MICROPOROUS MEMBRANES BASED ON CARBONIZATES OF PHENOL FORMALDEHYDE RESINS

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Microporous membranes approx. 0.1 mm in thickness were prepared by controlled carbonization of phenol formaldehyde sheet. The effects of carbonization temperature on sorption capacity, volume of micropores, size of micropores and transport properties were studied. Sorption of CO_2 at room temperature was evaluated on the basis of Dubinin-Raduskewich's isotherm. The diffusion coefficients and permeability for CO_2 were established from the time course of pressure drop during sorption. Microporous membranes on a macroporous carrier were also designed.

INTRODUCTION

Carbonizates obtained by heating organic precursors in an inert atmosphere can have a wide range of properties depending on the initial raw material and on the conditions of the preparation. Under carefully controlled conditions of carbonization, polymers with a dense lattice can be converted into microporous carbonic materials suitable as membranes for separation of gases. They have the advantage of high selectivity and resistance to high temperature, and of chemical durability. Bird and Trimm [1] were the first authors who examined the possibility of utilizing such a material in the form of membranes. They measured the diffusivity in the Wicke-Kalenbach cell (isobaric diffusion) on sheets 1.5 mm thick prepared by carbonizing at 700 °C. The results did not indicate an explicitly molecular sieve character of the membranes, as the permselectivities established were lower than expected and the temperature dependence did not always correspond to the character of activated diffusion. They explained this behaviour as being caused by the presence of fissures or larger pores which allowed the gas to bypass partially the microporous system. The behaviour may be obviously associated with a too high carbonization heating rate (7 K min⁻¹) which at the given wall thickness exceeded the so-called critical heating rate specified in the literature [2,3].

A genuinely selective carbon membrane exhibiting properties that corresponded to the microporous structure of molecular sieves was demonstrated by Koresh and Soffer [4]. It was a thin-walled capillary membrane prepared by controlled carbonization of a commercial polymer capillary membrane of a non-specified polymer.

Following activation, the membranes exhibited a high permselectivity for the O_2 - N_2 pair.

In view of the low strength of carbonizates, it is advantageous to fix the membranes to a strong macroporous and well permeable base. This, however, presents certain problems with the selection of a suitable carrier. Whereas a continuous thin layer of the polymer precursor can be easily applied to any macroporous carrier, the carbonized layer may crack as a result of contraction during the subsequent carbonization. A thin continuous layer of the UPILEX type polyimide was successfully applied to a permeable graphite carrier [5]. Two-layer membranes of carbonized aromatic polyimides were also described in the literature. The partitioning thin layer was of the polyimide film mentioned above, while macroporous polyimide served as carrier [6].

Phenol formaldehyde resins are currently used as precursors of glassy carbon. Compact objects of desired shapes can be readily prepared from liquid resins by gradual curing and hardening via the gel stage. Subsequent carbonization at 1000 °C converts the substance to glassy carbon, a heat-resistant and chemically durable material with a low porosity [7,8,9]. It can be made into the form of crucibles, medicinal prosthetic materials, carbon electrodes, etc. [10,11]. Carbonization at lower temperatures of 500 to 800 °C yields a microporous material exhibiting the properties of molecular sieves [12,13].

The present study is concerned with the preparation of microporous membranes by controlled carbonization of phenolic resins at 500, 600 and 700 °C, and with sorption and diffusion of CO_2 under isochoric conditions in the membranes. The possibility of preparing a composite membrane on a macroporous carrier is also discussed.

EXPERIMENTAL PART

Sheets 0.1 mm in thickness were prepared by thermal curing of type Umaform F resol (UMA Pardubice) using p-toluenesulphonic acid (5 %) as catalyst. The liquid was first polymerized for 24 hours at 60 °C. The gelated intermediate product was removed from the mould and cut into specimens approx. 8 × 20 mm in size, which were subject to final curing at 90 °C (4 hrs.) and 150 °C (2 hrs). The resite plates were then carbonized in nitrogen atmosphere up to the final heat treatment temperatures *HTT* of 500, 600 and 700 °C respectively, at a rate of 100 °C h^{-1} (sample designation C500, C600 and C700).

The foamed resite was prepared by thermal curing the Umaform F resin mixed with a foaming agent (low-boiling petrol fraction) to [18]. The macroporous resite was surface treated by dipping in 50 % xylene solution of dimethyl dichlorosilane and methyl trichlorosilane (10:1 by weight). Following evaporation in air, the process was repeated and the carrier cured for 2 hours at 150 °C. The solution of Umaform P of the composition described above was then applied onto the carrier.

The apparent density of the samples was determined by the hydrostatic method. Possible presence of larger pores was checked by electron microscopy.

The absorption measurements were carried out on the Sorptomatik 180 apparatus by Carlo Erba. Carbon dioxide at 20 °C under pressures of 0 to 150 kPa was used as adsorbate. The apparatus was adjusted for the purposes of the present study so as to allow the pressure in the adsorption vessel to be monitored continuously from the moment of introducing the sample to the establishment of equilibrium. The sample weight (2 - 3 g) was chosen to provide an isotherm comprising about ten points (i.e. 10 doses). Before the measurement, the samples were evacuated for 8 hours at 180 °C. The time course of pressure in the vessel was recorded continuously.

RESULTS AND DISCUSSION

When the preparation procedure was rigidly observed, the membranes did not contain any macropores discernible under the electron microscope at 550× magnification. The p_r equilibrium pressures were determined for all of the feed cycles. The equilibrium molar concentrations of the gas absorbed in the sample after the i-th feed ($C_r^{(i)}$) were calculated by means of the equation derived from the ideal gas balance :

$$C_r^{(i)} = C_r^{((i-1)} + \frac{N^{(i)}}{V_s} - \frac{p_r^{(i)} - p_r^{(i-1)}}{RT} \frac{V}{V_s} , \qquad (1)$$

where $N^{(i)}$ is the dose of gas (mol) in the n-th feed, R is the molar gas constant, T is temperature, V is the volume of gas in the adsorption vessel, V_s is the volume of the sample, $p_r^{(i)}$ is the equilibrium pressure.

Correction for the dead volume of the metering device, and the so-called effective temperature (cf. [14]) were taken into account in the dose calculation.

The experimental data is well described by the Dubinin-Radushkewich equation which we have rearranged to express concentration C_r:

$$C_r = C_r^{(\infty)} \exp -\left[\left(\frac{RT}{E} \ln \frac{f_r^{(\infty)}}{f_r} \right)^2 \right] , \qquad (2)$$

where f_r is the fugacity corresponding to pressure p_r. As the pressures employed were very low, we considered f_r to be equal to p_r. Fugacity $f_r^{(\infty)}$ was calculated from the saturating pressure of CO_2 multiplied by the fugacity coefficient [15]. The characteristic energy E and concentration $C_r^{(\infty)}$ corresponding to $f_r^{(\infty)}$ were determined by non-linear regression. Adsorption isotherms of CO_2 for carbonizates C500, C600, C700 are plotted in figure 1.

The procedure described by Medek [16] was used to calculate the mean r and the most probable pore radii r_{mode}, the surface area of micropores S_{micro} and porosity $\in$. The results are listed in table 1. They show that the volume of micropores over the range of 500 to 700 °C increases with carbonization temperature while the pore size remains almost unchanged.

Table 1. Equilibrium characteristics of C500, C600, C700 carbonizates.

		C500	C600	C700
$C^{(\infty)}$	(mol m^{-3})	4 321.15	6 259.38	7 963.05
E	(J mol^{-1})	9 949.70	10 071.75	10 338.79
$\in$	(vol.%)	23.09	30.80	39.41
r	(nm)	0.734	0.731	0.725
r_{mode}	(nm)	0.664	0.661	0.655
S_{micro}	(m^2 kg^{-1})	4.90 × 10^5	6.89 × 10^5	7.77 × 10^5

The time dependence of $p^{(i)}(t)$ obtained by CO_2 sorption measurements was evaluated on the basis of Fick's law. The shape of the samples allows the one-dimensional equation to be used in describing the gas transport[*]:

$$\frac{\partial C}{\partial t} = D_s \frac{\partial^2 C}{\partial x^2} . \qquad (3)$$

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[*] The top indices i signifying the sequence of dosing are omitted for reasons of better comprehension.

It is assumed that diffusion coefficient D_s does not depend on spatial ordinates nor on gas concentration. In view of the symmetry of the system, the equation may only be solved for one half of the body. The initial condition is considered to have the form:

$$C(x, 0) = C_0 = \text{const.} \qquad 0 < x < L \ , \qquad (4)$$

where L is half thickness of the platelet.

In formulating the boundary conditions the authors used the assumption that sorption of gases at the surface is much faster than the subsequent diffusion inside the body. During the entire process, the surface concentration will therefore be in equilibrium with the ambient pressure p:

$$C(L, t) = C_r(p) \qquad t > 0 \ , \qquad (5)$$

where C_r is the respective isotherm.

The boundary condition for $l = 0$ will obviously be

$$\left(\frac{\partial C}{\partial x} \right)_{x=0} = 0 \ . \qquad (6)$$

For momentary pressure p in the adsorption vessel, the following equation was derived:

$$p = p_0 + \frac{RT}{V} [N + V_s(C_0 - \overline{C})] \ , \qquad (7)$$

where p_0, C_0 are initial pressure and concentration respectively in the given cycle, and $\overline{C}$ is the mean concentration given by the integral

$$\overline{C} = \frac{1}{L} \int_0^L C \, dx \ . \qquad (8)$$

Diffusion equation (3) was solved numerically by the network method. The modified Dubinin--Radushkiewich isotherm (equation (2)) was chosen as the boundary condition. The D_s diffusion coefficients were determined by non-linear regression, by minimizing the squared deviations of experimental and calculated pressures separately for each feed cycle. The results are listed in table 2.

The D_s of all the carbonizates can thus be regarded as being independent of pressure. The mean values of $\overline{D_s}$ are given at the bottom of table 2.

Whereas the porosity of the carbonizates in question increases with carbonization temperature *HTT*, the maximum porosity values were attained at *HTT* = 600 °C. This is in agreement with the results published for water vapour sorption in carbonizates [12,13].

Table 2. Diffusivity of C500, C600 and C700 carbonizates.

Feed	C500		C600		C700	
	p_r (kPa)	$D_s \times 10^5$ (m²s⁻¹)	p_r (kPa)	$D_s \times 10^5$ (m²s⁻¹)	p_r (kPa)	$D_s \times 10^5$ (m²s⁻¹)
1	7.20	0.90	6.13	2.00	-	-
2	16.67	1.05	13.60	2.03	8.27	2.50
3	28.13	0.99	22.80	1.80	13.73	2.13
4	41.33	0.89	33.60	2.30	20.26	3.25
5	56.26	1.24	46.00	2.30	28.00	2.50
6	42.79	1.07	59.99	2.27	36.93	3.05
7	90.52	1.16	75.19	2.28	47.06	2.51
8	-	-	91.72	2.27	58.26	2.60
9	-	-	110.26	2.32	70.66	2.80
10	-	-	-	-	82.93	2.40
11	-	-	-	-	97.19	2.40
12	-	-	-	-	113.19	2.40
13	-	-	-	-	129.99	2.40
$\overline{D_s}$ (m²s⁻¹)	1.04		2.17		2.58	
a.d. (m² s⁻¹)	0.10		0.15		0.23	
st.d. (%)	9.55		7.09		8.96	

$\overline{D_s}$ - mean diffusivity, a.d. - absolute deviation, st.d. - standard deviation

Gas transport through the membrane is also associated with the diffusion rate. The gas migrates by first becoming adsorbed on the membrane surface, then penetrating the membrane by diffusion, and being desorbed on the other side. The gas flow J through the membrane can be characterized by permeability P which in a steady state is defined by equation

$$J = P \frac{(p_0 - p_1)}{l} \ , \qquad (9)$$

where l is the membrane thickness and p_0 and p_1 are pressures in front of and behind the membrane respectively.

The permeation rate is given by the slowest step, which is diffusion, as sorption and desorption on the membrane surfaces are much faster. The following equation can be readily derived for the relation between permeability and diffusivity:

$$P = D_s \frac{C(p_0) - C(p_1)}{p_0 - p_1} \ , \qquad (10)$$

where $C(p_0)$, $C(p_1)$ are surface concentrations on the two sides of the membrane respectively.

Permeability for a non-linear isotherm should obviously depend on pressure. For the carbonizates studied, permeability of CO_2 into vacuum ($p_1 = O$) was calculated by means of equation (10). Figure 2 shows the
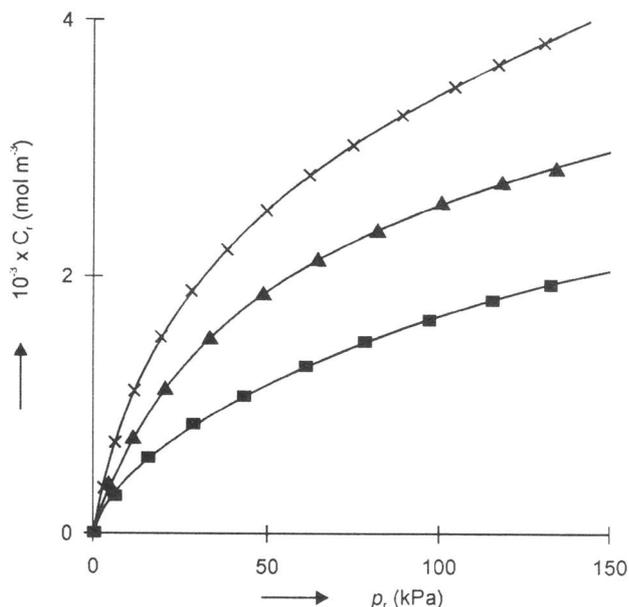
Figure 1. Adsorption isotherms of CO_2 for carbonizates C500, C600 and C700.
The curves were calculated from DR equation (2); ■ - C500, ▲ - C600, × - C700.
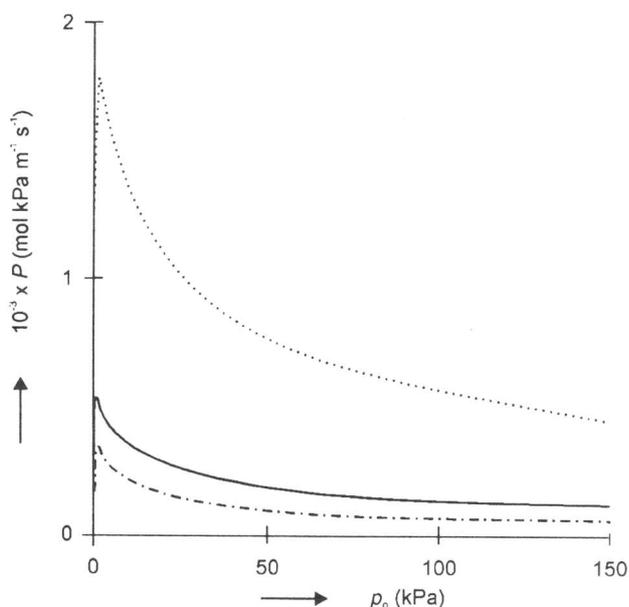
Figure 2. Permeability P vs. pressure in front of membrane (p_o) (calculated from equation (10)).
———— - C500, · · · · · · - C600, · — · — · — · - C700.

plot of permeability P calculated in this way vs. pressure in front of the membrane (p_o). The diagram shows that P attains the maximum value at low pressures and then decreases. A decrease of permeability with pressure was observed e.g. on CO_2 and CH_4 [17]. Contrary to this, permeability was found to be independent of pressure in the case of gases having small molecules, such as H_2 or He. This agrees with expectation as the gases exhibit a linear isotherm over the pressure range studied.

SUPPORTED MEMBRANES

Microporous carbon membranes are quite brittle, so that their practical application is possible only when they are supported by a suitable carrier. Selection of a suitable carrier represents quite a problem. Use of carriers of materials other than the membrane (such as foamed glass, etc.) leads to cracking as a result of contraction of the membrane in the course of carbonization and thermal stresses due to a difference in thermal expansion coefficients during cooling.

Macroporous resite appears to be a suitable carrier for membranes based on carbonized resites. The material was prepared by curing the Umaform P resin in the presence of a foaming agent (figure 3). The behaviour of resites prepared in the form of thin sheets and foam was
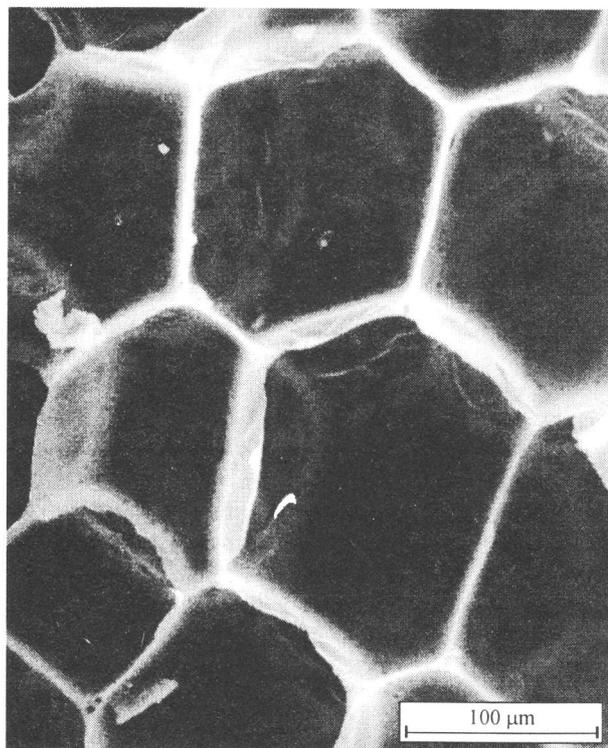
Figure 3. Structure of carbonized resite foam. Scanning electron micrograph.

studied in the course of carbonization. The contraction due to carbonization over the temperature range of 500 to 700 °C was found to be virtually identical with both types of resite. In principle, this fact allows reinforced microporous membranes to be prepared by carbonization of a resite layer applied in a suitable way onto resite foam. The danger of cracking is thus strongly suppressed because in the course of carbonization both layers behave in virtually the same way.

There are basically two possible ways of applying the resite membrane onto the resite foam: To prepare the polymeric membrane separately, to cement it onto the foamed carrier with phenol formaldehyde resin, and to carbonize the membrane after the adhesive has cured. This method is practicable only with planar carriers. The other way is to apply the surface layer in the form of its precursor, resol, and to cure and carbonize it. The other method is more difficult, as the surface forces prevent a thin layer to be formed because the solution tends to penetrate into the foamed carrier. The problem can be resolved by using a suitable intermediate layer. Good results were obtained with novolac resin which is a substance very similar to resols but subject to thermal curing and producing 30 % carbonization residue. This is why the macropores filled with this resin become for the most part reopened during carbonization. A thin layer of the resol solution can thus be applied onto the resite foam coated with the novolac resin. A supported microporous carbon membrane is then obtained after controlled curing and carbonization.

Acknowledgement

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MIKROPORÉZNÍ MEMBRÁNY NA BÁZI KARBONIZÁTŮ Z FENOLFORMALDEHYDOVÝCH PRYSKYŘIC

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Řízenou karbonizací polymerů lze za vhodných podmínek připravit mikroporézní karbonizáty s vlastnostmi molekulových sít. Tyto materiály mohou sloužit jako membrány k separaci plynů a pro membránové katalytické procesy. Vlastnosti karbonizátů závisí na druhu prekurzoru a na podmínkách přípravy, zejména na konečné teplotě (HTT). Na bázi fenolformaldehydové pryskyřice Umaform F byly při teplotách 500, 600 a 700 °C připraveny mikroporézní membrány s transparentními póry o průměru cca 1.2 nm.

Byla studována sorpce a difúze do těchto materiálů za teploty 20 °C a tlaku 0 - 150 kPa. Adsorpce probíhala za konst. objemu a kontinuálně se zaznamenával tlak v adsorpční nádobě jako odezva na dávku sorbátu. Sorpce byla vyhodnocena na základě Dubinin-Raduschkievichovy rovnice, která dobře vystihuje experimentální data. Vypočtené charakteristiky jsou uvedeny v tabulce 1.

Rychlost difúze CO_2 do karbonizátů byla určována z časové závislosti úbytku tlaku v adsorpční nádobě. Vyhodnocení difuzivit se provádělo na základě Fickova zákona pro jednorozměrnou difúzi do tělesa tvaru nekonečné desky. Difúzní rovnice byla řešena numericky a difuzivity D_s a P byly zjištěny u karbonizátů připravených za teploty 600 °C.

Výsledky naznačují, že studované karbonizáty by mohly být použity jako separační membrány pro plyny. Pro praktické použití je však třeba je aplikovat na vhodném nosiči. Byla navržena metoda přípravy vyztužených mikroporézních membrán. Vycházíme z makroporézního rezitu Umaform P s naneseným filmem neporézního rezitu. Šetrnou karbonizací tohoto systému lze připravit kompozitní membránu s neporušenou dělící vrstvou.