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ON THE PHENOMENOLOGY OF THE FINITE-DEPTH DIFFUSION OF OXYGEN INTO POLYMERS IN THE PROCESS OF THEIR RADIATION OXIDATION*

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A mathematical model of the finite-depth diffusion of air oxygen into a polymer exposed to ionizing radiation is proposed.

Introduction. The processes of heat conduction and diffusion are described by second-order partial-differential parabolic equations. For reacting media, the reactions occurring in them should be additionally taken into account. These reactions are considered as sources or sinks. In the stationary case, they are defined using time-independent variables.

Below we consider the indicated processes by the example of diffusion of air oxygen into polyethylene exposed to γ-irradiation. It was established experimentally that oxygen is absorbed in steady-state radiation-oxidation reactions that do not saturate in a wide range of absorbed-radiation doses.

The processes being considered were theoretically investigated with account for the above-indicated notions.

1. Experimental Procedure. We investigated the diffusion of air oxygen into high-pressure polyethylene (HPPE) (obtained in accordance with the State Standard 16337-77) exposed to a γ-radiation. The radiation source was ^{60}Co isotope, the absorbed radiation dose was about 1 Gy/sec, and the medium in which the irradiation was performed was air. The relative degree of radiative oxidation of the polyethylene was estimated using the infrared-spectroscopy technique by the radiation dose absorbed at a frequency of 1720 cm^{-1} corresponding to the absorption band of oxygen-containing polyethylenes. An infrared SPECORD M-80 spectrophotometer was used. The gradient of radiative transformations occurring in the bulk of the polyethylene was determined with the use of films closely packed into a stack under a pressure of 4–5 MPa at a temperature lower than the melting temperature of the polymer by 5–10 K [1, 2].

The sample (an HPPE film of thickness 100 μm) was isolated on both sides from oxygen by a pressed aluminum foil and irradiated to an absorbed-radiation dose of 1 MGy. After the foil was removed, the degree of oxidation of the polyethylene was estimated. We did not detect a marked change in the optical density of the absorption band at 1720 cm^{-1} and a marked radiation-induced oxidation of the polyethylene by the oxygen dissolved in it.

The sample (a stack of 10 films of thickness 100 μm) was irradiated to an absorbed-radiation dose of 2 MGy in a continuous regime. An analogous sample was irradiated to the same integral dose in the regime where irradiation was discontinued for 20 min every 12 hours. Subsequent analysis showed that the oxidation distributions over the thickness of the samples being investigated are identical and that, in the range of doses being used, the degree of oxidation of the polymer depends linearly on the absorbed-radiation dose.

It was established that the oxidation processes induced as a result of the absorption of integral γ-radiation doses ranging from 0 to 2 MGy do not saturate and the steady state is established for a time t much smaller than 12 h. Since, hereinafter, we will consider integral doses, the time of accumulation of which exceeds five days, the processes being investigated will be assumed to be stationary.

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TABLE 1. Distribution of the Optical Density of the Band at 1720 cm^{-1} over the Layers of a Stack (Numbering Proceeds from the Surface of the Sample) Depending on the Absorbed-Radiation Dose (1–5 are Layers)

Dose, kGy	1	2	3	4	5
125	0.169	0.103	0.018	0.009	0.009
250	0.357	0.226	0.035	0.019	0.019
500	0.643	0.387	0.058	0.034	0.033
1000	0.921	0.459	0.073	0.043	0.041
2000	1.297	0.686	0.124	0.066	0.065

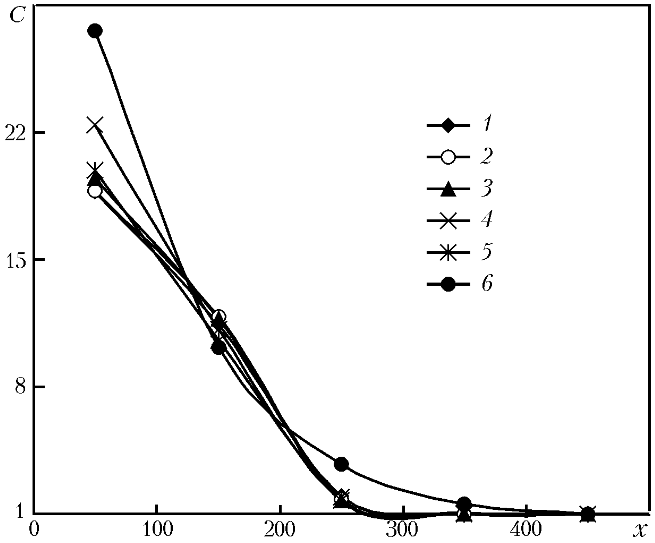

Fig. 1. Distribution of the relative oxidation of the HPPE over its volume: absorbed dose is 125 (1), 250 (2), 500 (3), 1000 (4), and 2000 kGy (5); 6) calculated dependence.

The model of oxygen diffusion into a semisphere and a layer, described below, was compared with experimental data.

Below we present experimental data obtained for a stack of HPPE films of thickness 100 ± 5 μm exposed to a γ-radiation. The total thickness of the stack was 1 mm (see Table 1).

Figure 1 shows the oxidation distributions over the volume of the HPPE exposed to different radiation doses. These dependences were constructed on the basis of rows of experimental data obtained at a definite absorbed-radiation doses and normalized to the degree of oxidation of the fifth (from the surface) layer, i.e., to the degree of oxidation of the polymer material located at the center of the stack at this dose. As is seen from this figure, the indicated dependences are practically coincident. This points to the absence of saturation processes across the depth (the distance from the surface) of the sample throughout the range of the absorbed-radiation doses investigated.

The coefficient of correlation of the experimental data with the theoretical curve is equal to 0.92. A hyperbolic cosine (see below) describes the two-dimensional diffusion of oxygen into the stack of films in the presence of oxidation reactions caused by the ionizing radiation. As is seen from Fig. 1, the oxidation of the surface layer is smaller than the theoretical one. This difference can be explained by the fact that, in the surface layer of an HPPE having a thickness of up to 100 μm, electron equilibrium is absent, i.e., a certain number of secondary electrons formed as a result of the interaction of the polymer with γ-quanta escape from the volume being considered. As a result of this effect, the dose of radiation absorbed in the surface layer of the HPPE accounts for 60–70% of the dose absorbed in its bulk [3]. Accordingly, the degree of radiation-induced oxidation of the polymer near the surface of the sample should be smaller than the calculated one.

Moreover, at all the doses investigated the oxidation at the level of the third and fourth (from the surface) layers was somewhat smaller than the theoretical one. The effect detected can be due to the appearance of a temperature gradient in the depth of the polymer in the process of its irradiation. This gradient increases the rate of recombination of free radicals in the bulk of the polymer volume increases, which leads to the formation of transverse bonds or a nonsaturation.

The experimental data were compared with the corresponding theoretical data by the method of least squares. A relatively high degree of correlation between the theoretical and experimental data allows the conclusion that the model proposed is sufficiently correct for absorbed-radiation doses falling within the range 0.1–2 MGy.

2. Diffusion into a Semispace. *2.1. Influence of irradiation of a polyethylene sample on the diffusion of oxygen into it.* The three-dimensional diffusion equation, as is known, has the form

$$\partial_x (D (\mathbf{x}, t)\, \partial_x C (\mathbf{x}, t)) = \partial_t C (\mathbf{x}, t) . \tag{1}$$

In the case of absorption of oxygen in a polyethylene sample as a result of the oxidation reactions arising in it under γ-irradiation, an additional term accounting for this effect appears in the diffusion equation:

$$\partial_x (D (\mathbf{x}, t)\, \partial_x C (\mathbf{x}, t)) = \partial_t C (\mathbf{x}, t) + k (\mathbf{x}, t)\, I (\mathbf{x}, t)\, C (\mathbf{x}, t) . \tag{2}$$

For a high-penetrability γ-radiation, it may be assumed that $I(\mathbf{x}, t)$ = const. In the absence of saturation, $k(\mathbf{x}, t)$ = const. Let us assume that $D(\mathbf{x}, t)$ = const. In this case, the diffusion equation for the stationary problem ($\partial/\partial_t C(\mathbf{x}, t) = 0$) will have the form

$$D (\mathbf{x}, t)\, \partial_x \partial_x C (\mathbf{x}, t) = k (\mathbf{x}, t)\, I (\mathbf{x}, t)\, C (\mathbf{x}, t) . \tag{3}$$

Let us consider the one-dimensional diffusion equation

$$D \frac{d^2}{dx^2} C (x) = kIC (x) , \tag{4}$$

where $x = x_3$ or

$$\frac{d^2}{dx^2} C (x) = q^2 C (x) , \quad q^2 = \frac{kI}{D} . \tag{5}$$

This equation is solved as

$$C (x) = C_1 \exp (- qx) + C_2 \exp (+ qx) . \tag{6}$$

For the diffusion of oxygen into a semisphere,

$$C (0) = C_0 , \quad C (+ \infty) = 0 \Rightarrow C (x) = C_0 \exp (- qx) . \tag{7}$$

For the two-dimensional diffusion of oxygen into a layer of thickness L

$$C (0) = C_0 , \quad C (L) = C_0 \Rightarrow C (x) = \left\{C_0/(1 + \exp (- qL))\right\} [\exp (- qx) + \exp (- q (L - x))] \tag{8}$$

or, what is the same,

$$C (x) = \left\{C_0/(\cosh (qL/2))\right\} [\cosh (q/(L/2 - x))] . \tag{9}$$

However, it should be noted that, at all values of the radiation intensity I, none of these solutions takes a zero value in the case where oxygen penetrates into the sample at a finite depth. This is in contradiction with the intuitive suggestion that, at any intensity of irradiation of a sample, a finite number of gas molecules diffuse into it at a definite depth.

2.2. Finite-depth diffusion of oxygen into a polyethylene sample. We will now consider the problem on the penetration of oxygen into a polyethylene sample at a finite depth. Equation (5) is solved, as earlier, in the form of relation (6), and the boundary conditions for it has the form

$$C(0) = C_0, \quad C(L) = 0.$$

In this case, we obtain

$$C(0) = C_1 + C_2 = C_0, \quad C(L) = C_1 \exp(-qL) + C_2 \exp(+qL) = 0. \tag{10}$$

It follows herefrom that

$$C_1 = C_0 \exp(+qL)/(\exp(+qL) - \exp(-qL)), \quad C_2 = -C_0 \exp(-qL)/(\exp(+qL) - \exp(-qL)). \tag{11}$$

As a result

$$C(x) = \{C_0/(\exp(+qL) - \exp(-qL))\} [\exp(+q(L-x)) - \exp(-q(L-x))], \tag{12}$$

$$C(x) = \{C_0/\sinh(qL)\} \sinh(q(L-x)). \tag{13}$$

At $x > L$, the solution is not physical because it corresponds to negative gas concentrations.

2.3. Features of the oxygen diffusion into a polyethylene sample at a finite depth. In the above-formulated problem, it is difficult to solve Eq. (5) for the case of penetration of oxygen into a polyethylene sample at a finite depth on the natural physical condition that the oxygen flow penetrating into this sample decreases to zero at the point at which the oxygen concentration is equal to zero. Let us assume that the oxygen concentration is equal to zero ($C(L) = 0$) at a finite depth L. It is natural that, in this case, $C(0) = C_0$ at the surface of the sample. Then, at this depth L, the oxygen flow penetrating into the sample should be equal to zero.

The last-mentioned condition is not of course a boundary condition because the second-order equation is completely determined by the two above-indicated boundary conditions. The requirement that the oxygen flow be equal to zero in the bulk of the sample is a criterion necessary for modification of the differential equation such that, at the above-indicated boundary conditions, the solution of this equation provided a zero flow at a definite depth of the sample. Therefore, we adopt the solution, described in Sec. 2.1, with a zero flow at the center of the sample but with a nonzero concentration. The solution with a zero concentration but with a nonzero flow at the point at which the concentration is equal to zero is purely mathematical. This solution is impossible from the physical standpoint since a nonzero flow arises at a nonzero concentration when the solution is continued to the region of negative values of C at $x > L$. From the physical standpoint, C cannot take negative values.

However, the last-mentioned system can be solved if Eq. (5) has the following solution:

$$C(x) = C_1 \exp(-qx) + C_2 \exp(+qx) - f. \tag{14}$$

In this case,

$$\begin{gathered} C(L) = 0 \Rightarrow C_1 \exp(-qL) + C_2 \exp(+qL) - f = 0, \\ \frac{d}{dx} C(x)\bigg|_{L=0} \Rightarrow C_1 (-q) \exp(-qL) + C_2 (q) \exp(+qL) = 0. \end{gathered} \tag{15}$$

Taking into account the boundary condition at the surface of the sample

$$C_1 + C_2 - f = C_0 \tag{16}$$

we obtain

$$C_1 = C_0 \exp (+ qL)/2 \, [\cosh (qL) - 1] \, , \quad C_2 = C_0 \exp (- qL)/2 \, [\cosh (qL) - 1] \, , \quad f = C_0/[\cosh (qL) - 1] \, . \tag{17}$$

However, solution (14) cannot be a solution of Eq. (5), which becomes evident if a simple substitution is done. This substitution shows that this equation should be modified in the following way:

$$\frac{d^2}{dx^2} C (x) = q^2 C (x) + q^2 f \, . \tag{18}$$

The modified equation is solved as

$$C (x) = \frac{C_0}{2 \, [\cosh (qL) - 1]} \left\{ \exp (- q \, (x - L)) + \exp (+ q \, (x - L)) - 2 \right\} , \tag{19}$$

or

$$C (x) = \frac{C_0}{\cosh (qL) - 1} \left\{ \cosh (q \, (L - x)) - 1 \right\} . \tag{20}$$

Expression (20) represents a solution of the problem on the diffusion of oxygen into a semispace at a finite depth.

2.4. Interpretation of the parameter f. From the formal mathematical standpoint, $f = C_0/[\cosh (qL) - 1]$ is nothing more nor less than a part of the concentration $C(x) = (C_0/[\cosh (qL) - 1]) \left\{ \cosh (q(L - x)) - 1 \right\}$ in the solution of the problem being considered. This concentration is obtained when the parameter corresponding to (–1) in the numerator is separated from the indicated solution. In its absence, the solution takes the "pedestal" of equal concentration at any point across the depth of a sample. The parameter $q^2 f$ in the diffusion equation serves to eliminate this "pedestal" in the solution. Therefore, it has the form of a constant absorption intensity at any point across the depth of the sample at a concentration of $f = C_0/[\cosh (qL) - 1]$ equal to the "pedestal" concentration.

From the physical standpoint, the change from Eq. (5) to Eq. (14) modifies the model of oxygen diffusion into a polyethylene sample as a result of the radiative-oxidation processes occurring in it.

In the new model, an additional term is introduced into the steady-state diffusion equation. It is assumed that f in it is a constant. In the case where the diffusion depth is finite, the length L should increase with increase in C_0 and decrease with increase in q because $f = C_0/[\cosh (qL) - 1] = \text{const}$ for this problem. Under such conditions, the quantity f will be constant and the relation between the quantities C_0, q, and L will be correct from the physical standpoint.

Thus, at $f = \text{const}$, Eq. (14) can be considered as a model adequately describing the finite-depth diffusion of oxygen into a polyethylene sample exposed to a γ-radiation.

However, it is difficult to interpret the physical processes described by the new term introduced. The quantity f, having dimensions of concentration, defines a constant gas concentration at any point across the depth of a sample; however, it is evident that the gas concentration decreases with depth. To explain the reason for the appearance of the additional term in Eq. (14), it should be noted that the problem on the finite-depth diffusion of oxygen into a polyethylene sample was formulated based on the assumption that a finite number of gas molecules are absorbed at a finite depth. This is not a necessary condition for a continuous medium but is a necessary condition for a discrete medium. Thus, the additional term in the indicated equation is nothing more nor less then a phenomenological estimate of the discreteness of the diffusing gas. Namely the molecular (discrete) model of oxygen diffusion into a polyethylene sample, as compared to the model of oxygen diffusion into a uniform medium, allows the intuitive conclusion that oxygen diffuses into the polyethylene sample at a finite depth. At the same time, the diffusion equation is a model of gas diffusion into a homogeneous medium. Therefore, it is impossible to propose a physically correct "mechanism" that would explain the necessity of introduction of the additional term. Its introduction should be considered as a phenomenology.

Conclusions. It may be suggested that the mechanism providing a finite-depth diffusion of air oxygen into a polymer material exposed to an ionizing radiation is based on the above-described phenomenology. However, this does not mean that there is no a need to develop a more detailed mechanism.

NOTATION

$C(\mathbf{x}, t)$, oxygen concentration; C_0, oxygen concentration at the boundary (surface) of a polyethylene sample, $C_0 = C(0, t)$; C_1, C_2, f, constants; $D(\mathbf{x}, t)$, diffusion coefficient; $I(\mathbf{x}, t)$, radiation intensity (dose rate); $k(\mathbf{x}, t)$, reaction constant; L, distance from the surface at which the gas diffused into the polymer is completely absorbed (finite-depth diffusion); q, coefficient; t, time; $\mathbf{x}$, vector from the origin of coordinates to the observation point; x, distance from the surface; x_3, depth of gas penetration into a semispace (third coordinate of the vector $\mathbf{x}$).

REFERENCES

1. Yu. M. Pleskachevskii, S. V. Kopylov, N. M. Kachalova, and V. P. Sel'kin, On the identification of the process of radiative oxidation in a stack of films and a polyethylene block, *Vestsi Akad. Navuk BSSR*, *Ser. Fiz.-Tékhn. Navuk*, No. 1, 116 (1982).
2. Yu. M. Pleskachevskii, N. M. Kachalova, V. P. Sel'kin, and V. M. Makarenko, Investigation of the anisotropy of radiative oxidation of polyethylene, *Dokl. Akad. Nauk BSSR*, **27**, No. 3, 235–237 (1983).
3. G. Z. Gochaliev, *Technological Dosimetry* [in Russian], Moscow (1984).