

# Preparation of Zeolite Filled Glassy Polymer Membranes

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## SYNOPSIS

The incorporation of zeolite particles in the micrometer range into polymeric matrices was investigated as a way to improve the gas separation properties of the polymer materials used in the form of membranes. The adhesion between the polymer phase and the external surface of the particles appeared to be a major problem in the preparation of such membranes when the polymer is in the glassy state at room temperature. Various methods were investigated to improve the internal membrane structure, that is, surface modification of the zeolite external surface, preparation above the glass-transition temperature, and heat treatment. Improved structures were obtained as observed by scanning electron microscopy, but the influence on the gas separation properties was not in agreement with the observed structural improvements. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

It has already been demonstrated that the incorporation of zeolites into a polymer matrix results in an improvement of the gas separation properties of the material used in the form of a membrane.<sup>1-3</sup> However, when a polymer in the glassy state at room temperature is used, the membrane contains a considerable amount of voids due to the poor adhesion of the polymer chains to the external zeolite surface.<sup>3</sup>

In this article an overview is given of the various glassy polymers investigated and the internal structures obtained by the normal casting–evaporation process. The different experimental methods applied to improve the internal structure are individually described. Finally, some conclusions are drawn and directions for further investigation are given.

## CASTING EVAPORATION

This preparation method is similar to the one used for rubbery polymers. Table I gives a list of polymers used. They are in the glassy state at room temper-

ature, except for the inorganic polyphosphazene ADP 300.

The experimental procedure consisted of dissolving the polymer in a suitable solvent and adding the desired amount of zeolite. After stirring at least one night, the solution was cast on a glass or a Teflon<sup>TM</sup> plate and the solvent was allowed to evaporate in a nitrogen atmosphere. The membranes were further dried in a vacuum oven. Figure 1 gives typical examples of internal structures observed for different polymers with silicalite-1 as zeolite.

It can be seen from figure 1 that in all cases the adhesion between the polymer and the external surface of the zeolite is very bad. The use of an inorganic polymer like the polyphosphazene did not give any better result, probably due to the crystallinity of this rubbery polymer.<sup>4</sup>

It is quite obvious that membranes with such an internal structure consist of three phases instead of two: polymer, zeolite, and voids around the particles. Table II gives some gas permeation results obtained with zeolite filled glassy polymer membranes prepared by a simple casting–evaporation process in comparison with the results obtained with unfilled polymers.

It can be observed that little or no improvement at all was obtained. In general, the gas permeability

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**Table I Polymer Overview**

Polymer Name (Abbreviation)	$T_g$ (°C)	Commercial Name and Origin
Cellulose acetate (CA)	80	Aldrich
Polysulfone (PSF)	190	Udel P3500, Amoco
Polyetherimide (PEI)	210	Ultem, General Electric
Poly(4-methyl-1-pentene) (TPX)	36	TPX MX001, Mitsui
Poly(2,6-dimethyl- <i>p</i> -phenylene oxide) (PPO)	210	General Electric
Polyimides (PI)	315	PIXU 218, Ciba Geigy
	310	UPJOHN 2080
Polydiphenoxyphosphazene	0	ADP 300, Atochem

increases when zeolite particles are added, but the selectivity decreases or remains about the same. This may be due to the fact that the zeolite is less selective and more permeable than the polymer phase. However, Figure 1 clearly shows that this is more likely the results of the interphase voids that drastically increase the permeability without affecting or decreasing the selectivity, except in the case of poly(4-methyl-1-pentene) (TPX) for which a slight increase in selectivity is observed.

Various methods were investigated to improve the internal structure of these membranes.

## SURFACE MODIFICATION OF ZEOLITE EXTERNAL SURFACE

### Principle

Problems of adhesion and wetting between an organic and an inorganic phase are encountered in many fields, for example the adhesion of polymer

films to a metal substrate or to glass fibers. Our situation is quite similar to this except that the substrate consists of a powder.

One way to solve this problem is to modify the surface properties of the substrate to make it more compatible with the organic phase. This can be achieved, for instance, by grafting some organic chains onto the inorganic surface by means of silane coupling agents. For a complete description of this concept, one is referred to the excellent book of Plueddeman,<sup>5</sup> a pioneer in this field, and to others.<sup>6-11</sup> The general chemical structure and the basic principle are shown in Figures 2 and 3.

The methoxy (or ethoxy) groups are first hydrolyzed by water traces followed by a condensation reaction with hydroxyl groups (silanol) present at the external surface of the zeolite particle. In this study, amino functional silanes were investigated.

## EXPERIMENTAL

Figure 4 shows the different silane coupling agents used. The experimental procedure to modify the external surface of the zeolite was adapted from Plueddeman.<sup>5</sup> The silane coupling agent is mixed with toluene and then the zeolite is added. The reacting mixture is then heated to 70°C and stirred overnight. After filtration and thoroughly washing with methanol to remove unreacted silane, the zeolite is dried at 80°C in air and then placed in a vacuum oven at room temperature.

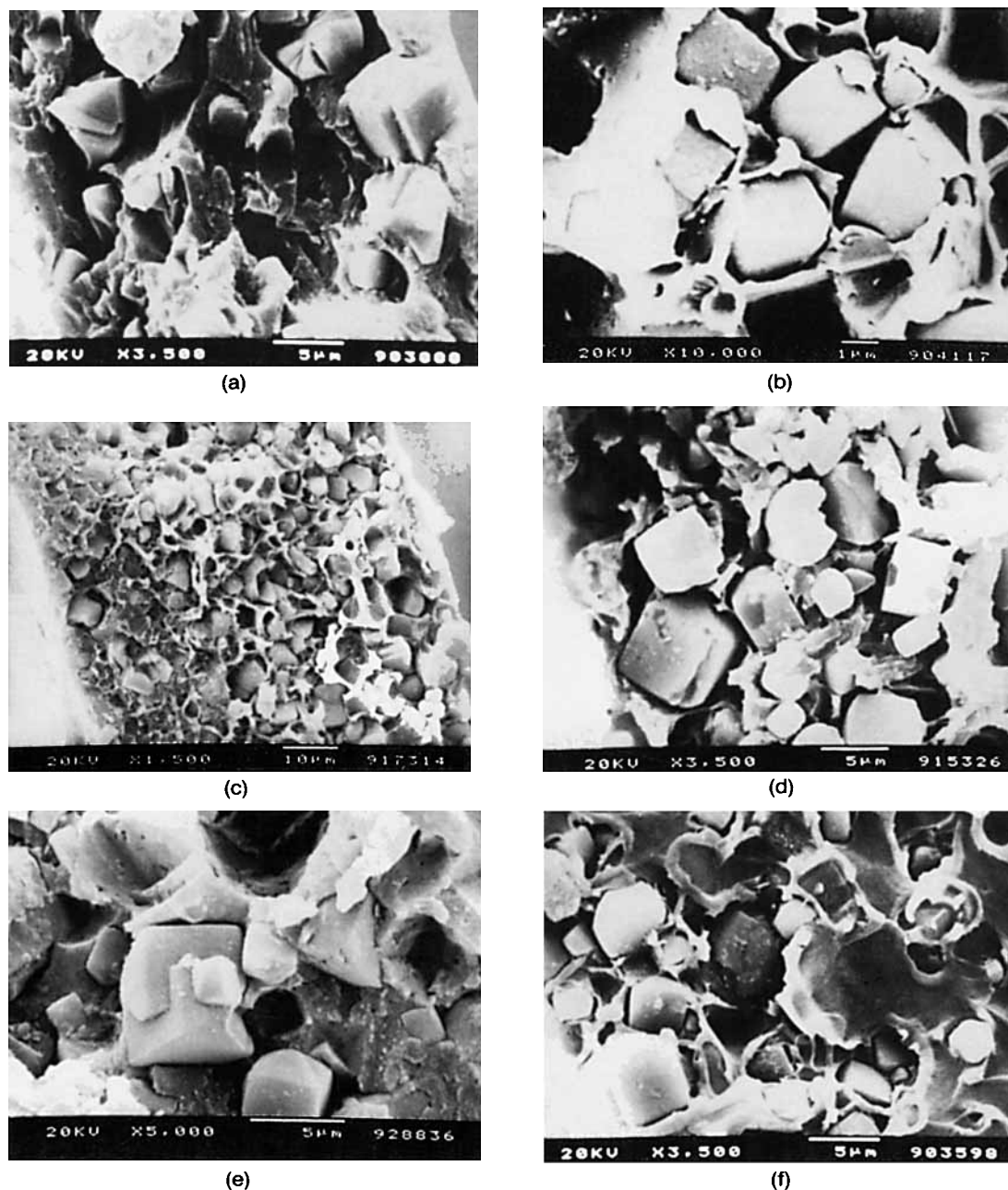
To determine whether the modification had actually taken place, two analysis methods were used. The first one was elementary analysis. The detection of more carbon and nitrogen than in nonmodified silicalite indicated that indeed some coupling agent remained attached to the zeolite surface (Table III).

The second analysis method was electron spectroscopy for chemical analysis (or X-ray photoelec-

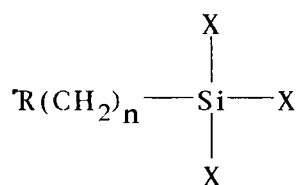
**Table II Gas Separation Results**

Membrane	$P_{CO_2}$ (Barrer)	$\alpha_{CO_2/CH_4}$
CA (from acetone)	11	41
CA + silicalite-1, 25 wt %	18	40
PEI (from NMP)	1.5	61
PEI + silicalite-1, 50 wt %	14.6	34
PEI + KY, 50 wt %	95	43
TPX (from TCE)	71	6.8
TPX + silicalite, 30 vol % (from TCE)	154	9.1
TPX (from PCE)	57	7.8
TPX + silicalite-1, 30 vol % (from PCE)	103	8.6

Results obtained with Zeolite filled and unfilled glassy polymer membranes. NMP: *N*-methyl-2-pyrrolidone; TCE: trichloroethylene; PCE: perchloroethylene.



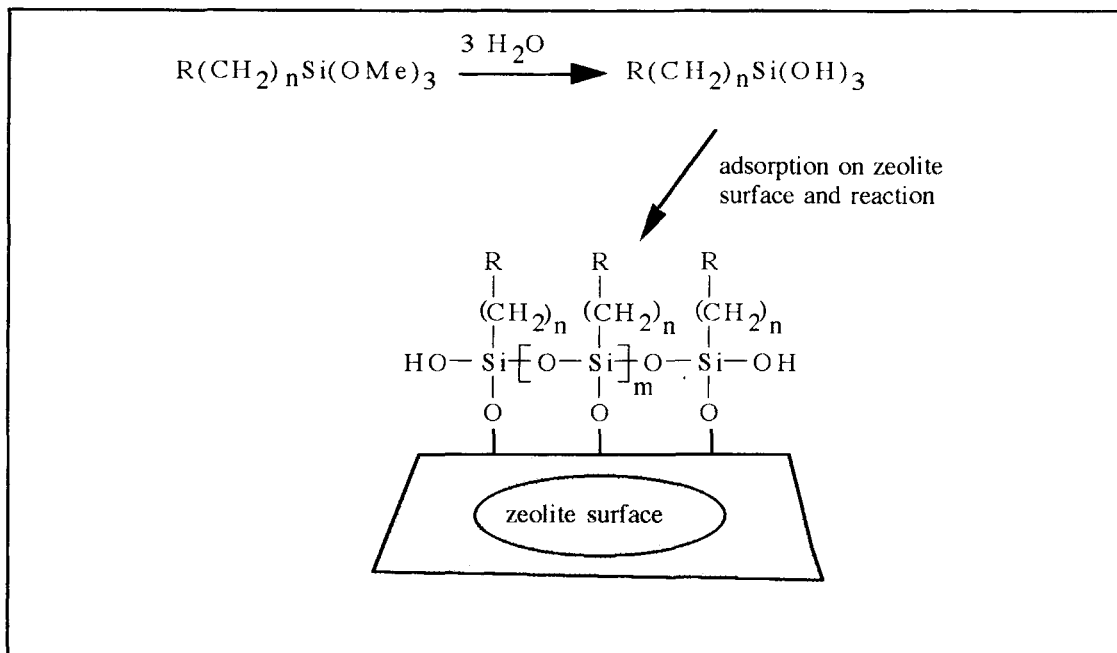
**Figure 1** SEM photograph of the cross section of zeolite filled polymer membranes: (a) CA + silicalite-1, 25 wt % ( $\times 3500$ ); (b) PEI + silicalite-1, 25 wt % ( $\times 10000$ ); (c) PPO + silicalite-1, 50 wt % ( $\times 1500$ ); (d) TPX + silicalite-1, 40 vol % ( $\times 3500$ ); (e) ADP 300 + silicalite, 50 wt % ( $\times 5000$ ); (f) PSF + silicalite-1, 20 wt % ( $\times 3500$ ).



X = hydrolyzable group, e.g. OMe, OEt,

R = organofunctional group, e.g. amino, epoxy

**Figure 2** General chemical structure of silane coupling agents.

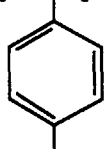


**Figure 3** Principle of coupling of organofunctional silanes onto zeolite surface.

tron spectroscopy). The apparatus used was a Kratos XSAM 800 with a Mg anode (15 kV, 15 mA). The zeolite powder was spread on an adhesive aluminum tape, pressed, and the excess powder removed. The sample was then evacuated at  $10^{-9}$  mmHg at room temperature. This method only gives results about the outer surface of the zeolite particles

because the method allows for a maximum measuring depth of 100 Å. Figure 5 shows a typical XPS spectrum for silicalite-1 powder before and after coupling with agent A-1120.

It can be seen that a peak appears at a binding energy of about 400 eV when the zeolite is treated with A-1120. This peak is representative of the ni-

chemical structure	commercial name and manufacturer
$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$ $\gamma$ -aminopropyltriethoxy silane	A-1100 (Union Carbide)
$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ N- $\beta$ -(aminoethyl)- $\gamma$ -aminopropyltrimethoxy silane	A-1120 (Union Carbide)
$(\text{CH}_3\text{O})_3\text{Si}(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{NHCH}_2$  CH=CH <sub>2</sub> .HCl Styryl amine functional silane	Z-6032 (Dow Corning)

**Figure 4** Chemical structures and names of the silane coupling agents used in this study.

**Table III Elementary Analysis of Silicalite-1 Before and After Coupling**

Zeolite	Al (wt %)	Si (wt %)	C (wt %)	N (wt %)	H (wt %)
Silicalite 1 before calcination	0.08	45	0.08 (±0.04)	0.03 (±0.02)	0.24 (±0.04)
Silicalite-1 after calcination	0.34	44.6	0.04 (±0.03)	0.07 (±0.02)	0.19 (±0.03)
Silicalite-1 + A-1120	0.21	41.6	6.31 (±0.02)	1.07 (±0.02)	0.85 (±0.03)
Silicalite-1 + A-1100	0.35	43.8	3.5 (±0.06)	0.10 (±0.02)	0.49 (±0.03)

trogen atoms of the amino silane. This means that some molecules of the silane coupling agent were grafted onto the external surface of the zeolite and that the results obtained by elementary analysis, which also show the presence of nitrogen atoms, are not only due to silane molecules that may be sorbed into the zeolite pores (these would not be detected so well by surface analysis).

## RESULTS AND DISCUSSION

The previous paragraph gave strong evidence that coupling of the silane agent took place at the external surface of silicalite-1. The next step of the study was then to investigate whether this surface modification had any effect on the internal structure of a silicalite-1 filled glassy polymer membrane.

### Scanning Electron Microscopy (SEM)

Figure 6 shows two examples of polyetherimide (PEI) filled with a modified silicalite-1 (with A-1100 and A-1120 agent, respectively).

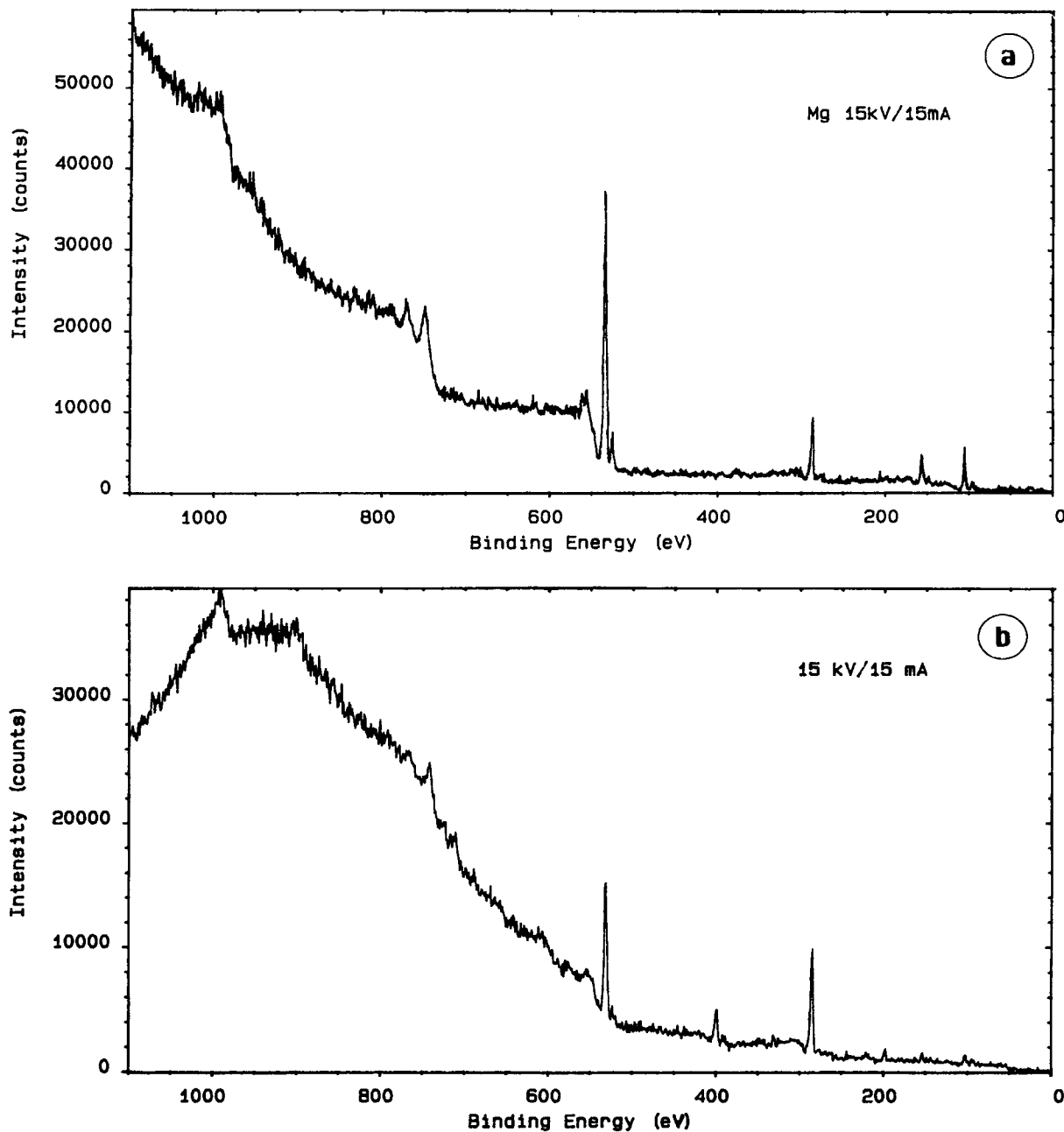
By comparing these two photographs with Figure 1 (b) it becomes very clear that the presence of coupling agent improves to a large extent the internal structure of the membrane. These membranes were prepared with 25 wt % of zeolite. However, the low density of the solvent (NMP,  $\rho = 1.03 \text{ g/cm}^3$ ) compared to the zeolite density ( $1.76 \text{ g/cm}^3$ ) and the low polymer concentration (15 wt %) resulted in sedimentation of the zeolite particles. The actual zeolite weight fraction in the layer where zeolite can be seen is thus much larger than 0.25. (An estimation based on the thickness of the membrane where zeolite is present relative to the total thickness gives a weight fraction in the particle rich region of 0.65.) Similar improvements were observed with polyimides (PIXU 218, UPJOHN) but not with polysulfone.

According to Pluedemann,<sup>5</sup> amino functional silanes are efficient in improving the adhesion of thermosetting and thermoplastic resins to mineral surfaces. The mechanism often assumed or postulated is the formation of an interpenetrating polymer network (IPN) at the mineral surface when no reaction between the amino group of the coupling agent and the polymer chain is possible. The improvement observed in this study might be the result of such a mechanism, that is, due to the formation of an IPN with the silane coupling agent; the polymer chains remains in contact with the mineral surface upon evaporation of the solvent. The silane coupling agent Z-6032 (Dow Corning) was used to improve the structure of silicalite-1 filled TPX membranes. However, no significant improvement was observed when the membranes were cast at room temperature despite indications of a good coupling between silane and zeolite (XPS analysis).

### Gas Permeation

Only a few membranes were tested with respect to their gas separation properties. Furthermore, the results obtained did not confirm the improvement observed by SEM; the selectivity remained lower than that of the pure polymer and the permeability for  $\text{CO}_2$  became higher. Figure 7 gives an example of variation of the separation properties for two PEI membranes filled with A-1100 modified silicalite-1.

The values for the unmodified silicalite-1 at the same weight fraction are  $P_{\text{CO}_2} = 15$  Barrer and  $\alpha_{\text{CO}_2/\text{CH}_4} = 34$  at steady state. This means that the modification of the zeolite only resulted in a (slight) decrease of the membrane permeability without affecting the selectivity. The improvement of the internal structure as demonstrated in Figure 6 accounts for the decrease in permeability compared to the membrane prepared with unmodified silicalite-1 because less voids can be observed. However, the

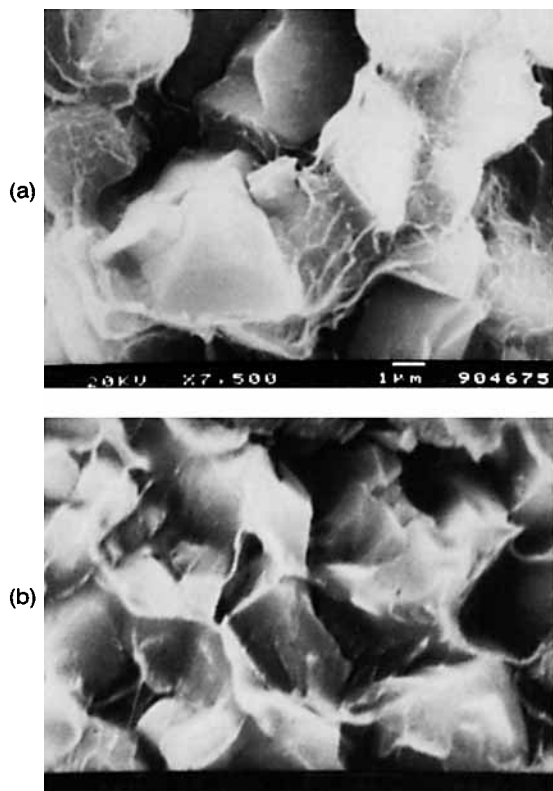


**Figure 5** XPS spectrum of silicalite-1 powder (a) before and (b) after coupling with agent A-1120.

selectivity remains the same and lower than that of the pure polymer. Three hypothesis can be made:

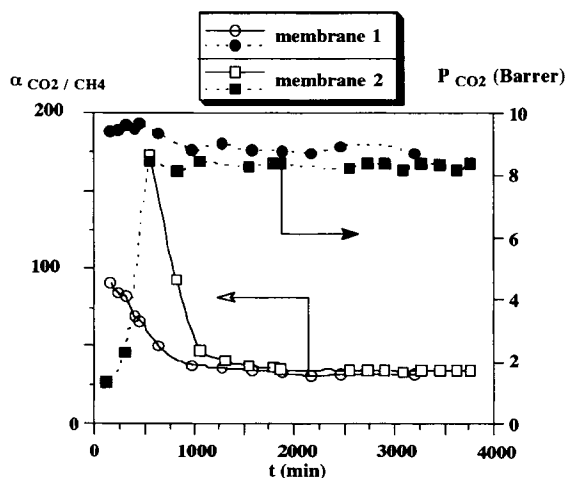
1. the internal structure is still not good enough;
2. silicalite-1 cannot improve the selectivity of PEI;
3. the silane coupling agent molecules present at the zeolite external surface hinder the diffusion of gas molecules through the zeolite pores.

The last hypothesis is not valid because if the zeolite pores were blocked by the silane molecules, no increase in permeability would be observed, that is, the opposite effect is expected. It is more likely that the improved internal structure is not good enough and that the increase of permeability is due to remaining voids. However, the second hypothesis cannot be ruled out because the experimental results reported by Duval et al.<sup>2,3</sup> suggest that silicalite-1 is less effective in improving the selectivity of an al-



**Figure 6** SEM photographs of PEI membranes filled with 25 wt % of silicalite-1 modified with (a) A-1100 ( $\times 7500$ ) and (b) A-1120 ( $\times 5000$ ); the membranes were prepared with *n*-methyl pyrrolidone (NMP) as solvent.

ready quite selective polymer ( $\alpha_{\text{CO}_2/\text{CH}_4} = 17$ ) compared to a poorly selective one. Hence when a polymer is used with a selectivity in the range of 40–60,



**Figure 7**  $\text{CO}_2$  permeability and  $\text{CO}_2/\text{CH}_4$  selectivity of PEI membranes filled with 50 wt % of A-1100 modified silicalite-1.

one might expect a relatively small effect of silicalite-1 on the separation properties.

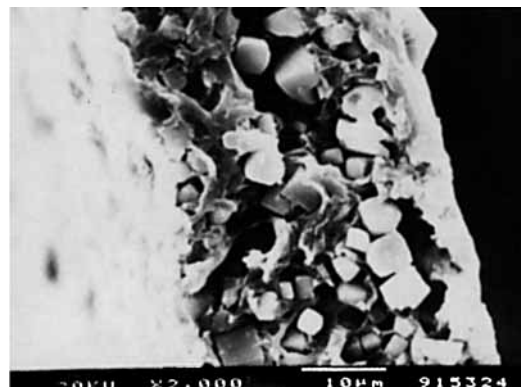
### Preparation of Membranes Above Glass-Transition Temperature

The problems encountered are obviously related to the glassy state of the polymer phase at room temperature. When rubbery polymers are used, no adhesion problems are observed.<sup>2</sup> By solvent evaporation from the zeolite-polymer solution at room temperature, the glass transition is crossed at a given polymer concentration. At this point the polymer chains become much less flexible than in the rubbery state and stress forces are created that might result in dewetting of the polymer from the zeolite external surface.

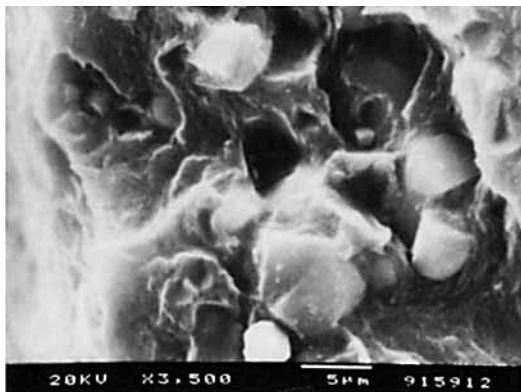
In the method investigated here the solvent is evaporated above the glass-transition temperature ( $T_g$ ) of the pure polymer. This implies that the whole process occurs above  $T_g$  of the polymer. TPX MX001 (Mitsui) with a  $T_g$  of  $36^\circ\text{C}$  as measured by differential scanning calorimetry (Perkin Elmer System 4 with a TADS 3600 data station) was used as polymer.

The membranes were cast from a hot polymer solution ( $60^\circ\text{C}$ ) on a hot glass plate in an oven ( $60^\circ\text{C}$ ) flushed with nitrogen. After evaporation of the solvent, the internal structure was observed by SEM. Unfortunately, this preparation method did not improve the wetting of the particles by the polymer phase very much (Fig. 8).

The only significant improvement of the structure was observed when the Z-6032 modified zeolite was used (Fig. 9). However, the nonhomogeneous dispersion of the zeolite particles into the polymer matrix (clustering) does not present any gas per-



**Figure 8** Typical example of the internal structure of a silicalite filled (40 vol %) TPX membrane prepared at  $60^\circ\text{C}$  with PCE as solvent ( $\times 2000$ ).



**Figure 9** Internal structure of a TPX membrane filled with Z-6032 modified silicalite (30 vol %) prepared at 60°C with PCE as solvent ( $\times 3500$ ).

meation results because all the membranes were leaking.

### Heat Treatment

This process was investigated with a PEI membrane filled with zeolite KY (50 wt %). This membrane was placed in a vacuum oven at 150°C for 4 weeks. The gas separation properties were measured again after this treatment. Figure 10 shows the variation of the carbon dioxide permeability and selectivity with time for this membrane.

It can be observed that both the selectivity and the permeability increase with time, which is similar to the results previously reported with rubbery polymers.<sup>2,3</sup> The selectivity increases from 8 to 52 over a period of about 10 days. In the meantime, the carbon dioxide permeability reaches a steady-state value after 3 days. This means that a further increase in selectivity is due to a decrease in methane permeability. The steady state  $\text{CO}_2$  permeability is 23 Barrer, which is much higher than the pure polymer permeability (1.5 Barrer after heat treatment) but the selectivity is somewhat lower (52 instead of 61).

However, the separation properties of the filled membrane before heating,  $P_{\text{CO}_2} = 95$  Barrer and  $\alpha_{\text{CO}_2/\text{CH}_4} = 43$ , should be taken into account. The heat treatment resulted in a large decrease in permeability and a slight increase in selectivity. This cannot be explained only by a large decrease of the number of voids in the membrane because it could be observed by SEM that some still remained after the heat treatment. The time dependency of the separation properties in this particular case is not really well understood.

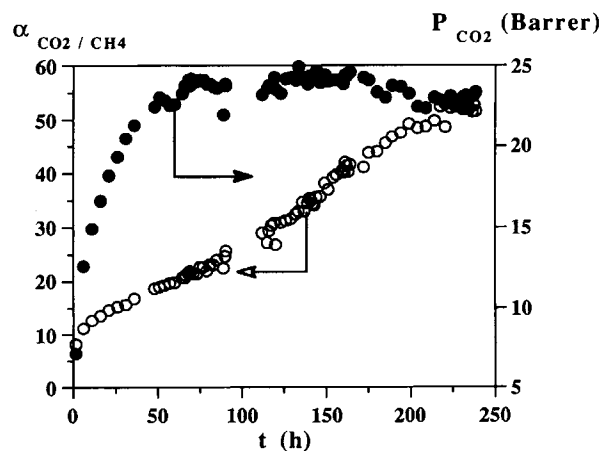
### Heat Treatment with Mechanical Pressure

In this method, a mechanical press (Laufer) was used to combine both mechanical stress and thermal treatment. The membranes were placed between two stainless steel plates that were in turn placed between two heating plates that can be adjusted to a certain mechanical pressure. TPX was used as polymer because of its relatively low melting temperature of 240°C.

At first polymer pellets were spread on the plates, then a weight of 6 T was applied on top of the plates and the temperature of the plates was increased up to 240°C. After 10 min the plates were cooled down and the TPX membrane was obtained [see Fig. 11(a)].

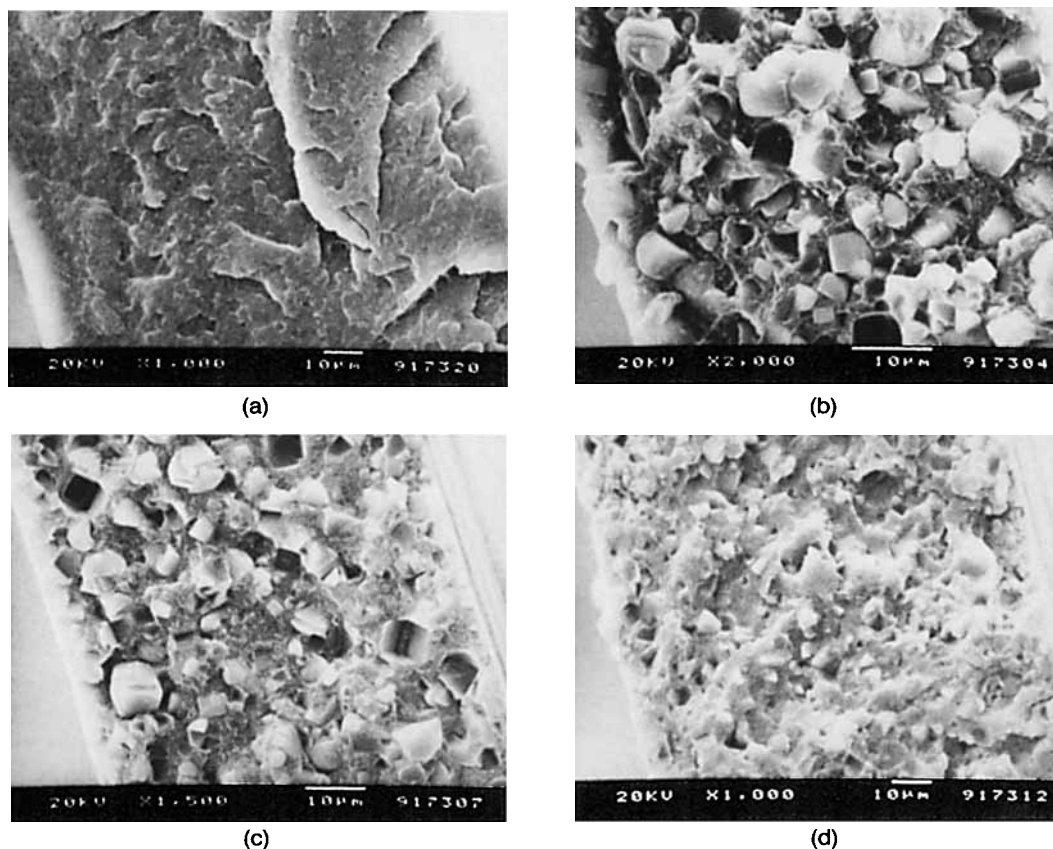
The same experiment was carried out with solution-prepared silicalite-1 filled TPX membranes and varying both the time under pressure and the temperature. Figure 11 (b–d) shows some examples of the structures obtained.

All filled membranes treated in this way were mechanically damaged and no gas separation properties could be determined. Furthermore, the membranes were brown after the treatment, indicating a possible degradation of the polymer phase. This was not expected because pressurizing the pure polymer at 240°C during 30 min does not result in any visible polymer degradation. However the presence of silicalite-1 might be the cause of the observed phenomena. Nevertheless, it can be observed that minimizing of exposure time at high pressure and temperature results in a better adhesion polymer-zeolite than in the case of a solution cast membrane,



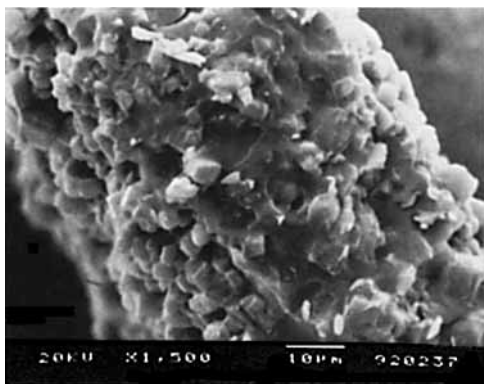
**Figure 10**  $\text{CO}_2$  permeability and selectivity over  $\text{CH}_4$  versus time for a KY filled (50 wt %) PEI membrane annealed at 150°C during 4 weeks.





**Figure 11** Filled and unfilled TPX membrane prepared in the molten state under mechanical pressure: (a) pure TPX, 6 T, 240°C, 10 min ( $\times 1000$ ); (b) TPX + 40 vol % silicalite-1, 6 T, 240°C, 10 min ( $\times 2000$ ); (c) TPX + 30 vol % silicalite-1, 6 T, 240°C, 2 min ( $\times 1500$ ); (d) TPX + silicalite-1, 30 vol %, 6 T, 240°C, press and cool down ( $\times 1000$ ).

although far from perfect. The same trend was observed with silicalite-1 filled PEI membranes, but here the membranes were also damaged after treatment.



**Figure 12** SEM cross section of a silicalite-1 filled TPX membrane treated at 250°C in nitrogen atmosphere under moderate mechanical pressure ( $\times 1500$ ).

The same experiment was carried out at 250°C with preevacuated membranes and under a nitrogen atmosphere. The membranes were placed between two Teflon plates. The result was the same, brown pieces of membrane. The structure obtained is shown in Figure 12.

However, a significant improvement of the structure can be observed, that is fewer voids between the zeolite particles and the polymer phase are left. Unfortunately, it was not possible to obtain pieces of membranes large enough to be tested for gas separation.

## CONCLUSIONS

The preparation of a zeolite filled membrane from a glassy polymer by the classic dissolution-casting-evaporation process results in a three phase membrane: zeolite, polymer, and voids. This might be due to stress forces occurring during the evaporation

step that led to the dewetting of the polymer chains from the zeolite external surface.

Surface modification of the zeolite particles resulted in a considerable improvement of the internal structure of silicalite filled PEI membranes. However, permeation results could not illustrate this improvement.

Evaporation of the solvent above the  $T_g$  did not give any positive result for the system TPX/silicalite-1.

High temperature treatments did improve the structure but damaged membranes were obtained and polymer degradation occurred.

From these experiments it can be concluded that the most promising approach is the modification of the zeolite's external surface by means of a coupling agent combined with the preparation of the membrane at high temperatures if the problem of polymer degradation can be solved. A possible new method may be the use of a zeolite whose external surface has been covered with a very thin layer of a polymer compatible with the matrix polymer. This thin layer could be grafted by means of a silane coupling agent in a first step, and the resulting adsorbent could be incorporated into the desired polymer.

Finally, an elegant way of dealing with this problem might be the direct polymerization of the matrix polymer around the zeolite particles by a bulk or interfacial polymerization.

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