MODIFICATION OF THE GAS-SEPARATING PROPERTIES OF ION-IMPLANTATION POLYMER MEMBRANES

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We have studied the gas-separation properties of industrial polyvinyltrimethylsilane (PVTMS) membranes, as well as of experimental specimens of polyarylate siloxane, modified with ions C^+, Ar^+, B^+, and N^+.

An important area in the practical utilization of polymer materials is membrane technology. The most important requirement imposed on polymer membranes as a structural material in gas-separation equipment is maximum output and a high level of separation in the processing of the mixture [1]. These parameters ultimately determine the dimensions of the equipment, the level of enrichment in the end-product of the mixture, as well as the expenditures of energy on the execution of the process. However, existing polymer membranes, in terms of their properties, do not always meet the requirements which are imposed on them in the solution of a number of scientific and engineering problems, and in this connection, a search is under way for various means of significantly altering their properties.

In addition to the traditional chemical methods of producing membranes of a specified composition and exhibiting specific properties, in recent times we have begun to resort to physical modification methods. The effect of thin-film carbon coatings (achieved by thermal deposition in a vacuum) on the gas-separation properties of polymer membranes has been established in [2, 3]. However, here the magnitude of the gas permeability of the modified membranes was sharply reduced, although the values of the selectivity coefficients increased. We should also make note of the fact that the reliability of these membranes is inadequate in actual use because of the poor adhesion of the coatings to the polymer substrate.

Ion implantation is a promising method of achieving goal-oriented changes in the physicochemical properties of polymers. Results from studies into the electrical, optical, structural, and mechanical properties of polymers can be found in reviews [4-7], and it is these properties that undergo significant evolution during radiation. The possibility of modifying the gas-separation properties of polymer ion-implantation membranes is demonstrated in [8, 9].

It is the purpose of the present study to undertake a comparative investigation into the gas-separation properties of polyvinyltrimethylsilane (PVTMS) membranes, as well as those made of polyarylatedimethylsiloxane (silar), modified through ion implantation.

Research Method. Industrial asymmetric PVTMS membranes and paper-based experimental silar specimens were used as the gas-separation membranes. Membranes exhibiting a thickness of 180-200 µm and a diameter of 45 mm were first degreased, and then placed into a radiation chamber. The treatment of the specimens with the ions C^+, Ar^+, B^+, and N^+ was carried out on a "Vesuvius" modernized installation with the following parameters: a vacuum of no less than 10^{-5} Pa, an ion energy of 30-150 keV, an ion-flux density of 0.5-2 mkA/cm^2, with the radiation dosage varied within the limits $8 \cdot 10^{14}$-10^{16} cm^{-2}. The asymmetric membrane was irradiated from the side of the diffusion layer, with the target temperature, governed by the ion bombardment and dependent on the radiation dose, did not exceed 300-330 K. The gas permeability of the membranes was studied on an experimental installation described in detail in [3]. Its main section is the diffusion cell which consists of an entry chamber and a measurement section, between which the test membrane is placed under airtight conditions. The gas being analyzed is passed under excess pressure into the entry chamber along

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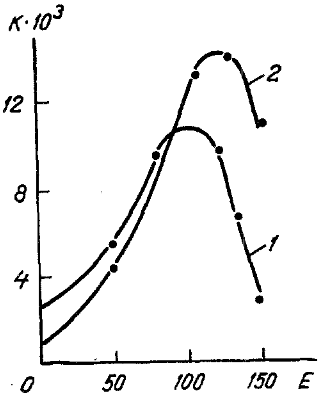

Fig. 1

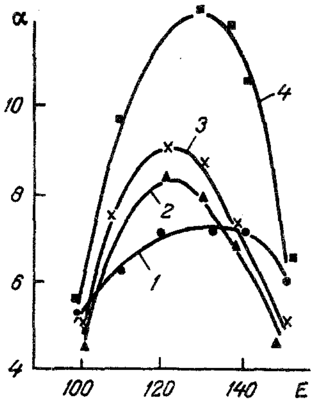

Fig. 2

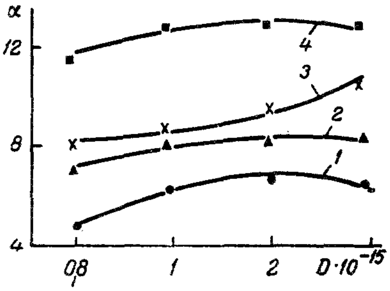

Fig. 3

Fig. 1. PVTMS (1) and silar (2) membrane water permeability as a function of the energy of the ions C^+ ($D = 2 \cdot 10^{15}$ cm^{-2}·const). K, liter/m^2·h·atm; E, keV.

Fig. 2. PVTMS (2, 3) and silar (1, 4) membrane selectivity coefficient for H_2/CO_2 and H_2/O_2, respectively, as a function of ion energy ($D = 2 \cdot 10^{15}$ cm^{-2}-const).

Fig. 3. PVTMS (2, 3) and silar (1, 4) membrane selectivity coefficient for H_2/CO_2 and H_2/O_2, respectively, as functions of the radiation dosage with ions C^+ (E = 100 keV-const).

TABLE 1. Gas-Separation Properties of Modified Membranes

Membrane type	Membrane radiation conditions	Gas permeability, liters/m^2·h·atm			Selectivity		
		H_2	CO_2	O_2	H_2/O_2	H_2/CO_2	CO_2/O_2
PVTMS	Control	2377	1398	457	5,2	1,7	3,1
PVTMS	C^+, $E = 100$ keV, $D = 4 \cdot 10^{15}$ cm^{-2}	11401	1629	1714	6,65	7,0	1
PVTMS	Ar^+, $E = 120$ keV, $D = 10^{15}$ cm^{-2}	—	209	51	—	—	4,1
PVTMS	B^+, $E = 100$ keV, $D = 10^{15}$ cm^{-2}	—	657	299	—	—	2,2
PVTMS	N^+, $E = 80$ keV, $D = 2 \cdot 10^{15}$ cm^{-2}	940	49,9	94	10	18,8	1
Silar	Control	310	1520	290	1,08	1	5,3
Silar	C^+, $E = 130$ keV, $D = 2 \cdot 10^{15}$ cm^{-2}	12300	1660	910	13,5	7,4	1,83

the membrane surface. The gas being diffused through the membrane was accumulated in the measuring chamber, initially evacuated to 10^2 Pa; this gas was analyzed by means of a chromato-effusion-mass spectrometer of the MKh-1312 type. Structural studies of the microrelief of the original and modified membranes was accomplished with the aid of an electron microscope, and an optical method was used to study the change in the composition of the surface layers.

Results and Discussion. Data on gas permeability and selectivity for the original and ion-implanted PVTMS membranes, as well as those of silar, can be found in Table 1 for various gases. Analysis of these results shows that in the case of ion implantation the gas-separation properties undergo significant change, and the level of these changes depends on the nature of the membrane material, the form and energy of the ion, and the radiation dosage. However, from all of the utilized ions (C^+, Ar^+, B^+, and N^+) only radiation with carbon ions yielded a positive effect, increasing both permeability to hydrogen, oxygen, and carbon dioxide, as well as the selectivity of the membranes. Proceeding from this, we can draw the conclusion that the change in the gas-selectivity properties of polymer membranes is a result not only of radiation defects which arise in the bombardment of the surface by any ions, but also a consequence of the formation of active capture centers (sorption) ascribed to the introduction of rigorously monitored concentration of carbon atoms in the surface layers which exhibit elevated selectivity for a particular gas. Given the identical parameters, the effect of irradiation is more significant for the silar which exhibits higher structural flexibility within the matrix of the polymer.

When the PVTMS is irradiated with nitrogen ions the permeability of all gases is reduced, but selectivity in terms of hydrogen and oxygen increased by a factor of 2, and for hydrogen and carbon dioxide it increased by more than an order of magnitude. Argon and boron high-energy ion implantation yielded no positive effect.

To determine the optimum treatment parameters, we studied the permeability and selectivity of membranes for hydrogen, oxygen, and carbon dioxide, as functions of the carbon ion energy and the radiation dosage. The results of these experiments can be seen in Figs. 1 and 2. The greatest effect in increasing the hydrogen permeability from radiation is achieved with an ion energy on the order of 100-130 keV, while for the selectivity coefficient the maximum is found at 130 keV. Thus, for example, the hydrogen permeability of silar increases by a factor of 30, while the hydrogen and oxygen selectivity increases by a factor of 10. With a further increase in the carbon ion energy the gas-selective properties of the membranes are impaired. The nature of the derived relationship can, apparently, be explained as follows: below 100-130 keV we have destruction of the polymer, destruction of the crystal structures, an increase in the nonsaturation of the molecular chains, and further, with an increase in ion energy, we have a significant change in the composition and structure of the surface areas of the film, due to the linking up of the polymer chains and the reduction in free volume, which leads to a reduction in the coefficients of gas solubility and diffusion, and consequently, to a reduction in permeability.

The dependence of the selectivity coefficients on the radiation dosage is less clearly expressed (Fig. 3), a consequence of the fact that the atomization of the surface is greater as the radiation dosage is increased. In this case, because of the predominant atomization of individual target components (the polymer) this process leads to the formation of a surface region exhibiting properties different from those of the original surface [10, 11].

In order to explain the results that we obtained, we conducted studies of the structure and composition of the surface layers in the polymer irradiated with carbon. We know that in the irradiation with high-energy ions complex radiation-chemical processes occur within the polymer. As a consequence of the excitation, weakening, breaking, and regrouping of the original chemical bonds, as well as because of the release of volatile compounds, atoms and radicals capable of reaction are formed, and these are the primary sorption centers. Electron-microscope and optical studies showed that in the case of radiation substantial structural reorganization and change in composition occurs within the surface layers. Band intensity is reduced in the IR spectrum of the PVTMS films, corresponding to CH bonds, while the expansion of the bands in the region 1400-1500 cm^{-1} is associated with the formation of multiple C—C bonds. Increasing the carbon radiation dosage from 10^{15} to $5 \cdot 10^{15}$ cm^{-2}, given a constant ion energy of 100 keV, leads to an intensification of this absorption band by a factor of almost 1.5. These changes in the IR spectrum confirm the conclusion that with radiation the bonds are broken and new bonds are formed, and that free hydrogen is released. Moreover, a band appears in the IR spectrum that corresponds to the carbonyl group C=O, which indicates the destruction of the irradiated PVTMS and its oxidation. With an increase in the radiation dosage the carbonization of the polymer becomes significant, and this brings about a noticeable change in the color of the film from light yellow in the case of a radiation dose of $2\cdot10^{15}$ cm^{-2} to dark brown for the case in which $D = 10^{16}$ cm^{-2}. Thus, modification of the polymer ion-implantation materials, given optimum radiation regimes, for appropriate ion-polymer systems, will yield a significant improvement in the gas-separation properties and it exhibits a number of advantages over other methods.

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STUDYING THE COEFFICIENT OF THERMAL CONDUCTIVITY FOR LIQUID METALS

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We discuss a method for an experimental study of the coefficient of thermal conductivity, specific heat capacity, and the specific electrical resistance of metals in the solid and liquid states, as well as the data that we have obtained with respect to the indicated properties of Bi, In, Cd, and Pb.

At the present time the coefficients of thermal conductivity for liquid metals have not been adequately studied [1]. This applies particularly to alloys. Such a situation can be ascribed to the limited development of reliable experimental methods, to the difficulties of carrying out such studies, particularly at high temperatures [2], and to the absence of sufficiently well-founded methods of calculating these properties [3].

In the present paper we examine a method intended for the experimental study of the coefficient of thermal conductivity λ, as well as of the specific electrical resistance ρ, and the specific heat capacity c_p for metals and alloys in the liquid and solid states. The method is based on one covered in [4-6] for the study of the thermophysical properties of metals in the solid state, and it essentially involves the following. Let a liquid metal of mass m be contained within a metal tube of length ℓ, and these two metals not reacting with each other chemically. We will assume that the cross-sectional area of the orifice

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