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Solid-Phase Technologies for Manufacture of Products from Polytetrafluoroethylene

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Abstract

The paper considers the main theoretical, experimental and technological results of the study of solid-phase processes of ram extrusion, compaction and die forging of polymeric materials based on polytetrafluorethylene. The experimental data were systematized; they allowed concluding about general regularities of the formation process and the structure formation in the materials. The rheological approach is proposed to find the optimal conditions for compacting polymeric powder billets. The main aspects of mathematical modeling of solid-phase extrusion and compaction based on direct consideration of structuring, densification and extrusion of viscoelastic polymer systems are discussed. The examples of practical application of solid-phase methods for manufacture of products from polymer materials are given.

Keywords

Solid phase technology; polytetrafluoroethylene; forging; polymer; composite; deformation.

Introduction

Manufacturing of products of a given shape and size from powder materials or solid preforms is an important issue of industrial application of polymers and composites based on them. In the most common traditional methods of processing polymeric materials, catalysts and solvents and long-term heating technological processes are used in products to transfer the material into a viscous-flowing or highly elastic state and its subsequent cooling. This raises a number of fundamental difficulties associated with the heterogeneous spatial-temporal temperature distribution, and the duration of operations limits the overall productivity of the processing equipment. In the manufacture of products from polymers, cost-effective methods of machining are often used; this method results in a large amount of waste in the form of chips. Therefore, it is important to create alternative technologies for the manufacture of products made of polymer materials. The development of environmentally friendly and resource-saving technological processes of solid-state technology, which are devoid of the aforementioned shortcomings, remain important. Using solid-phase technologies, materials with high quality parameters can be produced by plastic deformation of the material under conditions of high hydrostatic pressure (volumetric and sheet stamping, solid-phase and hydrostatic extrusion, pressing, rolling, etc.).

This paper discusses the main theoretical, experimental and technological results of solid-state processes of ram extrusion, compaction and die forging of polymeric materials obtained in the studies of the Basic Research Program of the OCHNM of the Russian Academy of Sciences No. 7 and No. III.5 “Safe and resource-saving chemical-technological processes. Testing processes to obtain experimental batches of substances and materials”. Particular attention is given to the methodological aspects of the insufficiently studied problem of forming polymeric materials. The moldability criterion as a property of the molding process is defined. The experimental studies have been systematized, making it possible to draw conclusions about the general laws of the molding process and the associated process of structure formation in materials. A method of free compression is proposed to determine the specified criterion, not tied to a specific technological equipment. A rheological approach to finding the optimum conditions for pressing polymer powder preforms is discussed. The main aspects of mathematical modeling of solid-phase extrusion and compaction based on direct consideration of the processes of structuring, compaction and extrusion of viscoelastic polymer systems are highlighted; this is the key to a correct understanding of the laws of high-temperature compaction and molding of finished products from fluoroplastic powders. The examples of practical application of solid-phase methods for obtaining products from polymer materials are given.

A rheological approach to finding optimal pressing conditions for powdered polymer performs

Powder materials are specific rheological objects. The study of their behavior during deformation, taking into account their porosity, constitutes an independent field of research and is of interest for obtaining products from polymer powders.

The most important question in the pressing of powders is the establishment of a relationship between the applied pressure and the density of compacts. For this purpose, a large number of experiments are carried out under conditions of static loading in the regime of constant pressure P = const [1]. However, in this case, there are methodological difficulties associated with the uncertainty of the experiment since the compaction process is essentially non-stationary and the degree of compaction is continuously changing with time. Therefore, the density corresponding to the preset pressure depends also on the duration of the pressing process. If we assume that the density should be understood as its maximum value, then this value also depends on the holding time under pressure. For different materials, the conditions for manufacturing integral preforms with an optimum density are usually found empirically.

In [2], a rheological approach to finding the optimum conditions for pressing polymer powders is discussed; according to this approach, the relative change in the density or volume of the material is deformation. The compaction of powders and their formability are considered as nonstationary deformation processes, which depend on rheological factors [3]. This approach makes it possible to understand the deformation mechanisms of powder materials and find their rheological properties. Its essence lies in the experimental study of stress-strain curves in the regime of constant rate of deformation (and non-constant pressure). These curves are invariant to the equipment and shape of the preform. It is important to note that these curves are obtained continuously from one experiment [4]. Thus, within the framework of the proposed approach, it is much easier to estimate the required pressure values that provide preset density values of the preform. On this basis, the necessary pressure is selected to ensure the given density value.

To study the effect of structural factors on the compaction kinetics of various fluoroplastic grades (different molecular weight of the polymer, the morphology of the powder particles and the regularity of their structure, particle size, flowability, etc.), 5 grades were chosen in [5–7]: F-4; F-4D; F-4M; “Forum”, “Fluralite”. Their choice is connected with the desire to investigate the compactability of a variety of produced and practically used fluoroplastics, differing in morphology, dispersion, specific surface area and contact area of particles.

Pre-pressing is the preparatory technological stage in the preparation of PTFE products, which precedes the thermal treatment of articles in the furnace at a temperature of 360–380 °C. The study of the compaction of powders is necessary to select the pressing conditions – pressing pressure and holding time under pressure. The pressing mode should provide the optimum value of density, which causes a certain level of strength properties of the preform for subsequent sintering. These structural factors affect the change in density during compaction. However, the effect of the initial structure of the powder on the compacting kinetics the powder material has not been studied sufficiently.

The experiments were carried out in a mold at room temperature in a constant speed mode. The loading rate in all cases was 5 mm/min. For all grades, the total weight of the sample was 4 g. The diameter of the mold-pouring chamber was 12 mm. The powder was poured into the mold and placed under the plunger of the universal testing machine “INSTRON” with a 2-coordinate recorder. The maximum force caused by pouring was 1 ton [5].

The height of the bulk layer for each brand was different. F-4 and grades F-4M, F-4D are hydrophobic materials that are easy to electrify and cake. During storage and transportation, these powders are caked in a lumpy, non-friable mass, which must first be loosened prior to pressing to break up the lumps and ensure uniform filling of the powder in the mold. Therefore, the concept of bulk density can be conditionally applied to these grades. Forum and fluralite have good flowability, so that the bulk density of these powders can be measured with great accuracy. As a result of the experiments, the pressure-time curves were plotted, on the basis of which the

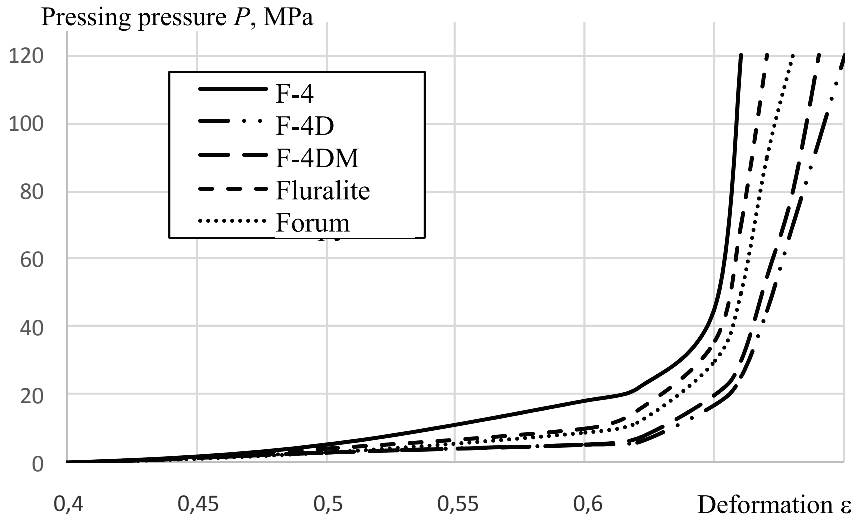


Fig. 1. Dependence of strain on pressure for fluoroplastic powders

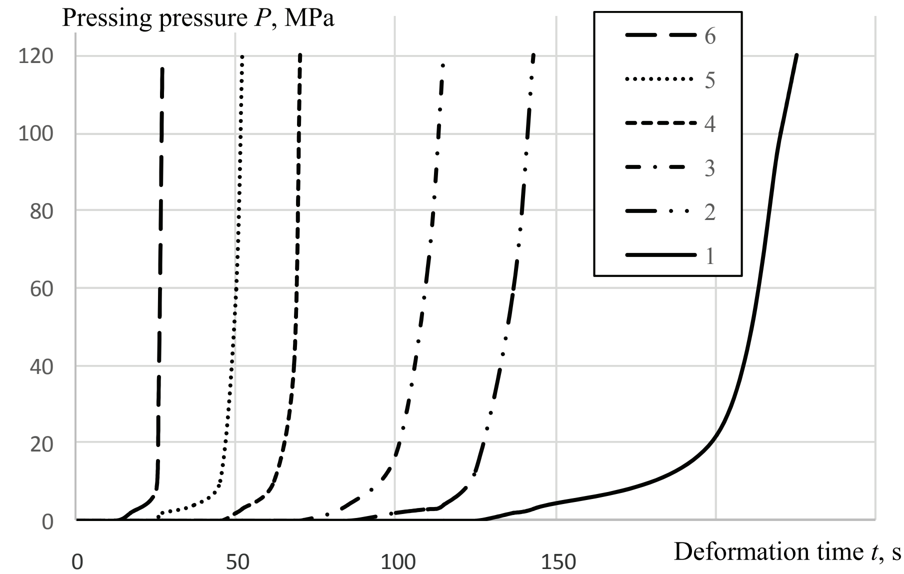


Fig. 2. "Pressing pressure-time" diagram for different loading rates for polymer F-4, mm/min:
1 – 5; *2* – 7.5; *3* – 10; *4* – 15; *5* – 20; *6* – 30

rheological pressure-strain curves were constructed, which made it possible to determine the rheological properties of the polymer material, to reveal deformation mechanisms, and to determine the optimal moldability conditions for the powdered polymer. The latter can be chosen through the analysis of the rheological curve of "pressure-deformation" (Fig. 1), constructed on the basis of the "pressure-time" curve. Deformation is calculated by the formula:

$$\varepsilon = \Delta h / h_{\text{in}},$$

where h_{in} is initial height of the bulk layer, Δh is change in the height of the bulk layer over time. In the assumption of uniformity of deformation, the stress can be assumed equal to the pressure on the plunger of the press.

The experiments have shown that the rate of deformation strongly influences the character of the dependence of the pressing pressure on time. For example, for polymer F-4, this dependence is shown in Fig. 2.

For the "pressure-deformation" dependence, there are 3 stages of deformation common to all brands (Fig. 3). The first (I) stage is accompanied by a linear increase in stresses with increasing deformation due to the movement of powder particles into the pores, and it does not require considerable effort.

The second stage of deformation in the range from 0.32 to 0.41 % corresponds to a nonlinear rise in stress with increasing deformation. At this stage, the movement of particles occurs due to their accommodation among themselves and partly due to the deformation of particles [8]. This stage requires great effort for further heterogeneous deformation of the material. It is this stage that is of greatest technological interest, since plastic deformation accumulates in the material. However, the plastic state does not occur at all points of the material [9], so it is difficult to choose the plasticity condition for porous materials [10].

In the third stage, when the stress is increased over a wide range, a small change in the strain occurs. In this case, the compaction process occurs, mainly, due to the growth of the contact surface during deformation of the particles.

For the selected systems, such properties as the compressibility modulus *G*, the finite value of deformation of the linear section of the stress-strain curve ε*, the compressibility coefficient k_{com} were determined. Table 1 shows the values of these properties for the investigated grades at a loading rate of 5 mm/min. The compressibility modulus is numerically equal to the tangent of the slope angle of the linear portion of the stress-strain diagram. The numerical value of the relaxation time can be

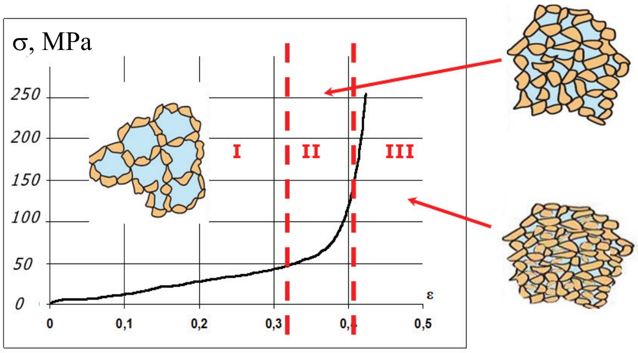


Fig. 3. Main stages of deformation of powder materials

Table 1

Rheological parameters of the investigated brands

Fluoroplastic grade	Parameters		
	G, MPa	ε^*	K_{com}, Pa^{-1}
F-4	1	0.5	1
F-4d, F-4M	10.24	0.57	0.09
Forum, Fluralite	13.89	0.59	0.07

determined by extrapolating the nonlinear part of the pressure-time curve to the time axis. The compressibility coefficient characterizes a reversible decrease in the height (volume) of the sample under the action of pressure and is quantitatively determined by the formula:

$$k_{com} = -\frac{1}{h_{in}}\frac{\Delta h'}{\Delta p'},$$

where $\Delta h'$ and $\Delta p'$ are limiting values of the height and pressure changes of the linear section. In terms of physical meaning, it characterizes the ability of the material to compact at the initial (linear) stage, during which the compaction intensity is maximal.

It is noteworthy that powdered polymers are an object of a special nature, and from the rheological point of view, little has been studied and an important question arises: how to correctly measure the rheological properties of these materials. Their specific features, in comparison with the objects of classical rheology, make it impossible to apply the known schemes and methods of experimental rheology, to make anew the study of viscosimetric flows, rheological coordinates, instruments and methods for solving the inverse problem. The solution of these problems, together with the development of the instrument base and the accumulation of experimental data, including the dynamics of structural transformations in the process of deformation, is the content of the scientific direction – rheology and rheodynamics of powder materials [11, 12].

Mathematical modeling of solid phase extrusion of fluoropolymers

The first experiments on the development of solid-phase extrusion processes revealed the need for technological parameters to enter the optimal area, for which the method of mathematical modeling proved effective. A theoretical description of the process of solid-state plunger extrusion of fluoropolymer materials was carried out in [13–17], taking into account rheodynamics, heat transfer, structuring, and kinetics of condensation of a compressible medium. A non-isothermal mathematical model of the process of solid-phase ram extrusion (**SPRE**) of a viscous structured material is presented. An important point of the theoretical description is the allowance for the dependence of viscosity on the density of the compressible material, temperature and structural parameter.

The development of the solid-phase extrusion process depends on a variety of effects: the mode parameters (the press plunger speed, the pressure on the plunger), the intrinsic properties of the material (bulk and shear viscosities and their dependence on density, temperature, structural parameters), thermal and boundary conditions, thermophysical properties and their dependence on density, geometry of the device and the sample. These factors determine the values of the characteristic times of the main processes: extrusion, compaction, thermal relaxation and structural transformations.

As part of the proposed approach, the dynamics of the deformation process of structured systems was analyzed. Using a numerical study of the problem for technological parameters corresponding to the solid-phase extrusion of fluoropolymers, the possibility of oscillatory modes of deformation was theoretically shown. The results of the investigations were compared with the experimental studies of the instability of solid-phase extrusion of fluoropolymers.

The SPRE experiments on fluoropolymer materials (F-4) in the velocity range 0.083–0.83 m/s were carried out on an Instron machine at room temperature [16, 17]. The rods were used as preforms, r_0 was the initial radius of the preform equal to $2.5 \cdot 10^{-3}$ m, H_0 is the initial height of the preform

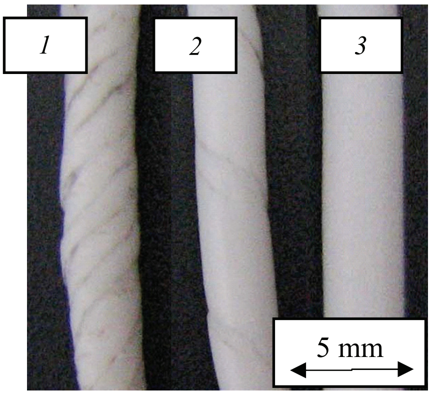


Fig. 4. Photo of the extrudate surface at different degrees of reduction: the radii (r_1) of the die:
1 – $r_1 = 1.1 \cdot 10^{-3}$ m; 2 – $r_1 = 1.25 \cdot 10^{-3}$ m; 3 – $r_1 = 1.9 \cdot 10^{-3}$ m

$15 \cdot 10^{-3}$ m, r_1 is the draw die radius that changed in the experiment ($1.9 \cdot 10^{-3}$ m, $1.25 \cdot 10^{-3}$ m, $1.1 \cdot 10^{-3}$ m).

Fig. 4 shows photographs of the extrudate surface for various degrees of reduction, which is equal to the fraction of the cross-sectional area of the loading chamber divided by the cross-sectional area of the capillary. For the maximum die radius, $r_1 = 1.9 \cdot 10^{-3}$ m, the average extrusion pressure P_{av} was 50 MPa, pressure oscillations in time are practically absent, as a result of which the surface of the extrudate is smooth (Fig. 4, sample No. 3). As can be seen, the extrusion process proceeded in an unstable mode – periodic oscillations arose over the entire surface of the sample, resulting in samples with an inhomogeneous extremely dense structure. In this case, the medium after the ultimate compaction became hard, and in the material periodic stress oscillations can occur in time. This result corresponded to the physical concepts of the onset of unstable extrusion modes of materials [12] in a solid state. For the intermediate diameter of the die $r_1 = 1.25 \cdot 10^{-3}$ m, the value of $P_{av} = 100$ MPa, which was twice as high as for $d_{die} = 3.8$ mm. There were significant fluctuations in pressure over time, as a result of which helical formations characteristic of flow instability propagated along the cylindrical surface of the extrudate (Fig. 4, sample No. 2). For the minimum diameter of the die $r_1 = 1.1 \cdot 10^{-3}$ m, the average value of the extrusion pressure was higher than in the two previous cases and was equal to 135 MPa (Fig. 4, sample No. 1). The frequency and amplitude of the pressure oscillations in time increased sharply, so that on the surface of the extrudate, spiral-like defects reduced the pitch and increased quantitatively. In this case, the sample lost integrity and broke up into separate spiral-like filaments.

For comparison with experimental data, numerical calculations of solid-phase rem extrusion of fluoropolymers at a given rate were performed. The parameters of the model corresponded to the experimental conditions. In Fig. 5 the pressures on the press plunger are plotted against time for two limiting cases: the time of structural changes was much longer than the deformation time (Fig. 5*a*, the small die radius) and the time of structural changes was much shorter than the deformation time (Fig. 5*b*, large die radius) . In the first case, the stress caused small-scale oscillations against the background of its general rise. It can be assumed that the result of these oscillations was the helical formations on the surface of the extruded sample observed in the experiment (Fig. 4, sample No. 1). In the second case, the samples were

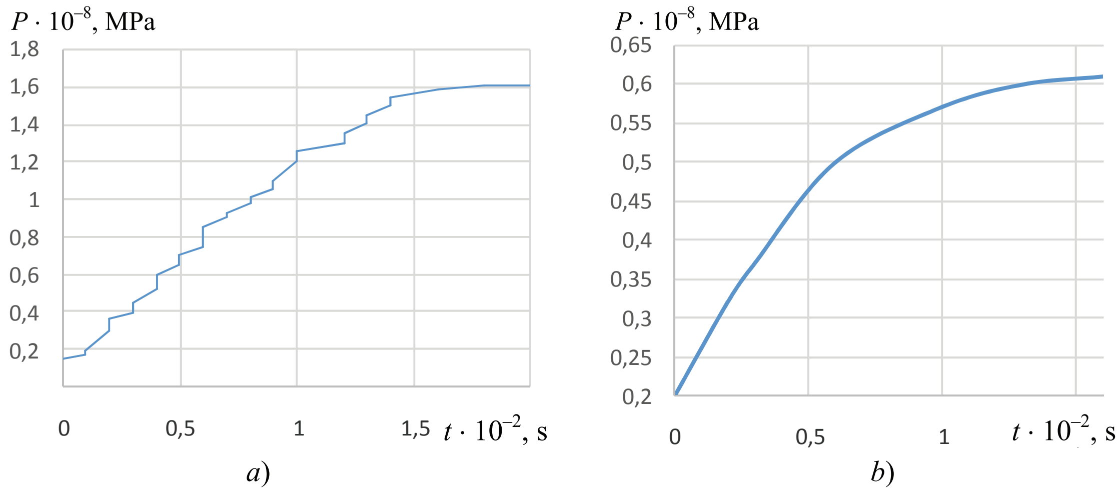


Fig. 5. Dependence of pressure *P* on time *t* for different degrees of reduction (different die radii r_1):
a – $r_1 = 1.1 \cdot 10^{-3}$ m; *b* – $r_1 = 1.9 \cdot 10^{-3}$ m; parameters: $r_0 = 5 \cdot 10^{-3}$ m; $t_{extr} = 180$ s; press velosity $V = 0.83 \cdot 10^{-4}$ m/s

obtained with a smooth surface, but they were not compacted. Transition modes of structuring and compaction lie between these extreme cases

To expand the capabilities of solid-phase methods of molding products, ultrasonic treatment is often used, which has a significant effect on the process of plastic deformation of materials and allows reducing porosity and improving the quality of products. However, in theory, the use of ultrasound in pressing and extrusion of powder materials has not been studied sufficiently. It is known that ultrasonic, as well as mechanical vibrations are often used to intensify various technological processes. Therefore, at first glance, it seems strange that ultrasonic exposure leads to an increase in the extrusion time, and not to a decrease in it. One can propose the following explanation for this experimental fact. In the extrusion of porous materials, there are cases of successive flow of compaction and extrusion processes. Since ultrasound affects both of these processes, the extrusion velocity of the material as it becomes denser slows down and the extrusion time increases.

To verify the presented explanation of the obtained experimental results, mathematical modeling of the effect of ultrasonic action on the process of deformation of porous viscoelastic material was made, taking into account the real rheological behavior of these materials and the process of structural transformations [18]. It was shown that the influence of a sound wave leads to a reduction in porosity and a decrease in its gradient, which should favorably affect the quality of the products. The theoretical justification was given for the experimentally observed increase in extrusion time under ultrasonic action. The mathematical model developed in this work makes it possible to qualitatively evaluate the influence of ultrasonic action on the properties of the material being extruded.

Molding of polymeric materials

One of the main issues in the development of solid-phase methods is the evaluation of moldability of polymeric materials, which is determined by the set of their rheological, thermophysical and physical-mechanical properties [19].

The description of the molding process can be constructed on the analysis of specific technological processes of extrusion, pressing or stamping. However, the approach based on the study of the general features of the molding process that is not related to specific process equipment is more important. This approach requires the solution of a number of methodological issues, and, first of all, the determination of the molding properties of the material itself.

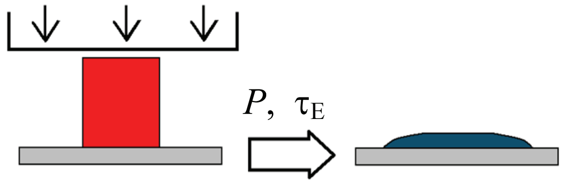


Fig. 6. The scheme of free uniaxial compression:
P – pressing pressure; t_E – time of aging of the material at a given pressure

To study the ability of polymeric materials to be molded, a free compression method is proposed. The essence of which lies in the deformation with constant velocity of cylindrical preforms from the polymeric materials under study at a given pressure and temperature of the initial heating (Fig. 6).

It is proposed to determine moldability for polymeric materials as a measure of the ability of a material to undergo shear deformation in a given pressure and temperature range. As a criterion for the formability of materials, it is proposed to use the degree of deformation:

$$\psi = (S_k - \text{Si}) / \text{Si},$$

where S_k is cross-sectional area of deformed material, Si is cross-sectional area of the initial preform. Thus, as a main property of the molding process, it is possible to use the dependencies of the degree of deformation of the material on the pressing pressure and the heating temperature of the initial samples.

For example, for fluoroplastic F-4 experiments were conducted at heating temperatures from room temperature to 100 °C and at pressures of 1 to 3.5 MPa (Fig. 7). As can be seen from the obtained dependences, without heating the preforms at low pressing pressures, the material exhibited a low plastic deformation ability. This result can be explained by the lamellar packing of PTFE macromolecules, which facilitated the sliding of the chains relative to each other, providing the ability to cool flow. When the pressing pressure was increased to 3.5 MPa, the degree of deformation increased to 0.77. When heating 60–100 °C in the whole range of pressure changes, the maximum value of the deformation $\psi = 0.95$ was achieved at low pressures (1 MPa), and further pressure increase did not lead to a marked improvement of the material formability. This range of temperature changes at low pressures of 1–1.5 MPa can be taken as optimal for processing PTFE in the solid phase. Using the experimental data obtained, the

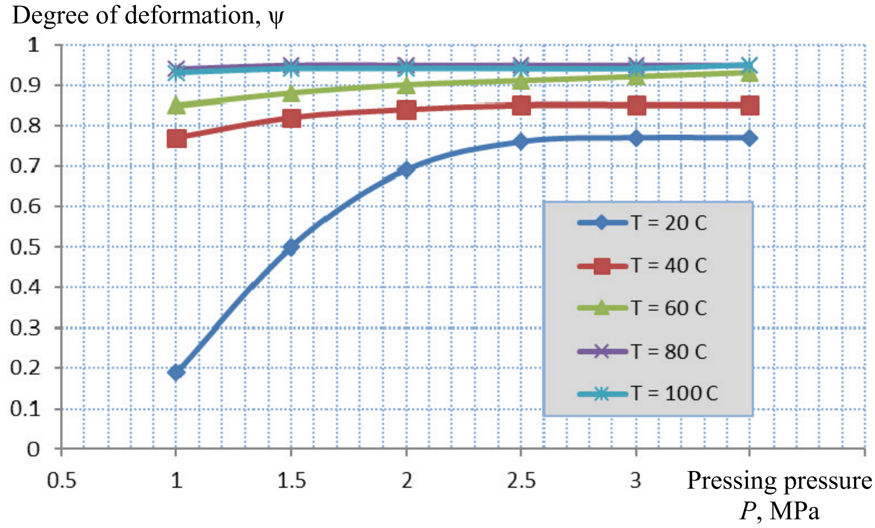


Fig. 7. Correlation between the deformation degree, the pressing pressure and the heating temperature for the initial samples of F-4

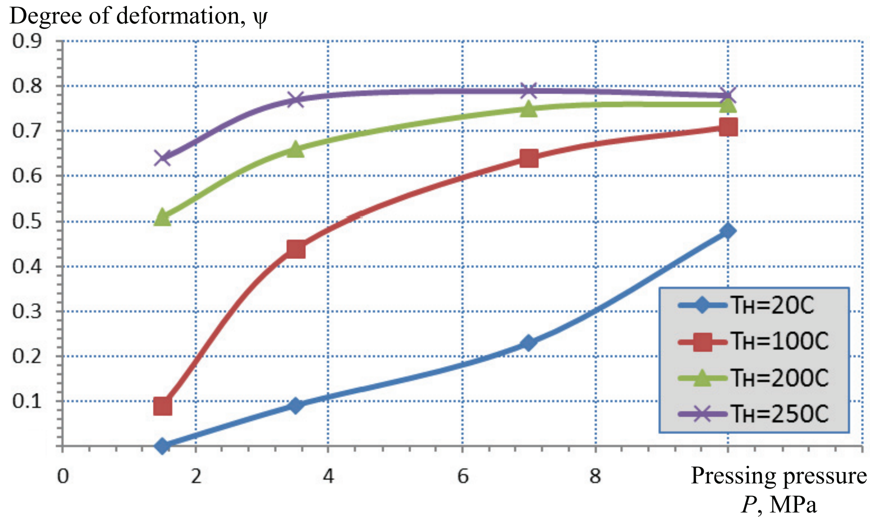


Fig. 8. Correlation between the deformation degree, the pressing pressure and the heating temperature for the initial samples of PA-6

optimum pressing pressure intervals and the heating temperature of the initial samples were determined without reference to the competitive equipment, and conclusions were drawn about the ability of the material to be molded.

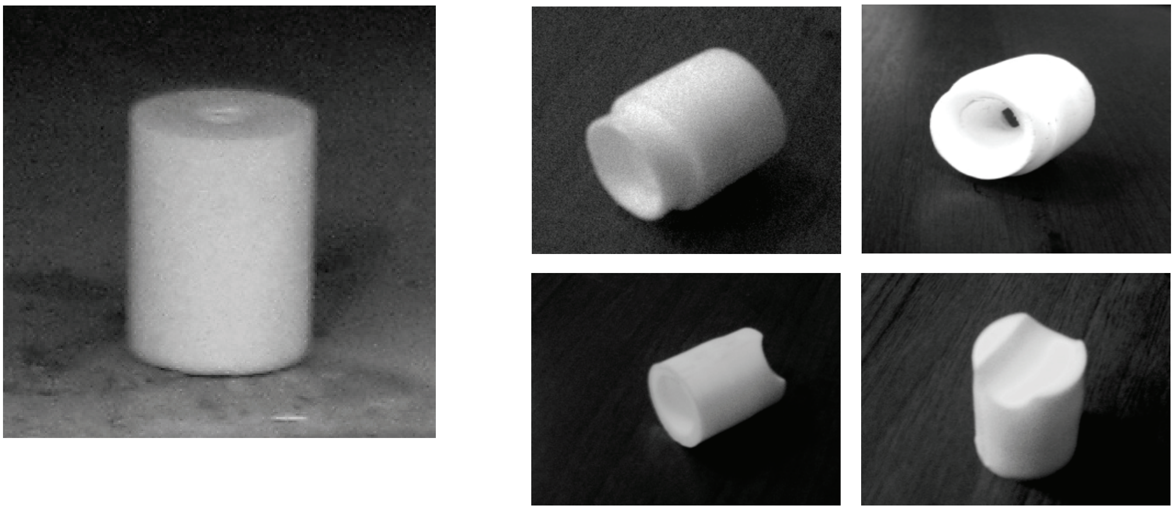
Polyamide PA-6 behaves in a similar way, but unlike fluoroplastic, it is more sensitive to pressure and temperature variations and does not have the ability to cool in the absence of heating. This is expressed in a more pronounced dependence of the strain on the pressing pressure and the heating temperature. Polyamide has good moldability when heated above 200 °C and pressing pressure 4 MPa and above. At low pressures and temperatures, solid-phase treatment is not recommended, since the formability of PA-6 under these conditions is low (Fig. 8).

Practical applications of solid-phase processes

Practical applications of solid-phase technological processes for manufacture of products from various functional gradient polymeric and composite materials are promising [20–22]. For example, die forging from fluoroplastic-4 in the solid state in a closed mold of the plunger type has its own peculiarities. The preform is a monolith, close in shape to the product (Fig. 9*a*). Preliminary the volume of the preform was calculated to obtain the required linear dimensions and the volume of the final product, taking into account the material compressibility of 7–8 %. Based on the theoretical and experimental studies, a pilot batch of insulators of various configurations was produced (Fig. 9*b*).

The most important parameters of the solid-phase stamping process are the preform temperature, the mold temperature, the holding time under pressure, and the pressure and molding speed. These parameters depend on the material, the configuration of the product, its shape and size. Compared with casting under pressure, the speed of manufacture by die forging is almost independent of the thickness or the total volume of products.

Fig. 10 shows the sealing cuffs of the hydraulic cylinders of the BELAZ vehicle suspension made of PTFE-4, obtained by industrial method (Fig. 10, *1*, *2*) and by die forging (Fig. 10, *3*, *4*). The experience has shown that product samples obtained by die forging are characterized by dimensional stability over a wider temperature range and less shrinkage than samples produced by an industrial method at a temperature above T_m, which is due to a reduction in the share of linear thermal shrinkage during deformation at a lower temperature. The products have elevated physicomechanical parameters caused by the physicochemical processes occurring in the material and the more ordered structure of the polymer.



a) *b*)

Fig. 9. Preform of fluoroplastic F-4 for the “Insulator” product (*a*), various configurations of the “Insulator” product (*b*)

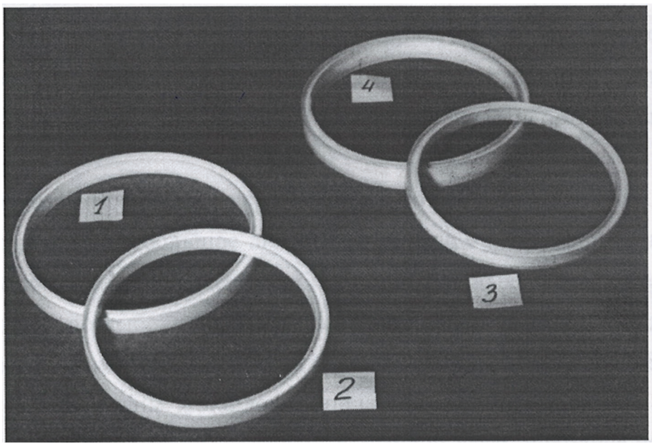


Fig. 10. Sealing cuffs made of fluoroplastic-4 for the hydraulic cylinders of BELAZ vehicle suspension made by the industrial method (*1*, *2*) and cuffs made by die forging from the circular preforms (*3*, *4*)

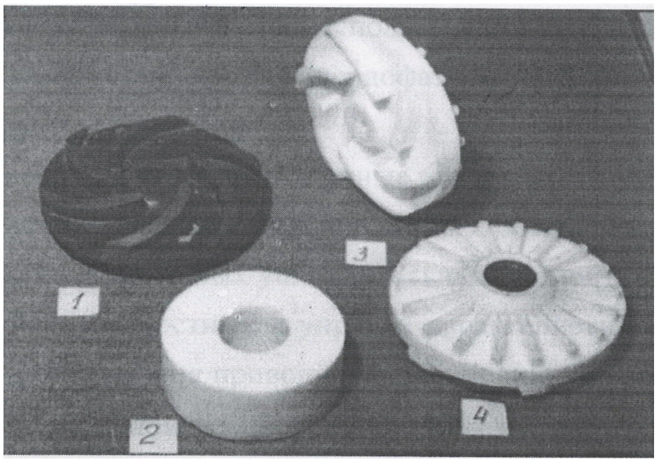


Fig. 11. Metal polymer impellers of a centrifugal pump:
1 – pump impeller from ATM-1; *2* – initial preform from F-4 for forging of the pump impeller; *3*, *4* – metal fluoroplastic impellers made by die forging

Fig. 11 shows metal fluoroplastic impellers of a centrifugal pump made by forging in a solid phase. Materials based on polytetrafluoroethylene largely meet the requirements imposed on the impellers of centrifugal pumps operating in an aggressive environment. Die forging of impellers of fluoroplastic pumps was performed on a 120-ton hydraulic press in specially designed molds. As materials for the research, pure polytetrafluoroethylene, as well as graphite-filled and coke-filled fluoroplasts 7B-2A and F-4K20 were used.

The obtained experimental data make it possible to recommend the method of solid-phase rem extrusion of PTFE and materials based on it in a solid aggregate state for the manufacture of parts of centrifugal pumps and other similar products of improved quality for chemical equipment. The experimental forged metal fluoroplastic impellers of centrifugal pumps passed production tests and were recommended for use at chemical enterprises.

Conclusion

The studies have revealed the following advantages of solid-phase manufacturing technology:

– increased technological parameters (low technological shrinkage, lower than that of cast moldings of similar shape and dimensions and, accordingly, high dimensional accuracy of the product), higher melt flow indices;

– increased performance characteristics of products: strength indices for various loading schemes are higher than those for the raw material (in one case – by 1.5–2.0 times, in the other cases – by dozens of times); heat resistance, dimensional stability is not lower than that of cast products;

– an increased economic and environmental performance: a sharp decline in material and energy costs, a reduction in harmful emissions, improved working conditions;

– the possibility of using existing press equipment for polymers and using cheaper equipment in comparison with traditional methods significantly increase the economic efficiency of solid-state technology.

With the expansion of the practical capabilities of solid-state technology, it has become expedient to use mathematical modeling of this process for solving a number of problem situations, and, most importantly, for giving recommendations and forecasts for manufacture of long-length products of large diameter. Using a numerical study of the problems, corresponding to the solid-phase extrusion of fluoropolymers, the possibility of vibrational modes of deformation has been theoretically demonstrated. The results of the investigations have been compared with the experimental studies of the instability of solid-phase extrusion of fluoropolymers.

It should be noted that for each specific practical application it is necessary to solve problems directly related to the technology of manufacturing products under consideration and the technical properties of these products. Practical applications of solid-phase processes for manufacture of various types of products from different functional gradient polymer and composite materials are promising. In this regard, there is an urgent need to continue research in three main directions:

– studying the possibility of changing the structure and properties of a number of composite materials by adding finely dispersed inorganic and carbon nanomaterials, molecular relaxation and physical and mechanical properties of the initial polymer systems that meet the requirements of the pressure treatment in the solid phase;

– studying physical processes and mechanisms of plastic deformation in real conditions of technological processes;

– studying the structure and performance properties of materials that have undergone solid-phase treatment (tests in shear, stretching, impact strength, microhardness, etc.).

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