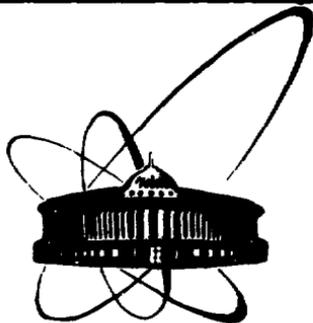


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**ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ
ДУБНА**

E12-89-762

V.V.Ovchinnikov

**THE DEFORMATION MECHANISMS
OF A POROUS STRUCTURE
OF THE POLY(ETHYLENE TEREPHTHALATE)
NUCLEAR TRACK MEMBRANE***

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*This paper is based on the author's Ph.D.thesis

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I. Introduction

For a large number of the presently known porous membranes, the membranes produced by nuclear-physical methods are of special interest. This type of filtration materials has appeared owing to the possibility of revealing latent tracks in the different polymeric materials irradiated by heavy ions [1,2] or by fission fragments [3], and then treated chemically. The so-called nuclear track membranes have a high uniformity of porous structure (the size and shape of pores) and, therefore, provide a high separation selectivity of various dispersive media.

To solve a variety of problems the nuclear track membranes are generally used in installations designed for long operation under normal conditions and at high temperatures. In the latter case one should note the manufacture of screen-vacuum insulation (thermal deposition of metallic layers onto the surface of a membrane) [4], periodical sterilization by autoclaving in medicine and food industry [5,6] as well as other processes that occur at temperatures above the room one. In this case the nuclear track membranes should have stable operating characteristics.

It is known that polymeric membranes can change their filtration productivity and selectivity spontaneously, for example, in the process of filtering liquid media [7]. This happens, primarily, because of the deformation changes by the discontinuous change of the hydrostatic pressure on the high-curved surface of channels. The smaller the radius of the channel, the greater the magnitude of the stress appearing on the pore surface. Other causes can also lead to porosity changes. The nuclear track membranes are not an

exception but rather a model porous medium that is convenient for investigation and control.

In the present investigation the time dependences of the pore radius of the nuclear track membrane from poly(ethylene terephthalate) (PET) in the wide temperature range (333-473 K) are plotted by the experimental way and the theoretical estimates of the experiment are made.

2. Membrane samples

The samples of nuclear track membranes were produced on the basis of partially-crystalline (the crystallinity rate is over 50%) PET film, which is usually used in capacitor, with biaxial orientation (the extrusion ratio is 1:3 and 1:3), thickness is 10 μm , average density is 1,4 g/cm^3 , average molecular weight is about 31000 and the modulus of elasticity is 3500-4000 MPa. The film was irradiated by a heavy ion beam and then treated in the conventional manner [1,2]. The porosity of the membranes did not exceed 1%, which permitted the pores available in the membrane material to be considered practically isolated one from another. The measured effective pore radius of the samples lies in the range from 4.5 to 170 nm.

3. Experimental procedure

The effective pore radius of the membranes was measured with the accuracy of about 2-3% in a set-up designed for gas-dynamical control at room temperature [8]. The samples were glued upon the metallic base of a filter holder having a calibrated hole with a diameter of (3.00 ± 0.05) mm. This allowed one to avoid additional manipulations during the process of thermal treatment and control of the samples.

The study of the deformation mechanisms of the PET nuclear track membrane structure was carried out in the temperature range

from 333 to 473 K. The samples were kept in a vacuum-dryer of SPT-200-type under a rarefaction of up to 10 Pa for a prescribed time. To reduce the processes of the thermal-oxidative destruction of the polymer, after each experiment argon was fed into the vacuum dryer and then the temperature was reduced to room one and the samples were removed for control.

4. Experimental results

The experimental time dependences of the gas-dynamical pore radius were obtained at various temperatures of the heat treatment. They are shown in Figs. 1 (a,b,c), 2 (a,b) and 3 (a,b). As a result of some dispersion of the pore shape and number, the initial pore radii R_0 of the membranes in different samples can vary within $\pm 10\%$.

The analysis of the dependences found reflects at least three existing forms of changes of the gas-dynamical pore radius: the healing, a small growth with the subsequent decrease to practically initial pore magnitude and a very visible pore growth [9,10]. Correspondingly, if the healing is observed in the whole temperature range, that irreversible pore growth is typically characterized by a pore size of 60 nm only at temperatures of 453 and 473 K. The behaviour associated with a small pore growth is noticed in practically all tests with pore radii above 20 nm.

As has been shown earlier by us [9], the healing of the pores is connected, in the first place, with the Laplace pressure on the pore surface leading, as the compliance increases (with temperature growth), to the more pronounced effect of the porosity loss. The pore growth at high temperatures was connected with the process of the polymer mass transfer to crystallization centres when the degree of the PET crystallinity increased. This was confirmed in experiments of measuring the weight-percent crystallinity ratio

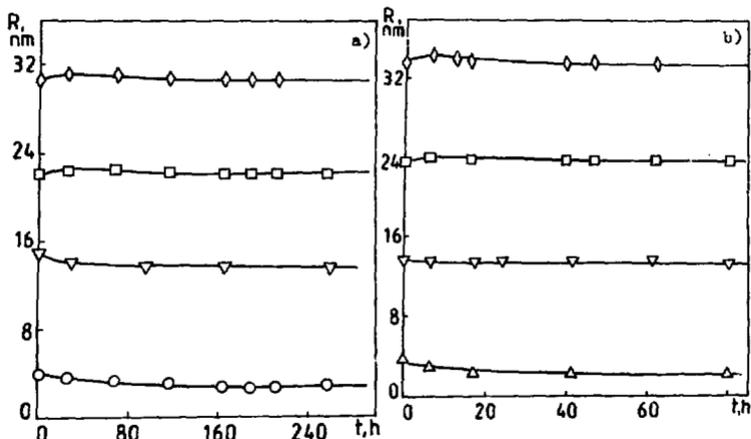


Fig.1. Dependence of the effective pore radius change on time.

a) $T=333$ K. $\circ, \Delta, \square, \diamond$ for $R_0=(4.00\pm 0.13); (14.8\pm 0.4); (22\pm 0.7); (30.5\pm 1.0)$ nm.

b) $T=343$ K. $\Delta, \nabla, \square, \diamond$ for $R_0=(3.60\pm 0.15); (13.5\pm 0.5); (24.0\pm 0.7); (35.0\pm 1.1)$ nm.

c) $T=363$ K. $\circ, \Delta, \nabla, \square, \diamond$ for $R_0=(3.15\pm 0.15); (4.85\pm 0.15); (16.1\pm 0.4); (22.7\pm 0.7); (32.0\pm 1.0)$ nm.

U_k of the PET nuclear track membrane with an effective pore radius of 25 nm (the treatment conditions are the same) - Fig. 4 [9].

The amorphous phase (and some part of the crystalline one) is removed into the solvent - the mixture of phenol and dichloroethane in

relation of 40-60 vol.% for a time of 30 min at a temperature of 358 ± 3 K (the regime was chosen experimentally). The coefficients of the crystallization rate K and the exponent n obtained on the

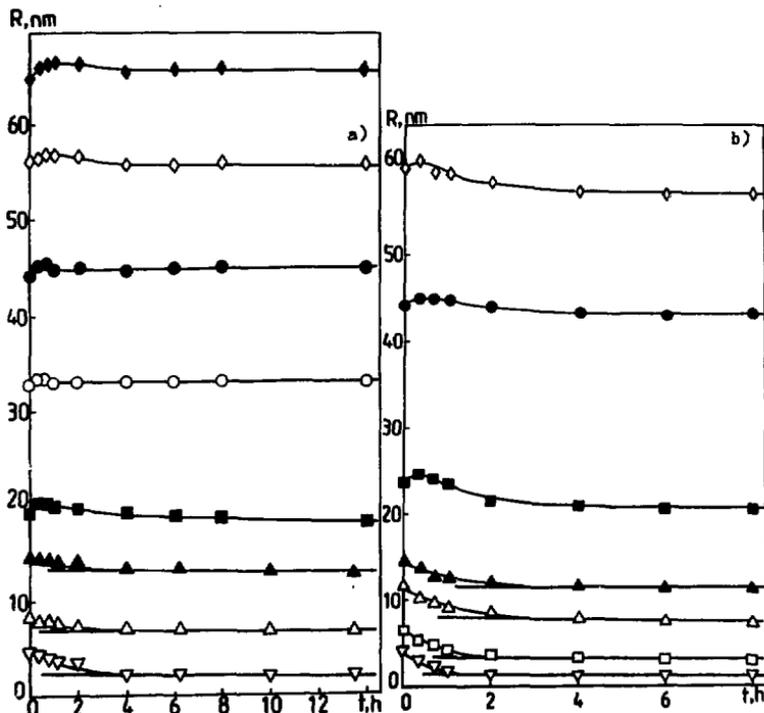
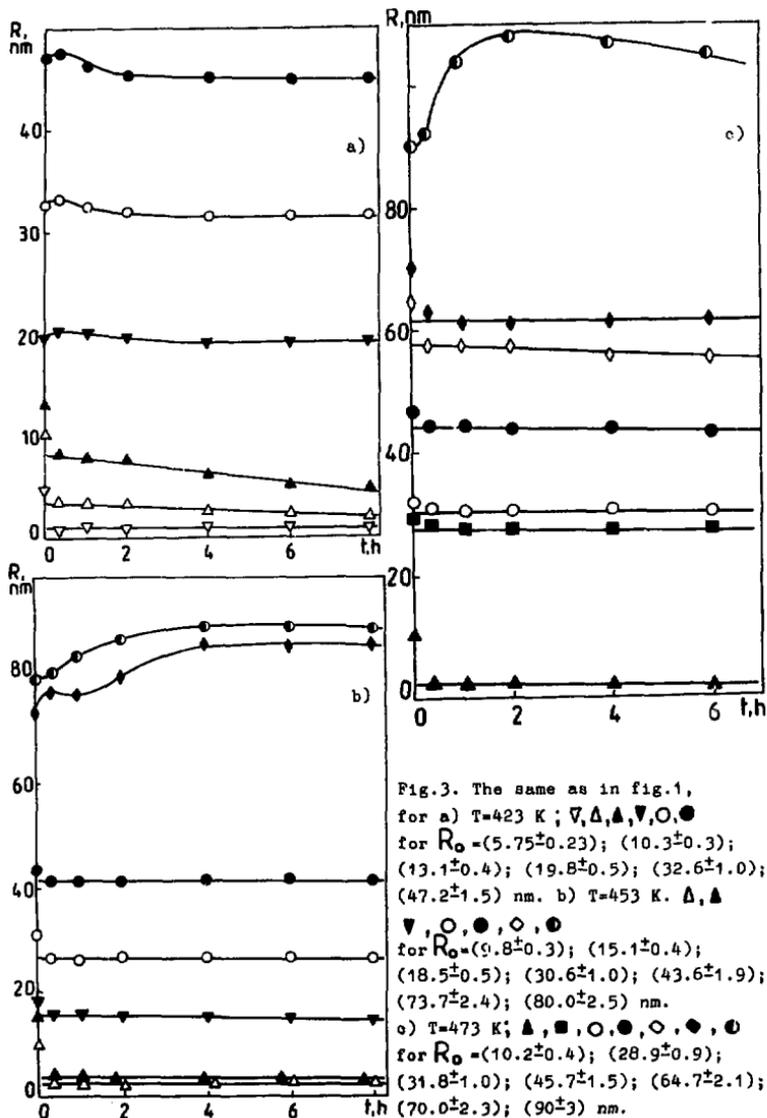


Fig. 2. The same as in fig.1 for a) $T=383$ K; $\nabla, \Delta, \blacktriangle, \blacksquare, \bullet, \circ, \diamond, \blacklozenge$
for $R_0 = (5.90 \pm 0.23)$; (8.35 ± 0.25) ; (14.6 ± 0.4) ; (19.4 ± 0.6) ;
 (32.7 ± 1.1) ; (44.4 ± 1.5) ; (56.3 ± 1.2) ; (64.8 ± 2.1) nm;
b) $T=403$ K; $\nabla, \square, \Delta, \blacktriangle, \blacksquare, \bullet, \circ, \diamond$ for $R_0 = (4.15 \pm 0.15)$;
 (6.60 ± 0.23) ; (11.7 ± 0.4) ; (14.6 ± 0.4) ; (23.0 ± 0.7) ; (44.3 ± 1.4) ;
 (60.2 ± 1.9) nm.



basis of the Avrami equation for secondary crystallization are shown in Table 1.

It should be noted that the exponent values of n lie in the range from 1 to 2 and correspond to the values obtained for the

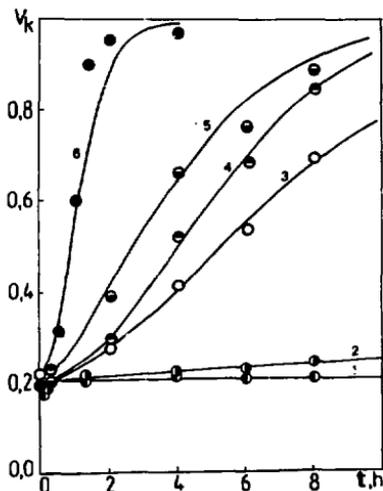


Fig. 4. Dependence of the weight-percent crystallinity ratio of the PET on time. $\bullet, \circ, \ominus, \oplus, \otimes, \odot$ for temperatures 343, 363, 403, 423, 433 and 453 K.

Table 1

The parameters of the Avrami equation for a PET membrane

T, K	343	363	403	423	433	453
K, h^{-n}	0.00078^{\pm} 0.00018	0.0035^{\pm} 0.0004	0.0321^{\pm} 0.0021	0.025^{\pm} 0.005	0.115^{\pm} 0.022	0.63^{\pm} 0.14
n	1.10^{\pm} 0.10	1.31^{\pm} 0.07	1.61^{\pm} 0.06	1.85^{\pm} 0.09	1.41^{\pm} 0.12	1.5^{\pm} 0.3

crystallization process in non-oriented PET [11]. The crystallization rate constant, naturally, is increased as the temperature increases in particular, from 433 to 453 K it is increased by a factor of 6. Just at those temperatures the irreversible pore growth is observed. The approximative curves are plotted in Fig. 4 on the basis of the obtained coefficients. From the shapes of these curves it can be proposed that near 373 K there lies the transition region from the glassy state to high elasticity one of the PET, and this corresponds to known results for oriented polymers [12,13].

For pore radii R_0 above 15-20 nm the Laplace pressure is negligible (it is visible only at temperatures over 473 K) and other processes begin to prevail in the deformation of the porous structure. Indeed, as known, the inner tensions exist in oriented polymers and, particularly, in the PET they are not relieved even after the technological heat setting of films [14]. Then any increase in the polymer temperature leads to some stress $\sigma(T)$ which can cause a small pore growth relaxing in time.

5. Theoretical estimates

5.1. Pore healing

The known solution to define the healing rate of the isolated pore into the solid medium can be written as [14]:

$$\dot{R} = -\alpha/2\eta, \quad (1)$$

where α is the coefficient of surface tension on the bound between the solid medium and the gas; η is the dynamic viscosity.

However the real polymer materials are characterized by the relaxation mechanism of deformation which manifests itself in the presence of the wide set of relaxation times (the spectrum) or in the appearance of the dependence of viscosity η on time t . If we use the Alfrey mechanical model with the set of Kelvin-Foigt-Meyer

elements [16] then the rate of the relative deformation of a polymer can be written as [8]:

$$\dot{\gamma} = \sigma \left[\sum_{i=2}^k \exp(-t/\theta_i) / \eta_i + 1/\eta_1 \right], \quad (2)$$

where η_i, θ_i are the dynamic viscosity and lag time of the i th Kelvin-Foight-Meyer element.

It is easy to show that the sum in the brackets is inversely proportional to the effective dynamic viscosity, i.e.

$$\dot{\gamma} = \sigma [1/\eta(t)]. \quad (3)$$

Then, on the basis of eqs.(1) and (2) the following expression can be derived:

$$\dot{R} = \frac{d}{2\eta_1} - \frac{d}{2} \sum_{i=2}^k \frac{1}{\eta_i} \exp(-t/\theta_i). \quad (4)$$

After integrating it has the form

$$R(t) = R_0 - \frac{d}{2} \left\{ \frac{t}{\eta_1} + \sum_{i=2}^k J_i [1 - \exp(-t/\theta_i)] \right\}, \quad (5)$$

where J_i is the compliance of i th Kelvin-Foight-Meyer element.

In eq.(5) one can consider the two extreme cases:

a) when $t \ll \theta_i$

$$R(t) = R_0 - \frac{d}{2} \cdot t \cdot \sum_{i=2}^k \frac{1}{\eta_i}, \quad (6)$$

b) when $t \gg \theta_i$

$$R(t) = R_0 - \frac{d}{2} \left(\frac{t}{\eta_1} + \sum_{i=2}^k J_i \right), \quad (7)$$

which are the equations of the straight lines.

5.2. Relaxation of the internal stresses

The temperature growth increases the mobility of polymer macromolecular segments which are expected to tend to an equilibrium

state with greater speed. The process can be connected with the appearance of the internal stress $\sigma_o(t)$ of which the relaxation can be described on the basis of the Alfrey mechanical model with the set of the l th elements:

$$\sigma(t) = \sigma_o(t) \sum_{i=1}^l \exp(-t/\theta_i). \quad (8)$$

However, the relaxation of certain polymer chains causes deformation in others and this leads to the appearance of new internal stresses. Deformation of this macromolecules can be modelled as a set of m th elements in the Alfrey model, in which the main role should be played by the relaxation times for stabilization of the system as a whole. Then, on the basis of eq.(8) it is possible to pass to the equation for polymer deformation [16]:

$$\gamma = \sigma_o(t) \sum_j^m (1/\eta_j) \int_0^t \exp(-t-\tau)/\theta_j \sum_i^l \exp(-\tau/\theta_i) d\tau, \quad (9)$$

where τ is the "ourent" time. After integrating eq.(9) we obtain:

$$\gamma = \sigma_o(t) \sum_j^m \sum_i^l j_i \theta_i [\exp(-t/\theta_i) - \exp(-t/\theta_j)] / (\theta_i - \theta_j). \quad (10)$$

Let us assume that the fractional change in deformation of a polymer is proportional to that in the area of the nuclear track membrane pores $\gamma = \pi n_o (R^2 - R_o^2)$ (here n_o is the pore density in the membrane, whereas for a small change in R :

$$R = R_o + \frac{\sigma_o}{2\pi n_o R_o} \sum_i^l \sum_j^m \frac{j_i \theta_i}{\theta_i - \theta_j} [\exp(-t/\theta_i) - \exp(-t/\theta_j)]. \quad (11)$$

The equation obtained describes the dependence with a pronounced maximum if the magnitude of the change in R will decrease with increasing n_o and R_o and increase with j .

5.3. Pore growth in the crystallization process of the polymer

The pore growth effect due to the polymer mass transfer during both the crystallization and the relaxation of internal stresses

can be estimated quantitatively. Indeed, the crystallization process is accompanied by increasing polymer density when the polymer volume decreases. We suppose that part of the released volume is spent on the pore size growth. In this case the fractional change in pore radius is expected to be proportional to the fractional change in the sample volume, i.e. $\gamma = \alpha(\rho_t - \rho_0) / \rho_0 = \mathcal{A} \mathcal{Q} (R^2 - R_0^2)$ (where $\rho_0 = \rho_k \omega_0 + \rho_a (1 - \omega_0)$ is the initial PET density; $\rho_t = \rho_k \omega_t + \rho_a (1 - \omega_t)$ is the PET density at the moment t ; ρ_k, ρ_a are the densities of the crystalline and amorphous phases; ω_0, ω_t are the degrees of the PET volume crystallinity (the initial and that at moment t); \mathcal{Q} is a coefficient). Then, on the basis of the Avrami equation for the weight crystallinity ratio of the polymer the pore radius can be written in the first approximation as

$$R = R_0 + \alpha (\rho_k - \rho_a) (1 - \sqrt[k_0]{1 - \exp(-Kt^{n_1})}) / 2\pi n_0 R_0 \rho_0 \quad (12)$$

From eq.(12) it follows that the porosity growth of the membrane is the higher, the larger the part of the amorphous phase in the original PET film.

6. Interpretation of experimental results and discussion

To describe the whole set of the experimental data it is necessary to take into account the three independent deformation mechanisms of the membrane porous structure. From eqs.(5), (11) and (12) one can obtain:

$$R - R_0 = \frac{\alpha}{2} \left\{ t \eta_t + \sum_{i=2}^k J_i [1 - \exp(-t/\theta_i)] \right\} + A \sum_{j=1}^e \sum_{i=1}^m J_j \theta_i [\exp(-t/\theta_i) - \exp(-t/\theta_j)] / (\theta_i - \theta_j) + B [1 - \exp(-Kt^{n_1})], \quad (13)$$

where $A = \sigma_0 / 2\pi n_0 R_0$, $B = a(\rho_k - \rho_a)(1 - \nu_{k0}) / 2\pi n_0 R_0 \rho_0$.

The interpretation of the experimental data using eq.(13) is very difficult because of the large number of unknown coefficients entering into the expression. For the convenient treatment of the results by the least-squares method (LSM) we used, in second term of eq.(13), only the first items in the sums ($l=m=1$) by introducing the two characteristic lag times θ_1 and θ_2 .

In addition, the treatment of the results can be carried out beginning from those pore radii for which the only mechanism of a change in membrane porosity manifests itself. So, at temperatures below 373 K the third term in eq.(13) can be neglected but in the sum of the first component only the first term can be retained [14]. The empirical coefficients obtained in this way are given in Table 2.

From Table 2 it follows that the compliance of PET J_2 (α changes weakly with temperature) in glassy state remains practically invariable. So, if α is assumed to be equal to 0.056 N/m [18], then J_2 will be equal to $(3.2 \pm 1.4) \cdot 10^{-8}$ m²/N and η_1 to about 10^{13} Pa·s, that is close to the value usually accepted for the glassy state of an amorphous polymer (greater than 10^{14} Pa·s) [19]. For the characteristic times θ_1 and θ_2 defining the relaxation of the internal stresses an evident temperature dependence is also observed. In this case θ_1 is always greater than θ_2 . Indeed, heating the polymer leads to residual relaxation of the stressed polymer chains with large times θ_2 . Meanwhile the departure from the quasi-equilibrium state of other macromolecules results in the appearance of their response in the form of the "rapid" relaxation of θ_2 . Taking into account the values of J_2 the estimate of η_2 ($\theta_2 = \eta_2 J_2$) gives the same order of magnitude as that for η_1 . In accordance with the defined parameters, the curves describing experimental data well are plotted in Fig.1.

Table 2

The coefficients of eq.(13) for temperatures below 373 K

T, K	333	343	363
$\lambda_2 d/2$, nm	0.9 ± 0.4	0.9 ± 0.3	0.8 ± 0.4
$d/2\eta_1$, nm/h	$(9 \pm 3) \cdot 10^{-3}$	$(3.5 \pm 1.6) \cdot 10^{-2}$	$(5.2 \pm 1.5) \cdot 10^{-2}$
θ_1 , h	76 ± 4	35 ± 15	35 ± 18
θ_2 , h	20 ± 5	7.0 ± 1.5	2.0 ± 0.3

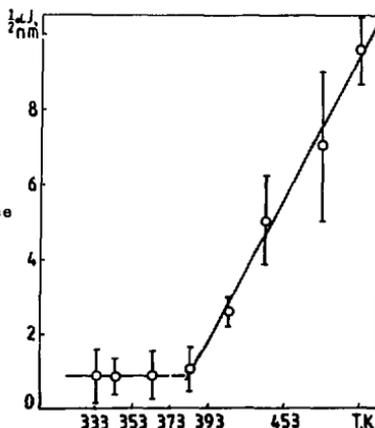


Fig. 5. Temperature dependence of the PET compliance

To describe the experimental results of temperatures above 373 K, in the first place, one should use the limiting cases of pore healing, i.e. eqs. (6) and (7). Indeed, as the evident exponential decrease in the membrane pore radius is observed only at 343-363 K (Fig. 2 (a,b)), at higher temperatures on the given time scale the exponent is not decided (the lag times are less than 1-2 h). In this case eq.(7) can be used LSM to determine the parameter $\lambda_2 d / 2$. In Fig.5 the calculated values are plotted as

functions of the temperature and are approximated as a linear function. The region of the vetrification temperature of PET is seen clearly. The behaviour of this dependence defines the mechanism of the pore healing in a nuclear track membrane over the whole temperature range. So, in the glassy state of the PET the healing value is practically independent of temperature, but in rubber state it increases with temperature. The latter leads to the healing of pores with R_0 above 20 nm in competition with the crystallization process of the PET, Fig. 3 (a,b). The basic parameters of eq.(13) obtained at high temperatures are shown in Table 3.

The obtained coefficients B allowed also to estimate the parameter Q to be about 0.1. That indicates that in the process of the secondary crystallization only about 0.1 of the polymer mass transferred leads to the pore growth but the rest of the polymer seems to be spent on the redistribution of the free volume [20] and on the growth of voids as is usually the case with polymer annealing [21].

The coefficients given in Tables 2 and 3 permitted the description of the whole set of experimental data on the basis of eq.(13) within an error of 5%.

Table 3

The coefficients of eq.(13) for rubber state of the PET membrane

T, K	383	403	423	453*	473*
θ_1, h	4 ± 4	5 ± 2	1.30 ± 0.22	-	-
θ_2, h	0.32 ± 0.16	0.20 ± 0.11	0.30 ± 0.08	-	-
B, nm	-	-	-	7.2 ± 2.8	16 ± 11

*Here the calculation for the crystallization process with eq.(13) is made taking into account the earlier defined parameters K and n of the Avrami equation.

Conclusion

The experimental study of the porous structure deformation of the nuclear track membrane from polyethylene (terephthalate) in the temperature range from 333 to 473 K has allowed one to reveal the three very likely processes. The first one prevailing for pore radii smaller than 15-20 nm characterizes the healing of the pores as affected by the Laplace pressure. The second process manifests itself at pore radii greater than 15-20 nm and is connected with relaxation of the internal stresses in the polymer material. The third process dominates at temperatures above 433 K and leads to visible pore growth when the crystallization process of the PET is accompanied by mass transfer.

On the basis of the Alfrey mechanical model of the viscoelastic deformation of polymers and the Avrami equation for PET crystallization, an expression was derived which describes satisfactorily the kinetics of the pore radius change in a nuclear track membrane in the investigated ranges of both temperatures and pore sizes.

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Механизмы деформирования пористой структуры
ядерной мембраны из полиэтилентерефталата

Экспериментальным путем исследуются механизмы деформирования пористой структуры ядерной мембраны из полиэтилентерефталата в диапазоне температур от 333 до 473 К. Показано, что размеры пор мембраны могут как уменьшаться, так и расти. Получено аналитическое выражение, базирующееся на механическом подходе Алфрея к релаксационному деформированию полимеров и удовлетворительно описывающее экспериментальные результаты во всем исследованном диапазоне температур и радиусов пор мембран.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

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Ovchinnikov V.V.

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The Deformation Mechanisms of a Porous
Structure of the Poly(ethylene Terephthalate)
Nuclear Track Membrane

The deformation mechanisms of a porous structure of the nuclear track membrane made of poly(ethylene terephthalate) are investigated in the temperature range from 333 to 473 K. It is shown that the pore size of the membrane can both decrease and increase. The analytical equation based on the Alfrey mechanical approach to the relaxative deformation of polymers describes the experimental data satisfactorily over the whole range of temperatures and pore radii of the membranes.

The investigation has been performed at the Laboratory of Nuclear Reactions, JINR.

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