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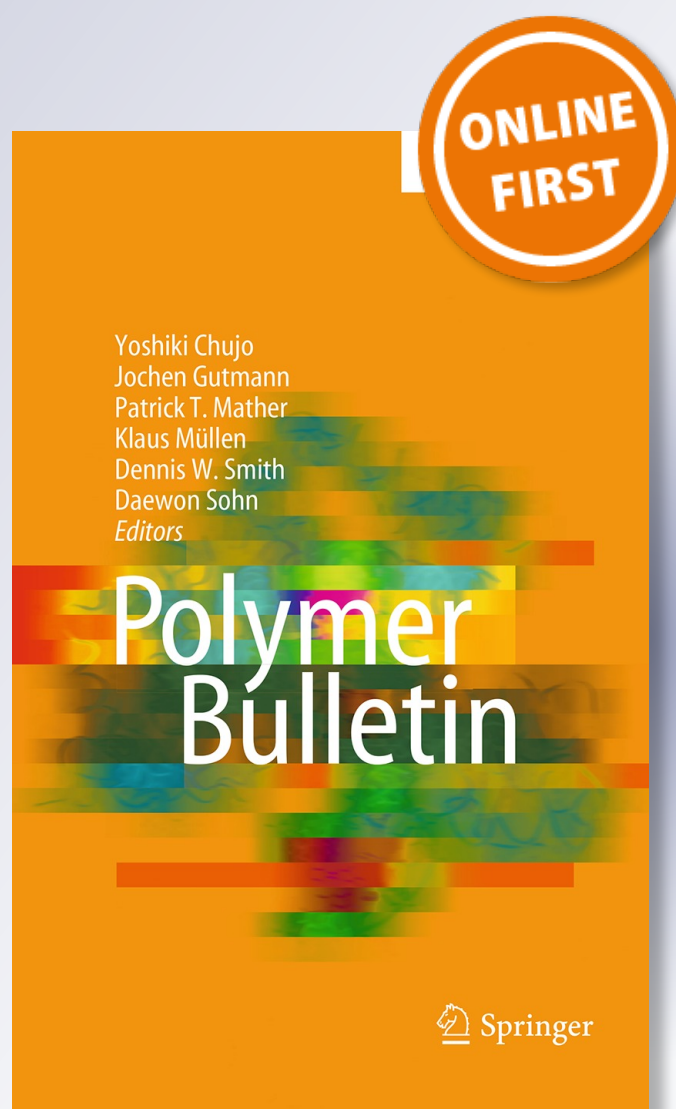
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Influence of silica and coupling agent loading on thermal, morphological and mechanical properties of hybrid membranes

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Abstract Hybrid polyetherimide-silica (PEI-SiO₂) membranes were synthesized via the sol-gel method through the hydrolysis of tetraethoxysilane (TEOS) with 3-aminopropyltriethoxysilane (APTEOS) as a coupling agent. The effects of silica content and the APTEOS/TEOS ratio in thermal, morphological and mechanical properties of the hybrid membranes were studied. Although many studies report improvements in the structure or properties of composite materials when a coupling agent is used, these contributions do not investigate the effect of the coupling agent loading on the properties of the new material synthesized. In this study, we prepared hybrid membrane with a fixed amount of APTEOS modifying TEOS content to analyze the silica content effect. Conversely, to determine the coupling agent effect, hybrid membranes were prepared varying the APTEOS content while the amount of TEOS was kept constant. All hybrid membranes have a dense and uniform internal structure and exhibit good thermal resistance with a degradation temperature above 544 °C. Membranes with 10 wt% of silica showed better tensile strength with a high modulus and low rupture elongation indicating an effective load transfer between the phases. Concerning the coupling agent effect, the maximum modulus was observed for membranes with 10 wt% of APTEOS, suggesting a greater interaction between the organic and inorganic phases.

Keywords Polyetherimide · Silica · Hybrid membranes · Thermal properties · Mechanical properties

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Introduction

It was proposed to incorporate inorganic fillers into polymeric matrices to improve the material properties so that the requirements of certain applications could be reached [1–4]. These composite materials can significantly improve the mechanical, thermal, and barrier properties of pure polymeric matrices. Studies have shown that successful implementation of these materials depends on the polymeric matrix selection, the inorganic filler, and the elimination of polymer–filler interfacial defects [5–10].

Regarding the application of these materials, our group investigated the use of gas separation membranes. Polymeric membranes used for gas separation offer many advantages such as low power consumption, operational simplicity, and good mechanical strength. However, these materials also have certain limitations since many applications require membranes more resistant and with better performance. Therefore, the development of new membrane materials is an important area of research. With the goal of contributing to the development of new polymer–inorganic filler systems, we proposed study hybrid membranes of polyetherimide (PEI) and silica.

Several studies were published using different polymeric matrices and incorporating silica as inorganic filler. Hybrid organic–inorganic composites could be prepared using commercial silica (fumed silica) [11–15] or are frequently obtained by generating the dispersed inorganic phase *in situ* by the sol–gel technique [5, 16–20]. The sol–gel process involves hydrolysis and condensation reactions, from an alkoxide precursor, which are typically catalyzed by an acid or base. While silicon alkoxides are used as precursors in the formation of hybrid membranes, tetraethoxysilane (TEOS) is the most extensively used [17, 21, 22].

To achieve a homogeneous internal structure, the use of a coupling agent is crucial as demonstrated in many published studies [7, 16, 18, 23]. The effects of the coupling agent are improving dispersion of the silica. It ensures a good adhesion between the phases, the creation of interactions with functional groups present in the polymer, as well as a change of the silica surface to avoid agglomerates formation. Although many studies reported these improvements in composite materials prepared by sol–gel process, these studies did not investigate the effect of modifying the amount of coupling agent used. To study the silica effect, the proportion of alkoxide precursor is generally the varying parameter. The coupling agent amount remains fixed [19, 20, 24]. In some studies, the authors set the coupling agent/alkoxide ratio and changed the amount of both reactants at a same time [7].

Even though a number of studies have now been carried out on the preparation and characterization of such hybrid or composite materials, the effect of coupling agent loading on the material properties offers no previous detailed reports.

In an earlier contribution [22], the influence of the reaction conditions on the membrane properties was investigated. It was found that the membranes with 10 wt% of silica showed an interesting permeability and selectivity trade off for the CO₂/CH₄ pair. We have focused our attention in this work primarily on the effect of the coupling agent on the hybrid membranes properties and to get better thermal, mechanical, and homogeneous materials. In the present work, the synthesis and

characterization of polyetherimide (PEI)-silica membranes with silica particles prepared via the sol-gel method, through the hydrolysis of TEOS and using 3-aminopropyltriethoxysilane (APTEOS) as coupling agent, are reviewed. A detailed discussion of the silica and APTEOS effects on the membrane properties is presented. Due the results obtained, we selected the silica and coupling agent load required to obtain a material with optimum properties. Thereafter, we are interested in continuing the study of these membranes in gas separation.

Experimental

Materials

Polyetherimide (PEI-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). Both Tetraethoxysilane (TEOS as a silica precursor) and 3-Aminopropyltriethoxysilane (APTEOS as a coupling agent) were from Sigma-Aldrich and were used for the inorganic material generation in the sol-gel process. Deionized water was used to carry out the alkoxide hydrolysis with HCl (37.5 wt%) as a catalyst. All the chemicals were used without previous purification.

Polyetherimide-silica hybrid membrane preparation

Dense PEI and PEI-silica hybrid membranes were prepared by the solution-casting technique [25]. PEI was dissolved (15 wt%) in NMP under stirring for 24 h. Hybrid membranes were obtained through the sol-gel process in situ, by hydrolysis, and condensation of TEOS in the polymer solution. Different methodologies followed to carry out the sol-gel reactions modifying synthesis parameters, such as temperature, stirring time, and solvents, were reported in a previous publication of our group [22]. PEI-silica hybrid membranes with a homogeneous internal structure were successfully synthesized when TEOS hydrolysis was carried out in situ in the polymer solution. A detailed experimental procedure for the membrane preparation can be found elsewhere [22].

Silica content 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). These membranes were denoted by PEI-X, in which X represents the silica content.

Coupling agent effect For the entire range of silica loadings studied, a 5 wt% of APTEOS/TEOS was used to prepare the hybrid membranes.

In order to study the effect of the coupling agent in the membranes properties, membranes with 10 wt% of silica were synthesized (middle amount of silica studied) by varying the amount of APTEOS. The weight percent of coupling agent was varied between 5 and 15 wt% respect to TEOS. These membranes were denoted by PEI-X-AY, in which X represents the silica content and A accounts for the APTEOS added in an amount Y.

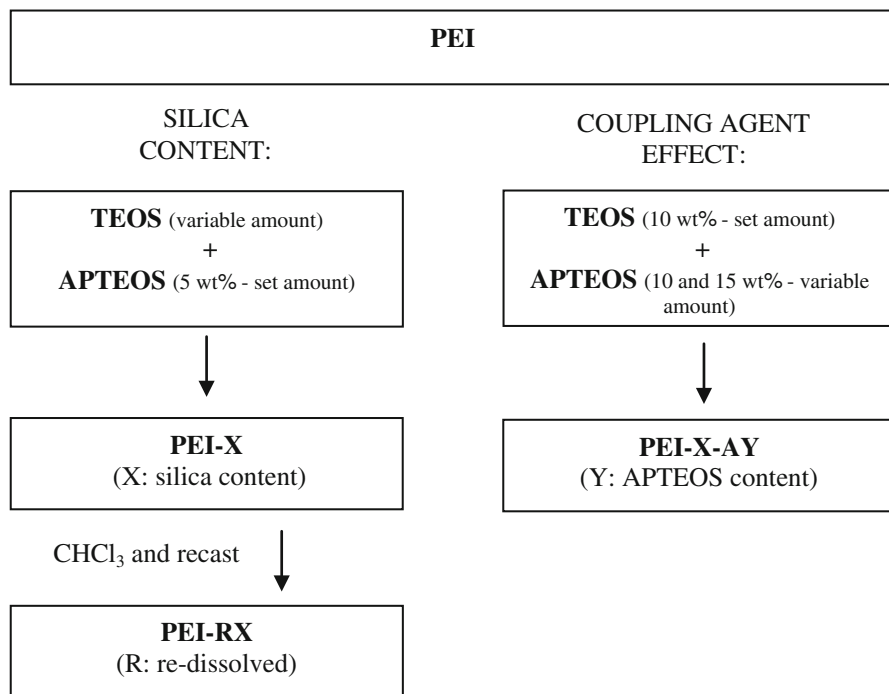


Fig. 1 Scheme with the hybrid membranes synthesized

Membranes re-dissolution Some of the membranes were re-dissolved in chloroform and recast. These membranes were denoted by PEI-RX, in which R is used for re-dissolved hybrid membranes.

The scheme with the hybrid membranes synthesized is shown in Fig. 1.

Membrane characterization

The membrane morphology was observed by electron scanning microscopy (SEM) (JEOL JSM-6480 LV). The samples were fractured in liquid nitrogen and metalized with gold.

Glass transition temperatures, T_g , were determined by differential scanning calorimetry (DSC) (Perkin Elmer DSC 7). The DSC measurements were carried out under an N₂ gas flow rate of 22.5 ml/min with a heating rate of 10 °C/min. Samples were heated twice from 50 to 300 °C. Thermal degradation and silica content in hybrid membranes were determined by Thermogravimetric analysis (TGA) (Perkin Elmer TGA 7). Samples were heated from room temperature up to 1,200 °C, at a heating rate of 10 °C/min.

The mechanical properties of the hybrid membranes were recorded on an SANS CMT 6104 universal tester at a constant traction speed of 3 mm/min. The samples had a rectangular shape (70 mm × 10 mm). The thickness of the membranes, measured by a micrometer, was in the range of 25–80 μm. The results deal with the average values of three samples of each membrane.

Results and discussion

Morphology

The synthesis procedure selected to prepare hybrid membranes (TEOS hydrolysis in situ in the polymeric solution) leads to dense homogeneous membranes with good silica dispersion [22]. This behavior was observed in the whole range of silica concentration (5–15 wt%). On the other hand, re-dissolved membranes are also homogeneous and dense. The use of a coupling agent is necessary to achieve a homogeneous internal structure.

In addition, the incorporation of both TEOS and APTEOS plays an important role in determining the morphology of the resulting polymeric structure improving the interaction between the materials in the reactive mixture. Several studies reported the advantages of the incorporation of the coupling agent to form hybrid membranes [7, 14, 16, 26].

Thus, Chen et al. [7] claimed that the coupling agent incorporation to prepare hybrid films by sol–gel process is required. The fracture morphology surfaces showed a finely interconnected or co-continuous phase demonstrating good miscibility between polymer and silica phases. However, in their work, the TEOS/coupling agent ratio was kept constant.

Nunes et al. [16] also stand out that coupling agent incorporation was necessary to obtain homogeneous films. The authors highlight that amine groups of the coupling agent interact with the imide groups of PEI. Due to this strong interaction, the hydrolysis goes on and the solutions containing small amounts of coupling agent have a tendency to gel. They found that only with proportions of 95/5 of TEOS/coupling agent, a stable solution (no gelation) was obtained.

To study the coupling agent effect, membranes with 10 wt% of silica (TEOS fixed content) but with higher amounts of coupling agent (APTEOS) were synthesized in this contribution. The SEM images of these membranes are shown in Fig. 2. The micrographics (a1) and (b1) show the complete membrane thickness, even as (a2) and (b2) showed a magnified cross-section image. A completely dense morphology is observed for membranes with 10 wt% (Fig. 2a) and 15 wt% (Fig. 2b) of APTEOS. Figure 2a1, b1 is consistent with the existence of a uniform structure across the membrane thickness.

A strong evidence of the coupling agent role in the sol–gel process is observed when hybrid membranes with higher APTEOS contents undergo the re-dissolving process. It was not possible to re-dissolve these membranes even after several days of stirring with the solvent. This observation shows that there is a modification in the structure formed, resulting in a new homogeneous material.

Glass transition temperature (T_g)

The glass transition temperature (T_g) is a parameter used as reference to evaluate changes in the thermal properties of the membranes by incorporating a filler. Table 1 shows the T_g of the hybrid membrane with 5 wt% of silica as well as the T_g corresponding to the unfilled polymeric membrane. For comparative purposes, the

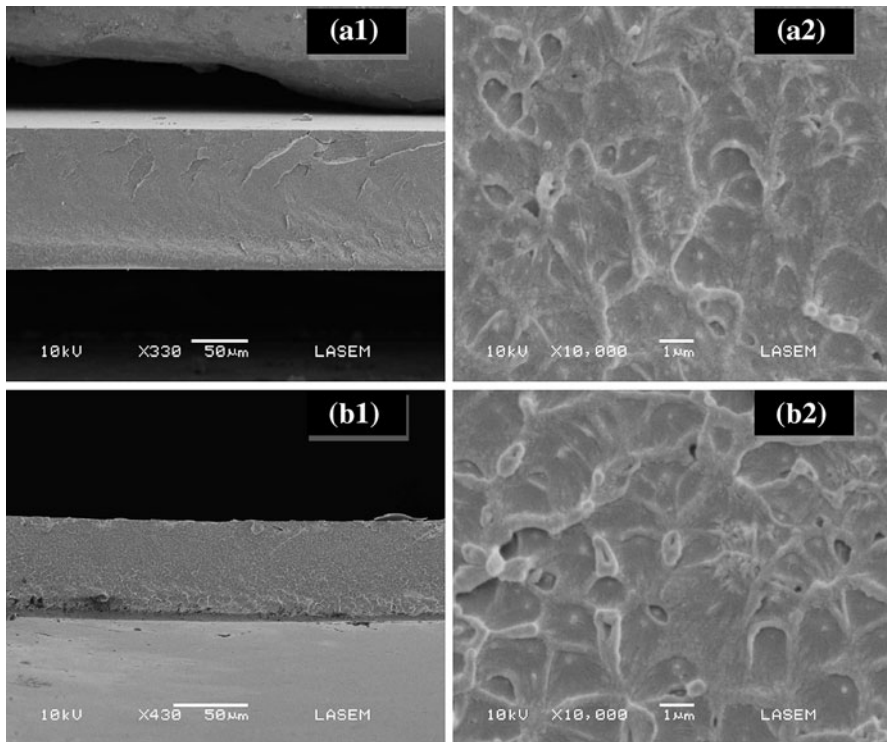


Fig. 2 SEM micrographs of cross-section membranes with 10 wt% of silica: **a** 10 wt% and **b** 15 wt% of APTEOS

Table 1 Glass transition temperatures of hybrid (5 wt% of silica) and pure polymeric membranes

Membrane	Silica (wt%)	T_g (°C)
PEI	–	181
PEI-5	5	185

glass transition temperature reported in the literature for polyetherimide is 210 °C [25].

Both membranes showed T_g values lower than those reported for pure PEI membranes. This effect cannot be related to the generation of silica from TEOS because the unfilled polymeric membrane presents an approximate value. This behavior could be attributed to a solvent effect since the drying conditions of the membranes may not be enough to remove all the solvent. The NMP could act as a plasticizer, reducing the T_g of the membranes. In order to ensure complete removal of the solvent, prior to the determination of T_g , the membranes were dried for 48 h in an oven at 200 °C. Ahn et al. [12] reported that membranes undergoing drying procedure are critical to remove residual solvent, which can cause decreases in T_g .

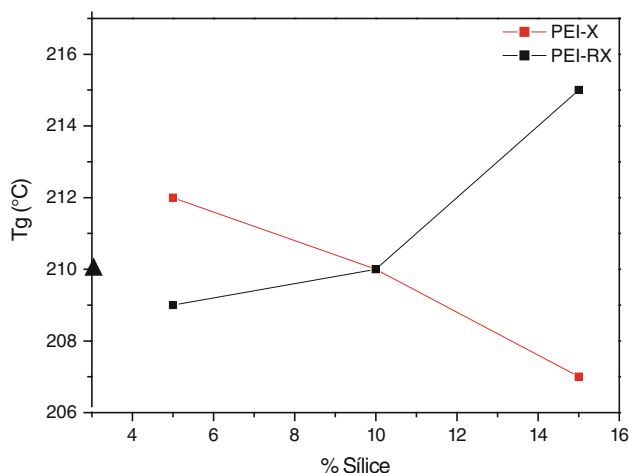


Fig. 3 Glass transition temperature (T_g) of the hybrid membranes before and after re-dissolution

Figure 3 reports the T_g of PEI and hybrid membranes obtained after following the aforementioned drying protocol. It was observed that the T_g values of the membranes differ from a range between 207 and 215 °C, which is consistent with the values reported in literature for this kind of membranes [16, 27–30].

For PEI-X membranes, it can be observed that T_g parameter slightly decreases as the silica content increases, in the range of silica studied.

Various effects on the T_g of the composite membranes were reported after the inorganic filler addition. Ahn et al. [12] observed a slight increase in the T_g of the polysulfone-silica membranes, but for a filler content higher than 20 wt%. The largest increase reported is 5 °C for a silica content of 30 wt%. The authors suggest that an increase in the T_g reflects a change in the segmental mobility of the polymer chains, as well as a greater rigidity in certain regions of the polymer generated by stresses created during formation of the membrane at the interface polymer-silica.

Li et al. [2] also reported that T_g rises with increasing silica content in ternary hybrid materials consisting of bismaleimide-polyetherimide-silica (an increase of up 19 °C for a 20 wt% of TEOS). The authors relate these increases in T_g with the interactions between the polymer matrix and silica, which are greatly improved by incorporating the coupling agent.

However, contributions were published in which no major differences were observed between the T_g values of the pure polymeric and nanocomposite membranes. Compton et al. [31] prepared polyimide membranes with silver or palladium nanoparticles generated in situ. The authors report just small differences in T_g , for the 13 wt% silver membrane suggesting that it takes place only in a small or negligible variation in the mobility of polymer chains near the nanoparticle surface. It is also possible that this variation could not be evidenced by a classical DSC analysis.

Moreover, in re-dissolved membranes (Fig. 3), an increase in the T_g with the silica content could be observed, showing a change in the segmental mobility of

polymer chains with a consequent increase in stiffness at the interface between both materials. An effect caused by the re-dissolution of the membranes could be the rearrangement of the silica network. A higher order of the inorganic phase in the PEI matrix can lead a greater steric hindrance of the polymer chains, leading to an increase of T_g . This observation is likewise consistent with the existence of good adhesion or compatibility between the two phases, which is also supported with the morphological analysis observed in the SEM images.

In addition, it is important to highlight the behavior of the membranes with 10 wt% of silica both PEI-10 and PEI-R10 which exhibit the same T_g value found in agreement with the T_g of the pure PEI membrane. Regarding this, we would infer that the silica network formed with that load of filler forms a structure which is able to interact very efficiently with the polymeric matrix.

In Table 2, the DSC results are presented for hybrid membranes with different APTEOS contents. The results show that there is no significant effect of the coupling agent in the T_g of the hybrid membranes.

Degradation temperature and silica content

Thermogravimetric analysis (TGA) was used to determine both the degradation temperature of the hybrid membranes as well as the silica content. Several published studies have determined the inorganic filler content using this technique [5, 24, 32–34]. This is justified by data that pyrolysis of most polymers occurs at temperatures below 700 °C in air and the silica network formed exhibits good thermal stability at those temperatures [5, 32]. In Table 3, the TGA results are reported.

It could be observed from the results that there is good correlation between the theoretical and experimental (residue obtained after heating samples up to 1,200 °C) content of silica. The residue increase by adding silica content in membranes suggests that there was an adequate incorporation of the filler in the hybrid material [34, 35] and that the sol–gel process was carried out almost completely [5, 24]. In some cases, the experimental silica content is greater than the theoretical one. This could be the result of a not completely homogeneous distribution of the silica in the membrane [32] or some fraction of polymer trapped in the silica network formed [35]. This latter hypothesis is evidenced by the color of the residue, which has a black color. If the residue was pure silica, it should have a typical white color. It is important to mention that the theoretical content of silica includes the amount of silica incorporated from TEOS, but not that from APTEOS, which also contributes to increase the amount of silica, although to a lesser extent.

Table 2 Glass transition temperature of hybrid membranes (10 wt% of silica) at different coupling agent amounts

Membrane	Silica (wt%)	Coupling agent (wt%) respect to TEOS	T_g (°C)
PEI-10	10	5	210
PEI-10-A10	10	10	207
PEI-10-A15	10	15	210

Table 3 Degradation temperature and TGA residue of hybrid membranes

Membrane	Silica ^a (wt%)	Ash ^b (wt%)	T_d (°C)
PEI	–	–	548
PEI-R5	5	5	545
PEI-R10	10	13	537
PEI-R15	15	18	546
PEI-10-A10	10	9	546
PEI-10-A15	10	20	544

^a Theoretical content of silica

^b Silica content determined from the TGA residuum obtained

The membrane with 10 wt% silica and 15 wt% APTEOS shows an experimental significant value above the theoretical one. It is important to notice that membranes with a higher percentage of APTEOS (10 and 15 wt%) could not be re-dissolved. This occurs due to a higher interaction between the phases causing the residue analyzed to contain part of the organic phase present.

Regarding the decomposition temperature, no significant changes were observed after incorporating the silica. Many studies report the effect of the fillers incorporation in PEI matrices on the thermal properties. Thus, Goh et al. [36] incorporated carbon nanotubes. These fillers were previously treated with surfactants with different charges to improve the interfacial adhesion with the polymer. The decomposition temperature for all samples started at about 550 °C, while observing a slight increase in this temperature in the PEI-nanotubes membranes. The increase (between 3 and 9 °C) was dependent on the type of surfactant used. This improvement in thermal stability was attributed to the higher heat resistance caused by the filler and the barrier opposed to the transport of volatile substances.

Kumar et al. [30] introduced carbon nanofibers in a PEI matrix. The authors observed a decrease in thermal stability of the membranes by introducing the nanofibers. However, all values are above 537 °C. This demonstrates the good thermal stability presented by hybrid membranes, although there was no increase in this property with the addition of filler.

In this regard, it can be stated that the hybrid membranes synthesized in this contribution exhibit good thermal resistance. The degradation temperature is above 544 °C and the performance of these membranes could be acceptable for many applications which have requirements of heat resistance.

Mechanical properties

Mechanical properties of composite materials, such as hybrid membranes, are determined for several factors. Among them, we could mention the proportion of filler and polymer, the size of the filler particles, the degree of dispersion of filler in the polymer matrix, and the adhesion or contact between the materials at the interface [1].

Table 4 shows the values (obtained from the average of three tests for each sample) of tensile strength (σ), Young's modulus (E), and rupture elongation (ϵ).

The tensile strength is defined as the maximum load resisted by the probe divided on its initial section. In the case of composite materials, the value obtained is related to the effectiveness of the stress transfer between the matrix and the filler, which is affected by the properties of the interface, i.e., the interactions present between both materials.

For PEI-RX membranes, the results show a maximum in tensile strength for the sample PEI-R10, with the maximum modulus and low rupture elongation compared to that of PEI pure membrane. It would indicate that the inorganic phase is highly dispersed in the polymer matrix with an effective load transfer between the phases.

On the other hand, we could think that at low silica loadings (PEI-R5), an inorganic structure is created that cannot properly interact with the matrix since the values of all parameters tested are lower for these membranes. This could indicate that there are no bonding sites between the organic polymer phase and the inorganic phase. In this case, the silica acts as non-reactive and non-reinforcing filler. However, good interaction would be achieved with 10 wt% silica. For higher loads, the formation of agglomerates of the filler particles can produce a decrease in tensile strength as it was observed by other authors [36–38]. This behavior could explain the results obtained for the membrane with 15 wt% of silica.

Concerning the coupling agent effect, PEI-10-A10 membranes showed a tensile strength value around PEI polymer matrix. However, the maximum modulus was observed with 10 wt% of APTEOS indicating that the coupling agent causes a greater interaction between the organic and inorganic phases [39].

Kumar et al. [30] observed an increase in modulus in PEI composites materials with the incorporation of surface modified carbon nanofibers. The authors attribute this modulus increase to improvements in both the interfacial adhesion and in the dispersion of nanofibers due to chemical interactions between the filler and the matrix. The interface bonds also enable a more effective load transfer. However, the effect of really working in the tensile strength is much lower.

Regarding the Young's modulus, an increase of E was observed in PEI-silica hybrid membranes except for membranes containing 5 wt% of silica. It could be explained by the rigidity of the inorganic particles which is generally much greater than that of the organic polymers [1, 37].

Table 4 Mechanical properties of the hybrid membranes

Membrane	Tensile strength (MPa) (σ)	Young's modulus (GPa) (E)	Rupture elongation (ϵ) (%)
PEI	57.8	1.57	7.63
PEI-R5	38.0	1.37	4.27
PEI-R10	66.0	1.89	5.50
PEI-R15	43.7	1.69	5.52
PEI-10-A10	56.2	1.92	6.03
PEI-10-A15	58.2	1.78	7.02

The rupture elongation values of hybrid membranes as a function of silica content are also shown in Table 4. In all the cases, a decrease of this parameter can be observed, which may be attributed to a cross-linking effect of silica, restricting the movement of polymer chains [7, 37, 39].

Conclusions

PEI-silica hybrid membranes containing 5–15 wt% of silica and with different coupling agent/TEOS ratio were successfully synthesized. Membranes with a homogeneous internal structure were observed in SEM micrographs. Particularly, when the APTEOS/TEOS ratio was increased dense membranes with uniform structure were obtained. These characteristics were also observed across the membranes thickness.

An increase of the glass transition temperature (T_g) of the hybrid membranes after the re-dissolution process reflects a change in the segmental mobility of polymer chains consistent with the existence of good adhesion or compatibility between the two phases. Moreover, there is no significant effect of the coupling agent in this parameter for hybrid membranes.

The silica content found experimentally by TGA tests is well-correlated with the theoretical values. The decomposition temperature of the hybrid membranes showed no significant changes in relation to the value of pure PEI membrane; however, all hybrid membranes exhibited good thermal stability.

Regarding the mechanical properties of re-dissolving membranes, there is a maximum in tensile strength for the sample PEI-R10. This membrane also shows the maximum Young's modulus. Nevertheless, a low strain at break is observed indicating that the inorganic phase is highly dispersed in the polymer matrix with an effective load transfer between phases. The sample with 10 wt% of APTEOS relative to TEOS showed the maximum modulus indicating that the presence of the coupling agent causes higher interaction between the organic and inorganic phases.

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