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Promising aspects of the structural modification of polymers and polymer composites with the aid of high pressures

V A Beloshenko, A A Askadskii, V N Varyukhin

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Abstract. The results of studies on the structures and mechanical properties of polymeric materials subjected to isostatic treatment and extrusion in the solid state, mainly rigid-chain and network polymers, polymer blends, and reinforced compositions, are described systematically and surveyed. The bibliography includes 204 references.

I. Introduction

The modification of polymers, the manufacture of which has been undertaken on an industrial scale, is one of the principal trends in the creation of materials with a required set of characteristics. Various procedures for the deliberate alteration of the structures and properties, including methods such as chemical and physical modification, are employed. Despite the advances achieved on these lines, the search for new modification methods, among which methods involving treatment by the application of pressure are promising, is being continued.

A high hydrostatic pressure induces both reversible and irreversible changes in the physical and mechanical properties of materials, promotes the formation of their new modifications, and makes it possible to achieve the synthesis of products the preparation of which is impossible under normal conditions.[1–7] The first experiments using high pressure were carried out more than 100 years ago but since then the interest in its employment for scientific and technological purposes has not weakened.

In order to obtain materials with the required performance properties, various methods based on the employment of high pressures, are used namely pressing, rolling, stamping, drawing, *etc*. They are distinguished by the scheme underlying the stressed state of the material and the hydrostatic component of the stress tensor.[8] Among the technological processes based on the direct application of a high hydrostatic pressure, the greatest development has been achieved in isostatic pressing and hydrostatic extrusion.[7,9–17] The isostatic pressing method is used basically in the treatment of powders. Its advantages include extremely effective mechanical characteristics of the final products, the possibility of obtaining articles of any shape, however complex, the simplicity of equipment, and the ease of automation. Virtually all the advantages of the plastic deformation of materials, including the most favourable scheme underlying the stressed state, the reduction to a minimum of frictional forces, and the plasticisation effect determined by the application of pressure, are applied in the hydroextrusion method. Using the advantages of the method listed above, it is possible to alter the structure and the strain – strength characteristics of the treated material.

Compared with other substances, for example metals, polymers are much more sensitive to the effect of pressure, but the first few studies which considered various aspects of the influence of high pressure on polymers were carried out comparatively recently.[18–22] Active interest in the study of the properties of polymers under pressure began to be manifested in the 1960s while the fundamental theoretical and experimental results, which clarify the role of high pressures in the establishment of a set of mechanical and performance properties of polymeric materials, were obtained in the 1970s – 1980s, which may be regarded as the period of the most vigorous development of this field.[23–30]

The methods for the treatment of polymers by the application of pressure, used for their structural modification, can be divided conventionally into two groups. The first comprises various procedures based on the application of an isostatic treatment; isostatic pressing of polymer powders, treatment by the hydrostatic compression of articles in the form of a block, and structure formation under pressure. This group of methods is characterised by a spherical external stress tensor. The second group includes methods based on the joint operation of a high pressure and shear stresses (the total external stresses tensor): deformation using Bridgman anvils, ultrasound, and shock waves; pressing; elastic-deformation grinding; solid-state extrusion; *etc*.

This review deals with structural modification methods, which are some of the most promising as regards practical employment — different versions of the isostatic treatment and solid-state extrusion. They are characterised by a high effectiveness, ease of technological application, and the possibility of treating comparatively large volumes of the polymeric raw material. The main bulk of studies devoted to isostatic treatment or solid-state extrusion have been carried out on flexible-chain amorphous or amorphous-crystalline homopolymers. Their results have been reflected to a large extent in a series of review articles and monographs, for example in the studies described in Refs 25, 26, 30, and 31. In the present review, attention is therefore

V A Beloshenko, V N Varyukhin A A Galkin Donetsk Physicotechnical Institute, National Academy of Sciences of Ukraine, ul. R Lyuksemburg 72, 340114 Donetsk, Ukraine. Fax (38-062) 255 02 08.
E-mail: bel@hpress.dipt.donetsk.ua (V A Beloshenko)
A A Askadskii A N Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, 117813 Moscow, Russian Federation. Fax (7-095) 135 50 85. Tel. (7-095) 135 93 98.
E-mail: andrey@ineos.ac.ru

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concentrated on the less well known aspects of the problem, namely on questions concerning the modification of rigid-chain and network polymers and polymer composites. New aspects of the development of the structural modification methods under discussion, in particular the solid-state extrusion of a powdered billet, are examined in greater detail.

II. Isostatic treatment of crystallisable polymers

1. Crystallisation under pressure

The vast majority of studies on isostatic treatment have been devoted to crystallisation under pressure. The main bulk of such investigations have been carried out on polyethylene (PE).[25, 32–39] In the first experiments, it was already observed that pressure not only increases the crystallisation temperature but also induces certain structural changes in the polymer. Thus Matsuoka and Maxwell [32] obtained at high pressures PE with an unusually high density, which they explained by more effective chain packing. Subsequently, Wunderlich [40] showed that crystallisation under a high pressure entails not only more satisfactory chain packing but also leads to the formation of crystals of a new type — crystallites with extended chains (CEC). The pressure corresponding to the onset of the formation of CEC is in the range 300–350 MPa according to the phase diagram.[41]

There are two main hypotheses concerning the appearance of CEC.[34] According to the first, the CEC are formed on nuclei consisting of straightened chains or packs of chains,[35] whilst according to the second, folded lamellae are thickened under pressure and are gradually converted into CEC.[36, 37]

The molecular mass distribution (MMD) has a significant effect on the course of crystallisation. For example, it has been shown [38] that the curves for the distribution of the thickness (length) of crystallites in the direction of molecular chains and of the molecular mass (M) distribution are identical for $M < 10\,000$. For $M > 10\,000$, mixed crystallites are formed. Fractions with narrow MMD crystallise in two stages,[42] while the crystallisation of specimens with a broad MMD usually involves a single stage. In mixtures of fractions, fractionation and segregation take place during crystallisation, which results in the formation of a eutectic-like mixture of crystallites comprising fully straightened molecules with a low M and crystallites made up of molecules with a high M having both straightened and folded shapes.[39]

The principal differences in the morphology of PE specimens, obtained at atmospheric and high pressures, are as follows. In the pressure-modified PE, the lamellar thickening occurs only up to a certain limiting extent, the twisting of the lamellae is not observed, and spherulitic formations with a fanlike structure are present. The latter are characterised by a tangential orientation of the C-axes.

The formation of CEC on crystallisation from the melt under pressure has been observed for a series of other polymers [43, 44] and copolymers.[45] Together with the formation of CEC, phase transformations occur in many polymers during crystallisation under pressure, as a result of which it is possible to obtain materials with a new crystal system. For example, it has been noted [23] that, together with the orthorhombic phase, a triclinic phase is present in PE crystallised at 436 MPa. If the crystallisation of syndiotactic polypropylene (PP) is carried out at pressures amounting to several hundreds of megapascals, it is possible to obtain a new crystalline modification.[46] Poly(vinylidene fluoride) (PVDF), crystallised at 507 MPa, consists of a mixture of two phases with different melting points (T_m); the PVDF obtained at atmospheric pressure consists of a single phase.[47] The transition to a new modification on crystallisation under high pressure has been noted also for polybut-1-ene.[25]

The study of the crystallisation kinetics showed that a high pressure as a rule slows down the crystallisation process, *i.e.* a higher degree of supercooling of the melt is required in order to attain the same rate of crystallisation as at atmospheric pressure.[48, 49] At the same time a nonmonotonic dependence of the rate of crystallisation of PE on pressure, due to changes in the kinetics of the growth of crystals and the phenomenon of topomorphy has also been discovered.[50]

The structural transformations listed above, which occur in polymers as a result of crystallisation under pressure, induce changes in their properties. As a rule, denser packing appears in the polymers and the degree of crystallinity and T_m measured under atmospheric conditions increase.[32, 40] Thus the differences between the densities (ρ) of high-density polyethylene (HDPE) specimens, obtained at normal and elevated pressures, amount to 2%.[32] The dynamic Young's modulus of pressure-modified polyethylene is twice as high, its strength is greater, but its plasticity is lower. A similar effect has been obtained for polytetrafluoroethylene (PTFE) and polypropylene.[25] The increase in the density of PE and the formation of CEC on crystallisation under pressure cause a decrease in its compressibility and in the intensity of γ-relaxation.[35]

2. Annealing under pressure

The influence of annealing under pressure has also been investigated mainly in relation to PE.[25] It was established that, when PE specimens comprising crystals with folded chains (CFC) are annealed, the rearrangement of the structure with CFC to a structure containing CEC is observed in the corresponding temperature ranges.[51] This has been confirmed by the appearance of a second (high-temperature) fusion peak and the results of morphological investigations; lamellae with transverse dimensions exceeding by more than an order of magnitude the dimensions of the lamellae in the unannealed specimens are formed after such annealing. There is a simultaneous increase in ρ for the annealed material, which reaches values characteristic of the structure with CEC. Slight changes in T_m, ρ, and morphology are observed during the annealing of specimens with the CEC structure, indicating a further improvement of their structural arrangement. It is assumed [40] that the formation of CEC during the annealing of PE under a high pressure takes place in accordance with a mechanism similar to the mechanism of crystallisation under the conditions of hydrostatic compression, *i.e. via* the isothermal thickening of lamellae.

Similar features (an increase in the degree of crystallinity, an improvement in the structure, and an increase in T_m and ρ) have also been established in the course of the annealing of other amorphous-crystalline isotropic polymer specimens.[25, 46] During annealing under pressure, oriented polymers exhibit a more complex behaviour. For example, uniaxially extended HDPE specimens undergo a phase transformation in addition to the increase in the thickness of the crystallites, in T_m, and in ρ already mentioned.[52] A proportion of the material undergoes the transition from the orthorhombic modification to the oriented triclinic modification. At the same time, there is a sharp increase in the degree of crystallinity: the intensity of the amorphous halo for the annealed specimen is five times smaller than for the original specimen.[52]

In the course of the annealing of oriented specimens of syndiotactic PP, the formation of a new high-pressure crystalline modification was observed.[46] The annealing of oriented PVDF specimens also induces a phase transition in the solid state with retention of the primary orientation.[46] The phase formed then has ρ higher by 10% compared with ρ for the low-pressure phase. Annealing under pressure (by crystallisation under pressure) of isotropic and oriented polymer specimens is reflected in their mechanical properties. In particular, a significant increase in the moduli of elasticity has been noted.[53, 54]

An improvement in the properties of the polymers can be achieved in a number of instances also by isostatic treatment at room temperature. The imposition of an hydrostatic pressure onto PTFE specimens with an increased porosity leads to the 'healing' of the micropores at pressures up to 80 MPa.[55] On further increase in pressure, the 'healing' process is retarded. Thermal activation analysis showed that the 'healing' of the

pores is associated with the viscous flow of the macromolecules. It continues until the free volume is 'exhausted'.

The contact between the polymer and the pressure-transmitting medium is very important in the isostatic treatment. In the absence of appropriate insulation, the negative effect of the medium can abolish the positive role of pressure or can impair the properties of the created material.[56]

3. Isostatic treatment of powders

The component methods for the treatment of polymer powders are extrusion, pressing with subsequent free sintering, pressing with sintering under pressure, and casting under pressure.[57] The choice of a particular procedure is determined both by the properties of the polymer and by the nature of the technical problem to be solved. The advantage of the pressing–free sintering scheme consists in the possibility of the effective manufacture of long articles by separating the pressing and sintering operations. However, in order to obtain good-quality articles, it is necessary to achieve the highest possible density and uniformity of its distribution with respect to length and the cross-section of the billet. It has been shown in relation to PTFE of brands F-2M, F-4, F-4MB, F-40, and F-40-P[58] that the isostatic treatment makes it possible to obtain the above properties with retention of the specified form of the article, provided that this operation is carried out after preliminary pressing of the powder. Hydrostatic pressures of 200–250 MPa are sufficient for the attainment of the state with the minimum porosity (Fig. 1).

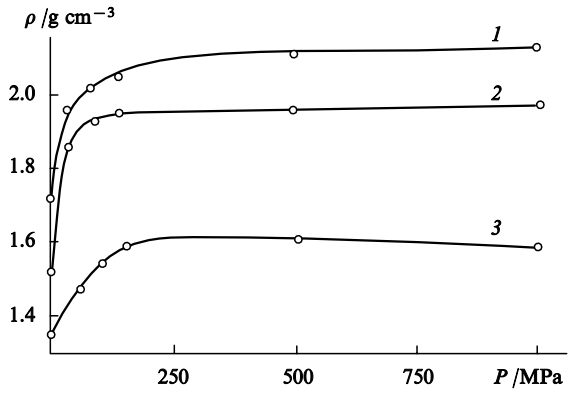


Figure 1. Pressure dependence of the density of polytetrafluoroethylenes for different powders: (*1*) F-4; (*2*) F-4MB; (*3*) F-2M.

A mathematical model describing the isostatic pressing of polymer powders and permitting the determination of the values of the principal technological parameter (the pressure) has been proposed.[59] The isostatic pressing process is regarded as consisting of two stages. The first stage is associated with the relative displacement and rotation of individual particles. The second involves elastic deformations of the particles filling the existing free space. After the removal of the external pressure, the polymeric material is loosened as a consequence of the reversibility of the elastic deformations and its density returns to the level attained at the end of the first stage. The relative density of the pressed polymer powder is therefore always less than unity. Comparison of the calculated and experimental $\rho(P)$ relations for PTFE confirms that the model is consistent with the isostatic treatment under consideration.[59]

In the practical application of powder technologies, moulding methods, differing from isostatic pressing, for example pressing in a rigid die of complex shape or pressing in special shells are widely used. The technological problems arising under these conditions are associated with the determination of the force necessary to attain the specified density, with the estimation of the pressure exerted on the walls of the die, with the calculation of the distribution of density with respect to the volume of the billet, *etc*. The parameters of the model,[59] found in experiments involving isostatic treatment, may be used to calculate the force parameters of the processes indicated.

III. Isostatic treatment of glassy polymers

1. The influence of pressure on the properties of amorphous polymers

There have been extremely few studies devoted to the influence of the isostatic treatment on the structure and properties of amorphous polymers. This is evidently associated with the possibilities for structural rearrangements which are much smaller than for crystalline polymers. Fairly detailed studies on polymeric glasses have been carried out.[60] It has been shown for a series of amorphous polymers that cooling of the specimens at 150 MPa from a temperature exceeding the glass transition temperature (T_g) to room temperature makes it possible to increase ρ compared with the original state by $\sim 1\%$. The state with increased density is metastable, but relaxation under atmospheric conditions proceeds slowly. With increase in temperature, this process accelerates, but at $T < T_g$ there is no complete transition to the original state. Compaction of the glass is characterised by increased values of the dynamic modulus of elasticity and a lower dielectric constant.

Higher values of ρ for a polymer vitrified under pressure have also been established in another study.[61] Here the instability of the material was noted. The nature of the recovery of ρ when the material is heated depends on the pressure employed: in the original stage of the recovery of ρ, the rate of the process is higher the higher the pressure P.

There have been few technological studies devoted to the application of a high hydrostatic pressure for the structural modification of polymers. Among them, mention should be made primarily of Shturman's studies[62,63] in which the favourable effect of annealing under pressure on the mechanical and performance characteristics of a series of polymers and polymer composites was demonstrated. For example, annealing of impact-resistant polystyrene promotes an increase in its strength, impact strength, and antifriction properties. A similar thermomechanical treatment of glass-reinforced polyamide specimens significantly increased their hardness together with an increase in the ultimate bending strength and impact strength. It is believed[62] that the strengthening effect is due to the compaction of the surface layer and the appearance in the latter of compressive stresses which increase the cohesive strength of the polymers. The molecular mass of the polymers also increases under the influence of temperature and pressure (the content of low-molecular fractions diminishes), which is correspondingly reflected in their properties.

2. The structures and properties of network polymers obtained under the conditions of hydrostatic compression

The chemical reactions as a result of which network polymers are formed are accompanied by the formation of a three-dimensional network structure. Compared with linear glassy polymers, one may expect new effects in the course of their isostatic treatment, in particular irreversible changes in structure and properties induced by the high pressure.

The study of the kinetics of the curing of network polymers under the conditions of hydrostatic compression showed that in the vast majority of cases the rate of this process increases with increase in pressure[64–69] and the increase is extremely significant. For a series of epoxide compositions, the increase in the reaction rate constant (k) at 250–350 MPa reaches several orders of magnitude.[64,67] The volume activation effect ($\Delta V^{\neq}$) for these reactions is negative and the increase in k with increase in pressure follows from the familiar relation.[70]

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\neq}}{RT}.$$

The nature of the influence of pressure is determined both by the type of the reagents selected and their proportions. For example, in the presence of an excess of an epoxide oligomer (EO) there is a possibility of the solvation of the reaction centres, which prevents their interaction, as a result of which the intensity of the effect of the pressure diminishes.[69] The results of studies by different investigators[64–69,71] involving the determination of k agree well. The shortening of the gel and glass formation times during the curing of EO by amines under the conditions of hydrostatic compression has been observed.[71]

Under the influence of pressure, the structure-formation process may be retarded as well as being accelerated. This result has been established, for example, in the curing of EO by an amine complex of boron trifluoride[66,67] and is associated with the influence of pressure on the equilibrium constant (K) for the dissociation of this complex to the amine (A) and BF_3, initiating the polymerisation

$$ABF_3 \rightleftharpoons A + BF_3 .$$

Under the influence of pressure, the equilibrium in this reaction shifts to the left and the concentration of BF_3 in the reaction mixture falls, which means that the rate of curing of the EO diminishes.

It has been established[65–69] that the differences in the kinetics of the chemical reactions occurring at pressures from 0.1 to 250 MPa are quantitative. This makes it possible to postulate the absence of an appreciable influence of pressure in the selected range (0.1–250 MPa) on the curing mechanism and hence on the molecular level of the structural arrangement of the epoxide polymers (EP). At the same time, the data obtained for poly(ethylene glycol dimethacrylate)[72] indicate that at sufficiently high pressures there is a possibility of changes in the structure of the molecular chains. Analysis of the IR spectra of poly(ethylene glycol dimethacrylate) showed that the nature of the disposition of the methacryloyl groups changes in the pressure range 600–2000 MPa, which is manifested by an increase in the probability of their 'tail to tail' addition. The most significant rearrangement of the molecular structure is observed at $P \leqslant 800$ MPa. An increase in pressure hardly influences the type of addition of the polymethacrylate chain units.

The influence of hydrostatic pressure on the topological and supermolecular structures of network polymers is more effective than its influence on the molecular level of the structural arrangement. Fig. 2 presents thermomechanical curves for specimens of a series of EP cured at different pressures.[73] The following compositions were employed: a blend of the epoxybisphenol A† resin ED-20 and polyepichlorohydrin cured with monocyanoethylenetriamine (EP-1); epoxyaniline resin cured with a eutectic mixture of aromatic diamines (EP-2); epoxybisphenol A resin cured with bis(4-amino-3-chlorophenyl)methane (EP-3); the epoxybisphenol A resin ED-20 cured with methyltetrahydrophthalic anhydride (EP-4); a blend of a flexible-chain block oligomer comprising an epoxide resin and acid oligomer and a diglycidyl ester cured with methyltetrahydrophthalic anhydride (EP-5); a blend of the epoxybisphenol A resin ED-20 and oligomeric diglycidyl esters based on diethylene glycol cured with triethanolamine titanate (EP-6); the epoxybisphenol A resin ED-16 cured with the methyltetrahydrophthalic anhydride (EP-7).

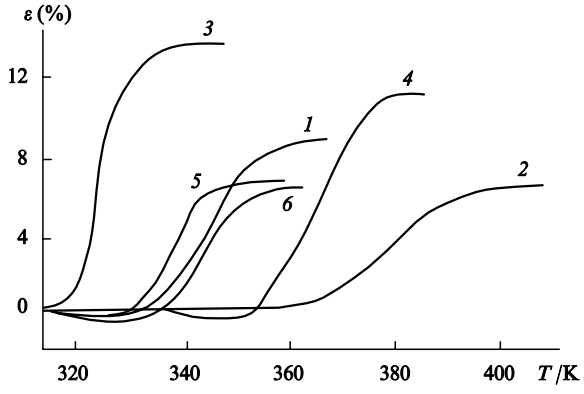


Figure 2. Thermomechanical curves for the epoxide polymers EP-4 (*1*, *2*), EP-5 (*3*, *4*), and EP-1 (*5*, *6*) at different pressures (MPa): (*1*), (*3*), and (*5*) 0.1; (*2*), (*4*), and (*6*) 200.

† Bisphenol A ('dian' in Russian) is 2,2-bis(4-hydroxyphenyl)propane (Translator)

Curing under pressure results in an increase in T_g and in the initial temperature of forced rubber elasticity and a decrease in the deformability of the polymers in the region of rubber elasticity. These facts indicate the intensification of intermolecular interaction. Pressure exerts the greatest influence on EP with large units (EP-4) or long chains between cross-links (EP-5). The increase in T_g reaches 30 K and the relative decrease in the quasiequilibrium elastic deformation reaches 30%. The latter is equivalent to the corresponding increase in the equilibrium modulus of elasticity, *i.e.* the increase in the rigidity of the polymer network. In the case of EP with compact units (EP-1), the changes under consideration are less pronounced. These findings indicate that the change in T_g under the influence of pressure is caused predominantly by the change in the packing of the units. The structure produced is 'frozen' at $T < T_g$ and is retained after the removal of the pressure. The appearance of anomalies on the thermomechanical curves for the modified EP-1 and EP-5 specimens in the vicinity of T_g is apparently a consequence of the relaxation of the 'frozen' compressive stresses.

The main parameter of the topological structure of the type of polymers considered is the concentration of the network cross-links (ν). Table 1 presents the values of ν for certain EP investigated.[74] For all the compositions, the curing under the conditions of hydrostatic compression promotes an increase in ν and the highest values of $\Delta\nu$ are attained for EP-4 and EP-5 ($\Delta\nu$ was estimated as the ratio of the increment in ν, caused by the pressure, to the value of ν for the control specimen).

Table 1. Effective concentrations of network cross-links in EP.[74]

Polymer	$10^{-20}\,\nu$ /cm^{-3}	$\Delta\nu$ (%)	Polymer	$10^{-20}\,\nu$ /cm^{-3}	$\Delta\nu$ (%)
EP-1	$\frac{7.3}{7.8}$	7	EP-4	$\frac{5.7}{8.1}$	42
EP-3	$\frac{12.1}{13.9}$	15	EP-5	$\frac{3.6}{4.4}$	22

Note. The values of ν above the horizontal line correspond to control specimens and those below the horizontal line were obtained at a pressure of 200 MPa.

The results of the thermomechanical analysis agree with pulse NMR data,[68] according to which structure formation under pressure increases the 'nuclear' glass transition temperature (T_g'), corresponding to the temperature of the appearance of two 'kinetic phases' with the nuclear magnetic transverse relaxation times T_{2b} and T_{2c}, and diminishes molecular mobility (Fig. 3). At $T > T_g'$, the changes in molecular mobility are observed only for the most mobile (T_{2b}) fragments of the polymer network, which indicates the influence of pressure also on the linear chains between the cross-links.

Differences between the internal friction spectra for the pressure-modified and control EP specimens have been demonstrated.[75] This indicates a lower intensity of the small-scale relaxation processes and a narrower set of relaxation times corresponding to these processes.

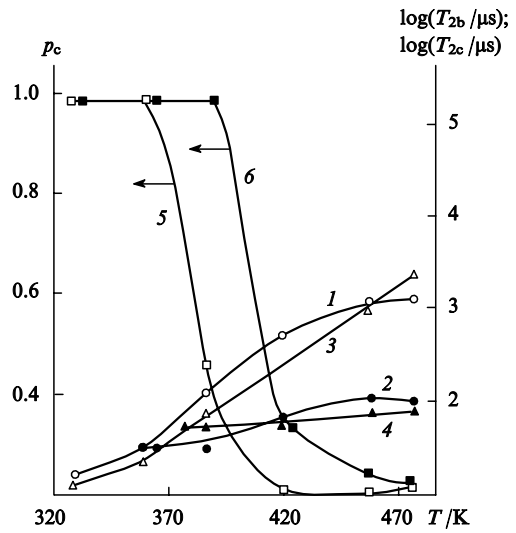


Figure 3. Temperature dependences of the nuclear magnetic relaxation times T_{2b} (*1*, *3*) and T_{2c} (*2*, *4*) and of the proton population p_c (*5*, *6*) for EP-1 at different pressures (MPa): (*1*), (*2*), and (*5*) 0.1; (*3*), (*4*), and (*6*) 150.

Three endothermic maxima appear on the differential scanning calorimetric (DSC) curves for the cured EP specimens (Fig. 4). They correspond to regions with different scales of the 'unfreezing' of molecular mobility: the low-temperature maximum *I* is associated with the 'unfreezing' of the noncooperative motion of segments at sites with a lower packing density (β-transition); the maximum *II* at 440 K corresponds to the cooperative glass α-transition; the high-temperature maximum *III* at 490 K is due to the molecular mobility in the rubbery state.[76] Comparison of curves *1* and *2* in Fig. 4 shows that treatment with pressure leads to a decrease in the intensity of the maximum *I* and its shift towards higher temperatures (*I′* on curve *2*), which is caused by the suppression of the small-scale molecular motion at the level of the segments (sections of the chain). The second maximum for the modified polymer is also located at higher temperatures (*II′* on curve *2*). The intensity of the molecular motion does not then change.

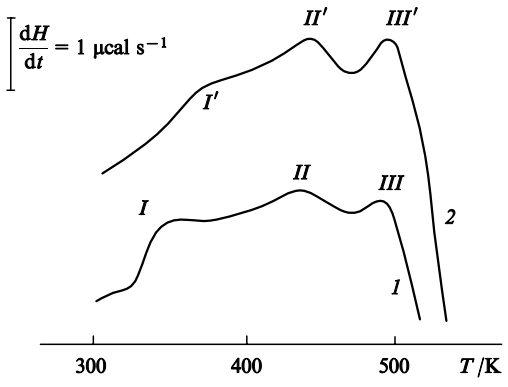


Figure 4. DSC curves for EP-1 at different pressures (MPa): (*1*) 0.1; (*2*) 100. *I*–*III* and *I′*–*III′* — see text.

Thus the set of data obtained by thermomechanical analysis, pulse NMR, internal friction spectroscopy, and DSC makes it possible to assume that the curing of the EP under the conditions of high pressures induces appreciable changes at the topological and supermolecular levels of the structural arrangement, manifested by an increase in the effective density of the cross-links and intensification of the intermolecular interaction.

This conclusion conflicts at first sight with the results of a study[77] in which the structure formation in EP was also investigated under the conditions of high pressures. According to these results, the specimens cured at 500–1000 MPa have lower values of T_g than those cured at atmospheric pressure. Estimation of the degree of cross-linking of the modified EP demonstrated that this process does not go to completion in the specimens indicated. Possibly the negative effect of pressure appeared because the investigators did not apply a correction for the temperature regime in the curing process. The change in T_g with increase in pressure is known to be 0.15–0.3 K MPa^{-1}. By tradition, in the epoxide resin curing practice the final curing temperature for the composition is chosen so that it exceeds the expected glass transition temperature.[79] In this case, the highest degree of conversion is attained. When the temperature regime corresponding to atmospheric pressure is applied in the region $P > 500$ MPa, the specimen is vitrified, for the reason mentioned above, before it attains the necessary degree of conversion. The reaction is inhibited and an undesirable result appears as a consequence.

There is also a possibility of another mechanism of the loosening of the polymer network on curing EP under pressure, which is analogous to that of Ozerkovskii *et al.*[72] In considering the pressure dependence of *v* for PDMA, the authors of this investigation suggested that in the network polymer cross-linked to the limiting extent an equilibrium is established between the cross-links, leading to a decrease in the volume of the system and the loosening cross-links. Calculation showed that at high pressures *v* decreases, because, starting with a certain critical concentration, the cross-links prevent the packing of the network skeleton.

In contrast to EP, for bis(methacryloyloxyethyleneoxycarbonyloxyethylene) oxide (MECDE) polymerised at 85–550 MPa, a decrease in the glass transition and enforced rubber elasticity temperatures as well as an increase in deformability in the rubbery state are observed with increase in pressure.[79] According to the authors,[79] this is caused by the changes occurring at the molecular level in the structural arrangement of MECDE. On polymerisation under pressure, there is an increase in the probability of the isotactic addition of units in the main macrochains of MECDE. Lower values of T_g are more characteristic of this modification than of the modification with the atactic type of addition of units.

A microstructure, the morphological unit of which is a globule, is at the uppermost level in the 'structural hierarchy' of network polymers[78, 80, 81] The globular character of the microstructure is manifested either on the surface of a section after etching or of the break produced by the application of a load. In the first case, the weakest sections of the polymer network are etched away, *i.e.* the globular relief reflects the chemical rupture front, the velocity of which is inversely proportional to the molecular packing density.[82] In the second case, the rupture takes place at the interglobular boundaries.[83] This makes it possible to regard the globule as a local thickening of the three-dimensional network, manifested as a particle on etching or mechanical rupture.[82]

Comparison of the microstructures of control EP specimens and specimens cured at high pressures shows that the dimensions of the globular formations and the thicknesses of the boundaries separating them diminish under the influence of hydrostatic pressure and the structure becomes more uniform.[62, 68, 84, 85] Table 2 presents the results of optical microscope studies of a series of epoxide compositions, illustrating this postulate. When the resolution of the microscope is high, it is seen that each globule consists of smaller formations. The results of electron microscope studies of the EP structure[84] are correlated with optical microscope data, which indicates a link between the observed morphological formations. The more finely disperse structure of the EP obtained under a high pressure compared with the structure of the EP cured at atmospheric pressure is due to the fact that the acceleration of the structure formation processes entails the

Table 2. The average sizes of the globules (d) and the content of groups of globules of different sizes at different pressures.[62, 68]

Polymer	P /MPa	d /μm	Content (%) of groups of globules of different sizes /μm										
			1–1.4	1.4–2	2–2.8	2.8–4	4–5.6	5.6–8	8–11.2	11.2–16	16–22.4	22.4–32	32–44.8
EP-1	0.1	5.6	–	0.2	0.4	16.4	41.7	30.8	6.8	3.4	0.2	–	–
	200	3.5	–	4.4	29.2	35.8	19.9	9.5	1.2	–	–	–	–
EP-3	0.1	9.8	–	–	0.9	6.2	11.3	20.3	24.1	28.6	7.8	0.6	0.2
	100	6.7	0.6	5.6	5.8	11.6	18.5	26.9	19.4	9.4	2.0	0.2	–
EP-6	0.1	6.0	0.8	6.0	11.4	16.1	16.1	21.3	20.1	6.8	1.2	0.2	–
	200	5.6	0.8	7.2	9.0	19.8	23.2	21.8	11.4	6.2	0.8	–	–

formation of a larger number of centres with reacted reactive groups, which create a basis for the subsequent formation and establishment of the heterogeneous morphology of the EP.[86]

The influence of pressure on the microstructure of MECDE is analogous to its influence on the structure of EP. Electron microscope studies [79] have shown that polymerisation under the conditions of hydrostatic compression is responsible for the decrease in the size of the globules from 500 Å (at 0.1 MPa) to 300–350 Å. Increasingly more pronounced aggregates with an elongated shape, consisting of a set of globules arranged one on top of another, are formed with increase in pressure.

An interesting result has been obtained in a study [87] devoted to the structure of a phenol–furfural composition based on iron tris(hydroxymethyl)phenoxide (Fe-TMP). In the original composition, the Fe-TMP forms ionic clusters which coagulate in the course of structure formation in the system with formation of associated species. High pressure promotes the latter process and leads to the appearance of larger metal-containing particles. At the same time pressure influences the physicochemical processes occurring in these particles during the curing of the composition, which alters their phase structure from amorphous to crystalline. The increase in the size of the cluster is accompanied by the appearance of a large amount of magnetite and an increase in the degree of order in its structure.

The pressure-induced changes at different levels of the structural arrangement of network polymers are reflected in their mechanical properties. In the first place, one should point to the increase in density, which has been noted in numerous investigations (see, for example, Refs 75, 79, and 85). This can be explained by the fact that pressure prevents the formation of macroscopic defects in the form of pores or cracks and promotes a decrease in free volume as a result of a more effective packing of the polymer. In the region of comparatively low pressures, the $\rho(P)$ relation is linear, but, as P increases, it approaches asymptotically a certain limiting value.[79]

Table 3 lists the strain–strength characteristics of MECDE specimens at different pressures, established in compressive tests.[79] Evidently, with increase in pressure, the modulus of elasticity (E) and the ultimate tensile strength (σ_t) increase to certain values. In the range 425–500 MPa, these parameters diminish. The extremum change in mechanical properties may be caused by the competition between the changes at the microlevels (ρ) and topological levels (v) of the structure and at the level of the macrochains. At a comparatively low pressure, effects associated with the increase in ρ and v predominate. The mechanism of the addition of methacryloyl groups predominates in the region $\geqslant$ 400 MPa.[72]

Table 3. The strain–strength properties of MECDE at different pressures.

P /MPa	$10^{-3}E$ /MPa	σ_t /MPa	P /MPa	$10^{-3}E$ /MPa	σ_t /MPa
0.1	2.20	230	340	2.60	250
85	2.35	235	425	2.55	245
170	2.35	220	550	2.40	230
255	2.45	230			

The results of compressive tests on EP specimens cured at atmospheric and elevated pressures agree [74, 85] with the data of the above study.[79] The more effective mechanical properties of the modified EP can be accounted for by the intensification of the intermolecular interaction and a decrease in structural inhomogeneity on curing under the conditions of hydrostatic compression. The most significant changes in properties are attained when the epoxide compositions deviate greatly from stoichiometry, whereupon the number of unreacted epoxide groups increases significantly. The intermolecular interactions at the boundary between the globular and interglobular phases are appreciably weakened under these conditions with a consequent sharp decrease in the strength characteristics of the control specimens. The density of the cross-links in the polymer increases under the influence of pressure (the degree of inhomogeneity diminishes) and the connectivity between the supermolecular formations is enhanced, which promotes the retention of fairly high strengths.

The data obtained in tensile tests on EP are similar. Fractographic investigations[75] have shown that modification by pressure does not entail a change in the rupture mechanism. The differences between the fractograms of the specimens compared are merely quantitative; in the modified EP, the structural elements of the fractograms are smaller.

A promising method of improving the mechanical properties of polymers is believed to be the cure under pressure of reinforced compositions, especially if one employs fillers with a low surface energy or fillers tending to undergo sedimentation. Fig. 5 presents the distribution of microhardness along sections of cylindrical

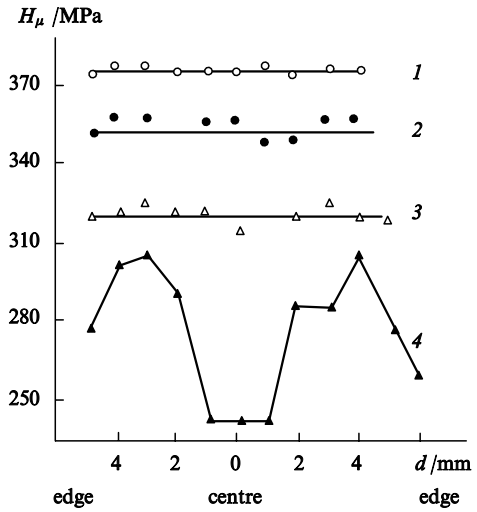


Figure 5. Distribution of the microhardness H_μ in cylindrical specimens of EP-2 (*1*, *2*) and EP-2 with 10 mass% of graphite (*3*, *4*) at different pressures (MPa): (*2*) and (*4*) 0.1; (*1*) and (*3*) 200.
d = Diameter of the cylinder.

EP-2 specimens obtained at different pressures. The level of microhardness H_μ for the modified polymer is higher compared with the control specimen, while the scatter of the values is approximately the same. When finely dispersed graphite powder is introduced, the picture changes sharply: a slight increase in inhomogeneity in the distribution of H_μ is observed for the polymer obtained under the conditions of hydrostatic compression, while in the control specimens the maximum deviation of H_μ from the mean reaches 20% for a filler content of 10 mass% – 30 - mass%. Such a change in H_μ in the latter case is caused by the separation of the composition into layers as a consequence of sedimentation processes. The viscosity of the cured composition increases under the influence of a high hydrostatic pressure, with a consequent suppression of the sedimentation processes, the microstructure of the composite becoming more homogeneous.

The dielectric properties of EP obtained at atmospheric and elevated pressures have been investigated.[75] It was established that the specific electrical volume resistance (ρ_v) of the modified polymers is higher than that of the control specimens and that the highest differences between the ρ_v are observed for specimens in the rubbery state. The EP investigated exhibited the ionic type of conductivity and the increase in ρ_v is therefore accounted for by the decrease in the mobility of the ions induced by the higher values of ρ and v for the modified polymers. The temperature dependences of ρ_v, the dielectric loss factor ($\tan\delta$), and the dielectric constant (ε') are correlated.[75] The maxima in $\tan\delta$ and ε' caused by the α-relaxation in the modified EP, as well as the corresponding break in the $\rho_v(T)$ relation, are located at higher temperatures compared with the corresponding maxima for the control specimens. Furthermore, the modified polymers have lower absolute values of ε'.

Studies on the thermal stability of EP showed [88] that appreciable differences between the characteristic temperatures of the objects compared were not observed for specimens in the form of a block. When the modified specimens are ground, an increase in the original thermal degradation temperature compared with the corresponding temperature of the control specimen is observed. Analysis of the change in the thermal degradation temperature in the course of the annealing of the ground specimens in oxygen and under an inert atmosphere led to the hypothesis that curing under pressure influences the nature of the packing of the molecular chains, as a result of which the most 'vulnerable' chemical bonds are shielded from oxygen.

Polymers based on interpenetrating polymer networks (IPN) have great potential possibilities for structural modification. Such polymers are obtained by simultaneous or consecutive curing.[89] In a series of studies, Lee and Kim [90–93] examined the influence of hydrostatic pressure on the structures and properties of simultaneously cured IPN in relation to the polyurethane – polystyrene (PU – PS) system. The characteristic features of the behaviour of the PU – PS compositions, consisting of blends of linear polymers or of polymers of the type of semi-IPN, were discovered. It was established that, in the course of synthesis under the conditions of hydrostatic compression, ρ of the final reaction product increases (the increase in ρ is observed in the range 0.1 – 250 MPa, while in the region of higher pressures ρ is independent of pressure). The nature of the temperature dependence of the mechanical loss factor also varies with increase in pressure. The $\tan\delta(T)$ relation for the compositions synthesised at atmospheric pressure has two maxima corresponding to each component of the composition (Fig. 6). In the synthesis under a high pressure, the positions of the temperature maxima are displaced towards one another and ultimately the maxima merge, forming a single peak. This peak is produced as a result of the degeneration of the PU maximum. The glass transition temperature of the dominant phase (PS) decreases with increase in pressure and this is the reason for the low slope of the relation $T_g(P)$ at $\sim$1000 MPa. The authors associate the observed effect with the increase in the compatibility of the phases both for the blend of linear polymers and for the semi-IPN and IPN (Fig. 7).

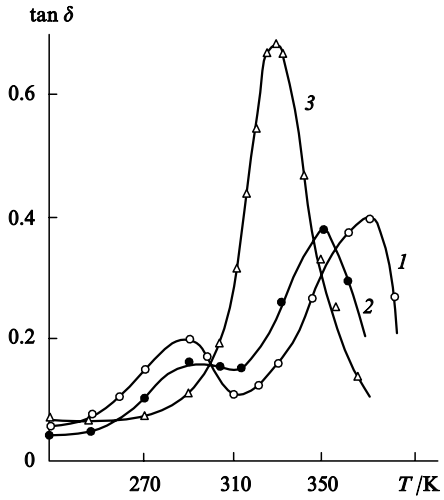


Figure 6. Temperature variations of the mechanical loss factor for the polyurethane – polystyrene IPN system containing 50 mass% polyurethane at different pressures (MPa): (*1*) 0.1; (*2*) 250; (*3*) 1000.

The results of electron microscope studies indicate that the morphology of the PU – PS system, synthesised at atmospheric pressure, consists of a fairly homogeneous structure made up of the PU and PS phases. With increase in the synthesis pressure, fully dispersed domains are formed in the PU phase, their size diminishing with increase in the compatibility of the phases. At 1000 MPa, the size of the domains is 30 – 50 Å, which corresponds to the molecular level of the blending. The size of the domains increases with increase in the cross-linking density in the IPN. The results of the study of the morphology of the IPN PU – PS system by dynamic mechanical analysis and electron microscopy agree satisfactorily.

In the case of the semi-IPN and the blend of linear polymers obtained at atmospheric pressure, the PU phase forms a matrix, but with increase in pressure a tendency towards the dispersion of this phase is manifested. Such a tendency is most notable for systems in which the PU component has a linear structure.

Prolonged annealing of the pressure-modified PU – PS blends at 0.1 MPa and $T < T_g$ promotes the partial restoration of the $\tan\delta(T)$ spectrum characteristic of control specimens synthesised under atmospheric conditions. With increase in the annealing temperature to $T > T_g$, complete phase separation (characteristic of the control specimens) takes place, which is indicated by the identity of the mechanical loss spectra of the annealed and control specimens.

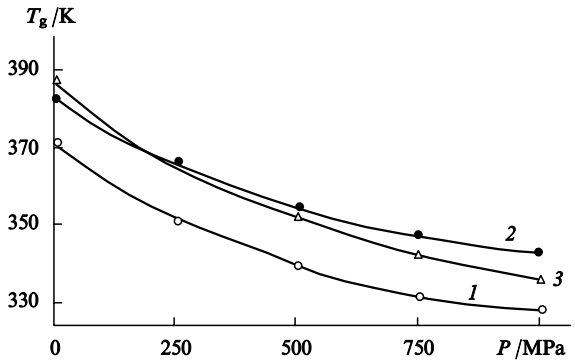


Figure 7. Dependence of the glass transition temperature T_g on the synthesis pressure for the polyurethane – polystyrene system. (*1*) IPN; (*2*) semi-IPN; (*3*) polymer blend.

The characteristic features of the structure formation in and the properties of the consecutively cured IPN synthesised under pressure have been investigated [94–96] in relation to epoxide allyl polymers. Diethylene glycol bis(allyl carbonate) (DEGBAC) and epoxybisphenol resins (EO) were used as the allyl monomers. The study of the prepolymerisation (formation of the allyl network) kinetics by rotational viscometry and by measuring ρ_v showed that together with accelerating the process and increasing the average degree of polymerisation, pressure induces or intensifies the gel effect. Under these conditions, even a comparatively slight increase in the original DEGBAC concentration alters the direction of the reaction towards the formation of the network product.

The pressure-induced changes in the structure and properties of the prepolymer are inherited on final curing of the composition (curing of the epoxide component) at 0.1 MPa. According to the results of thermomechanical analysis, high glass transition and rubber elasticity temperatures are characteristic of polymers obtained under pressure, but the vitrification temperature range is comparatively narrow. Fig. 8 presents the dependences of T_g for epoxide allyl compositions on the DEGBAC concentration corresponding to different conditions in the synthesis of the prepolymer. The increase in DEGBAC concentration, starting from a certain value, leads to a linear growth of T_g. The change in v induced by an increase in the content of the allyl component and by pressure is correlated with the 'behaviour' of T_g (Table 4).

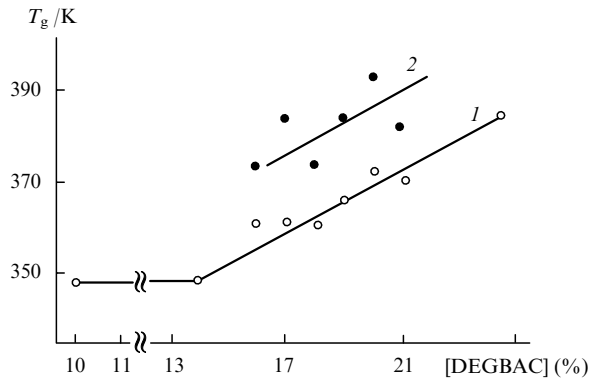


Figure 8. Dependence of the glass transition temperature T_g for epoxide-allyl polymers on the DEGBAC concentration. P (MPa): (*1*) 0.1 (control specimen); (*2*) 200.

Table 4. The structures and properties of epoxide-allyl polymers obtained at different pressures.

[DEGBAC] (%)	$10^{-20}\,v$ /cm^{-3}	T_g /K	ΔT_g /K	ΔC_p /kJ kg^{-1} K^{-1}	H_μ /MPa
16	6.0	343	50	0.24	150
	7.8	353	30	0.21	180
17	7.0	343	60	0.29	220
	9.2	358	30	0.21	180
18	7.6	343	60	0.38	250
	9.2	358	20	0.21	185

Note. The quantities above the horizontal line represent the characteristics of the control specimens and those below the horizontal line represent the characteristics of the specimens obtained using a pressure of 200 MPa.

The study of the relaxation and thermophysical properties of the polymers obtained at DEGBAC concentrations ensuring the formation of type IPN polymer–polymer structures demonstrated the following. In the region of T_g, a symmetrical $\tan\delta$ maximum and a jump in heat capacity (ΔC_p) are observed. Higher values of T_g, a narrower vitrification range (ΔT_g), and lower values of ΔC_p have been noted in pressure-modified polymer compositions.

The existence of a single glass transition temperature and its linear dependence on the concentration of the allyl component in the compositions investigated indicate a high degree of interpenetration of the epoxide and allyl polymers.[97,98] The influence of pressure on the change in the compatibility of the networks and the morphology of the polymers is difficult to trace for such systems. Nevertheless, the experimental results permitted a series of conclusions. The characteristic differences between the values of T_g, ΔT_g and ΔC_p for the polymers (Fig. 8 and Table 4), associated with the use of a high pressure in the prepolymerisation state, indicate the presence of a modifying effect of the pressure. Pressure affects primarily the degree of polymerisation of DEGBAC: for identical original concentrations of the allyl monomer, a higher degree of conversion of the prepolymer synthesised under the conditions of hydrostatic compression is observed and the probability of the formation also of a denser network of chemical bond cross-links therefore increases. In the curing of EO, the differences between the densities of the allyl networks are retained, which is reflected in the values of v and T_g for the polymers compared.

The uniformity of the polymer structures may be inferred to some extent from the values of ΔT_g and ΔC_p: ΔT_g and ΔC_p diminish with increase in homogeneity.[76] Hence it follows that pressure promotes the homogenisation of the structures of polymer compositions. This is indicated also by the results of small-angle X-ray scattering studies: the scattering intensity in the case of specimens obtained using hydrostatic pressure is much lower than in the control specimens (Fig. 9). This effect may be induced by different causes, for example, by the extensive penetration of the EO into the allyl network in the preparation of the prepolymer under a high pressure and also by the formation of a less defective allyl network. Ultimately the factors considered improve the compatibility of the networks.

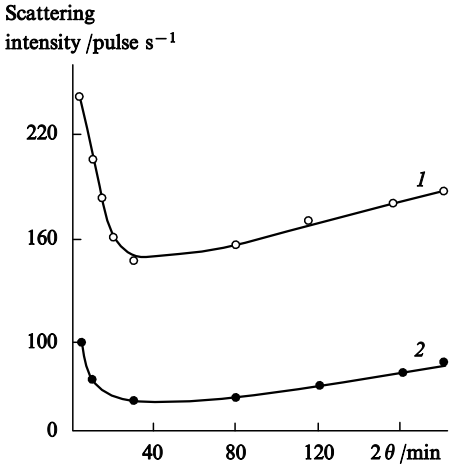


Figure 9. Results of the study of epoxide-allyl polymers (DEGBAC content 18 mass%) by the small-angle X-ray scattering method for prepolymerisation at different pressures (MPa): (*1*) 0.1; (*2*) 200.

The results of the measurements of the microhardness H_μ, which serves as a measure of the local plasticity (Table 4) agree with this conclusion. The lower values of H_μ for the pressure-modified polymers may be induced by the plasticisation phenomenon caused by the increase in the compatibility of the networks.[99]

3. Preparation of oligomeric products by fusion under pressure

The modifying effect of pressure may be used not only for the preparation of network polymers and polymer–polymer systems but also in the synthesis of their reactive components. The effect of hydrostatic pressure on the fusion of the epoxybisphenol A resin ED-22F and bisphenol A has been examined [100] and a study has been made of the fractional composition of the reaction product. In a study of the fusion kinetics, use was made of the method involving the titration of the reaction groups: the epoxide (E), alcoholic OH (A), and phenolic OH (P) groups. The fractional composition was studied by the gel-chromatographic method.

Figure 10 presents typical chromatograms of the reaction product obtained on fusion of the epoxide resin for 1 h. The assignments of the peaks are presented in Table 5. The influence of the duration of exposure and pressure on the fractional composition of the epoxide resins is reflected in the data in Table 6 and the change in the molecular parameters is reflected in the data in Table 7.

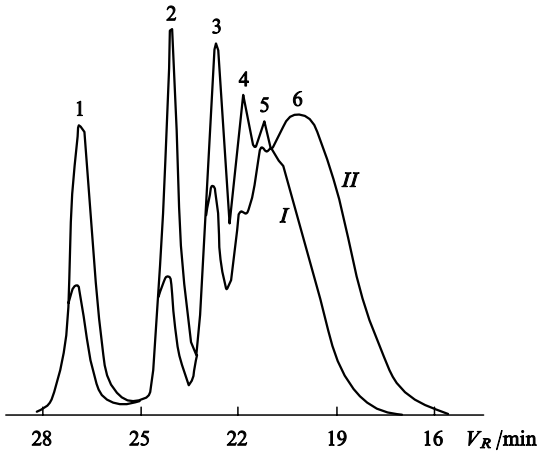


Figure 10. Chromatograms of the product of the fusion of an epoxide resin with bisphenol A. *P* (MPa): (*I*) 0.1; (*II*) 100; the numerals opposite the curves represent the numhers of the peaks in Table 5.

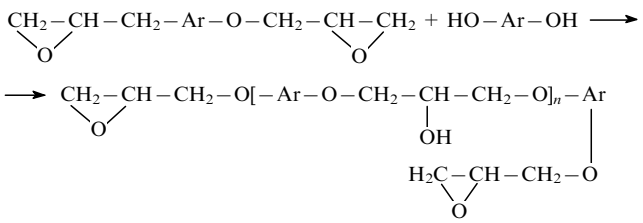
Table 5. The retention times (τ), the degrees of polycondensation (m), and the molecular masses of the product of the fusion of an epoxide resin with bisphenol A (Fig. 10).

No. of peak	τ /min	m	M	No. of peak	τ /min	m	M
1	26.9	0	340	5	21.5	4	1476
			—				1364
2	24.2	1	568	6	20.2	5	1592
3	22.8	2	908		19.4 [a]	7	1936
			796		18.2 [a]	10	2620
4	22.0	3	1136		17.0 [a]	14	3532

[a] These polymeric products are not represented by individual peaks on the chromatogram but are 'located' in the tail part of peak No. 6.

Despite a certain scatter of the parameters presented in Table 7, the acceleration of the process by the pressure can be clearly traced. Pressure leads to an increase in the proportion of the high-molecular fractions and in the degree of polycondensation (Table 6). On the other hand, an integral parameter such as polydispersity changes comparatively little.

The synthesis (chain growth) under pressure of oligomeric products may be represented by the following simplified scheme:[101–105]



It may be accompanied by a side reaction — chain branching:

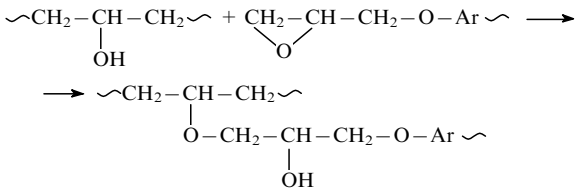


Table 6. Variation of the fractional composition of epoxide resins in the course of their synthesis.

Time /h	Content of fraction (%) for different degrees of polycondensation							
	0	1	2	3	4–6	7–9	10–13	⩾14
1.00	17.9 / 8.8	19.0 / 8.0	19.6 / 13.5	14.9 / 16.8	23.9 / 28.0	4.1 / 15.5	0.6 / 7.6	– / 1.8
1.25	15.8 / 8.0	17.4 / 6.0	22.0 / 14.0	6.6 / 19.0	32.2 / 27.1	5.2 / 15.8	0.8 / 8.0	– / 2.1
1.50	14.6 / 7.9	16.5 / 5.5	18.3 / 13.7	14.1 / 20.4	29.7 / 25.9	5.8 / 16.0	1.0 / 8.1	– / 2.5
1.75	12.9 / 7.5	15.0 / 5.4	17.0 / 13.4	15.1 / 21.1	32.3 / 25.5	6.5 / 16.1	1.2 / 8.2	– / 2.8
2.00	10.7 / 7.4	14.4 / 5.3	16.2 / 14.5	14.5 / 20.8	36.0 / 24.6	6.8 / 16.2	1.4 / 8.2	– / 3.0
2.50	8.6 / 7.3	12.3 / 5.1	15.0 / 13.3	12.3 / 22.2	43.3 / 24.4	7.0 / 16.3	1.5 / 8.3	– / 3.1

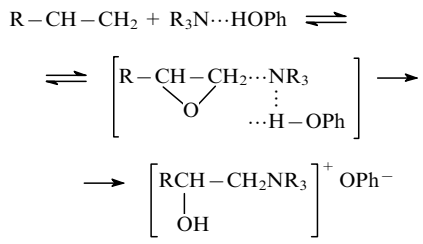
Note. Here and in Table 7 the quantities above the horizontal line were obtained for the control specimens and those below it refer to specimens synthesised at 100 MPa.

Table 7. Kinetic parameters of the synthesis and the molecular parameters of the epoxide resins obtained.

Time /h	$10^4\,k$ /s^{-1}	b	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	U	$\bar{f}_n^E$	$\bar{f}_w^E$	$\bar{f}_n^P$	$\bar{f}_n^A$
0.5	1.1 / 1.4	0.15 / 0.04	–	–	–	–	–	–	–	–
0.75	1.1 / 1.5	0.15 / 0.04	–	–	–	–	–	–	–	–
1.00	1.1 / 1.6	0.16 / 0.04	799 / 1059	1100 / 1548	1387 / 1968	1.4 / 1.4	1.6 / 1.4	2.2 / 2.0	1.1 / 0.8	1.4 / 2.6
1.25	1.1 / 1.6	0.16 / 0.04	863 / 1100	1215 / 1600	1547 / 2020	1.4 / 1.5	1.6 / 1.2	2.2 / 1.8	1.1 / 0.6	1.6 / 2.9
1.50	1.1 / 1.5	0.17 / 0.04	867 / 1100	1227 / 1600	1562 / 2000	1.4 / 1.5	1.5 / 1.2	2.1 / 1.7	1.0 / 0.5	1.7 / 2.9

Note. The average molecular masses (the number-average $\bar{M}_n$, the mass-average $\bar{M}_w$, and z-average $\bar{M}_z$ molecular masses) were calculated using chromatographic data, while the average functionalities were obtained from the formulae $\bar{f}_n^E = \bar{M}_w c_E/1000$, $\bar{f}_W^E = \bar{M}_w c_E/1000$, $\bar{f}_n^P = \bar{M}_n c_P/1000$, and $\bar{f}_n^A = \bar{M}_n c_A/1000$, where c_E, c_P, and c_A are the concentrations of the E, P, and A groups in the polymer blend. The selectivity is designated by b.

It is believed [105] that the polar complex tertiary amine (R_3N) – phenol (HOPh) interacts with the epoxy-group in the main reaction and that the reaction proceeds in accordance with the scheme



The kinetics of this process are described by the second-order equation

$$-d[E]/dt = k[E][R_3N]_0 ,$$

because the concentration of the reaction complex $R_3N \cdots HOPh$ is determined exclusively by the concentration of the tertiary amine. Bearing in mind that $[R_3N]$ = const in the course of the reaction,[102] the process considered may be described by a first-order kinetic equation for the specified R_3N concentration.

In reality the process is much more complicate, because the complexes P_m, $P_m E$, and $P_m A$ ($m = 1 - \infty$), where m is the degree of association of the phenol in the complex and A is the amine, are formed reversibly in the system. The complexes $P_m A$ with $m = 1$ and 4 are reactive. All these features significantly complicate the kinetic description of the fusion process because H-complexes and (or) contact ion pairs may be regarded as the reactive species in the chain propagation and branching reactions:[102]

$$A + \sim OH \rightleftharpoons \text{H-complex} \rightleftharpoons \text{contact ion pair.}$$

The low acidity of the alcohol formed in the chain propagation reaction precludes its competition with phenol in the complex formation process. For this reason, the side reaction is hindered in the presence of phenol and may be neglected to a first approximation.[101–103]

Table 7 presents the effective reaction rate constants (k) calculated from the consumption of the epoxy-groups (a first-order equation). Evidently, the approximate constancy of k is observed under the conditions investigated. This factor confirms the hypothesis that the main contribution to the rate of the given reaction comes from the amine – phenol complexes and not from the free ions.[102]

The fact that the formal-kinetic descriptions of the reactions at 0.1 and 100 MPa are the same may be interpreted as evidence in support of the constancy of the mechanisms of these processes in the system investigated. This permits the employment of the known pressure dependence of k (Zhulin [106]) for the calculation of the volume activation effect ($\Delta V_0^{\neq}$) corresponding to atmospheric pressure:

$$\log \frac{k_P}{k_0} = -\frac{\Delta V_0^{\neq} \Phi}{T} ,$$

where Φ is a function of pressure. With the aid of this relation and the values of k presented in Table 7 $\Delta V_0^{\neq} = -12.0$ cm^3 mol^{-1} was found. The value of $\Delta V_0^{\neq}$ obtained differs significantly from that established for the analogous polycondensation process:[67] $\Delta V_0^{\neq} = -27.0$ cm^3 mol^{-1} (interaction in the epoxide – amine system with formation of a network polymer). Consequently the influence of pressure on the interaction in the epoxide – phenol system is appreciably weaker than in the epoxide – amine system, which may be associated both with the differences in the transition states and with the solvation of the transition state in the epoxide – phenol system by oligomeric molecules, which may play the role of a 'solvent' (the volume activation effect for the viscous flow of such a solvent is positive [106]).

Using the approach based on the cascade theory of branching processes,[107] the selectivity of the process investigated was estimated [100] as the ratio of the rate constants for the side and main reactions. It was established that the synthesis of epoxide resins under the conditions of hydrostatic compression improves the selectivity significantly.

IV. Solid-state extrusion of polymers and polymer composites

1. Crystallisable polymers

Porter and coworkers were some of the first investigators who studied solid-state extrusion.[108, 109] They achieved the extrusion of PE through a capillary viscometer at temperatures close to the melting point. The transparent ultraoriented fibre thus obtained was characterised by high moduli of elasticity. In order to obtain a continuous oriented thread with the aid of a capillary rheometer, in a later study [110] PE was crystallised under pressure, after which it was extruded at $T < T_m$. This resulted in the appearance of a rigid strengthened fibre.

The structure of the polyethylene fibres obtained by solid-state extrusion is microfibrillar and is in the main similar to the structure produced in the usual stretching. The main bunch of microfibrils (fibrilla) is ribbon-shaped. The microfibrils are linked sideways by penetrating chains, which has been confirmed by X-ray investigations.[111] The amorphous component of the extruded specimens is also oriented, although to a lesser extent than the crystalline component. The maximum orientation of the amorphous phase is attained at extrusion temperatures close to the α-relaxation temperature.[112]

The properties of the extruded fibres depend both on the extrusion conditions (extrusion temperature; draw ratio $\lambda = d_b^2/d_d^2$, where d_b^2 and d_d^2 are respectively the diameters of the billet and the calibrating aperture of the die; the geometry of the deforming instrument) and on the original morphology of the polymer. It has been shown for HDPE that there is an optimum ratio between the CEC and CFC in the original material, which makes it possible to obtain the best set of mechanical properties. On the other hand, the maximum tensile modulus of elasticity is attained on extrusion in the vicinity of the α-process temperatures.[25] An increase in external pressure also corresponds to an increase in the modulus of elasticity.[113] The tensile strength is determined mainly by the value of λ.[25]

The solid-state extrusion method, used to obtain ultraoriented fibres, may be employed also for the preparation of films, which are likewise characterised by effective mechanical properties.[114] The solid-state coextrusion process has been frequently used in recent years for the uniaxial stretching of films.[115–117] HDPE is usually the material of the shell in which the film is placed. The choice of HDPE is determined primarily by its satisfactory deformability.

The characteristic features of the solid-state extrusion of block specimens of isotactic polypropylene have been investigated.[118, 119] The authors proposed a scheme for the process dynamics, incorporating nonstationary and stationary extrusion. The description of the process includes relations agreeing satisfactorily with experimental data. Within the framework of the chosen approach,[118] taking into account the occurrence of the marked orientational strengthening of polymers, the formation of spiral defects on extrusion with high draw ratios λ becomes understandable:[120] For such values of λ, the yield point (σ_y) becomes close to the ultimate tensile strength (σ_t) and any local inhomogeneity in the flow leads to the rupture of the extrudate.

A new series of publications on this question appeared in connection with the development of the hydrostatic extrusion method. When a liquid is used to transmit a high pressure, the most favourable conditions are created for solid-state moulding and it is possible to obtain rod-like and tubular articles with different profiles and a satisfactory quality of the surface and performance properties.[121]

The vast majority of studies on hydroextrusion have been carried out in relation to PE (see, for example, Refs 120 and 122–132). The very significant role of the technological process parameters, particularly extrusion temperature, the rate of deformation, and the angle of the drawing die (α) has been noted. It has been established [126, 128] that the most favourable deformation regime is the creep regime, in which the rate of emergence of the extrudate is $\sim 1 \times 10^{-3}$ m s^{-1}. The extrusion temperature range may be fairly broad but not unduly close to the melting point, where there is a possibility of the sticking of the material on the deforming instrument owing to its local fusion. At the same time, there is an optimum extrusion temperature for each draw ratio λ, which makes it possible to achieve the maximum effect (improvement of mechanical properties) due to orientation.

The data for the optimum value of α are contradictory,[123, 128, 133] but it is at least clear that it is in the range $20^\circ \leqslant \alpha \leqslant 60^\circ$. For low conical angles of the discontinuity, the nonuniformity of the distribution of deformations on the cross-section of the extrudate is small, but, owing to the increase in the contact area, there is an increase in the friction of the billet against the die, which increases the extrusion pressure. For large angles, there is an increase in the nonuniformity of the distribution of the deformations, which promotes an increase in the extrusion pressure and has an unfavourable effect on the distribution of properties over the cross-section of the extrudate.

With increase in λ, the variation of the density of the extruded PE passes through a minimum,[124, 126] the modulus of elasticity, the strength, and the hardness increase, while the plasticity diminishes.[25, 31, 124, 128] It is noteworthy that the increment in the tensile modulus of elasticity induced by hydroextrusion with high draw ratios, may exceed two orders of magnitude, while the stress may exceed one order of magnitude.[128] The capacity for strengthening is determined to a large extent by the molecular mass: in high-molecular PE, the increment in the modulus of elasticity is smaller than in low-molecular PE for the same technical parameters of the hydroextrusion process.[31, 124, 128] Together with the change in mechanical properties, an improvement of dielectric parameters has been noted for extrudates. Thus it has been observed [128] that the extruded HDPE is characterised by a greater resistance to the formation of incomplete electrical breakdown channels compared with the original material. This parameter increases with increasing draw ratio.

The study of the structures and properties of PE made it possible to put forward the following mechanism of the structural transformations in the hydroextrusion process.[120, 127] For low values of λ, the material has a typical fibrillar structure with slightly skewed crystallites and intra- and inter-fibrillar layers. With increase in λ, the crystallites become thinner in a transverse direction, are displaced relative to one another in the direction of the extrusion axis, the fraction of the interfibrillar amorphous layers diminishes, and the layers are partly drawn into the fibrils. On further increase in λ, the interfibrillar layers vanish and a structure made up of layers perpendicular to the extrusion axis arises. Dense interfibrillar strands of the type of CEC appear in the amorphous sections. The increase in the modulus of elasticity for small and moderate draw ratios is due to the increase in the degree of orientation of the structural elements considered and in the degree of crystallinity, but for high values of λ it is caused by the uniform distribution of the mechanical load over all the fibrils and by the growing role of the increasing number of intercrystallite strands. Overall, the proposed mechanism agrees with that discussed by Ciferri and Ward.[31]

Fairly numerous studies have been carried out on the hydroextrusion of PP. Features in the main similar to those characteristic of PE have been established for this material.[134, 135] In contrast to PE, the limiting draw ratios are significantly smaller for PP ($\lambda < 6$). A high degree of die swell (elastic recovery), characteristic of PP, reaching more than 30% for low values of λ, has also been noted.[134]

The characteristic features of the hydroextrusion process and the properties of the extrudates have been investigated to a lesser extent for other representatives of the class of amorphous-crystalline polymers. The results of studies carried out on PTFE have been published.[136, 137] The variation of the strength and elastic properties of fluoro-plastics as a function of the extrusion conditions obeys the same rules as in the case of other polyolefins, but the limiting degree of deformation on hydroextrusion does not exceed 4. The elastic and strength parameters for extension in the direction of the extrusion axis increase by a factor of 1.2–3.5. The breaking stress and tensile strength in the transverse direction also increase compared with the undeformed material. Extruded fluoro-polymers virtually lack cold fluidity.

The density, the mechanical properties in extension, and the linear coefficient of thermal expansion along the extrusion axis of hydroextruded poly-ε-caproamide have been investigated as a function of ratio.[138] The distribution of the densities of the axial and shear deformations has been obtained and comparative analysis of the experimental and calculated data on the extrusion pressure and the distribution of the deformations in the extrudates has been carried out.

An important performance characteristic of the oriented polymers is thermal shrinkage or the degree of recovery of the original dimensions (the shape memory effect). For HDPE, it does not exceed 10% and diminishes with increase in λ.[128] In the case of low-density polyethylene (LDPE), the degree of recovery is much greater: for low values of λ, it can reach $> 50\%$.[120] Numerous studies of the characteristic features of the thermal shrinkage of oriented specimens of crystallisable polymers have been carried out, but they were virtually all performed on films or fibres. The shrinkage characteristics and the shrinkage mechanism have been examined in detail for block specimens [139] in relation to LDPE deformed by hydroextrusion.

It was established that the thermal shrinkage of extruded LDPE specimens is a relatively rapid process in which the degree of shrinkage (ψ) increases with increase in the annealing temperature and with decrease in the extrusion temperature. Comparison of the maximum values of ψ for oriented PE films and specimens obtained by the hydroextrusion method showed that the latter exhibit a greater shape stability.[140–143] The changes in the maximum shrinkage stresses ($\sigma_{m.sh}$) and linear dimensions of LDPE as a function of λ and extrusion temperature are similar (Fig. 11) The shrinkage stresses vanish completely at temperatures corresponding to the fusion of the crystallites in the oriented LDPE.

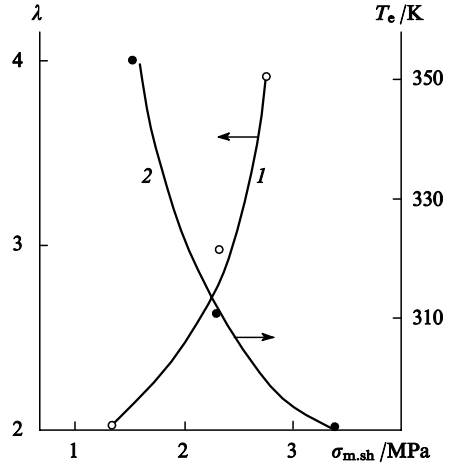


Figure 11. Relations between the draw ratio λ, the extrusion temperature T_e, and the maximum shrinkage stresses $\sigma_{m.sh}$ for LDPE. (*1*) $\sigma_{m.sh}(\lambda)$, $T_e = 313$ K; (*2*) $\sigma_{m.sh}(T_e)$, $\lambda = 4$.

During the orientation of LDPE, layered structures consisting of crystalline lamellae arranged perpendicular to the direction of stretching, arise in the extrudates. Stressed tied chains or clusters also appear as a result of the orientation. Heating of the oriented specimens shortens the extended macromolecules or parts of them: under the influence of entropy factors, the crystalline framework is transformed, which makes possible the shortening of the molecules.[140, 142, 144] The higher the temperature, the easier is the slip of individual sections of the macromolecules in the amorphous-crystalline polymer. With increase in extrusion temperatures, the number of stressed tied chains therefore diminishes, which decreases the stress and the degree of shrinkage. The decrease is caused primarily by the disappearance of the stressed tied chains in the defective crystallites, the disruption of which requires a low activation energy. At the same time, the displacement of the maximum on the temperature dependence of the shrinkage stress towards higher temperatures, which occurs with increase in the extrusion temperature,[139] is induced by the appearance of layers consisting of crystallites with increased transverse dimensions, the disruption of which requires a higher activation energy.

Yet another factor determining the structural rearrangement on heating of the extruded LDPE is the increase in the thickness of the lamellae during the annealing process. Individual segments are then 'drawn' into the body of the lamella, which induces the deorientation of the crystalline blocks and the appearance of internal stresses.[145, 146]

All the results examined above for the solid-state extrusion of crystallisable polymers were obtained in the extrusion of low-porosity monolithic billets. When highly-porous polymeric billets are employed, a kind of anisotropic structure, which makes it possible to achieve a state with a negative Poisson ratio (μ), may be formed in the extrudates.[147–149] The microstructure of such materials consists of grains joined by fibrils. These materials are interesting for a number of reasons: firstly, the effect of the negative μ may be used directly in clamps and seals; secondly, the presence of this effect influences favourably other mechanical properties, for example, the modulus of shear, the resistance to identation, *etc.*[150, 151] Finally, the complex microstructures responsible for the establishment of a negative μ may induce also other unusual phenomena associated with internal rotational degrees of freedom.[152, 153]

Not only monolithic but also powder billet may be subjected to solid-state extrusion. Strips, which were subsequently placed in HDPE were prepared from superhigh-molecular polyethylene (SHMPE) powder[154, 155] by pressing at elevated temperatures ($T < T_m$). Next the coextrusion process was carried out. Thus a highly modular high-strength state was achieved for the SHMPE. For example, the tensile modulus of elasticity achieved in one of the above investigations[155] amounted to ~ 60 GPa.

An even greater rigidity was attained on further stretching of the extruded materials by uniaxial extension. According to the data of Kanamoto *et al.*,[156] the modulus of elasticity of such films exceeded 100 GPa. Porter[157] obtained from powdered PTFE by the solid-state coextrusion method strips having a modulus of elasticity and an ultimate tensile strength of 3.2×10^4 and 3×10^3 MPa respectively. Oriented films have been obtained similarly[158] from polyacrylonitrile powder. They had effective strain–strength characteristics.

The difficulty of the process in which a polymeric billet is converted into a monolithic material, to be subjected to extrusion may in many instances render solid-state extrusion economically unjustified. This concerns particularly polymers with a high viscosity of the melt or reinforced compositions for which traditional highly productive processing methods (conversion of the billet into a monolithic material) are unsuitable. The solid-state extrusion method proposed in two investigations[159, 160] makes it possible to solve this problem. The procedure includes the following operations: compaction of the powder billet at room temperature, free heating of the billet, and extrusion using a heated high-pressure container and die. The process is fairly pro-ductive, since it can be made quasi-continuous, whereupon each successive billet, expels the mould residue from the preceding one.

It has been established empirically that the optimum extrusion temperature range for the extrusion of materials such as SHMPE is $(0.94-0.96)T_m$,[161] while for the polyetherketone based on isophthalic and terephthalic acids (brand PKIT) it is $(0.95-0.98)T_m$. At lower temperatures, the extrudates are obtained in a nonmonolithic form whilst at higher temperatures the polymer sticks to the deforming instrument, inducing an increase in the extrusion pressure and the formation of an uneven surface on the articles obtained (SHMPE) or the cracking of the extrudates (PKIT).

With increase in the degree of extrusion, the moduli of elasticity of the polymers considered increase and the increment in the modulus of elasticity for the flexible-chain polymer (SHMPE) is greater than for the semirigid-chain polymer (PKIT) (Table 8). The extrusion-induced changes in σ_t are small in both cases. At the same time, the plasticity diminishes with increase in the draw ratio. The results of mechanical tests on extruded SHMPE specimens are consistent with the familiar rules established for flexible chain crystallisable polymers,[126, 128] namely the increase in the modulus of elasticity is faster than the increase in the strength parameters associated with orientational extrusion. The conditions in the plunger extrusion of a polymeric powder billet differ fundamentally from the conditions in the traditional variants of solid-state extrusion and we shall therefore consider in greater detail the dynamics of the formation of the oriented structure in the extruded SHMPE specimens.

Figure 12 presents the dependence of the degree of crystallinity of SHMPE specimens on the draw ratio, obtained from

Table 8. The properties of polymer specimens obtained by the plunger extrusion of a powder billet.

Polymer	λ	$10^{-3}E$ /MPa	σ_t /MPa	ε_r[a] (%)
PKIT brand	1.0	2.0	80	–
	1.7	2.4	75	–
	2.3	2.5	70	–
	2.8	2.6	73	–
SHMPE	1.0	0.6	28[b]	9.7[b]
	3.0	0.7	32	11.7
	4.0	0.8	30	11.0
	5.0	1.1	30	10.0
	6.0	1.2	34	10.6
SHMPE–kaolin	1.1	0.7	31[b]	10.0[b]
	2.0	0.6	28	11.8
	3.0	0.7	31	10.0
	4.0	0.8	41	10.3
	5.0	0.9	40	9.2
	6.0	1.3	43	7.1
	7.0	1.5	47	7.0
SHMPE–Al	1.0	0.7	26[b]	8.1[b]
	3.0	0.8	37	7.4
	5.0	1.2	41	5.3
	6.0	1.1	40	5.4
	7.0	1.1	38	4.8
	9.0	0.9	34	6.1
SHMPE–$Al(OH)_3$	1.0	0.7	14[b]	4.5[b]
	3.0	0.8	19	3.0
	4.0	0.9	22	3.5
	5.0	0.8	17	3.0
	6.0	0.8	16	2.5
	7.0	0.4	13	4.9

[a] ε_r is deformation at the rupture point; [b] σ_y and ε_y are quoted respectively instead of σ_t and ε_r.

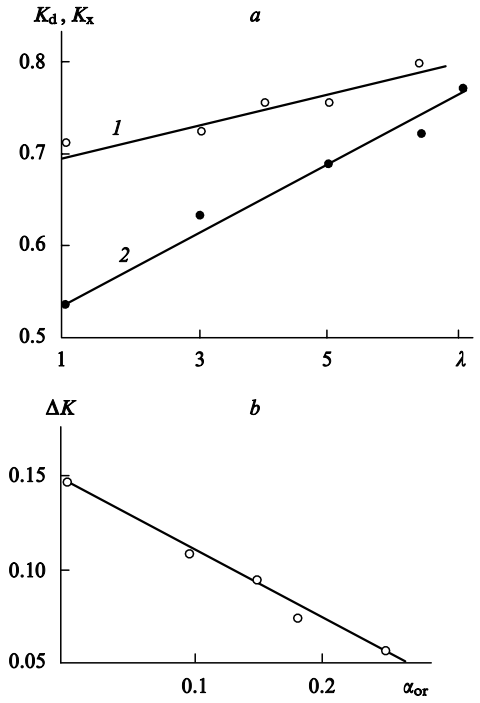


Figure 12. Dependences of the degrees of crystallinity K_d (*1*) and K_x (*2*) on the draw ratio λ (*a*) for SHMPE and of ΔK on the increment in the crystalline phase α_{or} (*b*).

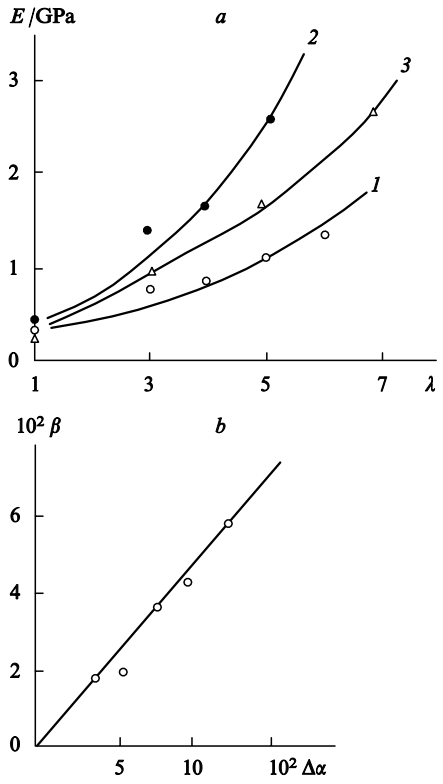


Figure 13. Dependence of the modulus of elasticity E for SHMPE and HDPE on the draw ratio λ (*a*) and of β on $\Delta\alpha$ for SHMPE (*b*). (*1*) SHMPE, compression; (*2*) SHMPE, bending; (*3*) HDPE, extension.

X-ray data (K_x) and from density measurements (K_d).[162] Evidently the absolute values of the X-ray degree of crystallinity are smaller than those found from the measurements of ρ. The observed difference between the values of K_x and K_d agrees with the available literature data [163, 164] and can have two explanations. According to Egorov *et al.*,[163] X-ray diffraction analysis yields the so called 'geometrical' degree of crystallinity, because the macromolecules arranged parallel to one another but without a three-dimensional order are detected by this method as disordered regions. On the other hand, in dilatometric measurements they can contribute to the crystalline phase. Mandelkern [164] expressed a different view, according to which the difference under discussion is caused by the presence of interfacial regions possessing a partial degree of order. In these regions, there is a smooth transition from long-range order (crystalline phase) to disorder (amorphous layers). Thus the quantity $\Delta K = K_d - K_x$ defines the fraction of either oriented macromolecules in the noncrystalline regions or the fraction of interfacial regions.

An increase in λ leads to an increase in the degree of crystallinity of SHMPE (Fig. 12), *i.e.* crystallisation due to orientation take place. The increment in the crystalline phase (α_{or}) can be expressed by the difference between the degrees of crystallinity (ΔK) corresponding to an arbitrary λ and $\lambda = 1$. The quantity K_x yields the true characteristic of the orthorhombic crystalline phase without taking into account the partial order in the noncrystalline regions and, by virtue of this factor, is accurate. It is therefore used to determine α_{or}. The parameter ΔK may be treated as the decrease in the fraction of oriented macromolecules in the noncrystalline regions [163] or in the volume of the interfacial regions.[164] Comparison of the data presented in Fig. 12 supports the second version, since, firstly, a decrease in the fraction of stretched through chains with increase in λ is unlikely; secondly, the values of ΔK for the undeformed SHMPE specimens are close to those established earlier by Mandelkern.[164]

The $E(\lambda)$ relations for SHMPE [156] and HDPE,[124] obtained in compressive, bending, and tensile tests, are similar (Fig. 13). Without dwelling on the discussion of the differences between the absolute values of E, we may note that, with increase in λ, one observes an increase in E which is steeper than a linear increase. There exist two limiting models describing the distribution of stresses in the oriented amorphous-crystalline monomers.[31] In the first, one postulates a uniform distribution of stresses in the crystalline block, where the tied chains are fairly uniformly distributed among the microfibrils formed in the stretching process. In the second, one postulates the complete independence of the tied chains and the crystalline blocks, the internal regions of the crystals alternating with amorphous layers which do not contain tied chains. The $K(\lambda)$ relations of the type presented in Fig. 12*a* correspond to the first model.[31] In this case, the volume fraction of the volume (β) occupied by tied chains is calculated by means of the simplified Takayanaga formula [31]

$$\beta = \frac{E}{E_{ax}(1 - K_x)},$$

where E_{ax} is the axial modulus of elasticity of the crystalline component.

Figure 13*b* presents the dependence of β on the fraction of the crystallised interfacial regions $\Delta\alpha$. The moduli of elasticity calculated from the results of compressive tests were adopted as E. A linear relation, passing through the origin of coordinates, is observed between β and $\Delta\alpha$. This means that the interfacial regions participate actively in the formation of the system of tied chains in the extruded SHMPE. The $\beta(\Delta\alpha)$ relation shows that ~45% of the macromolecules in the interfacial regions become tied chains. The result obtained agrees well with theoretical [165] and experimental [166] estimates.

Two components of the crystalline phase may be differentiated for the extruded SHMPE (taking into account the results examined above): the original crystalline phase transformed by deformation and the phase arising as a result of orientational crystallisation. The latter consists of crystallised amorphous sections and crystallised interfacial regions. Analysis of data on

the thermal shrinkage of extruded SHMPE specimens showed [167] that ψ increases with increase in α_{or} and $\Delta\alpha$, the absolute values of ψ and the corresponding α_{or} and $\Delta\alpha$ being similar. The above factors made it possible to postulate the fusion sequence for the components of the crystalline phase. The least perfect crystalline formations, obtained by the orientational crystallisation of the interfacial regions, melt initially. Their relatively high degree of imperfection can be explained by the presence in the interfacial regions of a large number of irregularities in the chains torn away from the crystallites. The next to melt are amorphous regions crystallised in the orientation process in which the number of irregularities is appreciably smaller. Finally, at higher temperatures the original crystalline phase melts. Thus the evolution of different structural components of SHMPE during the extrusion of a powder billet are described satisfactorily within the framework of the model of the three-component structure of the amorphous-crystalline monomer. The mechanism of this process has been examined in greater detail (resorting to fractal analysis and the cluster model of the structure of amorphous polymers) in another study.[168]

X-Ray diffraction investigations carried out on extruded PKIT specimens showed that the degree of crystallinity of all the specimens studied is $\sim$40% and changes little with increase in λ from 1 to 3. The specimens are characterised mainly by reflections which correspond to interplanar spacings of 5.71, 3.87, 3.19, and 4.79 Å. This state of PKIT is characteristic of an unstable crystalline modification,[169] *i.e.* the processing conditions are insufficient for a transition to the stable crystalline form having four principal reflections with interplanar spacings of 4.79, 3.91, 3.86, and 3.08 Å. Experiments showed that such an equilibrium form is formed on pressing at 623 K. It may be that the retention of the instability of the crystalline modification on extrusion in the temperature range 533–593 K is one of the causes of the insignificant change in the strain–strength characteristics of PKIT.

Porter and coworkers [157, 170] investigated the processes involved in the solid-state extrusion of a high-molecular PTFE powder billet. The extrusion was carried out in the temperature range 373–613 K until the attainment of the maximum values of λ. It was established that at a temperature below 373 K or above 613 K (this is higher than the melting point, which amounts to 607 K), the process under consideration cannot be achieved. In the range 373 K $< T_e <$ 553 K, the maximum value of λ is 10 and depends only slightly on T_e. On further increase in temperature, the limiting value of λ increases rapidly and amounts to 60 for T_e = 603–613 K. The structure and properties of PTFE are determined by the values of λ and T_e. In particular, the dimensions of the crystallites in both parallel and perpendicular directions relative to the extrusion axis increase with increase in λ. The presence of microfibrils, having a transverse dimension ($\sim$45 nm) greatly exceeding that usually observed for oriented monomers (6–20 nm), is characteristic of the highly oriented PTFE. The maximum value of the flexural modulus elasticity, corresponding to the optimum extrusion conditions (T_e = 613 K, λ = 40) reaches 20 GPa.

The method involving the solid-state extrusion of a powder billet proved to be fairly effective also in the case of thermoplastic polyimides.[171] The transition of the polymers to the molten state induces cross-linking of the macromolecules, which hinders their further processing. On the other hand, if the extrusion is carried out below T_m, using billets made up of powders pressed into discs beforehand, then for 563 K $\leqslant T_e \leqslant$ 593 K it is possible to obtain high-quality articles with a high degree of crystallinity.

2. Glassy polymers

There have been few studies of the properties of flexible-chain amorphous polymers extruded in the solid state. An increase in E and σ_t with increase in λ is observed for polymeric materials of this class, as for the amorphous-crystalline polymers, although it is not quite so pronounced. A distinctive feature of the flexible-chain amorphous polymers is that their plastic characteristics increase appreciably as a result of extrusion. For example, the deformation at the rupture point (ε_r) of poly(methyl methacrylate) subjected to tensile tests increased from several per cent for the control specimens to tens per cent for the extrudates.[172] A severalfold increase in impact strength has been noted for impact-resistant polystyrene.[173] The sharp increase in the plasticity of these polymers is attributed to the orientation of the molecular chains along the extrusion axis and the breaking away of side chains.[172–174]

The mechanical properties of polymers extruded in the solid state and of low-molecular substances, for example, metals, differ. The dependence of the strain–strength characteristic of oriented polymers on λ is determined to an appreciable extent by the scheme underlying the stressed state chosen in the test. Whereas on extension of polymers many investigators have noted an increase in the elastic and strength parameters with increase in the degree of orientation of the specimens, on compression the reverse effect is frequently observed or there are relations with a minimum. This applies both to crystallisable and flexible-chain amorphous polymers (Fig. 14).[175]

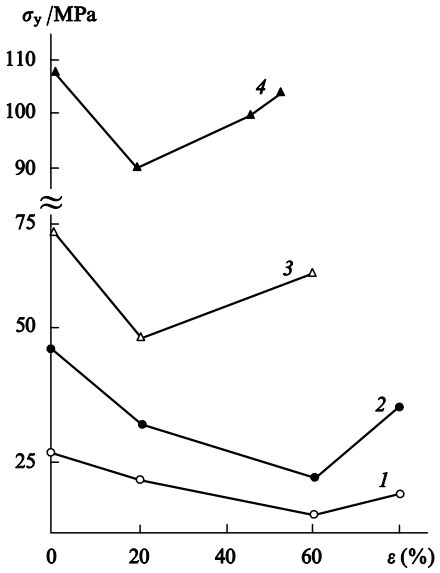


Figure 14. Dependence of the yield point σ_y in compression on the degree of deformation (ε) for polyethylene (*1*), polypropylene (*2*), poly(vinylchloride) (*3*), and poly(methyl methacrylate) (*4*).

The characteristic features of the solid-state extrusion of rigid-chain amorphous polymers have been scarcely investigated. In this connection, a definite interest attaches to data obtained in a study [176] of the influence of the deformation by hydroextrusion on the structure and properties of such materials in relation to the polyketones PAEKN (the product of the polycondensation of 4,4′-difluorobenzophenone and bisphenol A) and PAEKF (the product of the polycondensation of 4,4′-difluorobenzophenone and phenolphthalein, a card polymer). Table 9 presents the parameters of the hydroextrusion process: λ, T_e, the extrusion pressure P, and the properties of the extruded polyketones in compressive and microhardness tests. Evidently the pressure diminishes with increase in the extrusion temperature and increases with increase in the extrusion draw ratio. In the case of extrusion at room temperature, the extrusion pressure reaches such high values already at $\lambda > 3$ that the extruded materials are 'shot out' and break up.

Hydroextrusion improves the elastic characteristics of polyketones. For example, the modulus of elasticity of PAEKN increases with increase in λ and diminishes with increase in T_e. In the case of PAEKN, the highest value of E is observed at T_e = 488 K. The dependence of the characteristics σ_t and H_μ on

Table 9. The influence of hydroextrusion on the properties of polyketones.

λ	T_e /K	P /MPa	$10^{-3}E$ /MPa	σ_t /MPa	H_μ /MPa
Polymer — polyketone PAEKN					
1.0	–	–	2.0	80	180
2.2	293	800	2.5	70	170
2.4	293	900	3.0	70	165
2.8	293	1100	3.2	70	162
4.2	293	2000	–	–	–
2.5	488	30	3.6	120	237
Polymer — polyketone PAEKF					
1.0	–	–	0.7	56	143
1.8	443	3	0.9	63	135
2.6	443	25	1.1	58	126
1.8	453	1	0.7	55	130
2.6	453	3	0.8	48	122
4.0	453	15	1.0	59	127
6.0	453	27	1.3	64	133
1.8	463	1	0.7	40	135
2.6	463	3	0.7	38	132
6.0	463	17	0.8	50	136

the conditions in orientational extrusion is more complex. For PAEKN deformed at room temperature, these characteristics were lower than for the cast polymer ($\lambda = 1$). On the other hand, the extrusion of this material at an elevated temperature improves significantly the properties indicated. The values of σ_t and H_μ for PAEKF initially fall and then increase as λ increases, but the maximum values of these parameters for the deformed polyketone are smaller (H_μ) or of the same order ot magnitude (σ_t) than for the original material. The measurements of the density of PAEKF indicate the compaction of the polymer on deformation. This factor is associated primarily with the decrease in the volume of the pores, which are present in large numbers in the cast PAEKF according to optical microscope data.

The pattern in the scattering of X-rays by specimens of the original PAEKF consists of an amorphous halo. Annealing of the specimens for 2 h at 488 or 523 K with subsequent slow cooling does not alter it. Hydroextrusion at room temperature also does not change the pattern. At $T_e = 488$ K, the separation of the centre of the amorphous halo into two broad low-intensity reflections is observed, which indicates the onset of the crystallisation of the polymer. Cast PAEKF specimens are amorphous. Analysis of the X-ray diffraction data showed that hydroextrusion does not lead to any appreciable changes in the structure of the specimens.

Comparison of the results of mechanical tests and X-ray diffraction studies makes it possible to understand the characteristic features of the changes in the strain–strength properties of the aromatic polyketones studied. The slight increase in E and the nonmonotonic variation of H_μ observed with increase in λ (Table 9) for specimens subjected to hydroextrusion [175] are induced (as for flexible-chain amorphous polymers) by the orientation of polymer chains and the values of these quantities are determined by the degree of orientation and the structure of the polymer. The higher the extrusion temperature, the lower the degree of orientation, other conditions being equal. This is responsible for the low-slope of the $E(\lambda)$ and $H_\mu(\lambda)$ relations observed for PAEKF as T_e increases.

The strength of the polymer is to a large extent determined by the presence of different kinds of defects in it. The presence of a large number of micropores in cast PAEKF specimens and their 'healing' (elimination of microdefects) during hydroextrusion probably account for the nature of the $\sigma_t(T_e)$ relation. The effectiveness of the 'healing' increases with increase in pressure,[54] so that σ_t increases with decrease in T_e (this is accompanied by an increase in pressure) (Table 9). The $\sigma_t(\lambda)$ relation corresponds to the variation of the strength properties of flexible-chain amorphous polymers established by Nakayama and Inoue.[175]

It was noted above that the creation of oriented order in crystallisable polymers enhances more significantly their elastic and strength properties than in the case of amorphous polymers. Extrusion with $\lambda = 2.5$ and $T = 488$ K entails the transformation of the amorphous modification of PAEKN into a semi-crystalline modification. This tends to improve the mechanical characteristics of the given material.

The relaxation properties are well correlated with the results of mechanical tests and structural studies. Hydroextrusion increases the original and equilibrium values of the relaxing modulus (E_r) and stress (σ). The highest values of E_r and σ characteristic of PAEKN correspond to the modification with a partially crystalline structure. With the aid of the ideas developed by Askadskii [177] it has been possible to describe in detail the kinetics of the relaxation processes in the extruded aromatic polyketones. In particular, it has been established that the rate of interaction of the relaxators in the extrudates is higher than in the cast materials. This is quite reasonable if relaxators are understood as different kinds of microheterogeneities which are converted into nonrelaxing structures faster the higher the level of internal stresses (the latter naturally increases on deformation).

Large single deformations occurring without the disruption of brittle materials such as network polymers have been achieved as a result of the plasticisation effect during hydrostatic extrusion after the attainment of the oriented state.[68, 75, 178–180] EP — characteristic representatives of the class of network polymers — were selected as the object of study in the above investigations. It was established that the solid-state extrusion of EP induces a rearrangement of the structure at different levels of the structural arrangement, which is indicated by the results of NMR studies and optical-microscope studies.[68] Fig. 15 illustrates the variation of the molecular mobility of the structural fragments of high-crosslinked network EP, characterised by the nuclear magnetic transverse relaxation times T_2 for the mobile (T_{2b}) and more rigid (T_{2c}) 'kinetic phases' and also the variation of the fraction of relatively immobile protons (the p_c populations of the relatively

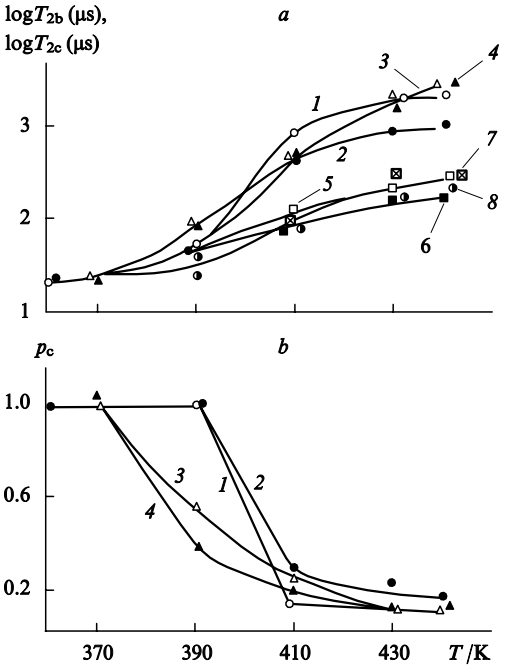


Figure 15. Temperature dependences of the nuclear magnetic relaxation times (*a*) and the proton population (*b*) for EP-7. (*1*)–(*4*) T_{2b}; (*5*)–(*8*) T_{2c}; ε (%): (*1*) and (*5*) original specimen; (*2*) and (*6*) 15; (*3*) and (*7*) 30; (*4*) and (*8*) 40.

immobile 'kinetic phase') as a function of the degree of deformation (ε) and temperature.

The differences between the kinetic properties of the fragments of the topological structure are induced by the differences between the numbers of degrees of freedom.[181] From these standpoints, the more mobile protons (characterised by the values of T_{2b} and p_b) belong to the linear chains between the cross-links and defective fragments of the network — the trifunctional cross-links CL_3 and chain branches. The less mobile protons (characterised by T_{2c} and $p_c = 1 - p_b$) belong to the tetrafunctional cross-links CL_4. The hierarchy of these fragments in order of decreasing mobility is as follows: linear chains between the cross-links and branches — CL_3 — CL_4. Mainly the molecular mobility of the more mobile structural elements changes on hydroextrusion (Fig. 15). The decrease in T_{2b} in the case of $\varepsilon = 15\%$ compared with the control specimen may be a consequence of the occurrence of orientational processes. Some of the mobile fragments are converted into the less mobile 'kinetic phase', which is manifested by an increase in p_c at $T > 410$ K compared with p_c for the original material.

For $\varepsilon \geqslant 30\%$, an increase in T_{2b} and a decrease in p_c are observed. This is apparently associated with the predominance of disordering processes over orientational processes. However, the significant decrease in the 'nuclear' glass transition temperature indicates that the disordering processes are accompanied by the mechanodegradation of the network, in the first place of CL_3 and CL_4 cross-links. The results of thermomechanical studies agree well with NMR data.[178]

The microstructure of the undeformed high-crosslinked network EP consists of globule-like formations made up of smaller elements. Hydroextrusion leads to characteristic changes in the morphology of the polymer. For $\varepsilon = 15\%$, the distinct boundaries separating the globules in the original material already vanish. A further increase in ε promotes the obliteration of the relief, which is observed on the etched surfaces of the specimens, bending, crushing, and twisting of the structural elements, and the formation of what resembles an 'eddy' structure.[14]

With increase in ε, the modulus of elasticity of the high-crosslinked network EP-7 ($\nu = 9 \times 10^{20}$ cm^{-3}) increases strongly in tensile tests and diminishes in compressive tests.[178] For individual specimens, deformed to the extent of 45%, the values of E obtained in extension exceed those for the control specimens by a factor greater than 2. The density varies nonmonotonically, reaching a maximum at $\varepsilon \approx 25\%$. The dependence of the strength parameters on ε, like the dependence on ρ, passes through an extremum (Fig. 16); on extension, σ_y and σ_t vary in parallel. In

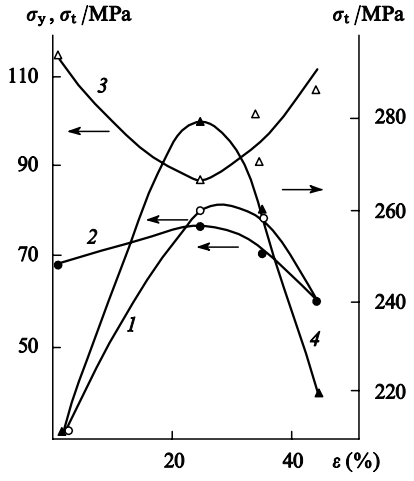


Figure 16. Dependence of the yield point σ_y (*1*, 3) and the breaking (tensile) stress σ_t (*2*, *4*) on the degree of deformation ε for EP-7. (*1*) and (*2*) extension; (*3*) and (*4*) compression.

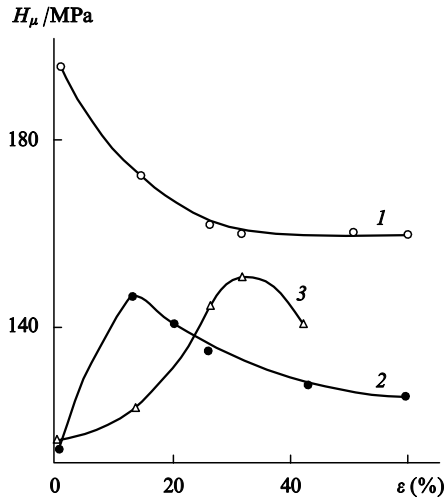


Figure 17. Dependence of the microhardness H_μ on the degree of deformation for EP-7 (*1*) and EP-5 (*2*, *3*). T_c(K): (*1*) and (*2*) 293; (*3*) 358.

compressive tests, σ_y and σ_t reach minimum and maximum values respectively at $\varepsilon = 25\%$. In both types of tests, ε_r increases and then decreases with increase in ε to 25%, while H_μ decreases monotonically for EP-7 as ε increases (Fig. 17).

The nonmonotonic variation of the $\rho(\varepsilon)$ relation for hydroextrusion is associated with the following factors. Deformation under a high hydrostatic pressure promotes the 'healing' of the micropores formed in the EP curing stage [25, 80] and the orientation of the polymer chains in the direction of the application of force leads under these conditions to the greater ordering of the structure compared with the original structure. All these features are responsible for the increase in ρ. At the same time, as ε increases, the material becomes loosened with formation of interfaces and microcavities and the intramolecular and intermolecular bonds are broken,[25, 182, 183] which leads in its turn to the appearance of cracks and a decrease in ρ. The changes in ρ noted above are undoubtedly reflected in the level of the mechanical properties of the hydroextruded polymer. This is indicated by the variation of σ_t and ε_r which is identical with that of ρ in both types of tests. The healing of the microcavities, predetermining to a large extent the strength of the continuous medium, leads to an increase in σ_t and ε_r, while the increase in porosity for $\varepsilon > 25\%$ induces an appreciable decrease in these quantities.

At the same time, the results of mechanical tests cannot be accounted for solely by the change in ρ. As already mentioned, processes involving the orientation of the chains of the macromolecules and mechanodegradation develop in EP on hydroextrusion. The orientation is probably achieved *via* the rotation of the elementary network, leading to the arrangement parallel to the direction of extrusion of the individual sections of the chains between the cross-links. For low values of ε, orientation processes predominate. They are responsible for the appearance in the polymer of internal microstresses, influencing the nature of the subsequent deformation of the specimen in tensile and compressive tests. As a result of the operation of the microstresses, the Bauschinger effect is observed:[184] the preliminary plastic deformation, induced by the extension, decreases the resistance to plastic deformation on compression. The moulding process during hydroextrusion can be regarded to a first approximation as deformation by extension (especially for a small angle of the die cone).[31] Therefore the decrease in σ_y, observed in compressive tests for specimens with $\varepsilon = 25\%$ compared with the original specimen, may be induced by the identity of the signs of the microstresses in the extrudates caused by the tension in the linear chains between the cross-links, and of the applied stresses. It is noteworthy that the changes established in the mechanical properties of the deformed high-crosslinked polymer network are similar

to the changes in the strain–strength properties of oriented crystallisable and amorphous polymers,[175] which indicates the similarity of the mechanisms of their deformation.

The study of the relaxation properties of the high-crosslinked network EP carried out on the original specimens and the extrudates has shown that, for $\varepsilon = 35\%$ and 45%, there is a sharp increase in molecular mobility induced by the loosening of the material and the partial mechanodegradation of the network.[178] The relaxation of the stress in the deformed polymer proceeds more vigorously than in the control specimen with increase in ε, the stress required for the maintenance of the specified deformation diminishes, the rate of relaxation increases, and the relaxation continues until the attainment of lower stresses. The fitting of the experimental relations with the aid of new relaxation memory functions [177] made it possible to establish that the stress relaxation process in the extruded high-crosslinked network EP is determined with equal probability by the kinetics of the interaction of the relaxators (microheterogeneities) and the kinetics of the diffusion of the nonrelaxators.[178] Compared with the original material, the number of microheterogeneities in the extrudates diminishes.

In order to increase the probability of breaks in the network, experiments have been carried out [71] on the hydroextrusion of an incompletely cured EP-1 epoxide composition. The curing of the specimens was completed after hydroextrusion. It was established that the elastic and strength properties depend only slightly on the degree of the preliminary deformation of the specimens. If the curing processes are not taken to completion, it is possible to detect at $\varepsilon = 50\%$ an increase in E by an order of magnitude compared with the undeformed specimens. Such an increase is induced by the orientation of the EP macrochain along the deformation axis. Probably a state with a high level of elastic and strength characteristics may be achieved for EP under appropriate experimental conditions when the time required for the completion of the curing of the extrudates is significantly shorter than the relaxation time of the oriented structure.

A study of the behaviour of the extruded EP having an open network ($\nu = 4 \times 10^{20}$ cm^{-3}) showed [179] that the nature of the dependences for σ_y and ε_r on ε in these materials is the same as for the high-crosslinked network EP. The difference consists only in the absolute values of σ_y and ε_r as well as the values of ε for which a change in the type of variation of σ_y and ε_r is observed; in the open network polymer (EP-5), the increase in σ_y and the fall of ε_r begin for higher values of ε. On the other hand, the dependences of E, σ_y and ρ on ε are qualitatively different. They increase over the entire range of ε. The microstructures of the original EP-5 specimens consist of globule-like formations of different dimensions. Deformation by hydroextrusion homogenises the microstructure and renders it finely disperse. On the other hand, an eddy structure is not formed up to $\varepsilon = 45\%$.

The observed differences between the changes in the microstructure, ρ, and the mechanical properties of the EP compared are associated with the different network densities and mobilities of the linear chains between the cross-links. In the more rigid polymer (EP-7), the plastic deformation processes accompanied by the rupture of the network of chemical bonds begin sooner and proceed more vigorously. In the case of EP with an open network (EP-5), they are scarcely manifested (for the range of ε investigated) in the behaviour of the integral macroscopic characteristics (ρ, E, σ_y, σ_t, ε_r). On the other hand, the use of a local method such as the procedure involving the measurement of microhardness made it possible to follow the evolution of network disruption processes even for low values of ε.[179] Fig. 17 (curve *2*) illustrates the variation of H_μ in the extrusion of EP-5 in the glassy state. The nonmonotonic variation of H_μ with increase in ε indicates competition between the orientational strengthening and disordering processes caused by the loosening of the network. In the case of EP-7, in which the degradation phenomena develop sooner, such a maximum in H_μ is probably displaced towards $\varepsilon < 15\%$, and for this reason one observes on the experimental curve only its right-hand (descending) branch (curve *1*). It is logical to suppose that, in creating more favourable conditions for the orientation of the internodal fragments in EP, the maximum under consideration should be observed for larger values of ε. The $H_\mu(\varepsilon)$ relation, presented in Fig. 17 (curve *3*), confirms this hypothesis. It was obtained for the EP-5 polymer deformed in the rubbery (non-equilibrium) state with subsequent 'freezing' of this state. Under conditions where the mobility of the linear chains between the cross-links increases significantly compared with the mobility of such chains in glassy polymers and the values of ε for which the disruption of the network is possible increase, this is reflected by the displacement of the maximum in the $H_\mu(\varepsilon)$ relation towards higher values of ε.

The behaviour in hydroextrusion of polymers of the IPN type with components differing appreciably in their rigidity is unusual. The results of studies [179, 180] carried out on the polyurethane–polyesteracrylate (PU–PEA) system suggest that mainly the elastic component (PU) undergoes orientational strengthening. The strengthening effect is achieved because the rigid network (PEA) prevents the relaxation of the stressed PU chains, creating constrains in the form of macromolecular entanglements. At a low PEA concentration, the deformation-induced strengthening, caused by hydroextrusion, is insignificant, because the density of such entanglements is low and the elastic component relaxes readily. With increase in the PEA concentration, the degree of orientational strengthening increases, but mechanodegradation processes begin to be manifested already for a PEA content of 30%. Both elastic and rigid chains are probably disrupted. The latter follows from the fact that, for PU : PEA $\geqslant$ 50 : 50, the possibility of the deformation of the IPN is reduced sharply.

The proposed explanation is supported by the following features. When the PU : PEA ratio changes from 90 : 10 to 70 : 30, the system undergoes phase separation.[185] This makes it possible to consider separately the evolution of the rigid and elastic networks during orientational stretching. It is known that in the solid-state extrusion of materials incorporating plastic and brittle (stronger) components with the former predominating, the weaker and more plastic component undergoes strengthening [186] Under these conditions the brittle phase may be disrupted with increase in ε. The role of such phases in the PU–PEA composition is assumed by the PU and PEA networks respectively.

The characteristic features of the thermal shrinkage of network polymers have been investigated [179, 180] in relation to EP and the PU–PEA system. It was established that the recovery of the original dimensions of the extruded EP when they are heated in a free state begins near the glass transition temperature ($T < T_g$) and terminates at $T \simeq T_g$ with attainment of the 100% effect. With increase in ε, the temperature of the onset of shrinkage diminishes. In contrast to linear amorphous and crystallisable polymers, network polymers have a narrower shrinkage temperature range and are characterised by the ability to retain the restored form at temperatures significantly exceeding T_g. The latter is known to be due to the presence of a network of chemical cross-links preventing the transition to the viscous flow state. The temperature of the onset of shrinkage is correlated with T_g (Fig. 18).

When extruded specimens with fixed ends are heated, the shrinkage stresses originally increase and then fall, this being accompanied by the disruption of the specimens in the vicinity of the clamps (Fig. 19). The maximum shrinkage stresses increase with increase in ε and ν. The latter fact reflects the $\sigma_{m.sh}(T_g)$ relation (Fig. 18), since ν and T_g vary in parallel in the case under consideration.[180] It is remarkable that the values of $\sigma_{m.sh}$ are approximately the same as for oriented block specimens of amorphous-crystalline polymers.

The characteristic features of the variation of the size of the oriented PU–PEA specimens during heating are on the whole similar to those established for EP: the shrinkage temperature range is comparatively narrow, the recovery of the original dimensions reaches 100%, and $T_{o.sh}$ diminishes with increase in ε. The temperature range in which the characteristic $\sigma_{sh}(T)$

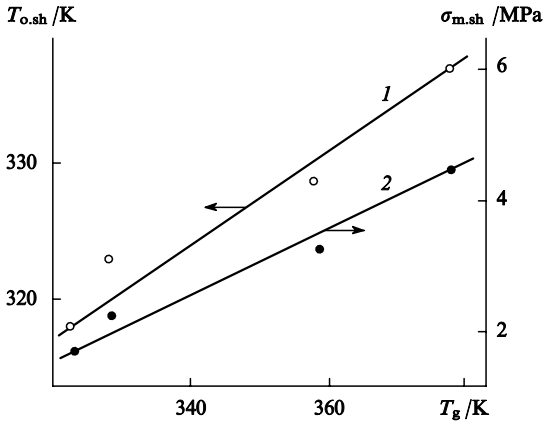


Figure 18. Dependence of the temperature of the onset of shrinkage $T_{o.sh}$ (*1*) and of the maximum shrinkage stresses $\sigma_{m.sh}$ (*2*) on the glass transition temperature T_g for EP-1.

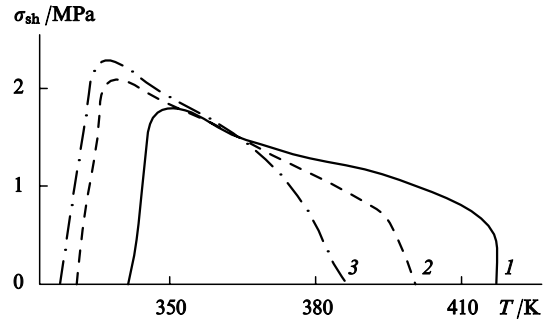


Figure 19. Temperature dependences of the shrinkage stresses (σ_{sh}) for EP-5. ε(%): (*1*) 15; (*2*) 20; (*3*) 25.

relations for the IPN investigated have an extremum (Fig. 20) indicates the dominant role of the elastic component, while the decrease in the half-width of the $\sigma_{sh}(T)$ maximum with increase in ε indicates an increase in the contribution of destructive processes (the specimens are disrupted earlier for the material with a defective structure in measurements of σ_{sh}) under these conditions. The fact that $\sigma_{m.sh}$ varies nonmonotonically (the relation has a maximum) with increase in ε is also striking. Such variation of σ_{sh} may be caused by the loosening of the network and hence by the partial relaxation of the stresses in the extrudate. The breaks on the right-hand branch of the $\sigma_{sh}(T)$ maximum for the

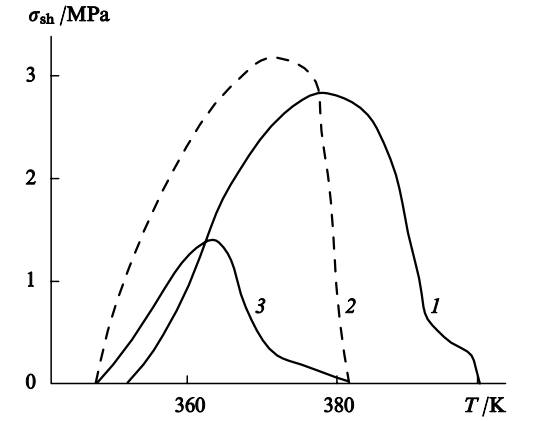


Figure 20. Temperature dependence of the shrinkage stresses for the PU–PEA IPN system containing 30 mass% of PEA. ε(%) (*1*) 25; (*2*) 30; (*3*) 40; T_e = 358 K.

PU–PEA system, preceding the disruption of the specimens, may be associated with the contribution of the rigid component.

The 'driving forces' of the thermal shrinkage of network and linear amorphous polymers [187, 188] are apparently the same. The difference consists in the fact that in the case of network polymers the twisting process involves not molecular chains but internodal fragments oriented along the deformation axis during extrusion. Evidently, depending on the nature of the molecular mass distribution, the nature of the thermal shrinkage spectrum, especially its width, should also vary in these materials. For IPN with a high degree of segregation of the components, the stress relaxation processes in different networks are separated by a temperature range. This makes it possible to identify them on the basis of the $\sigma_{sh}(T)$ relation (Fig. 20): by varying the composition and ratio of the components, it is possible to control the form of the relation, obtaining different versions of the shrinkage spectrum.

For amorphous polymers (in contrast to crystallisable ones), the version of solid-state extrusion involving the use of a powder billet has not so far come to be widely employed. Nevertheless, individual investigations indicate that this processing procedure is promising for the establishment of an oriented structure. The extrusion process and the properties of extruded DF-10 (an aromatic polyester), consisting of a composition based on a polyarylate and a copolysulfoneformal, have been investigated.[189] The results of these studies have shown that the optimum process is achieved if the extrusion temperature is 0.95–0.98 of the temperature corresponding to the transition of the polymer to the viscous flow state and $\lambda \approx 6-7$. Table 10 presents the strain–strength characteristics of DF-10 in tests involving compression and three-point bending (nicked specimens). Evidently, with increase in λ, the modulus of elasticity changes only slightly, whereas σ_y and σ_t increase appreciably. At the same time the plasticity of the material increase. These features are correlated with those established earlier for hydroextruded amorphous polymers.[172–175]

Table 10. The properties of DF-10 specimens obtained by the plunger extrusion of a powder billet.

λ	Compression					Bending		
	E /GPa	σ_y, /MPa	ε_y (%)	σ_t /MPa	ε_r /MPa	E /GPa	σ_t /MPa	ε_r /MPa
1	1.5	82	6.0	81	37	1.1	108	13
3	1.4	95	6.0	130	44	1.3	109	12
4	1.5	91	6.0	120	40	1.4	118	12
5	1.5	91	6.5	140	40	1.3	115	12
6	1.5	103	8.0	175	58	1.2	115	12
7	1.6	107	8.0	180	50	1.4	129	18

3. Polymer blends and reinforced compositions

Polymer systems consisting of polymer blends and reinforced compositions have been vigorously investigated in recent years. One of the reasons for the increased interest of investigators in these materials is their great potential possibilities as regards regulation of mechanical properties. However, there have been extremely few studies on the solid-state extrusion of polymer blends and reinforced compositions. The possibility of obtaining oriented block specimens of the LDPE–PP system by the hydrostatic extrusion method has been examined.[190] Uniaxial solid-state extrusion of such compositions is difficult owing to the weak interfacial interaction of the components caused by their thermodynamic incompatibility. In order to eliminate this obstacle, various procedures are resorted to, for example, radiation-induced or photochemical cross-linking.[191, 192] Deformation under the conditions of a high hydrostatic pressure made it

possible to abandon these procedures and to achieve higher values of λ without disruption of the material.[190]

The change in the mechanical properties of polymer blend specimens on compression and extrusion as a function of λ corresponds to the change in these properties established for extruded PE and PP specimens.[135, 175] The thermal shrinkage characteristics of the blends have a number of unusual features. An increase in the content of PP increases the shape stability of the extrudates (the residual deformation). At the same time there is an increase in the values of σ_{sh} and in the width of the shrinkage temperature range (Fig. 21). For all the PP concentrations, the increase in λ entails also an increase in $\sigma_{m.sh}$.

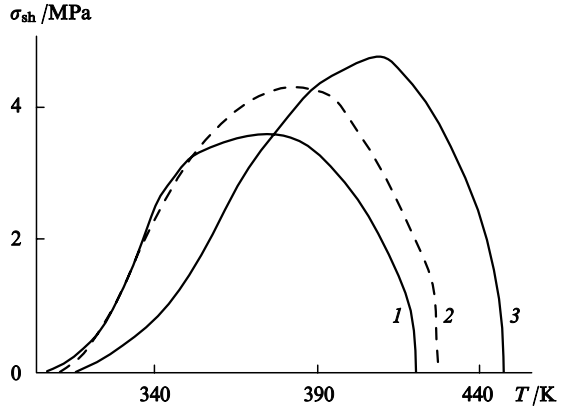


Figure 21. Temperature dependences of the shrinkage stresses σ_{sh} for the LDPE – PP blends. LDPE content (mass%): (*1*) 90; (*2*) 80; (*3*) 40; $\lambda = 3$

Analysis of the results of the study of Beloshenko *et al.*[190] established that the thermal shrinkage mechanisms in the LDPE – PP compositions and in LDPE are similar. At low PP concentrations, the stressed LDPE chains play the main role in the shrinkage process. With increase in the content of PP, the contribution of this phase to the establishment of the thermal shrinkage effect increases, which is manifested by the increase in $\sigma_{m.sh}$ and in the shape stability of the extrudates. The PP phase hinders the relaxation processes in the material: the temperatures at which the internal stresses are fully relaxed are displaced towards the region of higher T_m for the polyethylene phase. However, owing to the occurrence of phase separation, the observed changes are relatively small. The $\sigma_{sh}(T)$ relations for the blends in the region of the descending branch of the maximum differ from the relations established [191] for crosslinked compositions: at $T < T_m$ for polypropylene, the right-hand branch of the maximum passes to a plateau. This fact can be explained by the formation during cross-linking of a network of chemical cross-links intensifying the interfacial interaction. In the hydroextrusion of noncrosslinked compositions, one is dealing merely with the appearance of additional physical cross-links, the network of which is unstable during annealing, and also with a decrease in the stresses at the interfaces compared with the stresses in the course of uniaxial extrusion as a result of the favourable deformation scheme. Nevertheless the result obtained is of definite practical interest, since the expansion of the range of σ_{sh} increases the functional possibilities of the material.

The behaviour of amorphous and crystalline films specimens of the polyether-ether-ketone – polyester-imide (PEEK – PEI) system subjected to uniaxial extrusion by the coextrusion method has been studied.[116] The latter was achieved at temperatures below T_g (amorphous films) or below and above the crystallisation temperature (crystallisable films). The influence of extrusion on T_g, crystallisation and the degree of orientation was noted. In the case of amorphous films of the PEEK – PEI system, extrusion lowers the glass transition temperature of the polymer blend, although the density of the specimens increases somewhat under these conditions. The degree of orientation of these films increases with increase in the PEEK concentration. In the crystallisable films, the density diminishes monotonically with increase in A and extrusion intensifies the crystallisation process during the subsequent annealing of the films.

The traditional method for the preparation of reinforced polymer compositions is mechanical blending of the components. In the 1970s, a fundamentally new method for the introduction of fillers was proposed — the polymerisation filling method, which makes it possible to obtain polymer compositions directly in the course of the synthesis of the polymer.[193, 194] One of the promising aspects of the polymerisation filling method involves the creation of compositions based on SHMPE. Such materials have strain – strength parameters similar to those of SHMPE, but are harder, have a higher modulus of elasticity, and are more resistant to wear.[195] At the same time they are greatly superior to activation-reinforced compositions as regards deformability and impact strength.[195] The characteristic features of the solid-state extrusion process and the mechanical properties of extrudates of reinforced compositions based on SHMPE have been investigated.[161, 167, 196 – 200] The extrusion was carried out with the aid of the method proposed in a patent,[159] using polymer powder billets.

The extrusion parameters and the properties of the extrudates for a series of compositions investigated, measured in compressive tests, are presented in Table 8. The variation of E, σ_t, and ε_r for the SHMPE – kaolin system is analogous to that observed for SHMPE with the sole difference that the introduction of kaolin increases the limiting value of λ, the rigidity, and the strength, but reduces the deformability of the material. For other compositions, dependences of E and σ_t on λ with an extremum are observed, the values of λ corresponding to the maxima in the characteristics diminishing in the sequence kaolin $\rightarrow$ Al $\rightarrow$ Al(OH)$_3$. The last composition has the lowest level of strain – strength properties.

Comparison of the properties of the extruded compositions with those of control specimens obtained by hot pressing revealed an increase in rigidity and strength during solid-state extrusion for all the compositions investigated. The deformability diminishes at the same time. This feature is manifested even more strikingly in tensile tests.[196] Appreciable changes in ρ during the variation of λ have not been observed for the SHMPE – kaolin systems. For other compositions, ρ diminishes with increase in λ.

The extrusion draw ratio is known [201] not to reflect the real deformation of the macromolecules (λ_m) in oriented polymers. For reinforced compositions, the discrepancy between λ and λ_m is greater than for unreinforced ones, because the former quantity is calculated in relation to the entire volume of the polymer, whereas only part of it (the polymer matrix) is actually deformed. In order to eliminate this, a corrected molecular draw ratio has been introduced:[167]

$$\lambda'_m = \frac{\lambda_m}{1 - \varphi},$$

where φ is the volume degree of filling. The inequality $\lambda'_m < \lambda$ holds for SHMPE and $\lambda'_m > \lambda$ is valid for reinforced compositions. This relation between the parameters considered reflects the differences in the mechanisms of the deformation of SHMPE and the compositions based on it. For higher values of λ, the polymer macromolecules are disrupted at the polymer – filler boundary, which lowers the effective density of the network of macromolecular entanglements. This tends to increase λ'_m and has a positive effect on E. However, owing to the loosening of the interfaces, the fraction of free cavities increases with increase in λ, which leads to a decrease in E. For $\lambda > 5$, the second effect predominates and this induces a decrease in E for the reinforced compositions (Table 8).

The above conclusion has been confirmed by measurements of ρ and by the results of a study of the rupture surfaces of the extrudates.[198] For low values of λ, the surface relief of the break is homogeneous, which indicates a satisfactory adhesion between

SHMPE and the filler. In the case where $\lambda \geqslant 7$, the inhomogeneity of the relief, induced by the loss of adhesion at the polymer – filler boundary and hence by the rupture of the material at this boundary, can be easily seen.

For the majority of the compositions investigated, σ_t varies with λ in parallel with E and reaches the maximum values in the region $\lambda = 4-6$ (Table 8). Fig. 22 presents the dependences of the limiting extrusion draw ratio corresponding to the rupture of the specimen in mechanical tests (λ_r) as a function of the extrusion draw ratio. The values of λ_r were determined from the formula [202]

$$\lambda_r = 1 + \varepsilon_r .$$

Evidently λ_r increases with increase in λ (for oriented polymers, an increase in λ diminishes λ_r as a consequence of the exhaustion of the mobility of the molecular chains).[31] On the basis of the above findings, one can also postulate that the rupture of the extruded compositions is related directly to the presence of fillers, namely to the breakdown of the continuity of the specimens owing to the loosening of the polymer – filler boundaries and the formation of numerous microcracks. On deformation of the specimen in the course of mechanical tests, the microcracks formed during extrusion aggregate and the specimen is ruptured.

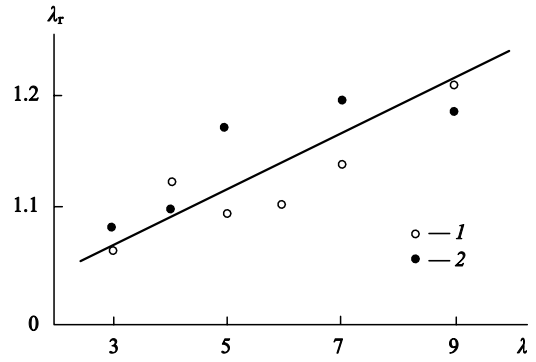


Figure 22. Dependence of the limiting draw ratio λ_r on the draw ratio λ for the SHMPE – 70 mass% Al (*1*) and SHMPE – 45 mass% of bauxite (*2*) systems.

The difference between the strain – strength properties of the SHMPE – kaolin compositions and the analogous properties of other compositions is caused primarily by the shape of the filler particles. The kaolin particles have the shape of plates, while the Al and $Al(OH)_3$ particles are spherical. The presence of particles anisotropic as regards shape promotes the appearance of an intense interfacial interaction, manifested in the partially cohesive mechanism of the destruction of the SHMPE – kaolin compositions.[203] At the same time, owing to the weak interaction at the polymer – filler interface, the fully adhesive rupture mechanism operates for the SHMPE – $Al(OH)_3$ system.

A mathematical model has been proposed for the solid-state extrusion of polymer composites.[204] It is based on the idea that the formation and 'healing' of microcavities are possible on deformation under conditions of high pressure. Relations have been obtained which make it possible to calculate the density of the extrudate and to plot it against λ. Comparison of the calculated and experimental values of ρ showed that the model describes adequately the plunger extrusion of a powder billet comprising polymerisation-reinforced compositions. At the same time, it can be used to predict the defectiveness of polymeric materials also in other processing schemes involving high pressures.

V. Conclusion

The data presented show that a high pressure is frequently used in theoretical and technological research and that its role in the structure modification of polymers is considerable and varied. The methods involving treatment with pressure examined in the review may be used for the effective control of shaping processes and of the structure and properties of polymeric materials with different structures. However, the functional possibilities of the different ways of achieving the modifying effect of pressure are not the same. Thus crystallisation or curing under pressure make it possible to obtain objects in the form of a block, as a rule cylindrical in shape, which limits the range of their practical applications. On the other hand, the substances formed in series-connected IPN (preparation of a prepolymer) or in oligomeric products serve as starting components for more complex compounds. The latter are manufactured under traditional conditions, which tends to expand their applications. For example, the IPN can be used as adhesives and also for the preparation of bulky polymeric articles of different shape and for different purposes. Finished articles, which do not require further mechanical treatment, can be usefully subjected to annealing under pressure, because favourable changes in the material take place to the greatest extent in its surface layer.

The results of the study of solid-state extrusion indicate the considerable potential possibilities of this method in the processing of not only flexible-chain polymers but also of rigid-chain network polymers, polymer blends, and reinforced compositions. As a result of the plasticising effect under the influence of high hydrostatic pressure, it is possible to achieve an orientational order in polymers and polymer composites which are brittle and difficult to work. The appearance of such order is accompanied by an improvement in the strain – strength properties of the materials or by the establishment in the latter of a qualitatively new state (the shape memory effect, a negative Poisson ratio).

One may hope that further studies of the application of the isostatic treatment or solid-state extrusion for the structural modification of polymers will help in discovering new aspects of the influence of high pressure which are of interest from both theoretical and practical points of view.

References

1. P W Bridgman *Rev. Mod. Phys.* **18** (1) (1946)
2. P W Bridgman *Studies in Large Plastic Flow and Fracture* (London: McGraw-Hill, 1952)
3. K Swenson *Physics at High Pressure* (New York: Academic Press, 1960)
4. M G Gonikberg *Khimicheskoe Ravnovesie i Skorost' Reaktsii pri Vysokikh Davleniyakh* (Kinetic Equilibrium and Reaction Rate at High Pressure) (Moscow: Khimiya, 1969)
5. H L D Pugh (Ed.) *Mechanical Behaviour of Materials under Pressure* (Amsterdam: Elsevier, 1970)
6. V I Zaitsev *Fizika Prochnosti i Plastichnosti Gidrostaticheski Szhatykh Kristallov* (The Physics of the Strength and Plasticity of Hydrostatically Compressed Crystals) (Kiev: Naukova Dumka, 1983)
7. A N Pilyankevich (Ed.) *Vliyanie Vysokikh Davlenii na Veshchestvo* (The Influence of High Pressures on Matter, Vol. 1) (Kiev: Naukova Dumka, 1987)
8. V L Kolmogorov *Napryazheniya, Deformatsii, Razrusheniya* (Stresses, Deformations, Degradations) (Moscow: Metallurgiya, 1970)
9. L V Prozorov, A A Kostava, V D Revtov *Pressovanie Metallov Zhidkost'yu Vysokogo Davleniya* (Pressing of Metals by a Liquid under High Pressure) (Moscow: Mashinostroenie, 1972)
10. A I Kolpashnikov, V V Vyalov *Gidropressovanie Metallov* (Hydropressing of Metals) (Moscow: Metallurgiya, 1973)
11. A A Galkin, A P Getmanskii *Pressovanie Metallov Zhidkost'yu* (Pressing of Metals by a Liquid) (Donetsk: Donbass, 1974)
12. B I Beresnev, E V Trushin *Protsess Gidroekstruzii* (The Hydroextrusion Process) (Moscow: Nauka, 1976)
13. M V Mal'tsev, E D Doron'kin, K I Ezerskii *Gidrostaticheskaya Obrabotka Tugoplavkikh Metallov* (Hydrostatic Processing of High-Melting Metals) (Moscow: Metallurgiya, 1978)

14. B I Beresnev, K I Ezerskii, E V Trushin *Fizicheskie Osnovy i Prakticheskoe Primenenie Gidroekstruzii* (Physical Foundations and Practical Use of Hydroextrusion) (Moscow: Nauka, 1981)
15. B I Beresnev (Ed.) *Vliyanie Vysokikh Davlenii na Veshchestvo* (The Influence of High Pressures on Matter, Vol. 2) (Kiev: Naukova Dumka, 1987)
16. B I Beresnev, K I Ezerskii, E V Trushin, B I Kamenetskii *Vysokie Davleniya v Sovremennykh Tekhnologiyakh Obrabotki Materialov* (High Pressures in Modern Technologies for the Processing of Materials) (Moscow: Nauka, 1988)
17. P J James (Ed.) *Isostatic Pressing Technology* (London: Applied Science Publ., 1979)
18. R B Dow *Chem. Phys.* **7** 201 (1939)
19. W Parks, R B Richards *Trans. Faraday Soc.* **45** 203 (1949)
20. C E Weir *J. Res. Natl. Bur. Stand.* **46** 207 (1951)
21. C E Weir *J. Res. Natl. Bur. Stand.* **50** 95 (1953)
22. P W Bridgman *J. Appl. Phys.* **24** 560 (1953)
23. K D Pae, S K Bhateja *J. Macromol. Sci., C* **13** 1 (1975)
24. S K Bhateja, K D Pae *J. Macromol. Sci., C* **13** 77 (1975)
25. S B Ainbinder, E L Tyunina, K I Tsirule *Svoistva Polimerov v Razlichnykh Napryazhennykh Sostoyaniyakh* (Properties of Polymers in Various Stressed States) (Moscow: Khimiya, 1981)
26. A Ya Gol'dman *Ob'emnoe Deformirovanie Plastmass* (Volume Deformation of Plastics) (Leningrad: Mashinostroenie, 1984)
27. K Kishore, R Vasanthakumari *High Temp.-High Pres.* **16** 241 (1984)
28. A L Kovarskii *Vysokomol. Soedin., Ser. A* **28** 1347 (1986) [a]
29. V F Skorodumov, Yu K Godovskii *Vysokomol. Soedin., Ser. B* **35** 214 (1993) [a]
30. E V Prut, in *High-Pressure Chemistry and Physics of Polymers* (Ed. A L Kovarskii) (Boca Raton, FL: CRC Press, 1994) p. 341
31. A Ciferri, I M Ward (Eds) *Ultra-High Modulus Polymers* (London: Applied Science Publ., 1979)
32. S Matsuoka, B Maxwell *J. Polym. Sci.* **32** 131 (1958)
33. T Takemura *Am. Chem. Soc., Polym. Prepr.* **20** 270 (1979)
34. D V Rees, D C Bassett *J. Polym. Sci., Part A-2* **9** 385 (1971)
35. P D Calvert, D R Uhlmann *J. Polym. Sci., Part A-2* **10** 1811 (1972)
36. A Peterlin *Polymer* **6** 25 (1965)
37. D V Rees, D C Bassett *Nature (London)* **219** 368 (1986)
38. B Wunderlich, L Melillo *Macromol. Chem.* **118** 250 (1968)
39. J L Kardos, H-M Li, K A Huckshold *J. Polym. Sci., Part A-2* **9** 2061 (1971)
40. B Wunderlich *Macromolecular Physics* Vols 1, 2 (New York: Academic Press, 1973, 1976)
41. D C Bassett, B Turner *Nature (London)* **240** 146 (1972)
42. S Matsuoka *J. Polym. Sci.* **42** 511 (1960)
43. Y Miyato, C Nakafuku, T Takemura *Polym. J.* **3** 122 (1972)
44. G P Andrianova *Fiziko-Khimiya Poliolefinov* (The Physical Chemistry of Polyolefins) (Moscow: Khimiya, 1974)
45. T Arakava, B Wunderlich *J. Polym. Sci., Part A-2* **4** 53 (1966)
46. R Hasegava, Y Tanabe, M Kobayashi, H Tadokoro, A Sawaoka, N Kawai *J. Polym. Sci., Part A-2* **8** 1073 (1970)
47. W W Doll, J B Lando *J. Macromol. Sci., B* **4** 889 (1970)
48. W W Doll, J B Lando *J. Macromol. Sci., B* **2** 219 (1968)
49. V M Baranovskii, A M Tarara, S I Bondarenko, V P Skvortsov, A I Nepomnyashchii *Plast. Massy* (3) 52 (1992)
50. A M Tarara, V M Baranovskii, S I Bondarenko, A A Khomik, V A Tsendrovskii, V V Lapinskii *Plast. Massy* (2) 13 (1995)
51. C L Gruner, B Wunderlich, R C Bopp *J. Polym. Sci., Part A-2* **7** 2099 (1969)
52. Yu F Zubov, V I Selikhova, M B Konstantinopol'skaya, F F Sukhov, N A Slovokhotova, N F Bakeev, A V Kryukov, V A Sokol'skii, G P Belov *Vysokomol. Soedin., Ser. A* **14** 2090 (1972) [a]
53. D C Bassett, D R Carder *Philos. Mag.* **28** 513 (1973)
54. D C Bassett, D R Carder *Philos. Mag.* **28** 535 (1973)
55. A I Petrov, M V Razuvaeva, A B Sinani, V I Betekhtin *Mekhanika Kompozit. Mater.* 1121 (1989)
56. A I Shul'gin, I O Kurochkina, V A Aulov *Vysokomol. Soedin., Ser. B* **33** 224 (1991) [a]
57. *Primenenie Poliolefinov, Polistirolov, Ftoroplastov i Polivinilatsetatnykh Plastikov. Katalog* [Application of Polyolefins, Polystyrenes, Fluoroplastics and Poly(Vinyl Acetate Plastics)] (Cherkassy: NIITEKhIM, 1981)
58. V A Beloshenko, V G Slobodina, S A Tsygankov, V M Shepel' *Fiz. Tekhn. Vys. Davl.* **1** (2) 85 (1991)
59. Ya E Beigel'zimer, V A Beloshenko, E V Prut *Vysokomol. Soedin., Ser. B* **37** 2085 (1995) [a]
60. R E Wetton, H G Moneypenny *Br. Polym. J.* **7** 51 (1975)
61. G J Kogowsky, F E Filisko *Macromolecules* **19** 828 (1986)
62. A A Shturman *Plast. Massy* (2) 47 (1989)
63. A A Shturman *Plast. Massy* (11) 51 (1990)
64. O E Ol'khovik, E M Blyakhman *Vysokomol. Soedin., Ser. B* **18** 36 (1976) [a]
65. V A Beloshenko, V I Zaika, M K Pakter, V M Shepel' *Fiz. Tekhn. Vys. Davl.* (33) 82 (1990)
66. V A Beloshenko, M K Pacter, B I Beresnev, V I Zaika, T P Zaika *High Pres. Res.* **6** 203 (1994)
67. B I Beresnev, M K Pakter, V A Beloshenko, V I Zaika *Dokl Akad. Nauk Ukr. SSR* **9B** 28 (1989)
68. M K Pakter, V A Beloshenko, B I Beresnev, T P Zaika, L A Abdrakhmanova, N I Bezai *Vysokomol. Soedin., Ser. A* **32** 2039 (1990) [a]
69. V A Beloshenko, M K Pakter, G I Sviridov *Ukr. Khim. Zh.*. **61** 68 (1995)
70. M G Evans, M Polanyi *Trans. Faraday Soc.* **31** 875 (1935)
71. J K Lee, K D Pae *J. Macromol. Sci., B* **32** 78 (1993)
72. B V Ozerkovskii, V D Plotnikov, V P Roshchupkin *Vysokomol. Soedin., Ser. A* **25** 1816 (1983) [a]
73. B I Beresnev, V A Beloshenko, M K Pakter, G T Evtushenko, E V Amosova *Dokl. Akad. Nauk Ukrainy* **3** 119 (1991)
74. V A Beloshenko, M K Pacter, V N Varyukhin *Acta Polym.* **46** 328 (1995)
75. V A Beloshenko, M K Pakter, B I Beresnev, T P Zaika, V G Slobodina, V M Shepel' *Mekhanika Kompozit. Mater.* 195 (1990)
76. V A Bershtein, V M Egorov *Differentsial'naya Skaniruyushchaya Kalorimetriya v Fizikokhimii Polimerov* (Differential Scanning Calorimetry in Physical Chemistry of Polymers) (Leningrad: Khimiya, 1990)
77. N Katsuhiko, N Takashi, A Xu, T Kohro *Polym. J.* **23** 1157 (1991)
78. V I Irzhak, B A Rozenberg, N S Enikolopyan *Setchatye Polimery. Sintez, Struktura, Svoistva* (Network Polymers. Synthesis, Structure, and Properties) (Moscow: Nauka, 1979)
79. A V Grachev, M R Kiselev Yu M Sivergin *Vysokomol. Soedin., Ser. A* **27** 1197 (1985) [a]
80. Yu S Zaitsev, Yu S Kochergin, M K Pakter, R V Kucher *Epoksidnye Oligomery i Kleevye Kompozitsii* (Epoxy-Oligomers and Adhesive Compositions) (Kiev: Naukova Dumka, 1990)
81. I Z Chernin, F M Smekhov, Yu V Zherdev *Epoksidnye Polimery i Kompozitsii* (Epoxy-Polymers and Compositions) (Moscow: Khimiya, 1982)
82. V G Khozin, A A Polyanskii, Yu M Budnik, V A Voskresenskii *Vysokomol. Soedin., Ser. A* **24** 2308 (1982) [a]
83. V S Kuksenko, M I Karyakina, N V Maiorova, T A Prokof'eva, A I Slutsker *Mekh. Polim.* **1** 157 (1974)
84. V A Beloshenko, M K Pakter, T P Zaika, G V Borisenko *Fiz. Tekhn. Vys. Davl.* **2** (1) 16 (1992)
85. V A Beloshenko, G V Borisenko, G T Evtushenko, G I Sviridov *Fiz. Tekhn. Vys. Davl.* **3** (4) 34 (1993)
86. V B Gupta, L T Drzal, W W Adams *J. Mater. Sci.* **20** 3439 (1985)
87. P G Babaevskii, I G Agapov, S V Bukharov, A E Chalykh, V V Matveev *Vysokomol. Soedin., Ser. B* **35** 1697 (1993) [a]
88. M K Pakter, V A Beloshenko, G V Borisenko *Fiz. Tekhn. Vys. Davl.* **2** (4) 115 (1992)
89. L Sperling *Interpenetrating Polymer Networks and Related Materials* (New York: Plenum, 1981)
90. D S Lee, S C Kim *Macromolecules* **17** 268 (1984)
91. D S Lee, S C Kim *Macromolecules* **17** 2193 (1984)
92. D S Lee, S C Kim *Macromolecules* **17** 2222 (1984)
93. D S Lee, S C Kim *Macromolecules* **18** 2173 (1985)
94. V A Beloshenko, L G Nechitailo, G I Sviridov, V F Stroganov, V P Privalko *Ukr. Polym. J.* **3** 49 (1993)
95. L G Nechitailo, V A Beloshenko, V P Privalko, V F Stroganov *Ukr. Khim. Zh.*. **61** 133 (1995)
96. V A Beloshenko, V F Stroganov, S P Bufistov, V V Korskanov *Ukr. Khim. Zh.*. **62** 138 (1996)
97. Yu S Lipatov, V F Rosovitskii *Dokl. Akad. Nauk SSSR* **283** 910 (1985) [b]

98. D Thomes, L Sperling *Polymer Blends* (Eds D R Paul, S Newman) (New York: Academic Press, 1978)
99. V F Stroganov, V M Mikhal'chuk, Yu S Zaitsev, L I Maklakov, Yu S Lipatov *Dokl. Akad. Nauk SSSR* **292** 670 (1987) [b]
100. M K Pakter, V A Beloshenko, A N Daragan, G I Sviridov *Zh. Prikl. Khim.* **66** 2086 (1993) [c]
101. M A Shcheblanova, S Z Rogovina, L V Vladimirov, A N Zelenetskii, M A Markevich, N S Enikolopyan *Dokl. Akad. Nauk SSSR* **226** 390 (1976) [b]
102. M A Tovmasyan, A N Zelenetskii, V V Ivanov, G A Grigoryan, O B Salamatina *Vysokomol. Soedin., Ser. A* **25** 862 (1983) [a]
103. M A Tovmasyan, A N Zelenetskii, V V Ivanov *Vysokomol. Soedin., Ser. A* **26** 1848 (1984) [a]
104. M F Sorokin, L G Shode *Zh. Org. Khim.* **2** 1463 (1966) [d]
105. M F Sorokin, L G Shode *Zh. Org. Khim.* **2** 1469 (1966) [d]
106. V M Zhulin, in *Fizicheskaya Khimiya. Sovremennye Problemy. Ezhegodnik* (Physical Chemistry. Current Problems. Yearbook) (Ed. Ya M Kolotyrkin) (Moscow: Khimiya, 1984) p. 144
107. S A Zahir, S Bantle, in *Epoxy Resin Chemistry. The 2nd Symposium of the 183rd Meeting of the American Chemical Society (Abstracts of Reports), Las Vegas, 1982* p. 245
108. J H Southern, R S Porter *J. Appl. Polym. Sci.* **14** 2305 (1970)
109. N E Weeks, R S Porter *J. Polym. Sci., Polym. Phys. Ed.* **12** 635 (1974)
110. N Capiati, S Kojima, W Perkins, R S Porter *J. Mater. Sci.* **12** 334 (1977)
111. J Clements, R Jakeways, I M Ward *Polymer* **19** 639 (1978)
112. W T Mead, C R Desper, R S Porter *J. Polym. Sci., Polym. Phys. Ed.* **17** 859 (1979)
113. J A Sauer, K D Pae, S K Bhateja *J. Macromol. Sci.* **8B** 631 (1973)
114. J H Southern, G L Wilkes *J. Polym. Sci., Polym. Phys. Ed.* **11** 555 (1973)
115. Y H Lee, R S Porter *J. Macromol. Sci., Phys.* **34** 295 (1995)
116. H L Chen, R S Porter *Macromolecules* **28** 3918 (1995)
117. R S Porter, L H Wang *J. Macromolecul. Sci., Rev. Macromol. Chem. Phys.* **C 35** 63 (1995)
118. A N Kryuchkov, A O Baranov, I Ya Dorfman, N A Erina, E V Prut, N S Enikolopyan *Vysokomol. Soedin., Ser. A* **26** 1993 (1984) [a]
119. I Ya Dorfman, A N Kryuchkov, E V Prut, N S Enikolopyan *Dokl. Akad. Nauk SSSR* **278** 141 (1984) [b]
120. A G Korchagin, M A Martynov, S A Tsygankov *Vysokomol. Soedin., Ser. B* **27** 335 (1985) [a]
121. N S Enikolopyan, B I Beresnev, G D Myasnikov, E V Prut, S A Tsygankov, A V Kryuchkov, N V Shishkova *Dokl. Akad. Nauk SSSR* **219** 368 (1986) [b]
122. A G Gibson, I M Ward *J. Mater. Sci.* **14** 1838 (1979)
123. R Gupta, P G McCormick *J. Mater. Sci.* **15** 619 (1980)
124. P S Hope, A G Gibson, I M Ward, *J. Polym. Sci., Polym. Phys. Ed.* **18** 1243 (1980)
125. S Abdul Jawad *Indian J. Technol.* **24** 709 (1986)
126. S A Tsygankov, N V Shishkova, B I Beresnev *Fiz. Tekhn. Vys. Davl.* (17) 77 (1984)
127. A G Korchagin, M A Martynov, S A Tsygankov *Vysokomol. Soedin., Ser. A* **26** 2529 (1984) [a]
128. S A Tsygankov, N V Shishkova, B I Beresnev *Fiz. Tekhn. Vys. Davl.* (19) 57 (1985)
129. S A Tsygankov, I Yu Khanukov, N V Shishkova, G D Myasnikov, B I Beresnev *Fiz. Tekhn. Vys. Davl.* (23) 70 (1986)
130. K Nakayama, H Kanetsuma *J. Mater. Sci.* **12** 1477 (1977)
131. J B Sahary, B Parsons, I M Ward *J. Mater. Sci.* **20** 346 (1985)
132. A A Turetskii, O Yu Zinov'eva, M B Konstantinopol'skaya, V A Aulov, Yu A Zubov, N F Bakeev *Vysokomol. Soedin., Ser. A* **31** 1644 (1989) [a]
133. N Inoue, T Nakayama *Technocrat* **10** 23 (1977)
134. H N Yoon, K D Pae, J A Sauer *J. Polym. Sci., Polym. Phys. Ed.* **14** 1611 (1976)
135. S A Tsygankov, N V Shishkova, B I Beresnev *Fiz. Tekhn. Vys. Davl.* (26) 74 (1987)
136. G D Myasnikov, S A Tsygankov *Plast. Massy* (2) 34 (1985)
137. B I Beresnev, N S Enikolopov, S A Tsygankov, N V Shishkova *Dokl. Akad. Nauk Ukr. SSR* **4B** 47 (1985)
138. E V Slavnov, V M Timofeev *Vest. Perm Gos. Tekhnol. Univ., Mekhanika* **2** 188 (1995)
139. P V Zamotaev, V A Beloshenko *Zh. Prikl. Khim.* **67** 1863 (1994) [c]
140. F Decandia, R Russo, V Vittoria *J. Polym. Sci., Polym. Phys. Ed.* **20** 1176 (1982)
141. W Chen, K Xing, L Sun *Rad. Phys. Chem.* **22** 593 (1983)
142. V I Dankin, V L Karpov *Vysokomol. Soedin., Ser. B* **25** 130 (1983) [a]
143. R J Yan, Y Luo, B Jiang *J. Appl. Polym. Sci.* **47** 789 (1993)
144. M Hoff, Z Pelzbauer *Polymer* **32** 3316 (1991)
145. P Zamotaev, T Privalko, O Mitukhin, V Bogdanovich *Ukr. Polym. J.* **1** 221 (1992)
146. J Spells, P Sadler *Macromolecules* **22** 3941 (1989)
147. B D Caddock, K E Evans *J. Phys. D., Appl. Phys.* **22** 1877 (1989)
148. K E Evans, B D Caddock *J. Phys. D., Appl. Phys.* **22** 1883 (1989)
149. K L Anderson, K E Evans *Polymer* **33** 4435 (1992)
150. R Lakes *Science* **235** 1038 (1987)
151. K E Evans *Chem. Ind.* **20** 654 (1990)
152. A C Eringen *J. Math. Mech.* **15** 909 (1966)
153. A C Smith *Int. J. Eng. Sci.* **6** 65 (1968)
154. P D Griswald, A E Zachariades, R S Porter *Polym. Eng. Sci.* **18** 861 (1978)
155. G T Pawlikowski, D S Mitchell *J. Polym. Sci., Part B, Polym. Phys.* **26** 1865 (1988)
156. T Kanamoto, T Ohama, K Tanaka, M Takeda *Polymer* **28** 1517 (1987)
157. R S Porter, in *Macroakron 94. The 35th IUPAC International Symposium on Macromolecules (Abstracts of Reports), Akron, OH, 1994* p. 598
158. T Kameda, A Yamane, T Kanamoto, M Ito, R S Porter *Vysokomol. Soedin., Ser. A* **38** 1152 (1996) [a]
159. USSR P. 1 839 148; *Byull. Izobret.* (47–48) 101 (1993)
160. Russ. P. 2 083 369; *Byull. Izobret.* (19) (1997)
161. V A Beloshenko, G V Kozlov, V N Varyukhin, V G Slobodina *Acta Polym.* **48** 181 (1997)
162. G V Kozlov, V A Beloshenko, V G Slobodina, E V Prut *Vysokomol. Soedin., Ser. B* **38** 1056 (1996) [a]
163. E A Egorov, V V Zhizhenkov, V A Marikhin, L P Myasnikova, A Popov *Vysokomol. Soedin., Ser. A* **25** 693 (1983) [a]
164. L Mandelkern *Polym. J.* **17** 337 (1985)
165. P J Flory, D Y Yoon, K A Dill *Macromolecules* **17** 862 (1984)
166. D Y Yoon, P J Flory *Polymer* **18** 509 (1977)
167. V A Beloshenko, G V Kozlov, V G Slobodina, E V Prut, V G Grinev *Vysokomol. Soedin., Ser. B* **37** 1089 (1995) [a]
168. G V Kozlov, V A Beloshenko, V M Varyukhin, V U Novikov *Zh. Fiz. Dosl.* **1** 204 (1997)
169. Ya V Genin, D Ya Tsvankin, S N Salazkin, V A Sergeev *Vysokomol. Soedin., Ser. B* **31** 74 (1989) [a]
170. H Okuyama, T Kanamoto, R S Porter *J. Mater. Sci.* **29** 6485 (1994)
171. Y D Wang, M Cakmak, F W Harris *J. Appl. Polym. Sci.* **56** 837 (1995)
172. N Inoue, T Nakayama, in *Proceedings of the 23rd Japan Congress on Material Research, Tokyo, Kyoto, 1980* p. 287
173. B I Beresnev, S A Tsygankov, N V Shishkova, K A Vylegzhanina, O K Belomutskaya, B S Polonskii, E E Manusevich *Dokl. Akad. Nauk Ukr. SSR* **7B** 42 (1987)
174. N Inoue, T Nakayama, T Ariyama *J. Macromol. Sci.* **19B** 543 (1981)
175. T Nakayama, N Inoue *Bull. Jpn. Soc. Mech. Eng.* **20** 688 (1977)
176. A A Askadskii, V A Beloshenko, K A Bychko, V V Shaposhnikova, A V Samoryadov, O V Kovriga, S N Salazkin, V A Sergeev, V G Slobodina, Ya V Genin *Vysokomol. Soedin., Ser. A* **36** 1143 (1994) [a]
177. A A Askadskii *Mekhan. Kompozit. Mater.* 403 (1987)
178. A A Askadskii, V A Beloshenko, M K Pakter, K A Bychko, M P Valetskii *Vysokomol. Soedin., Ser. A* **33** 2206 (1991) [a]
179. V A Beloshenko, V N Varyukhin, T P Zaika, S I Skiba, V I Sheludchenko *Fiz. Tekhn. Vys. Davl.* **6** (1) 65 (1996)
180. V A Beloshenko, P V Zamotaev, O P Mityukhin, L M Sergeeva, V F Stroganov *Zh. Prikl. Khim.* **69** 1203 (1996) [c]
181. V M Lantsov, M K Pakter, in *Reaktsionnosposobnye Oligomery i Materialy na Ikh Osnove. Khimicheskii Analiz i Fiziko-Khimicheskie Issledovaniya (Metody, Metodiki i Rekomendatsii po Ikh Primeneniyu)* [Reactive of Oligomers and Materials Based on Them. Chemical Analysis and Physicochemical Studies (Methods and

Recommendations Concerning Their Use)] (Cherkassy: NIITEKhIM, 1987) p. 75
182. A A Askadskii *Deformatsiya Polimerov* (Deformation of Polymers) (Moscow: Khimiya, 1973)
183. P G Cheremskoi, V V Slezov, V I Betekhtin *Pory v Tverdom Tele* (Pores in Solid) (Moscow: Energoatomizdat, 1990)
184. L S Moroz *Mekhanika i Fizika Deformatsii i Razrusheniya Materialov* (Mechanics and Physics of the Deformation and Fracture of Materials) (Moscow: Mashinostroenie, 1984)
185. Yu S Lipatov, L M Sergeeva, L V Karabanova, V F Rosovitskii, S I Skiba, N V Babkina *Vysokomol. Soedin., Ser. A* **30** 649 (1988) [a]
186. Yu F Chernyi, V Z Spuskanyuk, A A Lyadskaya, A I Opanashchuk *Gidropressovanie Instrumental'nykh Stalei* (Hydropressing of Tool Steels) (Kiev: Tekhnika, 1987)
187. N I Shishkin, M F Milagin *Mekhan. Polim.* **3** 323 (1966)
188. N I Shishkin *Mekhan. Polim.* **5** 787 (1972)
189. Russ. P. 2 105 670; *Byull. Izobret.* (16) (1998)
190. V A Beloshenko, P V Zamotaev, O P Mityukhin, V G Slobodina *Fiz. Tekhn. Vys. Davl.* **5** (3) 43 (1995)
191. P V Zamotaev, I Khodak, S A Sergienko *Zh. Prikl. Khim.* **66** 2071 (1993)
192. V P Gordienko *Radiatsionnoe Modifitsirovanie Kompozitsionnykh Materialov na Osnove Poliolefinov* (Radiation-Induced Modification of Composite Materials Based on Polyolefins) (Kiev: Naukova Dumka, 1985)
193. F S D'yachkovskii, L A Novokshonova *Usp. Khim.* **53** 200 (1984) [*Russ. Chem. Rev.* **53** 117 (1984)]
194. L A Novokshonova, I N Meshkova *Vysokomol. Soedin.* **36** 629 (1994) [a]
195. L O Bunina, V A Teleshov, V I Sergeev, S B Ainbinder, K I Tsirule *Plast. Massy* (8) 13 (1985)
196. V A Beloshenko, V N Varyukhin, G V Kozlov, V G Slobodina, iIn *High Pressure Science and Technology* (Ed. W A Trzeciakowski) (Singapore: World Sci. Publ., 1996) p. 153
197. G V Kozlov, M A Gazaev, V O Beloshenko, V M Varyukhin, V G Slobodina *Ukr. Fiz. Zh.* **40** 883 (1995)
198. G V Kozlov, V A Beloshenko, T P Zaika, V G Grinev *Plast. Massy* (6) 29 (1995)
199. G V Kozlov, V A Beloshenko, V G Slobodina *Plast. Massy* (3) 14 (1996)
200. V A Beloshenko, V G Slobodina, V G Grinev, E V Prut *Vysokomol. Soedin., Ser. B* **36** 1021 (1994) [a]
201. M P C Watts, A E Zachariades, R S Porter *J. Mater. Sci.* **15** 426 (1980)
202. A S Argon, M I Bessonov *Philos. Mag.* **35** 917 (1977)
203. I L Dubnikova, A I Petrosyan, V A Topolkaraev, Yu M Tovmasyan, I N Meshkova, F S D'yachkovskii *Vysokomol. Soedin., Ser. A* **30** 2345 (1988) [a]
204. Ya E Beigel'zimer, V A Beloshenko, A P Borzenko, V N Varyukhin *Mekhan. Kompozit. Mater.* **31** 834 (1995)

[a] — *Polym. Sci. (Engl. Transl.)*
[b] — *Dokl. Chem. Technol., Dokl. Chem. (Engl. Transl.)*
[c] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[d] — *Russ. J. Org. Chem. (Engl. Transl.)*