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Synthesis of polyetherimide/silica hybrid membranes by the sol–gel process: influence of the reaction conditions on the membrane properties

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Abstract Hybrid polyetherimide (PEI)–silica membranes were synthesized. The aim was to obtain improved materials for gas separation media. The inorganic material was prepared via the sol–gel method through the hydrolysis of tetraethoxysilane (TEOS). The influence of the reaction conditions on the final membrane morphology and properties were studied. Scanning electron microscopy (SEM), energy-dispersive X-ray analysis (SEM–EDX), and Fourier transform infrared spectroscopy (FTIR) were used to characterize the PEI and PEI–silica composite membranes. The evolution of TEOS hydrolysis and the condensation processes were verified by FTIR studies. The silica–polymer interaction was also analyzed. The SEM micrographs showed how the membranes distinct morphologies depended upon synthesis parameters and preparation techniques (presence of coupling agent, TEOS polymerization in situ or not, silica content and membranes redissolution). The permeation rates of CO_2, CH_4, O_2, N_2, and H_2 through the pure polymer and hybrid membranes were measured and showed an increase of gas permeability for hybrid membranes but, the CO_2/CH_4 and O_2/N_2 selectivities decreased compared to PEI membranes.

Introduction

Hybrid organic–inorganic materials have been investigated as an interesting alternative to overcome the single component limitations, or to enhance mechanical, thermal and transport properties. In order to improve the performance of polymer membranes used in gas separation, inorganic materials were incorporated into the polymer matrix. Porous inorganic fillers like zeolites and carbon molecular sieves (CMS) are used since they offer attractive permeation properties with permeabilities and selectivities, which are significantly higher than polymeric membranes [1–6]. Ideally, the incorporation of small volume fractions of inorganic fillers can result in a significant overall membrane separation efficiency increase. Alternatively, hybrid membranes were proposed with the incorporation of non-porous nano-sized particles [4, 7–10]. The function of the filler is to affect the molecular packing of the polymer chains, enhancing the separation properties of glassy polymeric membranes [11].

Hybrid organic–inorganic materials can be prepared using the sol–gel process. One method involves in situ reaction of an alkoxide with an organic polymer. Hydrolysis and condensation reactions take place in the alkoxide resulting in inorganic networks bonded to the organic polymer [12, 13]. The composite material morphology and physical properties depends on the reaction conditions and the degree of compatibility between both components.

When this hybrid material is designed for separation media, a key factor is to obtain a homogeneous structure. To achieve this objective, it is very important to have a membrane morphology control and to avoid phase separation. A good interaction between the organic and inorganic materials may be reached with the use of compatibilizers or coupling agents, leading to the required homogeneity [12, 14–21].

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A valuable membrane material that has attracted attention is PEI. This material has been used to produce dense films and asymmetric hollow fiber membranes.

Vu et al. [4] incorporated laboratory-synthesized CMS, into PEI matrix. CMS particles were formed via high-temperature pyrolysis of a polyimide (Matrimid). For PEI-CMS membranes, gas permeation test showed enhancements which range between 40 and 8% in CO_2/CH_4 and O_2/N_2 selectivity over the intrinsic selectivity of the pure PEI polymer matrix. The authors compared CMS with zeolites and highlighted several advantages of CMS as possible molecular sieves for the incorporation into mixed matrix membranes.

Husain and Koros [5] prepared asymmetric hollow fiber membranes using surface modified HSSZ-13 zeolite in a PEI polymer matrix. They underwent two different zeolite surface treatments to increase zeolite–polymer compatibility. The first method made use of a silane coupling agent to allow PEI polymer chains to be grafted onto the zeolite surface. Poor adhesion was observed between the materials in the mixed matrix hollow fiber membranes which did not improve selectivity. The second approach consisted of modifying the zeolite surface to improve compatibility with the polymer by replacing the hydroxyl groups with methyl groups. This hollow fiber showed a selectivity enhancement of 10 and 17% for O_2/N_2 and CO_2/CH_4, respectively.

Johnson and Koros [8] produced asymmetric hollow fiber membranes introducing nanoplatelet materials in a PEI matrix. They used nanoplatelet materials (nanoclays) due to the high aspect ratio of this material which presents advantages over zeolites or traditional molecular sieves. However, they found out that the direct dispersion process of the nanoplatelets did not produce the expected exfoliation. They also reported that the fibers were non-selective for the gases tested (N_2, O_2, and He).

Takahashi and Paul [22] prepared nanocomposite membranes based on PEI and three kinds of hydrophobically treated fumed silica. Their study was focused on the relation between voids or defects created in the membrane, and the permeation properties. They found that the nanocomposite membranes have lower selectivity than the polymer matrix due to particle agglomeration and voids formation. The particle dispersion in hybrid membranes had a direct relation with the surface treatment of the silica. The fumed silica particles with long chain treatment were severely aggregated. In a second article of these authors [23], nano-sized SiO_2 particles chemically bonded to the PEI polymer matrix via an amine-containing silane coupling agent were used. They prepared different nanocomposites membranes by solution casting and melt processing. All membranes showed particle agglomeration in the polymer matrix with larger sizes as SiO_2 content increased. They found that chemical coupling to the matrix reduced the void volume but did not eliminate void formation. Depending on the preparation method, the selectivity for gas molecules of these membranes decreases or is equivalent to the pure polymer matrix.

Nunes et al. [15] prepared organic–inorganic hybrids membranes of PEI and silica by in situ growth of the inorganic network through hydrolysis and condensation of tetraethoxysilane (TEOS) with addition of amino silane. Membranes were prepared by phase inversion method with the aim at being used as support of composite membranes for vapor separation under high pressures. The membrane morphology changed from finger-like to a sponge-like cavities structure with the addition of the inorganic component. Homogeneous films were obtained only when the amino silane was added to the PEI/TEOS solution. They concluded that membranes with higher inorganic content had a better mechanical stability and better performance as support of composite membranes for vapor separation.

It has already been demonstrated that the incorporation of silica into a polymer matrix can result in an improvement of membrane separation properties. It is also well known that each polymer–filler combination lead to different performances, with many reports on the hybrid systems used as support and not as a selective layer [15].

In this study, hybrid PEI–silica membranes were synthesized with silica particles prepared via the sol–gel method through the hydrolysis of TEOS aiming at exploring these membranes as a selective layer.

This contribution focuses on the investigation about the effect of reaction conditions on the hybrid membrane properties. The aim is to identify better conditions to obtain a homogeneous morphology. Evaluation of the resulting membranes was done by characterization of the modified chemical and physical structures as well as by measuring gas permeabilities of CO_2, CH_4, O_2, N_2, and H_2.

Experimental

Materials

Polyetherimide (ULTEM 1000) was obtained from GE Plastics. The polymer was dried at 60 °C before being used in the synthesis. The solvent was 1-methyl-2-pyrrolidinone (NMP). TEOS was used as silica precursor and 3-aminopropyltriethoxysilane (APTEOS) was used as the coupling agent. They both from Sigma-Aldrich were used for the inorganic material generation in the sol–gel process. Deionized water was used to carry out the alkoxide hydrolysis with 37.5 wt% HCl as catalyst. In some cases, ethanol was the solvent. All the chemicals were used without further purification.

Polyetherimide–silica hybrid membrane preparation

Dense PEI and PEI–silica hybrid membranes were prepared by the solution-casting technique [24]. PEI was dissolved (15 wt%) in NMP under stirring for 1 day. For the sol–gel process, 1:2:0.1 molar ratios of TEOS, water, and acid were used. When coupling agent was tested, 5 wt% of APTEOS/TEOS was used. Different methodologies were studied as shown in Table 1. In procedures 1-3 (P1, P2, and P3), a TEOS solution was prepared separately and then mixed with the polymeric solution. In the TEOS–ethanol (1:1 molar ratio) mixture, water, and acid were added with stirring using a water-cooled reflux column [16]. In procedures 4 and 5 (P4 and P5), hybrid membranes were obtained by in situ hydrolysis and condensation of TEOS in the polymer solution [12, 15, 17, 25]. In these cases, alcohol was not used as a solvent, to allow a shift of the reaction equilibrium toward hydrolysis [12]. In procedure 5, the APTEOS was first added to the polymeric solution and stirred for 24 h, before adding the TEOS.

Synthesis parameters such as temperature, stirring time, and solvents were modified. The silica content ranged between 5 and 15 wt% (weight percent of total silica in the hybrid material, as calculated from the initial amount of TEOS, assuming complete reaction).

The solution was cast on a flat glass plate and evaporated in an oven at 60 °C during 24 h. The thickness of the membranes measured by micrometer was in the range of 25–70 μm. Some of the membranes prepared following procedure 4, were redissolved in the solvent used for the synthesis and recast. These membranes were denoted by PEI-X, or PEI-RX, in which X represents the silica content and R is used for redissolved hybrid membranes.

Membrane characterization

The membrane morphology was observed by scanning electron microscopy (SEM) (JEOL JSM-6480 LV). The samples were fractured in liquid nitrogen and metalized with gold. Energy-dispersive X-ray analysis (SEM-EDX) was used to observe the silica content of the membranes.

Fourier transform infrared spectroscopy (FTIR) (GX FTIR Perkin Elmer spectrometer) was undertaken for both to confirm the sol–gel process and to evaluate the overall chemical changes in the hybrid organic–inorganic material. Attenuated total reflectance ATR-FTIR spectra of thin membranes films were collected with a 4 cm^{-1} resolution. The angle of incidence was 45° and the reference crystal was zinc selenide.

The synthesized membranes permeation properties were evaluated with pure gases (H_2, N_2, O_2, CH_4, and CO_2) using a constant volume/variable pressure method [26, 27].

The downstream and upstream chambers of the membrane cell were evacuated by a vacuum pump before beginning the gas permeation. The downstream pressure was detected by a pressure transducer. The membrane permeability was calculated by plotting the pressure in the permeate side versus time. The ideal selectivity (or permselectivity), α_{AB}, of membranes was calculated as

$$\alpha_{\mathrm{AB}} = \frac{P_{\mathrm{A}}}{P_{\mathrm{B}}}$$

where P_{A} and P_{B} are pure component permeabilities of gases A and B. The gas membranes permeabilities were measured at 3 bar and at a temperature of 30 °C.

Table 1 Synthesis conditions for the sol–gel process

Sol–gel procedures	Materials	Synthesis method	Solvent for TEOS hydrolysis	Stirring conditions
1	TEOS Water + HCl	TEOS hydrolysis separately	Ethanol	80 °C—1 h
2	TEOS Water + APTEOS + HCl	TEOS hydrolysis separately with coupling agent	Ethanol	80 °C—1 h
3	TEOS Water + HCl	TEOS hydrolysis separately	NMP	25 °C—1 h
4	TEOS + APTEOS Water + HCl	TEOS hydrolysis in situ with coupling agent	NMP	25 °C—20 h
5	APTEOS TEOS Water + HCl	Coupling agent in the PEI solution-stirring for 24 h	NMP	25 °C—30 h

Results and discussion

Morphology

Different conditions were tested to carry out the sol–gel reaction considering published studies that use silicon alkoxide precursors and organic polymers such as polyimide or PEI as matrices [12, 15–17].

The SEM images show that PEI pure membranes present a dense morphology (Fig. 1a). For membranes prepared following procedure 1, silica domains with sizes ranging from 1 to 6 µm can be observed (Fig. 1b, c). There is a poor adhesion between silica particles and the polymeric matrix. In membranes with a silica content of 10 wt%, the domains size is larger. Similar micrographs were observed in other polymer–silica hybrid materials such as polyimide–silica [28–30]. The authors reported that clear boundaries of the silica particles with some interfacial spaces showed that the pure organic and inorganic phases had poor interaction.

When the coupling agent was incorporated in an attempt to overcome the interface problem (procedure 2) (Fig. 1d), the adhesion between the materials was not improved.

Other synthesis methods were investigated to improve the internal structure of the membranes (procedures 3–5). Membranes prepared following procedures 3 and 5 were opaque. This is a strong evidence of a heterogeneous material [30]; since these membranes did not present a good visual homogeneity they were not characterized.

When TEOS hydrolysis is made in situ in the polymeric solution following procedure 4, better silica dispersion is observed (Fig. 2). This behavior is maintained in the whole range of silica concentration (5–15 wt%). On the other side, redissolved membranes are homogeneous and dense (Fig. 2b), probably because traces of water (from the hydrolysis reaction) were eliminated. By comparing these micrographs with Fig. 1, it became very clear that with this synthesis procedure, the internal structure of the hybrid membrane is improved to a large extent. On the basis of these results, we could conclude that synthesis via procedure 4 resulted in transparent films with silica well dispersed on the PEI polymer, which make these membranes suitable for gas separation. In this procedure both, the TEOS hydrolysis in situ in the polymeric solution and incorporate the alkoxide and the coupling agent at the same time, plays an important role in determining morphology of

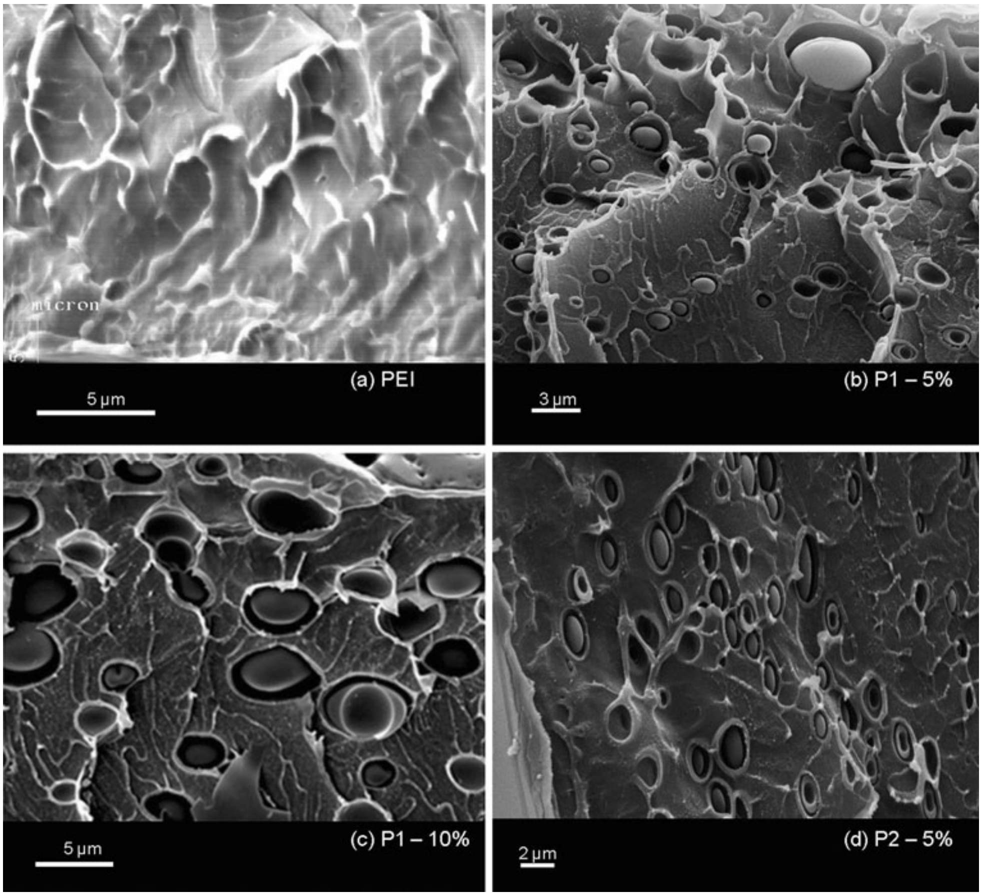

Fig. 1 SEM micrographs of cross section membranes: **a** pure PEI, **b** PEI-5 (procedure 1), **c** PEI-10 (procedure 1), and **d** PEI-5 (procedure 2)

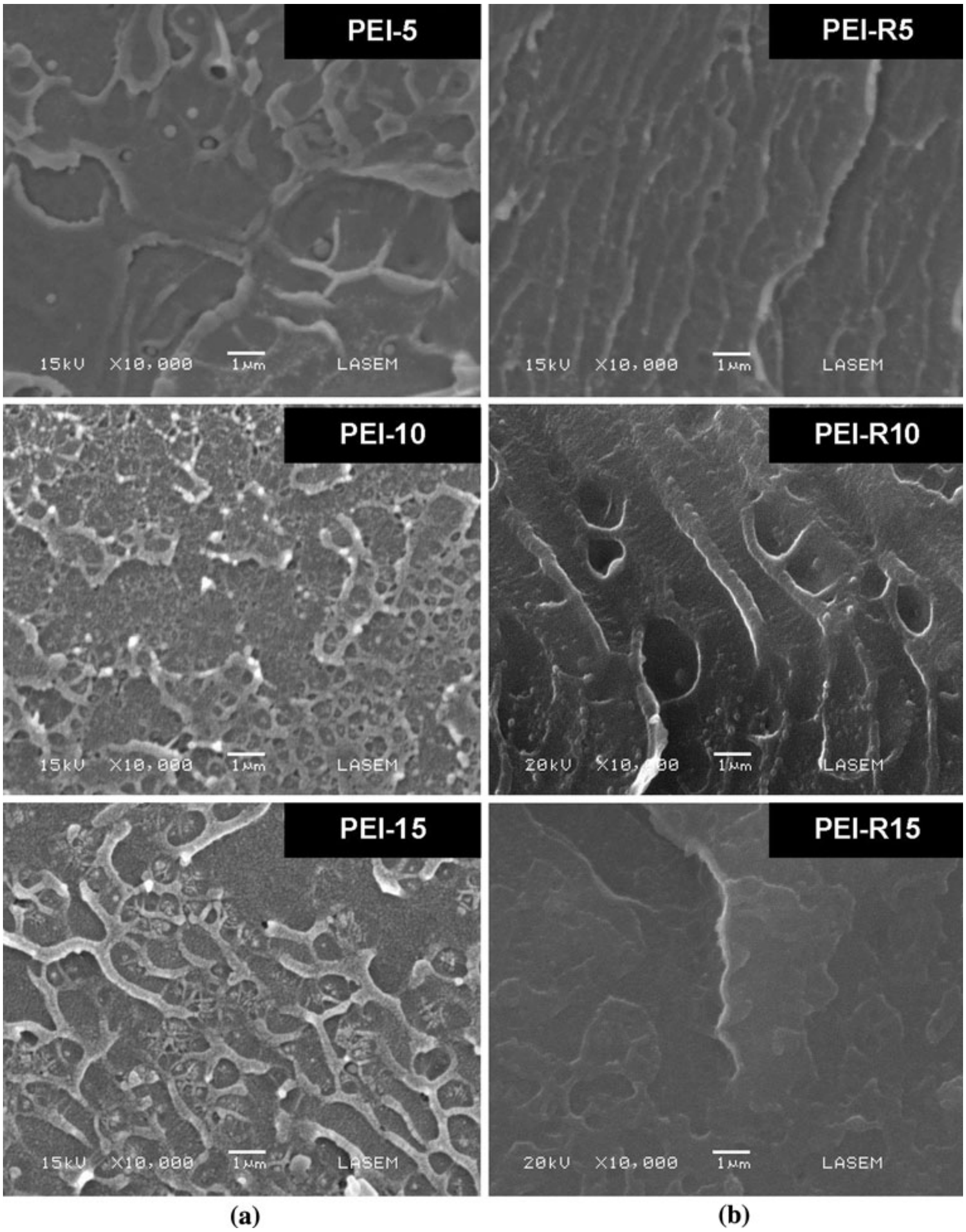

Fig. 2 Membranes cross section SEM micrographs: **a** TEOS synthesized in situ, **b** Redissolved membranes

the resulting polymeric structure improving the interaction between the materials in the reactive mixture. These membranes were selected for further evaluations.

To achieve a homogeneous internal structure, the use of a coupling agent is indispensable. Many studies reported the benefit of the coupling agent incorporation to form hybrid membranes [15, 17–19]. Their addition effect could be: to improve the silica dispersion and assure the adhesion between the phases [15, 31], the creation of an interaction with functional groups present in the polymer [15] as well as a change of the silica surface to avoid agglomerates formation [20] or to influence the silica structure by favoring the formation of linear inorganic network [18].

Nunes et al. [15] obtained a highly dispersed silica phase in PEI matrix. The authors reported that dispersion in the nanoscale was only possible with the introduction of small amounts of aminosilane, which do not only improve dispersion, but it also assures the adhesion between the inorganic phase and the organic polymer matrix, which is indispensable to avoid membrane defects formation. They also reported that the coupling agent amine groups strongly interacted to the imide groups of PEI. This kind of interactions is expected to be present in the hybrid membranes as well.

Kim et al. [20] reported that silane coupling agents are used to modify the silica surface through their unique bifunctional groups to enhance the compatibility with the polymer matrix. This surface modification is necessary because the silica nanoparticles have a high surface area covered by silanol groups. This hydrophilic surface is not compatible with the polymer matrix. In addition, the silica nanoparticles tend to adhere to each other through hydrogen bondings and form silica agglomerations.

Musto et al. [18] and Ragosta and Musto [21] reported that the presence of a coupling agent can also affect the structure of the inorganic network. They studied the incorporation of g-glycidyloxypropyltrimethoxysilane in the hybrid membrane, which demonstrates a strong influence on the silica phase by favoring the formation of linear (not cyclic), branched chains which make the structure loosely interconnected.

In this study, hybrid membranes with a homogeneous structure were reached with the incorporation of APTEOS as coupling agent, when the appropriate synthesis condition was used (procedure 4).

SEM–EDX analysis

The SEM–EDX analysis has also been carried out to show the presence of silica particles in the hybrid membranes (Fig. 3). This technique confirmed the increasing amount of inorganic filler in the membranes as one follows the peak corresponding to silicon.

FTIR analysis

An infrared spectrum of PEI polymeric films is shown in Fig. 4. Bands at 1776 and 1718 cm^{-1} corresponding to the asymmetric and symmetric stretching vibrations of C=O groups are observed. The absorption band at 1353 cm^{-1} is assigned to the bond stretching vibration of C–N in phthalimide rings. Vibrations at 1268, 1234, 1072, and 1014 cm^{-1} are due to aryl ether bonds [32].

It is interesting to analyze the spectra that results from the subtraction of the pure PEI membranes from the one of the hybrid membranes (Fig. 5). Several absorption bands between 1000 and 1200 cm^{-1} are observed due to asymmetric stretching vibration of siloxane groups (Si–O–Si) formed via the sol–gel process when TEOS was added.

Although IR spectra of silica systems have been extensively studied, there is no agreement with the structural significance of bands occurring at lower frequencies, in the 1000–1200 cm^{-1} range [33]. The frequency of the bands is of particular interest because it gives information about the molecular structure of the inorganic network. It is well known that silica gel is formed with cyclic and linear structures. In this study, we assigned the 1086 cm^{-1} peak to the asymmetric stretching mode of Si–O–Si units belonging to cyclic structures [12, 18, 33, 34]. This band is only observed in the PEI–silica film with 15 wt% of SiO$_2$ spectrum, suggesting that high silica loadings promote the formation of assemblies of Si–O–Si rings. The component due to the same vibrational mode in more linear and less

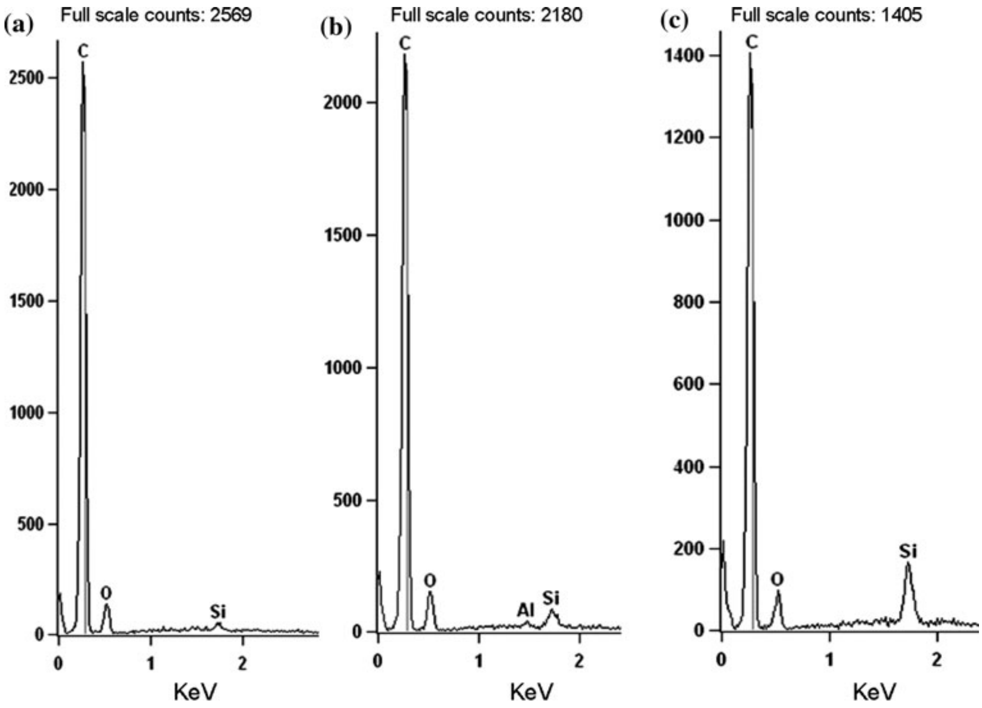

Fig. 3 SEM–EDX of hybrid membranes: **a** PEI-5, **b** PEI-10, and **c** PEI-15

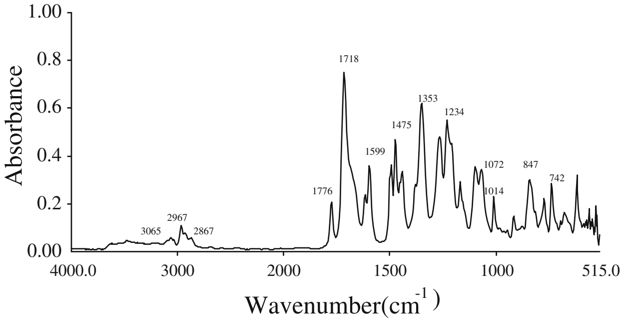

Fig. 4 FTIR PEI membrane spectra

cross-linked structures occurs at 1055–1060 cm^{-1} [18, 33]. The intensity of the last band mentioned increased with the silica content.

The presence of these bands are reported by Lenza and Vasconcelos [33] in their FTIR study of the sol-to-gel evolution of polymeric silica sols, obtained by hydrolysis and condensation of TEOS, using formamide as an additive. In the absence of formamide, the sol structure is poorly interconnected and 1040 cm^{-1} band is predominant. For sols containing formamide, condensation leads to small oligomers, a more cross-linked structure is obtained and the intensity of 1080 cm^{-1} peak increases. A similar assignment was done by Musto et al. [18] in polyimide/silica hybrids FTIR studies using a deconvolution technique. They attribute the splitting of the stretching vibration of Si–O–Si to a discrimination between cyclic (1093 cm^{-1}) and linear (1044 cm^{-1}) structures.

The band observed at 1117 cm^{-1} (Fig. 5) is related to the presence of Si–O–Si in linear structures [33]; however, a minor contribution of the Si–O–C asymmetric stretching modes cannot be ruled out [18].

An absorption band at 941 cm^{-1} is also clearly identified and represents the silanols groups (Si–OH) resulting from the incomplete condensation reaction in the silica network generation. The appearance of bands which are characteristic of condensed silica glass, the doublet around 1000–1100 cm^{-1} and the 941 cm^{-1} peak suggests that the sol–gel reaction was successfully carried out and confirms the almost complete development of the inorganic phase in the hybrid system. The displacement of these bands, compared to their position in neat silica spectra, could be due to polymer–silica interactions and could explain the novel properties of the hybrid membranes.

The FTIR hybrid membranes spectra are similar to the one of PEI membrane. This may be attributed to the low content of silica in the membranes and the overlap of the 1072 and 1014 cm^{-1} strong bands of the PEI (C–O stretching of aromatic ether) with the 1000–1100 cm^{-1} bands of the pure inorganic solid.

Gas permeabilities

The permeabilities of H_2, N_2, O_2, CH_4, and CO_2 in PEI and PEI–silica hybrid synthesized membranes are shown in Table 2. Permeability of the hybrid membrane with 5 wt% of silica (procedure 4) is higher for all gases compared to pure PEI membrane. However, CO_2/CH_4 and O_2/N_2 selectivity decrease significantly (Table 3). A possible reason could be the lack of proper adhesion between the silica and the polymer matrix, originating non-homogeneities at the interface. Gas transport mechanism would then

Fig. 5 FTIR substraction spectra of hybrid-PEI: *a* PEI-5, *b* PEI-R5, *c* PEI-R10, and *d* PEI-R15

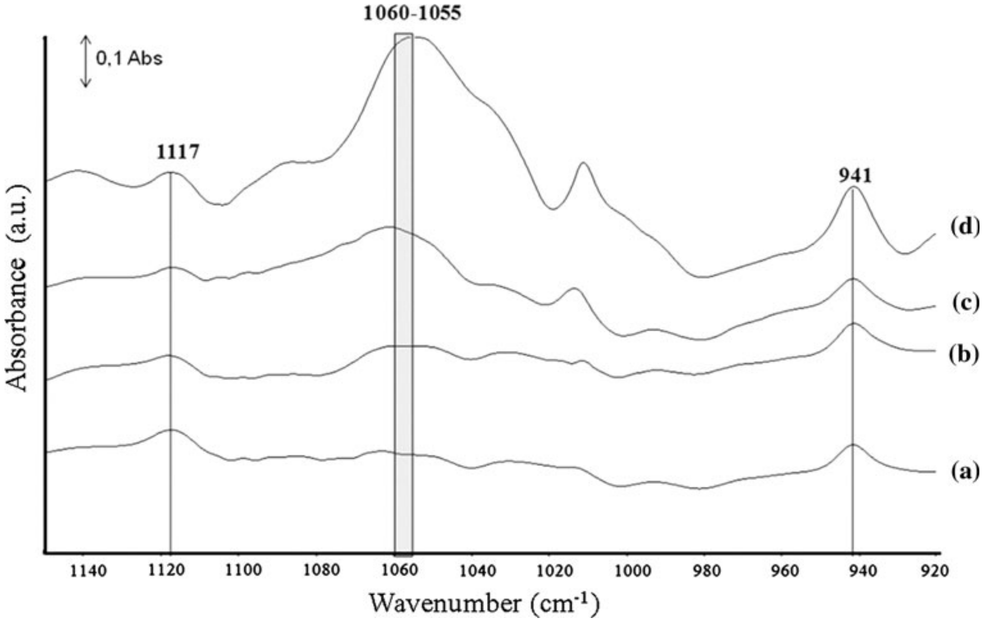

Table 2 Pure gas permeabilities (Barrer) of PEI and hybrid membranes

Membrane	Silica (wt%)	P_{H_2}	P_{N_2}	P_{O_2}	P_{CH_4}	P_{CO_2}
PEI	–	6.90	0.052	0.38	0.029	1.56
PEI-5	5	12.93	4.96	4.95	8.08	6.54
PEI-R5	5	4.65	0.097	0.38	0.088	1.70
PEI-R10	10	3.83	0.061	0.40	0.062	1.78

Table 3 CO_2/CH_4 and O_2/N_2 selectivities of PEI and hybrid membranes

Membrane	α_{CO_2/CH_4}	α_{O_2/N_2}
PEI	53.83	7.31
PEI-5	0.81	1
PEI-R5	19.32	3.92
PEI-R10	28.71	6.56

deviate from the solution-diffusion model of dense membranes, and rather be the result of a Knudsen diffusion type. This is suggested by the calculated Knudsen selectivities ($\alpha_{CO_2/CH_4} = 0.6$ and $\alpha_{O_2/N_2} = 0.94$).

For the redissolved hybrid membranes (PEI-R5 and PEI-R10), we could observe both a decrease in gas permeability and an increase in selectivity compared to the 5 wt% silica hybrid membranes. The permeability values of these membranes are comparable to that of pure PEI membrane, as SEM micrographs showed a dense morphology for both. The H_2 permeability was lower in the redissolved hybrid membranes, while other gas molecules showed in general higher permeabilities when compared with their values for the pure PEI membrane. From these results, we could infer that hybrid membranes have a microstructure which still contains some heterogeneity [1].

Although, we could not detect a direct relationship between gas permeability and silica content, the performance of PEI-R10 membrane suggested that interesting permeability–selectivity trade off can be sought and obtained for the CO_2/CH_4 pair. These results reflected the possibility of changing or optimizing the membrane transport properties modifying the synthesis conditions.

The relative enhancement in permeability (i.e., ratio of permeability of silica-filled membranes to that of unfilled membrane) is in the following order: $CH_4 > N_2 > CO_2 > O_2$. Ahn et al. [10] attributed these greater permeability enhancement of the larger penetrants compared to the smaller gas molecules to an increase in molecular spacing in the hybrid membranes, leading to a more pronounced effect on the diffusion coefficient and therefore on the permeability.

Thermal stability and mechanical properties can be improved when good interface bonding between the PEI matrix and the silica is reached [17, 28, 30]. So, one can still expect that this hybrid materials may be successfully used to prepare membranes with a promising combination of permeability–selectivity for gas separation.

Conclusions

PEI–silica hybrid membranes, containing 5–15 wt% of silica, with a homogeneous internal structure, as revealed by SEM, were successfully synthesized when TEOS hydrolysis was made in situ in the polymer solution.

Different morphologies were obtained depending on the synthesis method used to incorporate the inorganic material to get the hybrid membrane. FTIR spectra analysis turned out to be a reliable characterization technique to check if the sol–gel reaction was carried out. Gas permeation tests showed that the permeabilities of redissolved membranes are comparable to that of the PEI membrane. Hybrid membranes are more permeable than pure PEI membranes, without promoting, however, an improvement of CO_2/CH_4 and O_2/N_2 selectivity.

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