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Amorphous Perfluorinated Membrane Materials: Structure, Properties and Application

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Abstract—The structure and properties of glassy amorphous perfluorinated polymers are considered with an emphasis of their use as membrane material. The results of the study of free volume in these polymers and simulation of their nanostructure are discussed. The perfluorinated polymers are featured by unusual thermodynamic properties, so the influence of these properties on the parameters of the membranes based on them is examined. In conclusion, various applications of the membranes based on the perfluorinated polymers (predominantly amorphous Teflon AF) in separation processes are described.

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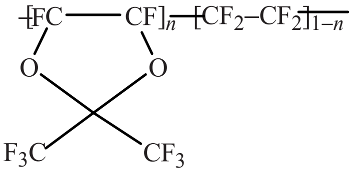
INTRODUCTION

Perfluorinated polymers are known since 30th of XX century when polytetrafluoroethylene has been discovered [1]. The amorphous perfluorinated polymers appeared more recently, in 70th [2]. They are the copolymers of the perfluorinated heterocyclic compound dioxolane with related compounds. By chemical properties they in much resemble polytetrafluoroethylene: exclusive chemical resistance that allows using them under aggressive conditions and in aggressive medium, in contact with oxidizers, acids and alkali.

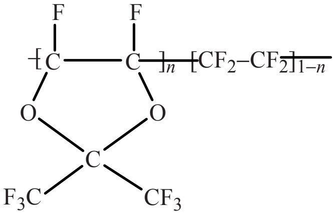
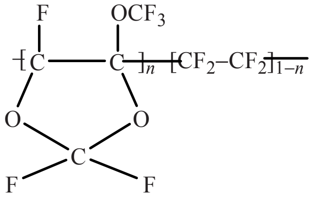
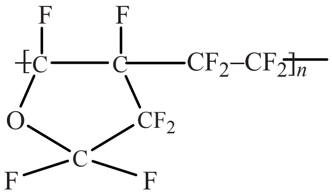
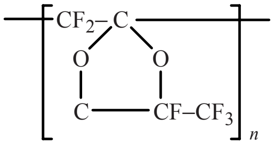
Thermodynamic properties of the amorphous perfluorinated polymers differ from those of hydrocarbon polymers. They are characterized by low solubility coefficients of gaseous hydrocarbons in them, are insoluble in common organic solvents, exert no swelling or damaging at the contact with petroleum products [3–6]. These features have not been explained theoretically yet [7], nevertheless they can be of great significance at the application of these polymers as a material for the gas separating membranes: the low solubility of the ordinary organic compounds in the perfluorinated polymers appears as diminished ability of the polymers to the plasticization which could decrease selectivity of the gas separation and pervaporation membranes [3]. For the perfluorinated polymers is typical low surface energy that retards deposition of a precipitate on the surface of a membrane produced from them. This is a very important property, because it is precipitate sedimenta-tion causes sharp decrease in the efficiency of porous ultra- and microfiltration membranes at their exploitation [8].

The interest to amorphous glassy perfluorinated polymers as the membrane material appeared due to the discovery of high gas penetration property of amorphous AF Teflons produced by DuPont [9, 10]. Such Teflons are the static copolymers of 2,2-bis-(trifluoromethyl)-4,5-difluoro-1,3-dioxolane and tetrafluoroethylene:



In the commercial scale two copolymers are produced, AF 2400 (n = 0.87) and AF 1600 (n = 0.65). They are soluble in perfluorinated solvents and therefore are appropriate for producing films and membranes that can be applied and studied. Also have been described the methods of the synthesis of other structurally related perfluorinated polymer with cyclic

Table 1. Structure and properties of some of amorphous perfluorinated polymers[a]

Polymer	Structure	T_c, °C	$P(O_2)$, barrer[b]	$\alpha(O_2/N_2)$	$P(H_2)$	$\alpha(H_2/CH_4)$	References
Teflon AF 2400 (87 mol % of dioxolane)		250	1140	2.0	2400	5.5	[10, 15]
Hyflon AD80X (80 mol % of dioxolane)		134	190	2.5	563	11.5	[16]
Cytop		108	7.0	3.5	28	25	[17]
Polyperfluoro-2-methylene-4-methyl-1,3-dioxolane		–	–	–	230	120	[18]

[a] (T_c) is glass transition temperature, (P_i) is permeability coefficients, ($\alpha_{ij} = P_i/P_j$) is separation factors (values for room temperature).

[b] 1 Barrer = 10^{-10} (cm^3 O_2) cm cm^{-2} s^{-1} cm Hg^{-1}. Here (cm^3 O_2) represents the quantity of oxygen that would take up one cubic centimeter at standard temperature and pressure, as calculated via the ideal gas law.

fragment in the main chain, Hyflon (statistical copolymer of 2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxolane and tetrafluoroethylene) [11] and Cytop [12], and their transport properties were investigated [3, 13, 14]. (Cytop is a homopolymer. Its structure is described in Table 1). Other amorphous perfluorinated polymers with the cyclic fragments in the main chain have also been described.

The structural formulas and some properties of the most detailed studied amorphous perfluorinated polymers are listed in Table 1. These data show strong influence of the structure of rings included to the polymers and copolymers on the properties of the obtained materials. The chain rigidity expressed by the glass transition temperature varies in the range from 108 °C to above 250 °C (2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxolane homopolymer). Increase in the content of the cyclic comonomer increases the glass transition temperature and gas penetrability. For example the copolymer AF 1600 containing 65 mol % of dioxolane has T_c = 156 °C, $P(O_2)$ = 170 Barrer [15], while increase of dioxolane content to 87 mol % increases noticeable these values: T_c = 250°C, $P(O_2)$ = 1140 Barrer.

Free Volume and Modeling the Structure of Amorphous Perfluorinated Polymers

The unusual transport properties of the amorphous perfluorinated polymers, and of the AF copolymers [9, 15, 19] first of all require study of their free volume (available space between the polymer chains). For this purpose several procedures of sounding have been applied, such as the method of the positron annihilation, reverse gas chromatography, and ^{129}Xe NMR spectroscopy. Principally the presence of large free volume in the amorphous glassy perfluorinated polymers is attested by their extremely low density. For example, the density of the amorphous AF Teflons (1.6–1.7 g cm^{-3}) is much below than that of polytetrafluoroethylene (2.15–2.20 g cm^{-3}) or tetrafluoroethylene and hexafluoropropylene copolymer FEP Teflon (2.12–2.17 g cm^{-3}). Note significant difference in the density of amorphous AF Teflons, and crystalline (2.35 g cm^{-3}) and amorphous (2.007 g cm^{-3}) phases of polytetrafluoroethylene [20]. This is reflected by a very high fraction of free volume in the AF copolymers, that by Bondi estimation [21], is about 0.3 [22]. The low density is characteristic also of the perfluorinated materials.

In Table 2 are listed the results of measuring free volume in perfluorinated polymers by means of several methods of sounding (the methodology of measuring free volume in polymers has been described in details in the review [23]). From the data of different methods the radii of the elements of free volume in the perfluorinated polymers R_{sp} and R_c are of higher values than in the hydrocarbon polymers. This situation indicates a certain similarity in the structures of perfluorinated polymers, which, however, has not been explained so far. Noteworthy that the estimations of free values demonstrate rather good consistence of different independent methods. Large values of the free volume elements has been established by sounding methods also for many polymers not containing fluorine but with high permeability, e.g., for polytrimethylsilylpropyne and other polyacetylenes [25–27].

The most detailed information about the nanostructure of the free volume in polymers can be obtained by the method of positron spectroscopy by measuring the time before annihilation, because it allows measuring not only average size of the elements of free volume (microcavities), but also their distribution by size and concentration. An important result that has been obtained for the highly permeable polymers (including amorphous AF Teflons) is elucidation of bimodal distribution of the microcavities by size [28, 29] (Fig. 1). Although the problem of adequacy of the bimodal distribution by size of the microcavities in glassy polymers from the data of annihilation measuring still an object of discussion (e.g., see [30]), nevertheless these data show unambiguously that amorphous AF Teflons contain unusually large cavities.

Very valuable information on the nanostructure of the amorphous Teflons has been obtained by means of computer modeling (with the method of molecular

Table 2. Radius of the elements of free volume (Å) in polymer from the data of a series of methods [24][a]

Polymer	^{129}Xe NMR spectra		Positron annigilation method		Reverse gas chromatography
	R_{sp}	R_c	R_{sp}	R_c	
Teflon AF 2400	8.04	5.12	5.95	6.33	6.4
Teflon AF 1600	6.66	4.43	4.89	5.43	5.8
AD 80X	6.12	4.16	–	–	
AD 60X	6.00	4.10	–	–	
Polytetrafluororethylene	5.69	3.94	4.20	4.90	
Polyphenylene oxide	2.92	2.56	3.40	4.20	3.4
Low density polyethylene	2.60	2.40	3.30	4.10	
Polycarbonate	2.48	2.34	2.90	3.80	
Polystyrene	2.52	2.36	2.88	3.76	

[a] (R_{sp}) is spheric model and (R_c) is cylindric model of an element of free volume.

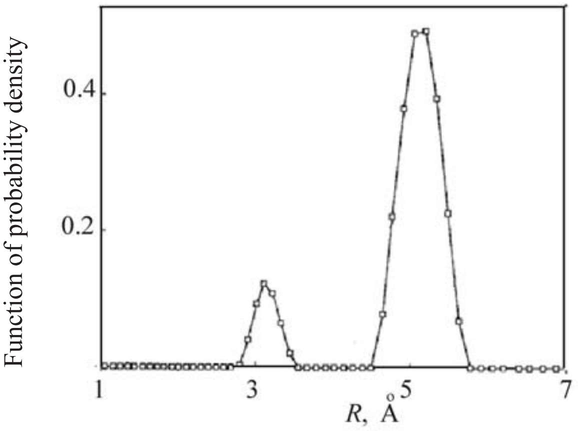


Fig. 1. Distribution by size of the elements of free volume in amorphous Teflon. By the data of the method of positron

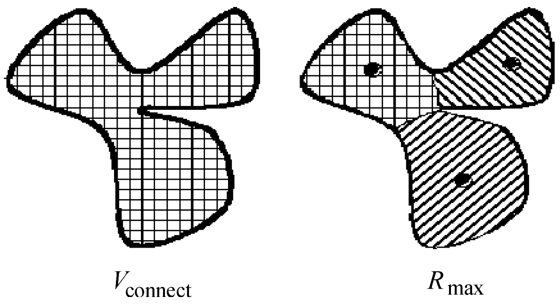


Fig. 2. Two possible models of a free volume element in polymers: $V_{connect}$ and R_{max} [31].

dynamics) [31]. For the analysis of free volume in glassy polymers were considered two models of the microcavities. By one approximation (marked as R_{max}) a microcavity of tentative form is divided into more compact quasi-spherical elements (Fig. 2). By another approximation ($V_{connect}$) a microcavity includes all the points where does not occur overlapping of atoms of the cavity forming polymer chains with a trial moiety, e.g., hydrogen-like atom of *o*-positron (*o*-Ps) in the method of annihilation of positrons (diameter 1.1 Å). The distribution over microcavity sizes obtained with such representation differs considerably depending on the applied model (Fig. 3). The R_{max} approximation gives wide distribution over sizes that cover the data on the microcavity sizes obtained by the sounding methods. The model $V_{connect}$ shows clearly the bimodal distribution but does not predict existence of large microcavities with the size ~18 Å, obtained as overestimation of the sounding methods. Probably actually there is superposition of both the models. Probably those for the *o*-Ps atoms that in the method of annihilation of positrons sound not all the regions in the microcavity of not regular shape are equally available. Then one can state better correspondence between the computer modeling of free volume and the results of the sounding methods. Noteworthy that very wide distribution over the cavity size in the AF 2400 copolymer has been obtained with the Monte-Carlo method [32].

The rate of diffusion through membrane depends not only on the size of the elements of free value, but also on their connectivity, that is, whether the elements form open or closed porosity. In this connection seems

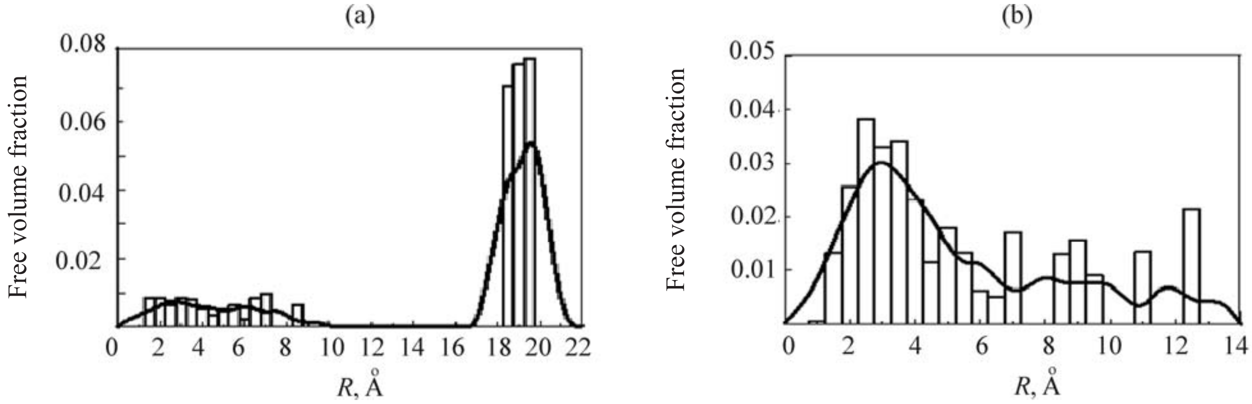


Fig. 3. Distribution by size of the elements of free volume in amorphous Teflon AF 2400 in the approximations: (a) $V_{connect}$ and (b) R_{max} [31]. Solid curves are obtained by averaging.

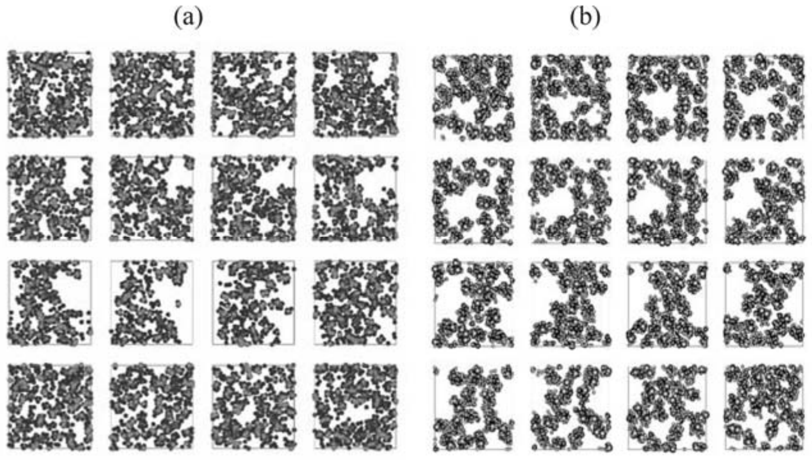


Fig. 4. Visualization of packaging the chains in the models of (a) amorphous Teflon AF 2400 and (b) polytrimethylsilylpropyne [31].

promising revealing the type of porosity by means of visualization of free volume that can be achieved by the method of molecular dynamics. This method assumes cubic package of the polymer macromolecules into the blocks (the cube edge 40–50 Å) and the sections of the model at a short distance (e.g., 3 Å) are considered. In Fig. 4 are shown such sections for the amorphous AF 2400 Teflon and for comparison for another highly permeable polymer polytrimethylsilylpropyne. The microcavity size in these polymers (by the molecular dynamics data and sounding methods) differs insignificantly. However, in Fig. 4 is seen a significant difference in the connectivity of the free volumes. In polytrimethylsilylpropyne it has character of the open porosity while in the amorphous AF 2400 Teflon the relatively large microcavities are surrounded by the dense packaged layers of the polymer chains. Such difference in the nanostructure is very significant for the transport properties of these polymers. In other words these “microscopic” structural features define “macroscopic” behavior of the considered polymers. The data in Table 3 demonstrate changes in the permeability coefficients for a series of *n*-alkanes through the amorphous AF Teflons and polytrimethylsilylpropyne. In the case of polytrimethylsilylpropyne occurs sorption controlled mass transfer [the permeability coefficients grow when the penetrant (diffusing molecule) size grows, like the case of changes in solubility coefficients], while in the AF Teflons occurs common for the glassy polymers the mass transfer controlled by diffusion (the permeability coefficients fall when the permeate size grows). This is connected with rather sharper dependence of diffusion coefficients on the permeating molecules size in the AF copolymers as compared with polytrimethylsilylpropyne (Table 4).

The large free volume and high gas permeability of the amorphous glassy perfluorinated polymers and of amorphous AF 2400 Teflon in particular, on the first glance seem not consistent with the current view on the connection between the structure and the gas separation properties of polymers. The strongest effects described in literature are defined by introduction of

Table 3. Premeability coefficients (*P,* barrer) of amorphous Teflons AF and polytrimethylsilylpropine toward gaseous alkanes C_1–C_3 [15, 33]

Gas	AF 2400	AF 1600	Polytrimethylsilylpropine
CH_4	435	41	15000
C_2H_6	252	16	31000
C_3H_8	97	2	38000

Table 4. Diffusion coefficients ($D\times10^7$, cm^2 s^{-1}) of gaseous alkanes in amorphous Teflon AF 2400 and in polytrimethylsilylpropine [15, 33]

Gas	AF 2400	Polytrimethylsilylpropine
CH_4	–	240
C_2H_6	3.60	110
C_3H_8	0.42	98
C_4H_{10}	0.24	–

bulky substituents to the main macromolecular chains. Among such side groups are known $Si(CH_3)_3$, Ge $(CH_3)_3$, $C(CH_3)_3$, and $CH(CH_3)_2$ attached directly or with a spacer to vinyl, polyene or another basic chain (e.g., see [34]). The design of the amorphous AF Teflons is quite another, so their properties can not be explained by the presence of bulky side groups preventing dense packaging of the chains.

As shown by quantum-chemical investigation [35] the nature of large free volume in amorphous perfluorinated polymers is connected with a very high rigidity of chains in these polymers at weak interchain interactions that is typical for all perfluorinated compounds. By the estimations in [35], the energetic rotation barriers between neighboring perfluorodioxolane rings are big enough. Thus, the rotation barrier for two neighboring 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxolane ring is about 60 kJ mol^{-1}. Replacement of two neighboring CF_3 groups in the ring by F atoms decreases it only slightly. The barrier falls at introducing–C_2F_4–links between the rings although its value remains high enough (ca. 20 kJ mol^{-1}). The height of rotation barrier correlates with the polymer glass transition temperature, and with the permeability, diffusion and solubility coefficients. Thus, the large free volume in the amorphous perfluorinated polymers is caused by the factors restricting dense packaging of the rigid chains.

Thermodynamic Properties of Perfluorinated Polymers

The thermodynamic behavior of perfluorinated compounds (both low molecular and polymers) differs from that of ordinary organic compounds. For first time it was discovered in the middle of XX century at the study of thermodynamic processes of mixing perfluorinated and hydrogen-containing organic compound and showed restriction of the Hildebrandt theory of regular solutions [36].

In the recent years the unusual thermodynamic properties were noted for various perfluorinated polymers. Both glassy and highly elastic perfluorinated polymers show higher solubility coefficients S of fluorocarbons than it would be expected from the known correlations of the ln S value with such parameters as critical temperature or boiling temperature [4, 6, 22, 29, 37]. However, it has been noted a lower solubility of fluorocarbons in hydro-carbon polymers [38]. Figure 5 illustrates considerable difference in the solubility coefficients of fluorocarbons and hydrocarbons in the amorphous perfluorinated resin, the copolymer of equimolar amounts of tetrafluoroethylene and perfluoromethylvinyl ether [6]. The nature of this effect which probably defines existence of some useful properties of perfluorinated polymers as membrane materials still remains to be an object of investigations [3, 7].

The permeability coefficients of gases P is defined as a dot $P = DS$, where D is diffusion coefficient and S is solubility coefficient of the gas in the polymer. The selectivity of a gas permeability $\alpha = P_i/P_j$ (the i and j indices relate to the gases of different nature) can be represented as diffusion selectivity $\alpha^D = D_i/D_j$ and sorption selectivity $\alpha^S = S_i/S_j$. The decrease in solubility of hydrocarbons in perfluorinated polymers S_j can lead to increase in selectivity of permeability of gas and hydrocarbons mixtures in these polymers. It is such regularities that often occur for the properties of the perfluorinated membrane materials.

In Fig. 6 is shown permeability–selectivity diagram for the pair N_2/CH_4 in respect of a series of polymers including amorphous perfluorinated polymers [3]. In such diagrams usually is emphasized so called upper limit that is the line confining at the top the area of points characterizing transport parameters of the membrane materials. Commonly the aim of investigators is obtaining a membrane material with the points in such diagram above the upper limit. As seen from Fig. 6, all the points of perfluorinated polymers are located above the upper limit line obtained for the set of hydrogen-containing polymers. The same is attested by a very high selectivity of He/CH_4 pair separation that is achieved with the membrane materials obtained by the complete fluorination of hydrocarbon polymers with molecular fluorine that leads to complete fluorine substitution for hydrogen in the modified polymer [39].

A serious restriction to the application of membranes to separation of the mixtures containing in a significant amount organic (mostly hydrocarbon) contaminants is plasticization of the membrane material that leads to decrease in the separation selectivity as compared to the ideal selectivity factors $\alpha = P_i/P_j$, where P_i and P_j characterize transport of the individual components. In the perfluorinated membrane materials this effect is much weaker due to low solubility of hydrocarbons. For example, at the separation of a propylene/propane mixture with a polyimide membrane the ideal separation factor $\alpha = P(C_3H_6)/P(C_3H_8)$ equals to 50. When the equimolar

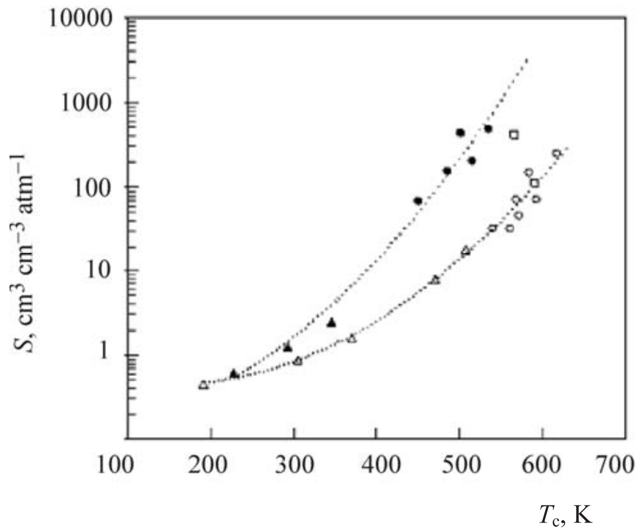


Fig. 5. Correlation of solubility coefficients of (dark dots) fluorocarbons and (light dots) hydrocarbons in the tetrafluoroethylene–perfluoromethylvinyl ether copolymet [6]. Triangles are the data of [37].

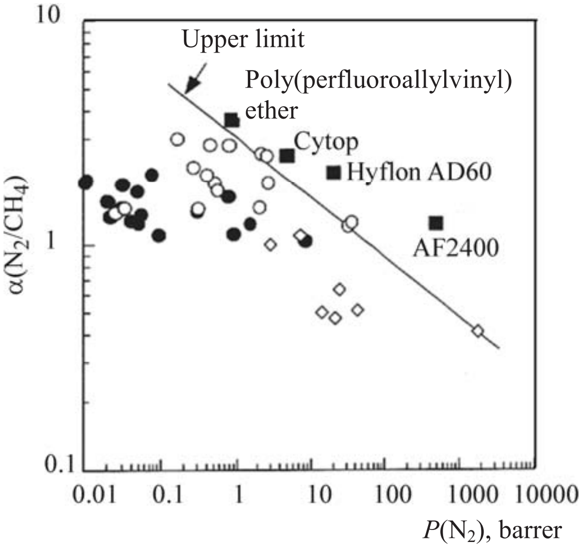


Fig. 6. Diagram permeability–selectivity for the pair nitrogen–methane. (●) are polyimides containing no fluorime, (○) are fluorinated polyimides, and (◊) are polyacetylenes [4].

mixture of these hydrocarbons is feed with the pressure over the membrane 4 atm, the real separation factor equals 8 only, and at the pressure 8 atm it is less tan 2. On the other hand, at the separation of the same mixture with the membrane based on the perfluorinated polymer Cytop the real separation factor does not depend on the pressure of the feeding flow and remains equal to 5 up to 12 atm pressure [3].

Processes of Separation with the Membranes Based on the Perfluorinated Polymers

The membranes based on the amorphous perfluorinated polymers found application to the separation of the components of air into the flows enriched with either oxygen or nitrogen. Feeding with the air enriched with oxygen to the content 25–35% O_2 allows to increase power of diesel engines and to decrease toxic exhausts at the engine cool start. In this case is used the permeate, that is, the flow passed through the membrane. The air enriched with oxygen was also supposed to apply as a furnace blast. It was supposed to use the retentate (the flow not passed through a membrane) for the lowering NO_x exhaust at the work of diesel engine. Such flow can contain up to 90–95% of N_2. The air flow enriched with oxygen by means of application of the membranes based on perfluorinated polymers (as well as with other polymers , e.g. polyvinyltrimethylsilane) was supposed to use for medicine purposes in a portable respirator, while the air enriched with nitrogen can serve as the inert atmosphere for the storage of fuel, of fruits and so on.

The main advantage of the amorphous perfluorinated polymers is high gas permeability, and hence low enough specific surface of membrane that allows designing compact gas separating devices. At the same time, the not high selectivity at the separation of oxygen–nitrogen mixtures [$\alpha(O_2/N_2) \approx 2$ for the amorphous AF 2400 Teflon] restricts the degree of the permeate enrichment. The permeate obtained with the membrane based on AF 2400 can not contain more than 35% of O_2. But ever such low enrichment gives a way to the realization of many practical challenges [40–44].

Such a challenge is creation of a versatile method of gasification of low sort (high-ash) coals. Such solid fossil fuel is accessible and abundant energy source but its gasification with air feeding meets many problems. It has been shown that cheap and effective method of processing such coals can be created on the basis of application of the air enriched to 27–33% of O_2 by the membrane method [45]. Practical realization of this process is connected with the high enough permeability of the existing membranes. Thus, the permeability on oxygen of flat asymmetric gas separating membrane based on polyvinyltrimethyl-silane is 0.6 l m^{-2} h^{-1} atm^{-1}. At the same time the permeability of composite membrane based on AF 2400 copolymer is higher by an order of magnitude. Hence, for obtaining the same flow of the air enriched with oxygen, e.g., 300 m^3 h^{-1}, the surface of the hole fiber module based on AF 2400 should be of the area 10–70 m^2, while with the membrane of polyvinyltri-methylsilane it should be of 1000–2000 m^2. Respective membrane modules will differ in size even more [46].

The exclusively high chemical stability of the perfluorinated polymers opens another pathway for the application of the membranes based on these polymers: For feeding with ozone the system of purification of sewages and for disinfection. A disadvantage of many existing processes of ozonation is the loss of ozone fed with ejectors or bubble columns, owing to its relatively low solubility in water. This loss can be decreased sharply by feeding with the ozone flow through nonporous polymer membrane (the process of pertraction). But practically all organic polymers exert destruction at the contact with ozone. A promising solution is application of perfluorinated polymers that combine high chemical stability and effective permeability as the membrane material [47–49].

The insolubility of amorphous perfluorinated polymers in organic solvents opens also a perspective route for their application; namely, use them as the materials for the pervaporational separation of liquid organic mixtures or for removing organic contaminants from aqueous solutions [50, 51]. Here the advantage of such membrane material is also owes to the features of thermodynamic properties of the perfluorinated compounds and their high permeability. The membranes based on the perfluorinated polymers are especially perspective for the organoselective pervaporation, that is, for the separation of mixtures of organic compounds. There are many objects for such separation in the petroleum chemistry and in the chemistry of basic organic synthesis. To the moment has been demonstrated versatility of the membranes based on amorphous AF 2400 Teflon for the separation of methane chlorine derivatives and for purification of containing them sewages. One can expect that application of high permeable membranes of this type with thin selective layers will be perspective also for the separation of other mixtures.

CONCLUSIONS

Amorphous perfluorinated polymers constitute a relatively new class of the membrane materials possessing a complex of unusual structural, thermodynamic and transport properties, opening various pathways of their application to the separation of gas and liquid mixtures.

Besides the examples of their application considered in this review, there are perspectives of their application in other directions. Due to their low surface energy of these amorphous polymers (as well as of partially crystalline perfluorinated materials) there is unique possibility of their application as porous membranes to the processes of ultra- and microfiltration. For them is not typical sedimentation of precipitates that sharply decrease efficiency of membrane in the process of exploitation. The same properties of the perfluorinated polymers makes extremely desirable to use them for the membrane contactors (the devices for selective injection of the gas mixture components to liquid phase by feeding through the membrane or by desorbing through the membrane of dissolved gases), in membrane bioreactors and in other new membrane technologies. A serious difficultness to the introduction of amorphous perfluorinated membranes appears due to restricted assortment of such polymers, and this makes urgent solving the problem of the synthesis and investigation of new perfluorinated materials.

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