

PIM-1/MIL-101 Hybrid Composite Membrane Material: Transport Properties and Free Volume

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Abstract—A hybrid composite membrane material based on the PIM-1 polymer of intrinsic microporosity and MIL-101 nanoparticles of mesoporous chromium terephthalate has been prepared and tested. Fourier-transform IR spectroscopy has revealed the presence of interaction between the polymer matrix and the nanoparticles introduced into it. The addition of MIL-101 nanoparticles leads to an increase in the permeability and diffusion coefficients for gases (He, O₂, N₂, CO₂) compared to the original polymer. Using positron annihilation lifetime spectroscopy (PALS), it has been shown that these changes result from an increase in the free volume in the polymer composite material.

Keywords: hybrid composite membrane materials, permeability, diffusion, free volume

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INTRODUCTION

Gas separation membranes and membrane materials based on polymer composites containing various additives of nanoparticles have attracted much attention from researchers [1, 2]. Nanoparticles containing internal cavities of a certain size (zeolites, metal–organic frameworks (MOFs), or carbon nanotubes) are of particular interest. In addition to the disturbances generated in the polymer matrix and an increase in free volume and gas permeability that accompanies these disturbances, they provide the possibility of selective sorption of certain penetrants and thereby an increase in the selectivity of the resulting membranes. The choice of the polymer forming a continuous matrix is extremely important. In selecting the polymer material, preference should be given to materials for which, even in the absence of additives of nanoparticles, data points in the Robeson plots [3] lie in the immediate vicinity of the so-called “upper bounds.” One of these polymers is a PIM-1 polymer of intrinsic microporosity, which advantageously combines permeability and selectivity [4].

Recently, it has been shown that a composite material based on PIM-1 and a ZIF-8 zeolitic imidazolate framework exhibits fairly attractive transport properties and a high free volume [5]. It would be of interest to study other hybrid systems based on the same polymer and other frameworks. This task is implemented

in this study, which focuses on the examination of a PIM-1/MIL-101 system. MIL-101 is mesoporous chromium(III) terephthalate that exhibits an exclusively developed specific surface area (4000 m²/g according to the BET model [6]) and high chemical and thermal stability [7]. This combination of properties is responsible for particular interest in MIL-101 as a sorbent of gases and an active filler for composite membrane materials. In this study, the coefficients of permeability, diffusion, and solubility of gases in this composite have been determined. Using positron annihilation lifetime spectroscopy (PALS), the free volume of the composite has been examined. Spectral studies of the PIM-1/MIL-101 system have been conducted.

EXPERIMENTAL

Materials

The PIM-1 polymer was synthesized as described in [4] and kindly provided by Prof. P.M. Budd (University of Manchester, United Kingdom). The polymer structure is shown in Fig. 1.

Crystalline MIL-101 was prepared at the Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences by hydrothermal synthesis as described in [6]. To synthesize the composite, a dispersion of MIL-101 in chloroform was prepared

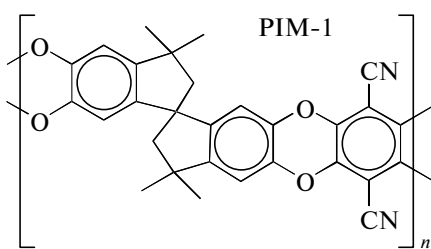


Fig. 1. Chemical structure of the PIM-1 polymer of intrinsic microporosity.

by sonication using a UZDN instrument. The resulting dispersion was mixed with a solution of PIM-1 in chloroform. After the removal of the residual solvent (to constant weight), the resulting film contained about 33 vol % MIL-101. The choice of this high concentration of the additive was based on the observation that significant changes in transport properties typically occur only at an addition content of more than 20%.

Measurements

Coefficients of permeability (P), diffusion (D), and solubility (S) were determined by the barometric method using an MKS Barotron system. The P and D values were found by the Daynes–Barrer time lag method, and the solubility coefficient was determined as the $S = P/D$ ratio.

Spectral studies of the sample surface were conducted in the reflection mode using a HYPERION-2000 IR microscope coupled to a Bruker IFS-66 v/s FTIR spectrometer (150 scans, a resolution of 1 cm^{-1}). For measurements in the attenuation total reflection (ATR) mode, a Ge crystal was used; the spectra were recorded in a range of $4000\text{--}600\text{ cm}^{-1}$.

The free volume of the PIM-1/MIL-101 composite was measured by PALS. A standard EG&G Ortec PALS instrument with a time resolution of $\text{FWHM} = 300\text{ ps}$ was used to process the spectra employing the PATFIT software. A source of positrons was a ^{44}Ti isotope (a half-life of 48 years; manufactured by Izotop, Russia) with a radioactivity of 0.76 MBq. The energy of the “primary” quantum was 1.159 keV. The lifetime spectra were described in terms of a four-component model; in addition, lifetimes τ_3 (intensity I_3) and τ_4 (intensity I_4) were attributed to o -Ps annihilation [8]. A stack of films, each having a total thickness of about 1 mm, was placed on both sides of the source. The annihilation times were measured in an inert atmosphere (N_2) to eliminate the “quenching” of positronium by atmospheric oxygen. Each measurement lasted for about 3 h to collect statistics for about 10^6 events.

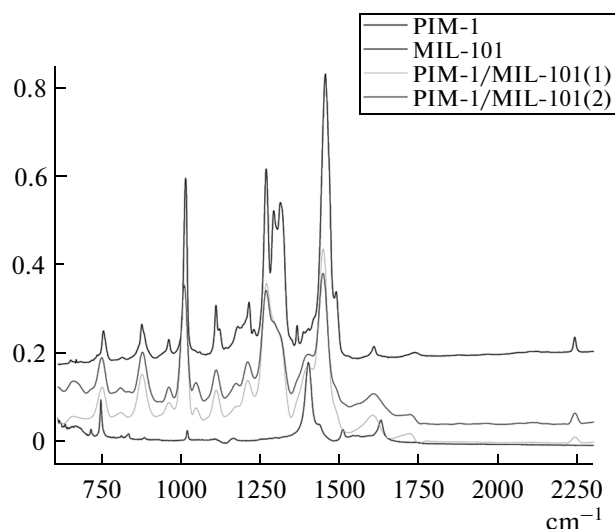


Fig. 2. Spectra of the starting components (PIM-1 polymer and MIL-101 additive) compared to the spectrum of the composite membrane.

RESULTS AND DISCUSSION

Spectral Studies

An important issue in the study of hybrid composite membranes with additives of nanoparticles, which has not yet been adequately addressed, is the interaction between the introduced nanoparticle and the polymer matrix. In this study, an attempt to approach this problem using IR spectroscopy was made. Individual spectra of the polymer (PIM-1), MIL-101 particles, and a composite containing 33% of the additive were recorded. These spectra are compared in Fig. 2. Bands of PIM-1 and the MIL-101 additive are clearly evident in the spectrum of the composite membrane.

Before proceeding to comparison of these spectra, it is necessary to say a few words about the spectra of the components. The spectrum of PIM-1 is fully consistent with its structure. The bands at 3055 , 3006 , 1607 , 1490 , and 754 cm^{-1} are attributed to the stretching and bending vibrations of the aromatic rings; the band at 2242 cm^{-1} corresponds to the stretching vibration of the nitrile group, while the intense bands at 1312 , 1291 , 1269 , and 1013 cm^{-1} are ascribed to the stretching vibrations of the C–O–C bonds. The bands at 2929 , 2957 , and 2866 cm^{-1} correspond to the stretching vibrations of the saturated C–H bonds; 1455 cm^{-1} , the bending vibrations of CH_2 in the spiro-pyran rings; 876 cm^{-1} , the skeletal vibration of the five-membered spiro-pyran rings; and 1370 cm^{-1} , the bending vibrations of the methyl groups.

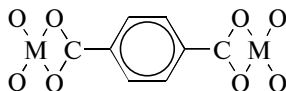
The ATR IR spectra of MIL-101 powders exhibit bands of the para-substituted aromatic ring: 1631 and 1510 cm^{-1} ($\nu_{\text{C}=\text{C}}$), 1018 and 1018 , 748 , and 717 cm^{-1} (δ_{CCH}). The most intense band in the spectrum at 1402 cm^{-1} is attributed to the highly delocalized carboxylate ion; the broad band at 666 cm^{-1} corresponds

Table 1. Gas permeability and gas separation selectivity of the PIM polymer and the PIM/MIL-101 composite

MIL-101, vol %	P , Barrer*				Selectivity, $\alpha = P_i/P_j$		
	He	O ₂	N ₂	CO ₂	O ₂ /N ₂	CO ₂ /N ₂	He/N ₂
0	1180	701	174	3250	4.0	19	6.8
33	1200	1010	232	8440	4.4	36	7.0

* 1 Barrer = 10^{-10} cm³ (STP) cm/(cm² s cm Hg).

to the M–O bonds. That is, the spectrum describes a structure of the following type:



with highly delocalized (sesquialteral) C–O and M–O bonds.

It should be noted that in the composite membrane, all the bands of both MIL-101 and particularly PIM-1 are strongly broadened and even exhibit a peak shift compared to the spectra of the starting components. This fact in itself suggests that the sample comprises two mutually interacting chemical compounds rather than merely a mechanical mixture. That is, the sample most probably contains both the individual components (PIM-1 and MIL-101) and mutually interacting components. To reveal the cause of this interaction, it is necessary to examine the MIL-101 and PIM-1 bands that undergo the greatest changes in the spectrum of the composite membrane. These changes are observed in the absorption region of the PIM-1 C–O–C bonds at 1300–1250 and 1013 cm⁻¹, in which some bands are not detectable and a strong shift and a change in the intensity ratio occur. In terms of structure, these changes in the spectrum are suggested to be due to fairly strong noncovalent bonding of the dioxane ring unit of PIM-1 to the metal cation in MIL-101 (apparently, in the region of crystal lattice defects). In this case, since both components comprise regions of conjugated bonds, this interaction cannot but affect the broadening and shift of the bands of other structural units: the aromatic rings in both components and the saturated groups in the spectrum of PIM-1, because the conformation of the polymer in the spiropyran ring obviously changes. The interaction of the oxygen atoms of PIM-1 with the metal cation in MIL-101 is also evidenced by a shift of the M–O band (666 cm⁻¹) and a significant increase in its intensity in the spectrum of the composite membrane compared to the spectrum of the MIL-101 powder.

It is of particular interest to study possible chemical changes that occur in the composites under the action of ultrasound. The fact is that almost all preparation techniques for composites involve sonication of nanoparticle slurries in solutions of matrix polymers [1, 2]. This issue has not been given sufficient attention in the

literature either. MIL-101 dispersions in chloroform were subjected to sonication for 2 and 4 min. The recorded spectra were compared with the spectra of the original MIL-101 sample. Changes in the IR spectra were observed at 1750 and 1650–1500 cm⁻¹. The absorption bands at 1630 and 1509 cm⁻¹ can be attributed to the stretching vibrations of C=C in the aromatic ring; changes in the structure are most pronounced in the region of 1560–1537 cm⁻¹. After sonication, an absorption band at 1750 cm⁻¹ appears. This band can be attributed to the vibrations of the free C=O groups in carboxylates in the absence of charge delocalization. Most probably, during sonication, the crystal lattice of MIL-101 undergoes partial destruction resulting in the appearance of carboxyl groups without delocalized bonds.

Gas Permeability

The transport properties of the resulting composite membrane and the original PIM-1 polymer were compared. The permeability coefficients and separation factors are listed in Table 1.

It is evident that, for most of the gases, the permeability coefficients increase along with a certain increase in the separation factors. The result is that the point corresponding to the composite membrane containing MIL-101 is considerably shifted compared to the upper bound in the Robeson plot, which is shown in Fig. 3.

It is known that the permeability coefficient comprises a diffusion component, i.e., diffusion coefficient D , and a thermodynamic component, i.e., solubility coefficient S ($P = DS$). It is of interest to determine which of these parameters is responsible for changes in the transport properties of the composite containing the MIL-101 additive. Table 2 shows the diffusion coefficients of the different gases in the pure PIM-1 polymer and in the composite.

It is evident that the composite is characterized by significantly higher diffusion coefficients for all the gases. In addition, no considerable decrease in the diffusion selectivity is observed. At the same time, the solubility coefficients remain almost unchanged upon the introduction of MIL-101 additives into the polymer matrix, as evidenced by Table 3. Thus, an increase in the permeability coefficient is mostly caused by an

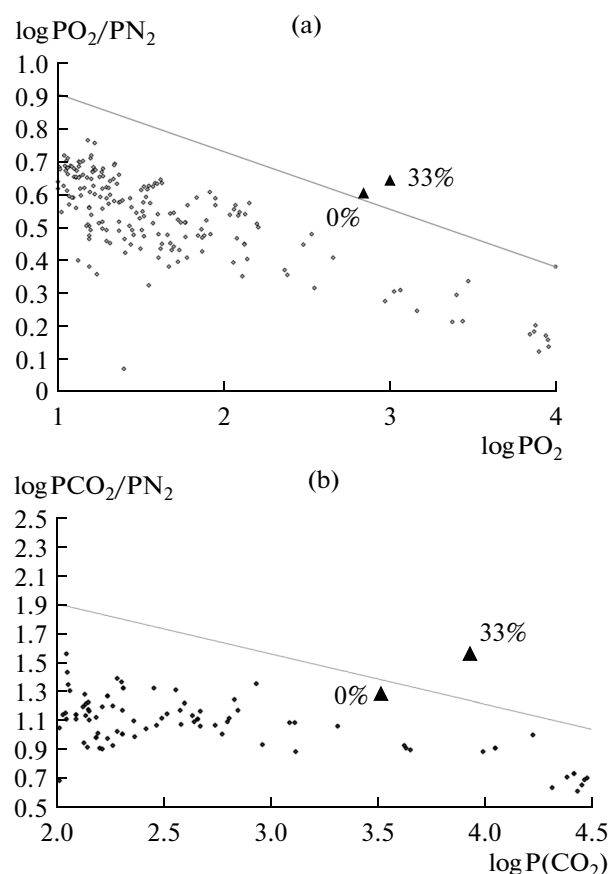


Fig. 3. Fragments of the Robeson diagrams for pairs of gases: (a) oxygen/nitrogen and (b) carbon dioxide/nitrogen and experimental data.

increase in the diffusion coefficients. Note that it is this behavior that has been previously found in studies of another hybrid composite membrane of the PIM-1/ZIF-8 system [5].

Free Volume Studies

The concept of PALS is based on the idea that a long-lived (orthopositronium) component or components τ_3 and τ_4 can be used as a measure of the free-volume element size in polymers. It should be noted that, in conventional glassy polymers, only one long-lived component τ_3 is observed; however, in highly per-

meable materials, such as polytrimethylsilylpropyne, the observed positron lifetimes are much longer and the spectrum is split into two components τ_3 and τ_4 [9]. The relationship of lifetimes τ_3 and τ_4 with radius R of the spherical free-volume element is determined by the semiempirical Tao–Eldrup equation

$$\tau_i = \left\{ \lambda_0^T + 2 \left[1 - \frac{R_i}{R_i + \Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R_i}{R_i + \Delta R} \right] \right\}^{-1},$$

where τ_i (ns) is the orthopositronium lifetime and R_i is the respective radius of the free-volume element, $R_0 = R_i + \Delta R$, where adjustable parameter ΔR is usually assumed to be 1.66 Å. Lifetimes τ_3 and τ_4 , respective intensities (statistical weights) I_3 and I_4 , and the radii of the free-volume elements found from the above formula for the pure PIM-1 polymer and the composite are listed in Table 4.

The table shows that both the pure PIM-1 polymer and the composite based on it exhibit a bimodal distribution of τ , which is consistent with the results of previous studies [10, 5]. The introduction of a MIL-101 additive into the matrix of PIM-1 leads to an increase in both τ_3 and τ_4 , i.e., to an increase in the free-volume element size. This behavior is also observed for other hybrid composite membranes, in particular for the previously studied PIM-1/ZIF-8 system [5]. In terms of the proposed models (e.g., [11]), this behavior may be indicative of an increase in the free volume at the interfaces between the nanoparticles and the polymer matrix. Changes in intensities I_3 and I_4 upon switching to the composite membrane are somewhat unexpected. These quantities are commonly regarded as an estimate of concentrations of free-volume elements of an appropriate size. The table shows that the introduction of a MIL-101 additive results in a sharp increase in I_3 and a slight decrease in I_4 . This fact can be interpreted as a change in the size distribution of free-volume elements. Note that a qualitatively similar behavior was previously observed for a PIM-1/ZIF-8 composite membrane [5]. The increase in the diffusion and permeability coefficients correlates with changes in free-volume element size R_4 .

Thus, the introduction of an additive of MIL-101 nanoparticles into the PIM-1 polymer is accompanied by the same phenomena that were observed for the PIM-1/ZIF-8 system, namely a simultaneous

Table 2. Diffusion coefficients and diffusion selectivities of the PIM polymer and the PIM-1/MIL-101 composite

MIL-101, vol %	$D \times 10^7, \text{cm}^2/\text{s}$				Diffusion selectivity, $\alpha^D = D_i/D_j$		
	He	O ₂	N ₂	CO ₂	O ₂ /N ₂	CO ₂ /N ₂	He/N ₂
0	540	12	3.1	4.1	3.9	1.3	170
33	690	16	4.0	8.4	4.0	2.1	170

Table 3. Solubility coefficients and solubility selectivities of the PIM polymer and the PIM/MIL-101 composite

MIL-101, vol %	$S \times 10^3, \text{ cm}^3 (\text{STP})/\text{cm}^3 \text{ cmHg}$				Solubility selectivity, $\alpha^S = S_i/S_j$		
	He	O ₂	N ₂	CO ₂	O ₂ /N ₂	CO ₂ /N ₂	He/N ₂
0	2.2	58	56	790	1.0	14	0.04
33	1.7	63	58	1000	1.1	17	0.03

Table 4. PALS spectrum parameters and radii of the free-volume elements

MIL-101, vol %	τ_3 , ns	I ₃ , %	τ_4 , ns	I ₄ , %	R_3/R_4 , Å
0	1.59 ± 0.08	5.5 ± 0.2	5.9 ± 0.1	13.2 ± 0.3	2.45/5.17
33	1.86 ± 0.04	21.7 ± 0.3	6.8 ± 0.2	7.8 ± 0.3	2.73/5.51

increase in permeability and selectivity caused by an increase in the free volume and diffusion coefficients.

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