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REVERSIBLE CHANGES IN THE GAS PERMEABILITY OF POLYMERS DURING GAMMA IRRADIATION

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It is known that, as a result of the action of ionizing radiation, the entire complex of properties of polymers changes in accordance with the structural-chemical changes occurring in them (^1).

Very few studies have been carried out on the diffusion of gases in irradiated polymers, and the available works are devoted mainly to the question of the influence of radiation on the gas and vapor permeability of polyethylene (2,4). These studies have demonstrated the dependence of the permeability constants of gases on the integral dose received by the polyethylene. However, the diffusion of gases through polymers located in the irradiation field, despite the practical and theoretical importance of this phenomenon, has not been studied.

Mokul'skii and Lazurkin (^5) investigated the mechanical properties of polymers under irradiation by a nuclear reactor. They discovered reversible radiation-mechanical effects. Some part of these changes arose during irradiation and disappeared when it was stopped. Naturally, one could expect an analogous reversible effect of irradiation on the diffusion of gases through polymers. Establishing this effect was the aim of the present work.

The investigations were carried out by a manometric method on a source of γ-radiation, Co^60, with an activity of 20 kg-equiv. radium (^7), at dose rates up to 700 rad/sec.

The layout of the apparatus on which the permeability constants were measured is shown in Fig. 1.

The apparatus consists of three main units: 1. A diffusion cell, in which the film under study is clamped between two flanges with a lead sealing ring (Fig. 1, 1). On one side of the film there is gas (under a pressure of 600–700 mm Hg), and on the other side, vacuum. The area of the film surface varied from 1.5 to 1.7 cm^2, depending on the seal. Films of thickness 90 and 120 μ were studied. 2. A movable vacuum post, located on a trolley, consisting of a fore-vacuum pump and a mercury diffusion column (Fig. 1, 2). 3. A manometer for remote pressure measurement (Fig. 1, 3)*, operating on the principle of a change in the inductance of the sensor coil when the core, made of a ferroresonance alloy, is displaced. The sensor coil is located on a U-shaped mercury manometer

Fig. 1. Schematic of the apparatus

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with a reservoir. A core floats on the mercury. When the pressure in the system changes, the float moves together with the mercury, and the inductance of the coil changes accordingly; this is recorded by an EPVI-14 instrument (accuracy of the instrument measurements $±$0.05 mm Hg). Measurements of the permeability constant were made by measuring the increase of pressure with time in the vacuum chamber.

The assembled diffusion cell, together with a chamber filled with inert gas, was checked for tightness. The cell was connected by means of ground joints—the vacuum post and a remote manometer were connected. After creating a vacuum in the system, the vacuum post was disconnected and removed from the irradiation chamber.

Before introducing the source, the rate of increase of pressure in the vacuum part of the system was measured and the dependence of pressure on time, $p = f(\tau)$, was determined. After making sure that a steady diffusion rate had been established and that the dependence $p = f(\tau)$ was linear, the radiation source was introduced. The rate of pressure rise in the vacuum chamber increased sharply while the linearity of $p = f(\tau)$ was preserved. The rate remained constant during pressure measurements over the time during which the integral dose received by the film did not cause noticeable structural changes in the polymer. After removal of the source, the initial diffusion rate was established.

Fig. 1. Schematic of the apparatus

A correction for the pressure increase resulting from gas evolution by the film and by the grease of the ground joints during irradiation was determined in advance. For this purpose the hermetically assembled system was evacuated, the diffusion cell was placed at the center of the source, and it was irradiated continuously for 6 h. During this time the pressure remained constant to within ±0.05 mm Hg. Thus, the correction for gas evolution from the irradiated film and grease could be neglected.

In Fig. 2 the dependence $p = f(\tau)$ is shown graphically for helium before irradiation and during irradiation of polyethylene at 10° at a dose rate of 730 rad/sec. As can be seen from Fig. 2, the pressure increases immediately after introduction of the source, and not gradually as the source approaches, as might have been expected. This is explained by the fact that at lower dose rates, of the order of 100 rad/sec, as special experiments showed, no acceleration (at 20–22°) is practically observed. To maintain a constant temperature, which was

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* The design of the manometer was proposed by V. B. Osipov.

Fig. 2. Increase of helium pressure in the vacuum part of the apparatus with time for polyethylene at 10°. I, III, and V—without irradiation; II, IV, VI—during irradiation

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regulated by means of a heating element and a thermoregulator, during the experiment the cavity of the cylindrical source was cooled with running water through a metal jacket.

Fig. 2. Increase of helium pressure in the vacuum part of the apparatus with time for polyethylene at 10°.
I, III, and V—without irradiation; II, IV, VI—during irradiation.

The results of measurements of the permeability of helium and xenon through polyethylene at different dose rates are presented in Table 1. The permeability constants were calculated from Fick’ s equation for a steady-state flux.

As can be seen from Table 1, the process of diffusion acceleration depends strongly on the dose rate. The greater the dose rate, the greater the effect of relative acceleration of diffusion. Thus, for helium ($t = 17°$) the diffusion process at an irradiation dose rate of 300 rad/sec is accelerated by approximately a factor of three, and at 730 rad/sec ($t = 10°$)—on average by a factor of 10.

Table 1

Experiment No.	Temp., °C	Polymer	Gas	p_0 (from graph)	Permeability in the absence of irradiation, $p_0 \cdot 10^{10}$	Permeability in the radiation field, $p_1 \cdot 10^{10}$	$\frac{p_1}{p_0}$	Dose rate, rad/sec
1	17	Polyethylene	Helium	1.8	–	4	2.22	180
1	17	Polyethylene	Helium	1.8	2.44	–	1.65	180
2	17	Polyethylene	Helium	1.8	1.92	6.0	3.12	300
2	17	Polyethylene	Helium	1.8	2.68	5.6	2.08	300
2	17	Polyethylene	Helium	1.8	2.56	5.67	2.22	300
2	17	Polyethylene	Helium	1.8	2.93	5.25	1.79	300
3	10	Polyethylene	Helium	1.12	1.0	6.1	6.1	730
3	10	Polyethylene	Helium	1.12	1.08	12.5	11.6	730
3	10	Polyethylene	Helium	1.12	1.15	14.8	12.9	730

Experiment No.	Temp., °C	Polymer	Gas	p_0 (from graph)	Permeability in the absence of irradiation, $p_0 \cdot 10^{10}$	Permeability in the radiation field, $p_1 \cdot 10^{10}$	$\frac{p_1}{p_0}$	Dose rate, rad/sec
4	15	Polyethylene	Xenon	0.24	—	2.55	10.6	730
4	15	Polyethylene	Xenon	0.24	—	3.70	15.4	730
5	40 ± 2	Polyethylene	Xenon	5.25	—	15.6	3.1	180
5	40 ± 2	Polyethylene	Xenon	5.25	5.05	15.7	2.8	180
6	15	Polytetrafluoroethylene	Helium	—	8.0*	14	1.75	560
6	15	Polytetrafluoroethylene	Helium	—	6.79	12.2	1.70	560

* The film was tested after irradiation with a dose of 0.7 Mrad.

For xenon this effect is more pronounced. At a dose rate of 180 rad/sec ($t = 40^\circ$), the diffusion process during irradiation increases by approximately a factor of 3, and at 730 rad/sec (15°)—by a factor of 10-15.* The effect of acceleration of diffusion during irradiation increases with each insertion of the source, but only at comparatively low dose rates. At low values of the dose rate, when the acceleration effect is relatively small ($p/p_0 = 2$–3), no increase in the ratio p/p_0 after repeated irradiation was observed (experiments 2 and 5, Table 1).

After the source is removed, the rate of the process again changes sharply, approaching the initial rate, but remaining somewhat higher than it. There remains, as it were, an "aftereffect," and this effect increases after each period of irradiation. As can be seen from Table 1 and Fig. 3, after four irradiation periods with a total duration of 160 min, the permeability constant increased from $1.92 \cdot 10^{10}$ to $2.93 \cdot 10^{10}$ cm^3/cm^2 sec • cm/atm. However, in some cases this effect is insignificant, for example in experiment 3.

Fig. 3. Increase in helium pressure in the vacuum part of the apparatus with time for polytetrafluoroethylene at 15°. I, III—without irradiation; II—under irradiation.

Acceleration of the diffusion process during irradiation was also found for the helium—polytetrafluoroethylene system (Fig. 3, Table 1). However, owing to the low radiation resistance of polytetrafluoroethylene, the test time was very

* In view of the low rate of xenon penetration through polyethylene at 15° and the limited pressure-measurement range of the remote manometer, it was not possible to measure the permeability constant of xenon at 15°. Therefore, values of p for xenon were used from the graphical dependence of $\lg p$ on $1/T$ (Fig. 4),

Fig. 4. Temperature dependence of xenon permeability through polyethylene

Figure 3: Fig. 4. Temperature dependence of xenon permeability through polyethylene

obtained by us in testing polyethylene film at different temperatures on an analogous apparatus with a MacLeod manometer. The data obtained are presented in Table 1. For comparison, data on helium permeability in polyethylene are also given.

limited at high dose rates (500-600 rad/sec). At the same time, at lower dose rates (30, 130, and 200 rad/sec) practically no effect of acceleration of the permeability of polytetrafluoroethylene was observed. At a dose rate of 560 rad/sec, the process of helium diffusion through polytetrafluoroethylene is accelerated much less than in the case of polyethylene and helium at the same temperature —only by a factor of 1.5. Thus, the process of acceleration of gas diffusion during irradiation is observed both for polymers undergoing crosslinking and for polymers undergoing degradation. It might have been expected that, during irradiation, the incident energy of the γ-radiation would cause heating of the diffusion cell and the film, as a result of which the gas permeability of the film would increase. Measurements of the temperature of the vessel and the film showed a certain increase in temperature (of the order of 3°), which causes an acceleration of the diffusion process in the case of helium by 20% and in the case of xenon by 50%, whereas p/p_0 reaches values of $\sim$ 3–10, respectively. Consequently, the overall heating of the film has no substantial influence on gas diffusion.

Fig. 4. Temperature dependence of xenon permeability through polyethylene.

Apparently, the acceleration of diffusion is associated with local excitation of molecules and an increase in their flexibility as a result of the primary acts of absorption of γ-quanta and the secondary reactions of the excited particles formed. During irradiation, ruptures occur in the main and side chains, which may cause changes in mechanical characteristics, for example creep. However, these ruptures can hardly be the cause of the acceleration of diffusion, since the diffusion rate at a sufficiently high molecular weight of the polymer does not depend on the length of the macromolecules.

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CITED LITERATURE

1. L. T. Bugaenko, T. S. Nikitina et al., *Chemical Action of Ionizing Radiations*, Moscow, 1958.

2. I. Sobolev, J. A. Meyer, V. Stannett, M. Szwarc, J. Polym. Sci., **17**, No. 85, 417 (1955).

3. H. A. Bent, J. Polym. Sci., **24**, No. 107 (1957).

4. C. E. Rogers, A. W. Myers et al., *Plastics Progress*, London—N. Y., 1957, p. 45.

5. M. A. Mokul' skii, Yu. S. Lazurkin et al., DAN, **125**, No. 5, 1007 (1959).

6. A. Kh. Breger, V. A. Belynskii et al., Proceedings of the All-Union Scientific-Technical Conference on the Use of Radioactive and Stable Isotopes and Measurements in the National Economy and Science, Publishing House of the Academy of Sciences of the USSR, 1958.

7. T. S. Nikitina, E. V. Zhuravskaya, A. S. Kuz' minskii, *The Action of Ionizing Radiations on Polymers*, Moscow, 1959.

Note: Figure translations are in progress. See original paper for figures.