Change in the Porosity of Polytetrafluoroethylene during Radiation Modification above the Melting Temperature[1]

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Abstract—The X-ray degree of crystallinity, χ, and the density, ρ, of suspension-polymerized polytetrafluoroethylene after its irradiation above the melting temperature of the crystalline phase are studied. A comparison of dose dependences of χ and ρ makes it possible to infer that pores occur in the initial polytetrafluoroethylene and that porosity substantially decreases during irradiation. The time of pore contraction in polytetrafluoroethylene after its radiation modification above the meting temperature is estimated with respect to the order of the magnitude. This estimate is based on the consideration of viscous flow under the action of surface-tension forces.

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Polytetrafluoroethylene belongs to the class of polymers that degrade under the action of ionizing radiation. The signs of degradation are as follows: accumulation of terminal macroradicals resulting from the scission of polymer chains, isolation of low-molecular-mass fluorocarbon products of radiolysis, and a decrease in mechanical stability [1−3]. An increase in the radiation temperature above room temperature is accompanied by a further increase in the yield of the products of PTFE degradation [3].

After the melting temperature (327°C) is passed, the monotonous character of the dependences of characteristics of PTFE on irradiation temperature is violated. As was shown in [4, 5], the irradiation of PTFE in melt gives rise to a change in the direction of radiation-chemical processes; crosslinking, rather than degradation, of polymer chains appears, and the mechanical properties are improved. To date, this phenomenon has been studied with the use of a wide range of modern analytical methods [6−10].

In [11, 12], a change in the morphology of polymers due to accumulation of the products of radiation degradation (scissions of chains, short-chain branches, isolated double bonds, low-molecular-mass products, and others) was proposed as the cause of the abnormal behavior of PTFE near the melting temperature.

Note that it is hard to obtain direct evidence of crosslinking in the case of PTFE, for example, via the gel-fraction method or through molecular-mass determination, because this polymer is insoluble in all solvents and the morphology of the polymer may change owing to both crosslinking and degradation.

An abnormally pronounced change in the characteristics of PTFE after irradiation above the melting temperature remains an unsolved problem. According to the data from [12], the increase in the wear resistance of PTFE irradiated in melt is unprecedentedly high (more than four orders). Other properties (creep rate, radiation resistance, and recoverable strain) change from one to several orders of magnitude [12]. These substantial effects are observed at very small (from the viewpoint of radiation chemistry) absorbed doses (from 50 to 200 kGy). All these facts make it possible to suppose that, in addition to molecular mechanisms (crosslinking or degradation), other processes play an important role in the radiation modification of PTFE; as a result, radiation effects are enhanced.

This study concerns one of the possible processes affecting macroscopic properties: namely, the decrease in the porosity of the polymer matrix during irradiation due to the action of surface-tension forces and the decrease in the viscosity of the system.

EXPERIMENTAL

Research Objects

The research objects were sintered suspension-polymerized PTFE block samples (Kirovo-Chepetsk Chemical Works). The samples were fabricated as rods

with a diameter of 50 and height of 100 mm from PN powder through standard uniaxial pressing and subsequent sintering.

Irradiation

The irradiation of PTFE rods was performed at 335°C, above the melting temperature of crystallites (327°C), in an inert medium (argon) on a KSV-500 γ-ray unit (Karpov Institute of Physical Chemistry) with ^{60}Co γ-quanta with an average energy of 1.25 MeV. The samples were placed in a radiation-chemical apparatus [13] whose construction made it possible to set the required conditions of irradiation.

Density

The density of the studied rods was measured via hydrostatic weighing at 22°C. The rod weight was 440 g. For each experimental point (the value of the absorbed dose), density was determined through averaging of the results of independent measurements (no less than five rods). The weights of rods in air and distilled water were measured with a Vibra HJR-620CE balance (Japan) with a reading discreteness of 1.0 mg.

The average density of the rods was calculated according to the equation

$$\rho = \frac{\rho_w m_0}{m_0 - m_w},$$

where ρ is the sample density; ρ_w is the density of distilled water at a given temperature; and m_0 and m_w are the weights of a sample in air and in water, respectively. The error of density measurements at the specified experimental parameters was ±0.001 g/cm³.

Crystallinity

The X-ray degree of crystallinity was measured with the use of samples in the form of pellets 20 mm in diameter and 2 mm in height that were cut from the central part of the rods. X-ray diffraction studies were conducted at room temperature on a Bruker D-8 diffractometer using filtered $CuK_{\alpha 1}$-radiation. The experimental spectra were recorded in the pointwise scanning mode with a step of 0.01° (on the 2θ scale) and an accumulation time of 60–90 s at each point. For a series of samples, the recording mode remained unchanged; the total time of scanning was kept constant. Additional rotation of the sample during recording made it possible to minimize the effect of axial texture along direction [001]. The diffractograms were processed with the use of the X'Pert (Philips) and PROFIT complex of X-ray crystallographic programs [14]. As a result of profile analysis of complex experimental spectra, exact values for not only the positions of diffraction reflections and amorphous components but also their half-widths and integral intensities were obtained.

Table 1. X-ray degree of crystallinity and density of suspension-polymerized PTFE at various radiation doses D above the melting temperature

D, kGy	ρ, g/cm³	χ, %
0	2.160	72.5
10	2.174	77.6
20	2.180	77.1
50	2.191	81.6
100	2.202	78.6
200	2.204	76.2
500	2.210	69.0

The X-ray degree of crystallinity was calculated as the ratio of the integral intensity of reflection 100 to the total integral intensity of diffraction in the range of Bragg angles from 10° to 25° minus the background under the reflection curve. The average size of coherent scattering blocks and the size distribution of crystallites were determined as described in [15]. A LaB$_6$ standard (NIST, United States) was used as a reference in order to allow for the effect of the spectral width of the used radiation and instrumental widening.

Figure 1 shows the examples of diffractograms measured for initial and irradiated PTFE samples.

RESULTS AND DISCUSSION

In order to compare porosities of initial and irradiated PTFE samples, their density ρ and X-ray degree of crystallinity χ were measured. The relevant data are shown in Fig. 2 and Table 1. Depending on the absorbed dose, the density of the samples monotonically increases from 2.16 g/cm³ for the initial PTFE to 2.21 g/cm³ at a dose of 500 kGy (Table 1; Fig. 2, curve 1). In this case, χ initially increases from 72.5% for the initial PTFE to 81.6% at a dose of 50 kGy and then decreases to 69.0% at an absorbed dose of 500 kGy (Table 1; Fig. 2, curve 2).

Such a pattern of the dependence of the fraction of the crystalline phase on the absorbed dose during irradiation of PTFE in melt with a maximum of ~100 kGy is well-known. In [16], this dependence was observed with the use of X-ray diffraction and DSC.

In the ideal case, the density of a semicrystalline polymer is determined from the amorphous-to-crystalline phase ratio:

$$\rho = k\rho_c + (1 - k)\rho_{am} \qquad (1)$$

where ρ_c and ρ_{am} are the densities of the crystalline and amorphous phases, respectively, and k is the volume fraction of the crystalline phase. The volume and weight fractions of the crystalline phase are related via
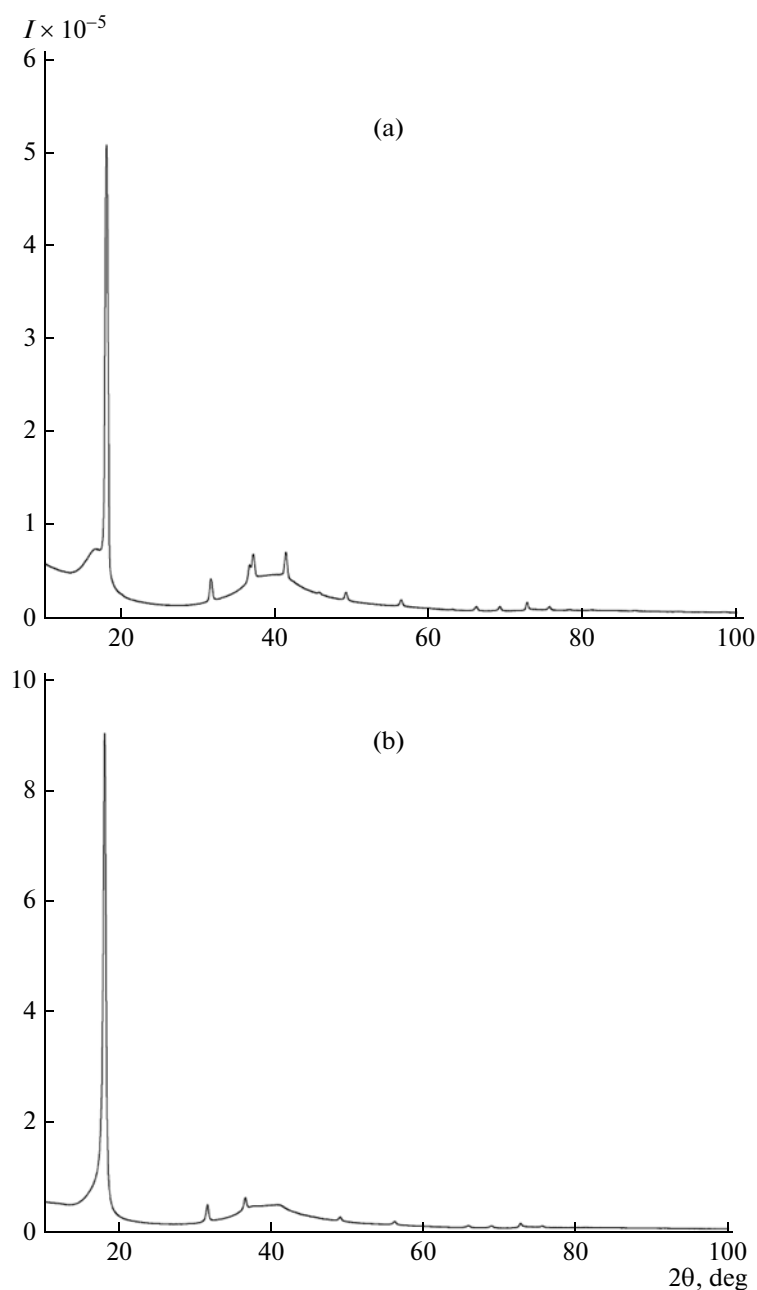
Fig. 1. Diffractograms of suspension-polymerized PTFE (a) prior to and (b) after irradiation with a dose of 200 kGy at 335°C.

the relationship $k = (\rho/\rho_c)\chi$. After substitution of the latter relationship into Eq. (1), we arrive at

$$\rho = \frac{\rho_{am}}{1 - (1 - \frac{\rho_{am}}{\rho_c})\chi} \qquad (2)$$

There is a certain scatter in the values of ρ_{am} obtained for PTFE with the use of various methods [17]. In [18], the density of the amorphous phase is estimated as 2.0 ± 0.04 g/cm^3. On the basis of the volume of the crystal lattice of PTFE, the density of the crystalline phase is 2.302 g/cm^3 [17]. With allowance

for the low value of $(1 - \rho_{am}/\rho_c)\chi \leq 0.13$, Eq. (2) may be linearized:

$$\rho \approx \rho_{am} + \rho_{am}\left(1 - \frac{\rho_{am}}{\rho_c}\right)\chi \qquad (3)$$

The maximum deviation of linear approximation (3) from precise Eq. (2) is 1.7% [17]. That is, the dependence of the density of a material on the X-ray degree of crystallinity is close to linear.

Table 2 lists the calculated (expected) densities of the samples, ρ_c, obtained with the use of experimental X-ray degrees of crystallinity as well as the calculated
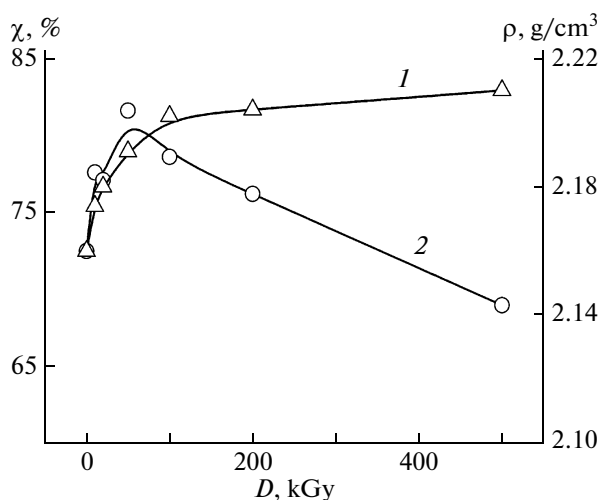
Fig. 2. (*1*) Density and (*2*) X-ray degree of crystallinity of suspension-polymerized PTFE vs. absorbed dose at an irradiation temperature of 335°C.
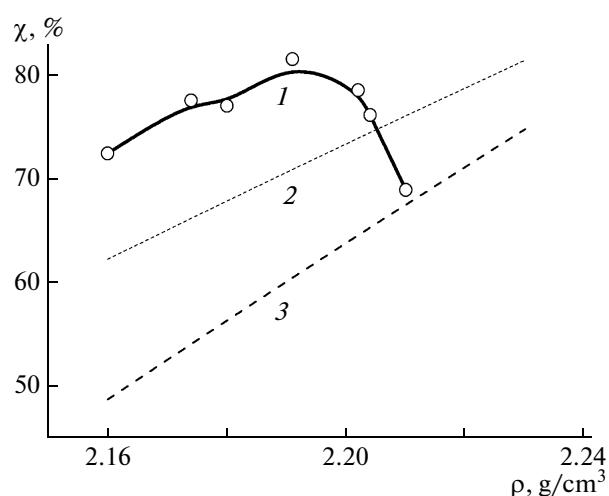

Fig. 3. Diagram for (*1*) experimental and (*2, 3*) theoretical values of the density and the X-ray degree of crystallinity of PTFE samples irradiated at various doses at 335°C.

X-ray degrees of crystallinity, χ_c, obtained from the experimental values of density. The values of χ_c and ρ_c were calculated through Eq. (2). Table 2 shows the scatter in the values of χ_c and ρ_c that arises with the use of the minimum (1.96 g/cm^3) and maximum (2.04 g/cm^3) densities of the amorphous phase taken from [17].

As follows from Table 2, the calculated values of the density and the degree of crystallinity differ substantially from the experimental values. However, with an increase in the absorbed dose, the experimental and calculated values show a tendency to converge.

Figure 3 shows the diagram obtained for the experimental and theoretical values of the density and the X-ray degree of crystallinity for the samples of interest. It is evident that, by definition, the region of experi-

mental values cannot be under curve *3*; i.e., structures with densities higher than that of crystallites cannot occur in the sample. The finding that the experimental points on curve *1* are above and out of the region between *2* and *3* confirms the presence of structures with densities smaller than the density of the amorphous phase in the sample, that is, voids (or pores).

In addition, changes in χ and ρ should be symbate; with an increase in the degree of crystallinity, the density of the sample increases. However, for the samples irradiated with a dose above 50 kGy, the values of χ and ρ change in opposite directions (Fig. 2, curves *1, 2*; Fig. 3, curve *1*) and the decrease in crystallinity is accompanied by an increase in density.

The above results can be explained by the presence of porosity in the sample and by its change during irra-

Table 2. Calculated values of X-ray degree of crystallinity χ_c and density ρ_c of suspension-polymerized PTFE at various radiation doses above the melting temperature

D, kGy	χ_c, %	$\Delta\chi_c^*$	ρ_{cr}, g/cm^3	$\Delta\rho_c^*$ (±0.01), g/cm^3	φ, %	$\Delta\varphi^*$, %
0	57	±6	2.210	3	2.3	±0.6
10	61	±6	2.227	2	2.4	±0.5
20	63	±6	2.225	1	2.0	±0.5
50	66	±5	2.240	0	2.2	±0.4
100	70	±5	2.230	0	1.3	±0.5
200	71	±5	2.222	2	0.8	±0.5
500	72	±4	2.199	5	−0.5	±0.5

Note: Parameters χ_c and ρ_c are the values of the X-ray degree of crystallinity and the density, respectively, calculated with the use of the experimental values from Eq. (2).

* The parameter $\Delta\chi_c = \pm(\chi_{c,min} - \chi_{c,max})/2$, $\Delta\rho_c = \pm(\rho_{c,min} - \rho_{c,max})/2$, $\Delta\varphi_c = \pm(\varphi_{c,min} - \varphi_{c,max})/2$ is the scatter of values of the X-ray degree of crystallinity, the density, and the porosity calculated at minimum (1.96 g/cm^3) and maximum (2.04 g/cm^3) densities of the amorphous phase.

diation. The value of porosity is determined through the following relationship:

$$\varphi = \frac{V_p}{V} = 1 - \frac{V_c + V_{am}}{V} = 1 - \frac{\rho_{exp}}{\rho_c}, \qquad (4)$$

where φ is porosity, V_p is the volume fraction of pores, V_c is the volume fraction of the crystalline phase, V_{am} is the volume fraction of the amorphous phase, V is the total volume of pores in the crystalline and amorphous phases, ρ_c is the density calculated from Eq. (2) with the use of the experimental values of the degree of crystallinity, and ρ_{exp} is the experimental value of density.

Table 2 shows the values of porosity for the test samples that were obtained through Eq. (4). At low absorbed doses (up to 50 kGy), porosity changes insubstantially and is close to the corresponding value for the initial PTFE (2.3%). A further increase in dose results in a drastic decrease in porosity. At an absorbed dose of 500 kGy, the porosity of PTFE is practically absent within the limits of error of its determination.

A change in the porosity of PTFE during irradiation above the melting temperature may be qualitatively explained by the contraction of voids under the action of surface-tension forces.

The PTFE melt (especially near the melting temperature) on the crystallite size scale should be considered an anisotropic, inhomogeneous medium. However, if we distract our attention from the above feature of this polymer, an extremely simple model of the behavior of an isolated spherical cavity in an infinitely homogeneous and isotropic medium may be applied. This task has a well-known solution.

If a spherical cavity with a radius of R_1 is formed in an ideal liquid with surface tension coefficient α and a gas occurs in this cavity under excess (relative to the pressure of this gas at infinity) pressure p_1, then, $p_1 = 2\alpha/R_1$ is the condition of equilibrium.

The excess pressure is positive. Consequently, the gas from the cavity diffuses infinitely and each cavity always disappears after a time determined by the gas permeability of a liquid. The PTFE melt is a viscoelastic material with a very high viscosity that depends strongly on the rate and value of strain; therefore, its behavior differs from that of an ideal liquid.

Let us further assume that the gas permeability of the PTFE melt is sufficient for the excess pressure of atmospheric gases in the cavity to become lower than $2\alpha/R_1$ after a time measured in hours. That is, this pressure may be disregarded. In addition, the radial elastic deformation in this case is determined by $\alpha/2G$ with a value on the order of 3 nm at $\alpha = 7 \times 10^{-3}$ N/m and at shear modulus $G = 10^6$ Pa; that is, this elastic deformation may likewise be disregarded.

Thus, the time dependence of the cavity radius is set by the simplest relationship $\sigma = 2\eta\dot{u}$, where $\sigma = 2\alpha/R$ is the radial stress on the cavity surface; η is

the viscosity, which depends on the time, rate, and value of strain; $\dot{u} = -\dfrac{2}{R}\dfrac{dR}{dt}$ is the radial component of the strain-rate tensor; and R is the cavity radius.

Hence, the rate of change in the cavity radius is

$$\frac{dR}{dt} = -\frac{\alpha}{2\eta}$$

and, at a constant viscosity, this value is radius-independent.

The viscosity of the PTFE melt is $\sim 10^{11}$ Pa s [19, 20], the surface energy is 7×10^{-3} N/m, and the rate of a change in the cavity radius is $\sim 3.5 \times 10^{-5}$ nm/s. The typical time of sintering of block PTFE samples with a characteristic size of 50 mm is 20 h. Only cavities with radii less than 2.5 nm can disappear during this time. If we suggest that a cavity with a radius of 100 nm contracts for 20 h, then the relative strain rate is lower than 10^{-5} L/s for cavities with radii above 100 nm, and the decrease in viscosity may be disregarded at these relative-strain-rate values [21].

Thus, even submicron cavities cannot disappear via the viscous-flow mechanism under the action of surface-tension forces during sintering in the fabrication of block PTFE. A different situation is observed during the radiation modification of PTFE above the melting temperature. During this process, the decrease in viscosity may be rationalized in terms of at least two causes: degradation of polymer main chains and a decrease in the molecular mass and radiation-induced creep [22].

Let propose that molecules remain linear after radiation modification. In what follows, we will use the data from [23] on the dependence of the molecular weight of PTFE on the radiation dose. At a dose rate of 10 kGy/h used in this study, the parameter of polymolecularity for radiation degradation is assumed to be 2. These data may be approximated via the following equation:

$$M_w(t) = 14.4 \times 10^9 (s)/t(s)$$

The viscosity of the PTFE melt may be approximated through a general empirical equation [21]:

$$\eta = 10^{14.5} \, (\text{Pa s})(M_w(t))^{3.4} \qquad (5)$$

Then, at a dose rate of 200 kGy, the viscosity should be less than 10^4 Pa s; i.e., it is extremely far from reality. The viscosity of the melt of radiation-modified (at a dose of 200 kGy) PTFE that was estimated through measurements of the rate of change in the residual strain of the sample at a constant load of 0.1 MPa takes a value of $\sim 10^9$ Pa s at strains of $\sim 10\%$.

Thus, although the radiation modification of PTFE is accompanied by a two-fold decrease in viscosity, this decrease is not as substantial as could be anticipated under the assumption that the molecules obtained during radiolysis are linear.

In [24], the concentration ratio between branching points and terminal groups was measured with the use of ^{19}F NMR spectroscopy. The value of this ratio during irradiation of PTFE with a dose of 500 kGy at 340°C was above unity (~1.15), thereby suggesting the branching character of polymer chains. In empirical Eq. (5), which determines viscosity as a function of the weight-average molecular mass, the exponent for branched molecules may differ from 3.4.

Nevertheless, let us use Eq. (5) for qualitative estimation. To this end, the time dependence of molecular mass is changed in such a manner that, after 20-h irradiation, viscosity will correspond to the value mentioned above (~10^9 Pa s):

$$M_w(t) = 1.5 \times 10^{11}(s)/t(s)$$

In addition, it should be taken into account that, during radiation treatment in the melt, a certain amount of low-molecular-mass products is dissolved in the bulk material. As a result, a constant excess pressure in cavities that corresponds to the concentration of these products at a given temperature and dose rate is created.

Note also that, for a viscous vertical cylinder, the base radius should increase with time (this cylinder should "spread out"). Because no substantial spreading out of the base was observed after radiation treatment of cylinders with a height of 150 mm, yield strength σ_f should be presumably introduced for the PTFE melt. The presence of the yield strength can be explained by the fact that the regions of orientational order can exist in PTFE melt for a long time. In the PTFE melt, in contrast to liquid crystals, these regions may be linked by tie chains of macromolecules; hence, creep in the direction parallel to the axes of orientation of fragments of macromolecules is restricted and is related to the destruction threshold of orientational order.

Thus, the stress on the cavity surface should be written as follows:

$$\sigma = \frac{2\alpha}{R} - (p \pm \sigma_f),$$

where p is the pressure formed in a cavity by low-molecular products, the plus sign is taken when the radius decreases, and the minus sign is taken when the radius increases. If the initial radius satisfies the relationship

$$\frac{2\alpha}{p + \sigma_f} < R < \frac{2\alpha}{p - \sigma_f},$$

its value does not change.

Finally, the phenomenon of radiation-induced creep should be taken into account too. In [21], the time constant of radiation-induced relaxation of stresses was measured at room temperature in the preliminarily stressed PTFE film at various dose rates. On the basis of the data of this study, the equivalent viscosity that describes radiation-induced creep of PTFE at room temperature can be evaluated. This value was found to be $\eta_r \sim 10^9$ Pa s. In [21], a model in which radiation-induced creep is described in terms of the predominant scission of stressed bonds was used.

Under the assumption [24] that the radiation-chemical yield of terminal CF_3 groups during radiation of PTFE in melt is 5 times greater than the corresponding yield at room temperature, it is reasonable to suggest that the above-introduced viscosity is $\eta_r \sim 2 \times 10^8$ Pa s at 335°C.

In general, the dynamics of a bubble is described by the Rayleigh–Plesset equation [25]. The relative contributions of inertial and viscous properties of a medium to the dynamics of the bubble may be estimated with the use of the dimensionless parameter

$\mu = \dfrac{\eta}{R\sqrt{\rho p}}$, where ρ is the density of a medium [25]. In our case, this parameter is on the order of 10^{10}. This circumstance makes it possible to disregard the inertial contribution to the dynamics of the bubble and to regard it only as the balance of the surface tension, the viscoelastic properties of the medium, and the pressure within the bubble.

Assuming that viscous flow and radiation-induced creep are independent processes caused by the same stress, let us write the equation of motion for the surface of a cavity of radius R as follows:

$$\left(\frac{1}{\eta} + \frac{1}{\eta_r}\right)\left(\frac{2\alpha}{R} - (p \pm \sigma_f)\right) = -\frac{4}{R}\frac{dR}{dt} \qquad (6)$$

The solution to Eq. (6) evidently looks as follows:

$$R(t) = \frac{2\alpha}{p \pm \sigma_f} - \left(\frac{2\alpha}{p \pm \sigma_f} - R_1\right)\exp\left(\frac{p \pm \sigma_f}{4}\int\left(\frac{1}{\eta} + \frac{1}{\eta_r}\right)dt\right)$$

In Fig. 4, the family of dependences $R(t)$ is given at various R_1 for the conditions of $p = 8500$ and $\sigma_f = 1500$ Pa and at the above-mentioned values of viscosity and surface tension. As is seen, the voids of radius $R_1 < 1$ μm disappear during the typical time of treatment, while the voids of radius $R_1 > 2$ μm can increase infinitely. At the above viscosity parameters, radiation-induced creep makes the major contribution to this dependence.

The presence of porosity in the initial PTFE with an intrinsic void size less than 1 μm is confirmed by electron microscopy [26]. The effect of an increase in the void radius (and porosity) during radiation modification of PTFE was confirmed as well. In this case, the industrial samples of PTFE in the form of 50-mm-dia rods that were obtained through the standard procedure of horizontal pressing with further sintering were exposed to modification.

These samples usually have substantially lower densities (from 2.08 to 2.12 g/cm^3) and higher porosities than those of the samples obtained via uniaxial vertical pressing. After modification with a dose of
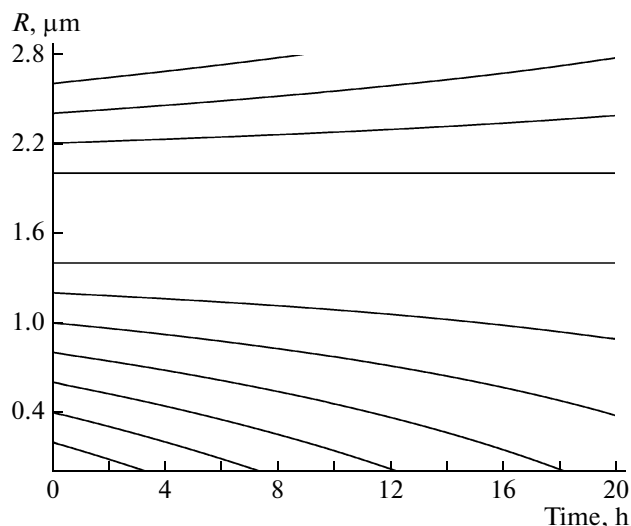
R, μm

Fig. 4. Pore radius vs. irradiation time at various values of the initial radius.

200 kGy at 335°C, the densities of these samples further decrease to 1.7–2.0 and the porosities (and pore sizes) increase to such an extent that the samples undergo a change in geometry ("inflate").

The effect of porosity on the properties of polymers may be related to the ratio between the average diameter of a pore and the average distance between pores; this ratio is close to the cubic root of porosity. At a porosity of 0.1%, the distance between pores is a factor of 10 greater than their diameter; i.e., there is no interaction between pores. Therefore, this porosity can affect only the strength properties of the material. At a porosity of 1%, the distance between pores is a factor of 5 greater than their diameter; this distance may be considered the conditional threshold of the formation of interaction between pores. At a porosity of 3%, the distance between pores is only three times larger than their diameter; interaction between pores may influence the pattern of stress–strain curves of the material during loading, that is, the elastic modulus and the yield strength.

Thus, viscous flow under the action of surface-tension forces during the radiation modification of PTFE above the melting temperature may considerably contribute to the healing of defects of a polymer and thus cause a decrease in its porosity and improvement of physicomechanical properties.

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