

Incorporation of Hydrophobic Porous Fillers in PDMS Membranes for Use in Pervaporation

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Three types of hydrophobic porous fillers (carbon blacks, in situ methylated silicas, and silylated silicas) were incorporated in PDMS (polydimethylsiloxane) membranes in order to find out under which conditions these filled membranes were advantageous for pervaporation of aqueous solutions. The properties of these fillers were changed systematically in order to maximize fluxes and selectivities in the pervaporation of aqueous ethanol, tertiary butyl alcohol, or aroma solutions. Many fillers were able to realize an increased membrane selectivity, but none of them could combine this with an increased organic flux. In this respect, silicas silylated with TMCS (trimethylchlorosilane) were found to be the best fillers. The filler addition was most beneficial when applying feed mixtures that induced low swelling in the membrane.

Introduction

For the removal of organics from aqueous solutions, polydimethylsiloxane (PDMS) membranes were found to be very suitable. When using silicalite-filled PDMS, improved separations^{1–8} were mostly observed. In many cases however, the observed increase in selectivity was accompanied by a decreased flux of the desired organic compound. This was reported for aroma compounds,^{1–3} chlorinated hydrocarbons,^{4,5} and alcohols.⁶ The negative effect of incorporated silicalite on the flux of these composite membranes can be ascribed to the molecular sieving properties of the zeolite. This sieving effect was observed in gas separations,^{10–14} and a negative influence on the gas permeability was proven for molecules with a kinetic diameter larger than 3.6 Å. In pervaporation,⁴ a value of about 5.5 Å was mentioned, corresponding very well with the theoretical limiting value to allow transport, being the pore size of the zeolite. However, it was proven in a homologous series of alcohols,⁶ that only ethanol benefits from fillers with such structure. Even though diffusion of all other alcohols through the zeolite can surely take place, transport was faster through the PDMS phase for the given feed concentration. By studying the influence of the zeolite on the performance of filled PDMS membranes, we realized that the presence of meso- and macropores^{1,4} in the filler combined with a high hydrophobicity of these pores is most ideal for good separations. The incorporation of such porous structures forced us to develop a new synthesis method¹⁵ which leaves all pores open and gives a good particle dispersion. In this paper, we report on two different kinds of fillers that fulfill the requirements of being hydrophobic and containing meso- and macropores: carbon blacks and modified silicas. Their performance is investigated in the separation of ethanol, tertiary butyl alcohol, and aroma compounds from water.

Experimental Section

Materials. The Printex and the Special Black carbon blacks were provided by Degussa. They will be referred to as the P-series and the SB-series. Their main properties are listed in Table 1. They were chosen so as to have two sets of fillers

TABLE 1: Dibutyl Phthalate Absorption (mL/100 g), pH-Value in an Aqueous Dispersion, Particle Size (nm), and BET (m²/g) Values of the Carbon Blacks As Given by the Manufacturer

	DBP (mL/100 g)	pH	particle size (nm)	BET (m ² /g)
Special Black 100	94	3.3	50	30
Special Black 350	45	3.5	31	65
Special Black 550	47	2.8	25	110
Printex G	96	9.0	51	30
Printex 35	42	9.0	31	65
Printex 55	45	9.5	25	110
114A		4.5–7.0		850
BL				1000

with different pH values, in which specific surface and dibutyl phthalate (DBP) values differed. Carbon blacks 114A and BL were provided by Chemviron and were added because of their high BET value, indicating the presence of lots of micropores.

Methods. Preparation of the Silicas. TEOS (75 mL, tetraethoxysilane, 98%, Janssen Chimica) was added to 150 mL of water, acidified to pH = 2 with HCl (37%, UCB). This was stirred overnight to ripen the sol. By titrating it with a 25 wt % NH₃ solution (Merck, p.a.), the pH was adapted to 6. The silicas were dried at 120 °C for 24 h and then calcined at 400 °C for 12 h. When preparing organo-substituted silicas, a certain mol % of TEOS was replaced by the same amount of PhTEOS (phenyltriethoxysilane, 98%, Janssen Chimica) or DDEOS (dimethyldiethoxysilane, 97%, Janssen Chimica).

Silylation of the Silicas. Silylation was done as described in Vankelecom et al.¹⁶ Silylation was repeated until subsequent silylations resulted in an unchanged water sorption of the silica.

Sorption Experiments. The water sorptions of the fillers were measured after equilibrating the samples for at least 24 h in an atmosphere with a constant relative humidity of 80% (saturated ammonium chloride solution). The samples were pretreated at 150 °C under vacuum.

Pretreatment of the Fillers. Before adding the carbon blacks to the polymer solution, they were sieved (0.16 mm) and pretreated at 150 °C under vacuum for 90 min. The silicas were milled to a fine powder and dried overnight at 400 °C.

Membrane Preparation. Membranes were prepared following Vankelecom et al.¹⁵ An 8 vol % solution of the PDMS cross-linker (RTV-615B, General Electric) and the PDMS

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prepolymer (RTV-615A, General Electric) was prepared in chloroform (99%, Janssen Chimica) with a cross-linker/prepolymer ratio of 1/10. The solution was mixed for 1 h at 70 °C, after which the carbon blacks were added and stirring was continued for another hour at room temperature. The mixture was poured in a petri dish, from which the solvent was evaporated overnight. The polymer was cured at 150 °C under vacuum for 45 min, after which the membrane was removed from the petri dish. A PDMS concentration of 15 vol % in chloroform was used in the membrane synthesis with silylated silicas.

Pervaporation. Three different feed mixtures were applied: a 6 wt % aqueous ethanol (Riedel-deHaën, 99.8%) solution, a 6 wt % aqueous tertiary butyl alcohol (Aldrich, 99.5%) solution, and an 800 ppm mixture containing eight different aroma compounds (100 ppm each: ethyl acetate, isoamyl acetate, valeraldehyde, hexanal, ethanol, isoamyl alcohol, 2-hexanone, 2,3-butanedione, all with a purity of more than 98%). All fluxes were normalized to a membrane thickness of 100 μm . For the alcohol/water separations, pervaporations lasted for 45 min. The actual collection of permeate was started after 1 h of permeation to be sure to reach steady state conditions. When aroma compounds were pervaporated, 90 min of pervaporation was done to reach steady state conditions, after which a new feed mixture was introduced to do the actual pervaporation measurement. This one started after another equilibration period, taken as one-eighth of the pervaporation time needed to collect 1 g of permeate. Before applying the membranes in the pervaporation apparatus, they were equilibrated by placing them in a 3 L bottle containing the aroma solution at 35 °C.

All pervaporations took place in an apparatus obtained from GFT-Le Carbone, at 35 °C with a vacuum below 3 mbar and a feed flow of 50 L/h for a membrane area of 182 cm^2 . The feed and permeate solutions were analyzed by using GC (CP-SIL-5 CB packing). The detector was at 300 °C and the injector at 290 °C with a column head pressure of 62 kPa. For the aromas, analysis was isothermal at 110 °C and cyclohexanol was used as external standard. The standard was added to feed solutions as a 4000 ppm solution, and to permeates as a pure compound, after dilution of the permeate with acetone to make one phase. For ethanol analysis, 2-propanol was added as external standard, and the analysis was isothermal at 70 °C. Ethanol was used as a standard for the isothermal analysis at 90 °C of the tertiary butyl alcohol solutions. The enrichment factors are expressed as a ratio of wt % aroma present in the permeate over the wt % present in the feed. For the alcohols, selectivity is defined as $(y_a/(1 - y_a))/(x_a/(1 - x_a))$ in which x_a and y_a are the weight fractions of alcohol in the feed and in the permeate respectively.

Results and Discussion

1. New Synthesis Procedure. With the former synthesis method,¹⁷ it was impossible to incorporate structures that combine large pores with large pore volumes. In the new synthesis method,¹⁵ the fillers are added to the polymer solution when a partially cross-linked polymer network is formed already. As shown by Jia et al.,¹³ such a prepolymerization keeps the filler better dispersed when the suspension is cast to form a membrane. In contrast to Jia et al.,¹³ the filler is added here after—and not during—the prepolymerization. This constitutes an important advantage since the partially cross-linked polymer chains can no longer enter the filler pores. This was proven for PDMS membranes filled with zeolite Y in a 20 vol % loading. When applying this membrane in the pervaporation of an aqueous aroma mixture, fluxes drastically increased from 107 $\text{g/m}^2\cdot\text{h}$ to 722 $\text{g/m}^2\cdot\text{h}$ when using membranes prepared

TABLE 2: Pervaporation of a 6 wt % Ethanol Solution Using Carbon Black Filled PDMS Membranes: Normalized Ethanol, Water, and Total Fluxes ($\text{g/m}^2\cdot\text{h}$) and Selectivity

	ethanol	water	total	selectivity
PDMS	23.0	43.1	66.1	8.4
SB100	17.5	32.2	49.8	8.5
SB350	15.4	27.9	43.3	8.7
SB550	15.3	28.3	43.6	8.5
PG	18.7	32.3	51.0	9.0
P35	14.2	26.2	40.4	8.5
P55	15.8	28.3	44.1	8.7

TABLE 3: Pervaporation of a 6 wt % Tertiary Butyl Alcohol Solution Using Carbon Black Filled PDMS Membranes: Normalized Alcohol, Water, and Total Fluxes ($\text{g/m}^2\cdot\text{h}$) and Selectivity

	tert-butyl alcohol	water	total	selectivity
PDMS	29.4	31.1	60.5	14.9
P35	21.2	22.9	44.0	14.5
SB350	18.3	23.2	41.5	12.7
BL	18.9	26.9	45.8	11.0
114A	18.1	25.2	43.3	11.3

following this new preparation method. As selectivity is maintained, this clearly proves that the zeolite pores are no longer obstructed.

2. Pervaporation Using Carbon Black Filled PDMS. 2.1.

Ethanol. Table 2 shows the total fluxes as well as the compound fluxes measured in the pervaporation of a 6 wt % aqueous solution of ethanol. Most striking is the very high permeability of unfilled PDMS. In the filled membranes the carbon blacks cause additional cross-linking.¹⁸ This induces reduced swelling possibilities in the membrane, leading to lowered fluxes and somewhat increased selectivities. Irrespective of the particular properties of the carbon blacks, fluxes and selectivities of all carbon black filled membranes hardly differ. There is only a slight tendency for the fillers with the highest DBP value to have the highest fluxes. Indeed, it wouldn't be illogical for an open filler structure to accelerate transport.

2.2. Tertiary Butyl Alcohol. It was thought that no positive effect of the filler structure could be observed in the pervaporation of ethanol/water mixtures, because the transport of the small ethanol molecule through the PDMS matrix is too fast.⁶ Furthermore, the strong coupling between ethanol and water also diminishes the influence of the filler: following the strong interactions between the alcohol and water, the filler does not effectively discriminate between both molecules. That is why a larger and less hydrophilic alcohol such as tertiary butyl alcohol was chosen now. Only one representative of the P- and SB-series was used here, but two high-BET carbon blacks were added to the series.

The higher selectivities (Table 3) for tertiary butyl alcohol than for ethanol are due to the weaker interactions between this alcohol and water, leading to reduced coupling. Here again, however, no positive influence of the filler can be observed. Probably, the more hydrophobic alcohol makes the membrane swell too much⁶ so that transport still happens through the polymer matrix by preference, in spite of the size of the molecule. Furthermore, the high-BET carbon blacks even lead to strongly reduced selectivities as compared to the unfilled PDMS membrane. Probably, their high amount of micropores slows down the transport of the bulky alcohol, or maybe their micropores are not completely interconnected.

2.3. Aroma Compounds. As observed in the above pervaporations, 6 wt % solutions of alcohols induced such a strong swelling in the polymer part of the composite membranes that no positive influence of the incorporated carbon blacks on

TABLE 4: Pervaporation of an 800 ppm Aroma Mixture Solution Using Carbon Black filled PDMS Membranes: Normalized Aroma, Water, and Total Fluxes (g/m²·h) and Enrichment Factors

	aroma	water	total	enrichment
PDMS	10.2	41.2	51.4	248
PG	9.6	28.0	37.6	319
P35	8.6	24.0	32.5	329
P55	7.7	21.7	29.4	327
SB100	9.7	28.7	38.4	316
SB350	7.2	21.2	28.4	317
SB550	8.1	20.7	28.8	350

TABLE 5: Pervaporation of a 6 wt % Tertiary Butyl Alcohol Solution Using PDMS Membranes Filled with Organo-Substituted Silicas: Normalised Alcohol, Water, and Total Fluxes (g/m²·h) and Selectivity

	organic	water	total	selectivity
PDMS	29.4	31.1	60.5	14.9
Silica	17.4	36.8	54.2	7.4
5DDEOS	19.9	34.5	54.4	9.1
10DDEOS	20.8	29.6	50.4	11.0
15DDEOS	17.5	32.7	50.2	8.4
20DDEOS	19.1	34.2	53.3	8.8
10PhTEOS	22.6	36.1	58.8	9.8
20PhTEOS	16.7	24.8	41.5	10.5
30PhTEOS	20.0	34.8	54.8	9.0
40PhTEOS	17.8	28.3	46.1	9.9

the transport could be observed. In this respect, a mixture of aroma compounds with a total organic concentration of only 800 ppm was pervaporated. It was expected that the limited swelling of the membrane caused by these strongly diluted organics would restrict diffusion through the polymer. That way, both sorption in and diffusion through the particle would gain significance.

This time, the water fluxes are more reduced than the organic fluxes, reflected in increased global enrichment factors for all carbon black filled membranes (Table 4). The low swelling excludes water molecules from the polymer phase and forces a larger part of the transport to go through the hydrophobic filler, ensuring selective uptake. With reduced swelling, diffusion through the polymer becomes more difficult. The introduction of a fixed pore system in the fillers becomes interesting then for fast transport, especially for rather bulky molecules. The results demonstrate an enhanced performance for carbon black filled membranes in the pervaporation of mixtures inducing low swelling of the membrane. However, the increased enrichment factor is accompanied by a decreased aroma flux. Possibly, the carbon black pore system contains several dead-end pores. In an attempt to combine the high enrichment with high organic fluxes, some other fillers were incorporated.

3. Pervaporation Using PDMS Filled with Organo-Substituted Silicas. *3.1. Tertiary Butyl Alcohol.* Dewitte et al.¹⁹ reported that hydrophobic silicas could be obtained by adding organo-substituted precursors of TEOS in the synthesis solution of silicas. Apart from decreasing the water sorption of the synthesized silicas, these substituted compounds change the particle texture. When substituting TEOS by DDEOS, total pore volumes and BET values go through a minimum for a substitution degree of 20 mol %. Applying PhTEOS as substituent, water sorptions were found to be even lower than for DDEOS-substituted silica fillers, while having comparable BET values.

Incorporation of pure silica induces the lowest selectivity (Table 5). Indeed, this filler is very hydrophilic. None of the silica-filled membranes realize a higher alcohol flux nor an increased selectivity than the unfilled PDMS membrane. Compared with PDMS, the fillers clearly decrease the overall

TABLE 6: Pervaporation of an 800 ppm Aroma Mixture Solution Using PDMS Membranes Filled with Organo-Substituted Silicas: Normalized Aroma Water, and Total Fluxes (g/m²·h) and Enrichment Factors

	organic	water	total	enrichment
PDMS	10.2	41.2	51.4	248
Silica	9.2	39.8	49.0	235
5DDEOS	10.4	45.6	55.9	231
10DDEOS	7.9	28.0	35.9	276
15DDEOS	6.8	37.0	43.8	194
20DDEOS	7.2	41.3	48.5	186
10PhTEOS	9.9	36.8	46.7	266
20PhTEOS	7.7	24.7	32.5	297
30PhTEOS	7.1	32.2	39.3	226
40PhTEOS	6.5	24.7	31.2	261

TABLE 7: Water Sorption (wt %) on Silicas as a Function of Silylating Agent and Number of Silylations

number of silylations	TMCS	TPCS
0	38.1	38.1
1	30.3	20.7
5	4.9	3.1

TABLE 8: Pervaporation of an 800 ppm Aroma Mixture Solution Using PDMS Membranes Filled with Silylated Silicas: Normalized Aroma, Water, and Total Fluxes (g/m²·h) and Enrichment Factors

	organic	water	total	enrichment
PDMS	10.2	41.2	51.4	248
Silica	9.2	39.8	49.0	235
TMCS 1	8.0	36.1	44.0	227
TMCS 5	9.1	24.7	33.8	337
TPCS 1	7.5	31.8	39.3	238
TPCS 5	7.0	20.7	27.8	317

membrane permeability due to their cross-linking action. Furthermore, the organo-substituted silicas do not seem to be sufficiently hydrophobic to exclude water from their pores when comparing their fluxes with the ones of the silica-filled PDMS. Just as for carbon black filled membranes, high feed concentrations clearly have no advantage of such fillers, irrespective the texture of the particles.

3.2. Aroma Compounds. This situation changes when 800 ppm solutions of aroma compounds are pervaporated (Table 6). Some composite membranes have fluxes that are comparable with those of the unfilled reference membrane, and several have even higher enrichment factors. Water fluxes are remarkably higher for the dimethyl-substituted silicas when comparing fillers with the same amount of organic groups. The more hydrophobic character of the phenyl groups—reflected in the strongly reduced water sorptions²⁰—can explain that. As organic fluxes are comparable, the phenyl-substituted silicas consequently show slightly higher enrichment factors in general.

4. Pervaporation with Silylated Silicas as Filler. The best results were obtained when applying an alternative manner to prepare large pore fillers with hydrophobic character via silylation of a pure silica after its synthesis. Silylation of a USY (ultrastable zeolite Y) with TPCS (triphenylchlorosilane) was found already to lead to an increased hydrophobicity.¹ Incorporation of this filler in PDMS increased both organic fluxes and selectivities.

Water sorption is depicted in Table 7 as a function of the number of subsequent silylations and shows that phenyl groups are more effective in shielding the polar silica wall. In Table 8, the clear correlation between the decreasing water sorption of the fillers and the decreasing water flux of the respective composite membranes is obvious. As the organic flux is decreasing to a lesser extent than the water flux, high enrichment factors can be realized with the best silylated samples. Organic

fluxes are always slightly lower for the TPCS silylated samples than for the TMCS (trimethylchlorosilane) silylated silicas. Irrespective of the silylating agent, the resulting fluxes of the composite membranes are always lower than the organic flux of the PDMS membrane in which unsilylated silica is incorporated. It might indicate some pore blocking due to silylation, being more important in the case of the larger TPCS molecules. This kind of hydrophobic filler clearly seems to be most promising.

Conclusions

The effect of incorporation of carbon blacks in PDMS for the pervaporation of a 6 wt % alcohol solution in water is situated on the level of the PDMS (reduced swelling due to cross-linking), more than on the level of the structure of the filler. When pervaporating feeds leading to low PDMS swelling, the carbon black fillers create more selective membranes, but strongly reduce fluxes, possibly due to a non-interconnected pore system.

When using PDMS membranes filled with hydrophobic silicas, the best results were obtained with silylated silicas. Very high enrichment factors were combined with only slight drops in organic fluxes. A further optimization of the silylation of the fillers and their synthesis method is the subject of future research.

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