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Original Research

Graphene oxide and reduced graphene oxide as additives in polysulfone hybrid membranes for gas permeation

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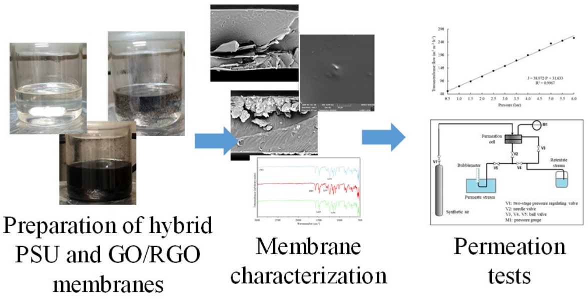

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Abstract: Hybrid polymeric membranes with the addition of graphene and derivatives are currently being developed and studied due to the unique properties of this material, whose addition in membranes is related to the enhancement of physical and mechanical properties and separation performance. In this study, polysulfone (PSU) membranes containing graphene oxide (PSU/GO) and reduced graphene oxide (PSU/RGO) were developed at a concentration of 0.5 wt.%, and their morphology, physical-chemical and thermal properties, and separation performance were evaluated. Membrane morphology was evaluated by SEM, thermal stability by TGA/DTG, functional groups and material structure by FTIR, mechanical properties by pressure test, and gas permeation using synthetic air. Agglomeration of GO and RGO was verified, a factor that may have interfered with the performance of the membranes. There was no change in the thermal stability of the membranes with the presence of GO/RGO, nor the occurrence of new bands observed in FTIR spectra, indicating that the interactions between PSU and GO/RGO were physical. All membranes resisted the maximum system pressure (6 bar), and it was not possible to identify whether the addition of graphene-derived materials had a positive effect on the mechanical strength. PSU/GO membranes had a better performance regarding synthetic air permeability in the gas permeation test than PSU and PSU/RGO membranes, possibly due to the functional groups present in GO, which facilitated the mass transfer within the polymer structure.

Keywords: Additives, gas permeation, hybrid membranes, membrane separation process, permeability.

Introduction

Membrane separation processes have stood out relative to classic separation methods, such as conventional filtration and absorption/adsorption. This is because, in general, membrane-based systems have greater selectivity when compared to conventional separation processes [1,2].

According to Wee et al. [3], the main separation processes that employ membranes as selective barriers include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, dialysis, electrodialysis, gas permeation, and pervaporation.

The gas separation process using dense membranes has become one of the most used technologies in the industry due to its operational flexibility, compact design, and high selectivity, generating permeate streams with high purity. In gas permeation, the main driving force is the chemical potential gradient, due to the difference in partial pressure and concentration of the components. In dense membranes, permeation occurs by sorption of gas molecules on the face of the membrane in contact with the feed, with diffusion occurring inside the membrane and, finally, the desorption of permeant molecules on the side of lower pressure, corresponding to the permeate stream [1,4].

One way to control/adjust membrane performance is through the addition of additives that enhance the mass transfer process through the membrane. Thus, to increase the efficiency of polymeric membranes applied on a large scale, hybrid membranes are developed. Hybrid membranes are formed by polymers (continuous phase) plus additives (dispersed phase), generally called fillers or carriers in the literature [1,5]. Therefore, the preparation of hybrid polymeric membranes is presented as an alternative of interest and an active field of study in membrane technology. The use of additives aims to improve specific characteristics for a given application, such as thermal and chemical resistance, increase in the diffusion/sorption rate, or improvement of mechanical properties [5,6].

The permeability, selectivity, mechanical, chemical, and thermal resistance, and the useful life of the membranes are characteristics that can be altered through the use of specific additives. According to Rodrigues [7], the most used polymers for the preparation of hybrid membranes are polysulfone (PSU), polyvinyl acetate (PA), polydimethylsiloxane (PDMS), polylactic acid (PLA), and polyetherimide (PEI), among other polymers.

Polysulfone (PSU) is an amorphous, hard, rigid, and resistant thermoplastic polymer, known for its high performance as an engineering material. Its chain is composed of sulfone, aryl, and ether groups. PSU is characterized by high mechanical strength, high hardness, and satisfactory thermal and oxidative resistance [8,9].

Among the different inorganic materials used in the development/production of hybrid membranes, graphene and its derivatives have been studied as potential additives in the production of hybrid membranes [4,10,11]. The addition of graphene in the synthesis of hybrid membranes improves the physical-chemical properties and the mechanical, chemical, and thermal resistance of membranes containing this additive [12-14]. Some studies addressed the potential use of graphene oxide (GO) or reduced graphene oxide (RGO) in the production of hybrid membranes [12-14].

Studies employed graphene oxide in the production of hybrid membranes. According to Lyu et al. [10], membranes based on GO have nanopores in their structure and the presence of oxygenated groups confers hydrophilicity to the membrane. However, in GO there are also non-oxidized regions, which are hydrophobic. Therefore, GO can be considered an amphiphilic material.

Zhao et al. [13] evaluated the characteristics of poly (ethylene oxide-b-amide-6) hybrid membranes with the addition of GO at concentrations of 1.0 – 3.6 mg·L^{-1} for water permeation. The membranes composed with 3.85 vol.% GO had a 56 % increase in Young modulus and a 98 % decrease in stress at break, in addition to an increase in the degree of crystallinity.

He et al. [12] developed composite PA membranes added with GO nanosheets at concentrations of 0.005, 0.030, 0.060, 0.120, and 0.300 wt.%, for seawater desalination. There was an increase in the hydrophilicity of the membranes with the increase in GO concentration from 0.06 to 0.30 wt.%. Consequently, there was a decrease in the surface energy of the hybrid membranes when compared to those without additives. The insertion of graphene oxide also caused an increase in water flux (which ranged between 13 – 80 % in all additive-enhanced membranes) when compared to pure PA membranes, without affecting salt (NaCl) selectivity. The authors also commented that the hybrid membranes showed antimicrobial activity 2.6 times higher than the non-hybrid membranes, considering GO as a potential antifouling material regarding biofouling.

Silva [4] addressed the implementation of 0.5 wt.% GO and RGO in polyurethane (PU) nanocomposites in gas permeation membranes and steel coating. The solvent used in the preparation of the membranes was tetrahydrofuran. Nitrogen and carbon dioxide were used in the experiment. It was found that the membranes produced with GO and its reduced form showed lower permeability for both gases than pure PU membranes. Furthermore, membranes with the addition of RGO showed an 11 % increase in selectivity compared to membranes produced with the pure polymer. The membranes with the addition of GO did not show significant improvement in terms of selectivity.

However, it is important to point out that, although GO and RGO can be similar in terms of chemical structure and potential to be used in Membrane Science, the intrinsic differences regarding the presence of polar groups in GO, which exist to a lesser degree in RGO, may influence the physical-chemical and interaction properties between different polymer matrices and these additives. Few studies addressed the potential effects of these differences between GO and RGO in the development and application of hybrid membranes composed of these materials, even as additives.

Thus, the present work aimed to synthesize polymeric polysulfone membranes with the addition of graphene oxide and reduced graphene oxide and to evaluate their potential effects on the physicochemical properties of the membranes in gas permeation processes.

Experimental Section

The base polymer used in the preparation of the membranes was the commercial polysulfone (PSU, CAS: 25135-51-7), supplied by Sigma-Aldrich, in pellets, with an average molar mass (Mw) of 35 kg·mol^{-1}. The GO and RGO additives used were prepared using the Staudenmaier method [15], supplied by the Pontifical Catholic University of Rio Grande do Sul (PUCRS, Porto Alegre, Brazil). Thermal annealing was the process used to reduce GO, remove the oxygenated functional groups, and generate the RGO.

Flat sheet membranes were prepared from solutions with 18 % w/v PSU in chloroform (99.8 % purity, Cinética Ltda., Brazil), and the solution was stirred with a magnetic stirrer at approx. 900 rpm for 1 h at 25±2 °C. For the synthesis of membranes incorporated with graphene derivatives, concentrations of 0.5 wt.% GO and RGO were added relative to PSU mass in the polymeric solutions. After the additives were incorporated, the polymeric solutions were stirred for another 20 min and then sonicated for 30 min at room temperature, with a frequency of 40 kHz, to avoid/reduce particle aggregation.

The polymeric solution was spread over a glass support using a stainless-steel spreading knife, maintaining an approximate thickness of 0.3 mm between the knife and the support. The technique used for the synthesis of the membranes was phase inversion by solvent evaporation, followed by immersion of the resulting films in a coagulation bath using distilled water as a non-solvent, at room temperature, as described by Favero [16].

A simplified scheme of the study's experimental procedure is shown in Figure 1.

Three types of membranes were prepared. Initially, pure PSU membranes were produced (without the use of additives) and then PSU membranes were produced with the addition of 0.5 wt.% GO and with the addition of 0.5 wt.% RGO.

The morphology of the produced membranes was evaluated by scanning electron microscopy (SEM). For the observation of the cross-section, the membranes were cryogenically fractured using liquid nitrogen (-196 °C). The samples were metalized with a thin layer of gold. The analyzes were performed using the Mira Tasco 3 microscope (Tescan, Czech Republic), with a magnification range of 250x to 100,000x and an accelerating voltage of 10 kV.

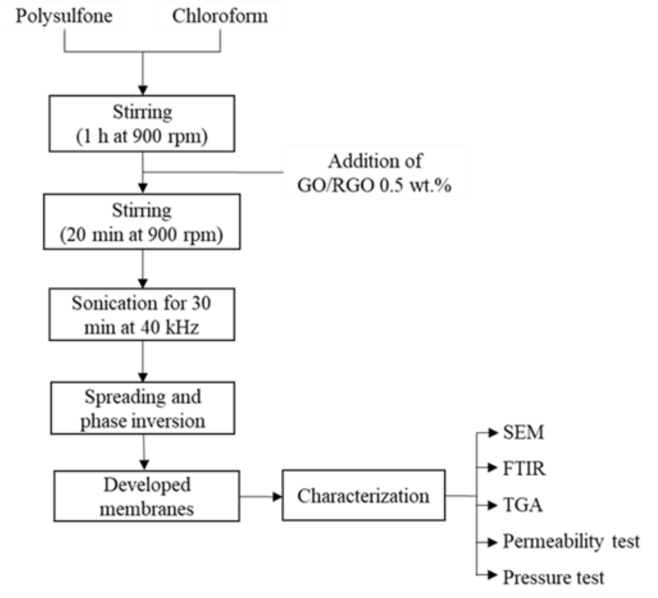

Figure 1. Simplified diagram of the hybrid membrane synthesis process and characterization steps.

FTIR assays were performed using a Nicolet iS10 equipment (Thermo Scientific, USA). The analysis was performed with an average of 32 scans, using the Total Attenuated Reflectance (ATR) method, with a germanium (Ge) crystal at an angle of 45°. Spectra were obtained in the wavenumber range of 4000 – 400 cm^{-1}. with a resolution of 4.0 cm^{-1}.

Thermogravimetric analysis (TGA) was performed using a TGA-50 thermobalance (Shimadzu, Japan). The heating rate used was 10 $°C \cdot min^{-1}$, starting from room temperature (approx. 25 °C) to 910 °C, using nitrogen as an inert gas (50 $mL \cdot min^{-1}$), and a platinum crucible.

The thickness of the membranes was measured using a digital micrometer with a measurement capacity of 1 µm to 25 mm (Mitutoyo, Japan). At least ten measurements were made at different points on the membranes and, after that, the arithmetic mean and standard deviation of the measurements for each membrane were calculated.

Pressure tests were performed using synthetic air as the fluid to be permeated, composed of 78 vol.% nitrogen gas, 21 vol.% oxygen gas, and 1 vol.% of other gases and water vapor. The test was carried out with the aid of a gas permeation system, as shown in Figure 2. The system pressure was varied between 0.5 bar and 6.0 bar (maximum operating pressure of the system), with an increase of 0.5 bar every 10 min. The test was performed at 25±2 °C.

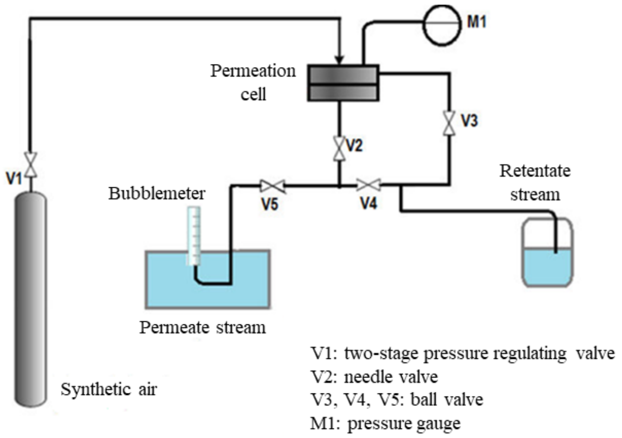

Figure 2. Scheme of the gas permeation system used in the study (adapted from Trentin [4]).

The permeability tests performed on the membranes followed a process like that described in the pressure tests, being performed at 25±2 °C. In the same gas permeation system, the flow of synthetic air that permeated through the membranes was measured. The pressure was varied from 0.5 bar to 6.0 bar, with an increase of 0.5 bar. At each pressure change, a time of 10 min was allowed for stabilization of the flow in the membrane to measure the gas flow. To measure the volume of gas, a container with water and a test tube was used as a bubble meter. Four collections were made for each pressure variation, where a certain volume of gas was collected in a time of 10 s, after which the average flow of the membranes was calculated. At 6 bar pressure for the PSU/RGO membrane, the flow was collected for 1 h due to low gas flow. Transmembrane flux was calculated using Equation 1 [17].

$$J_p = \frac{V_p}{A_m \cdot t_m} \tag{1}$$

Being J_p the permeate flux ($L \cdot m^{-2} \cdot h^{-1}$), V_p the volume of permeate obtained in time t (L), A_m the permeation area of the membrane (m^2), and t_m the process time (h).

The useful permeation area of the membranes in the system was 4.91 cm^2. As the objective of the work was to test only the permeate flux of the different synthesized membranes, only synthetic air was used in this analysis, and the individual flux and permeability of the feed components (N_2 and O_2) were not measured.

The tests were performed in four replicates and the results were submitted to analysis of variance, followed by Tukey's multiple range test at a 5 % probability of error. Statistical analyzes were performed using the Statistica 12 software (StatSoft, USA).

Results and Discussion

Scanning electron microscopy

The SEM micrographs of the surface area and cross-section of the developed membranes are compiled in Figure 3.

Figures 3a and 3b show the micrographs of the membrane synthesized with pure PSU. The membrane presented a homogeneous surface and dense morphology, suitable for gas separation. In the notch at 20,000x magnification, a small defect in the membrane can be seen, possibly formed during the spreading of the solution on the glass plate. It is also possible to observe the formation of some pores from the membrane production process, which may have been formed during the evaporation of the solvent or the immersion process. However, these have not changed the dense morphology of the obtained membrane.

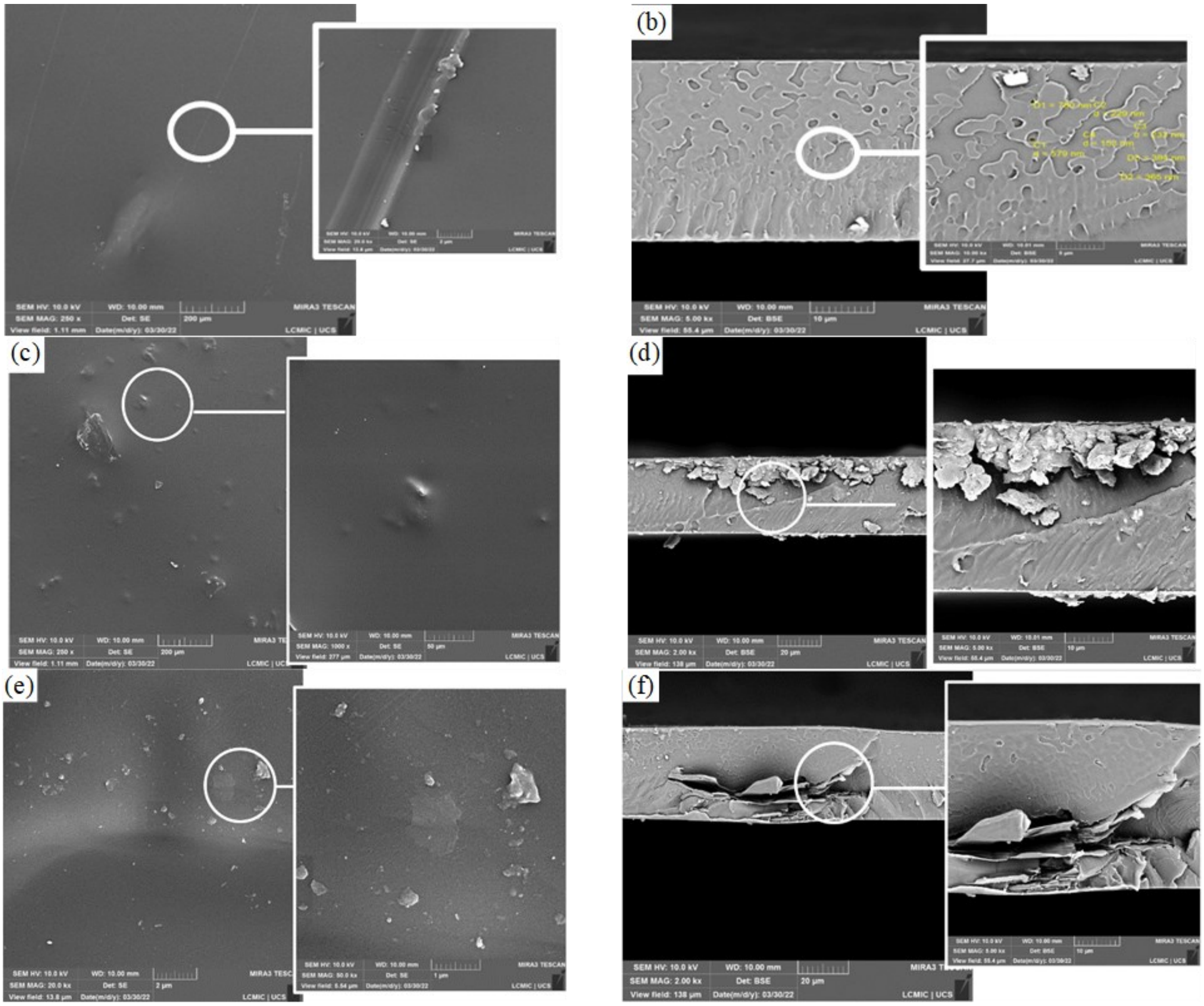

Figure 3. Micrographs of the surface and cross-section of the produced membranes. a) PSU – surface; b) PSU – cross-section; c) PSU/GO – surface; d) PSU/GO – cross-section; e) PSU/RGO – surface; f) PSU/RGO – cross-section.

The morphology of the PSU/GO membrane can be seen in the micrographs in Figures 3c and 3d. A concentration of 0.5 wt.% GO was added, causing difficulty in dispersing the material. The sonication step helped to disperse the GO in the polymer. However, it is possible to notice that there was an agglomeration of the additive even with sonication. A similar result was reported by Silva [4] in the preparation of PU membranes for gas permeation with the addition of GO and RGO. The author attributed this agglomeration to existing attractive forces between the additive particles.

Micrographs of PSU/RGO membrane morphology are compiled in Figures 3e and 3f. A result like that found in the PSU/GO membrane can be observed, with the occurrence of agglomeration of RGO particles in the polymeric matrix [18].

One of the biggest difficulties reported in the literature is efficiently dispersing and homogenizing graphene-based materials in polymers. When graphene is added to a polymeric matrix, it tends to be held together by attractive forces. Therefore, these forces must be reduced or canceled so that there is deagglomeration and dispersion of the material in the polymer [4]. As the GO and RGO used came from graphite, in which the graphene sheets are maintained through Van der Waals forces, it is expected that these materials will agglomerate in the polymer due to the presence of this type of intermolecular force [19].

Other preparation methods can be used to prevent the agglomeration of graphene-based materials when added into polymers, such as dissolution blending, melt blending, and in situ polymerization. In dissolution blending, the solvent is used to create an organic solution with the polymer, adding the material to be dispersed. In melt blending, the polymer melts and the additive is added. In *in situ* polymerization, the material is added to the reactor during the polymer synthesis process. Also, a covalent graft of graphene in the polymeric

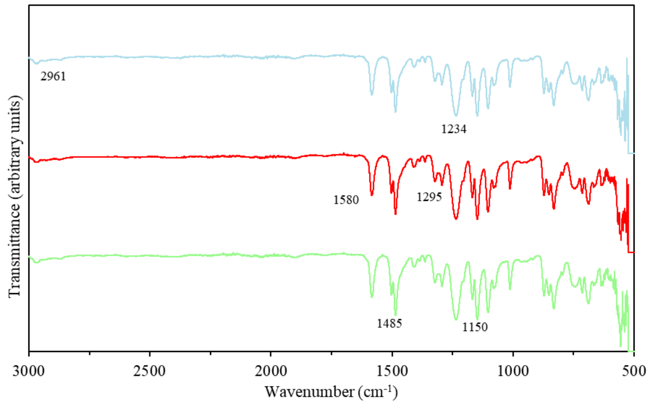

Figure 4. FTIR spectra of PSU (green line), PSU/GO (red line), and PSU/RGO (blue line) membranes.

Analyzing the spectrum, it is possible to identify the presence of functional groups and structural groupings of the samples and verify if there was any kind of chemical interaction between the polymer and GO or RGO. From 4,000 cm^{-1} to 3,000 cm^{-1} there were no relevant signs. For both samples, at a wavenumber close to 2,960 cm^{-1}, asymmetrical axial deformation of the CH bond occurred [22]. In the region from 1,480 cm^{-1} to 1,590 cm^{-1}, aromatic C=C stretching vibrations occurred, represented at approximately 1,580 cm^{-1} [23,24]. The group that corresponded to aromatic ether (COC) was observed at 1,234 cm^{-1} and the band referring to the hydroxyl group was observed close to 1,485 cm^{-1}, and both bands are related to the presence of phenol groups [23,25].

Asymmetric and symmetric stretching vibrations of polysulfone, resulting from O=S=O bonds, are usually identified in the bands located in the regions of 1,290 cm^{-1} and 1,100 cm^{-1}, corresponding to the bands detected at approximately 1,295 cm^{-1} and 1,150 cm^{-1} [23,25]. Signals in the wavenumber range of 900 cm^{-1} to 500 cm^{-1} corresponded to aromatic CH bonds, such as deformation vibrations [26].

It is important to observe that FTIR analysis may indicate the occurrence of chemical reactions between moieties and functional groups of the polymeric matrix and the additives. This would show whether the type of interaction between the constituents of the membrane is of physical or chemical origin. Chemical modifications in the polymeric structure may be desired or undesired, depending on the separation pattern aimed and the overall effect on membrane characteristics [23,24].

Analyzing the spectra obtained, the three produced membranes showed characteristic signals of pure PSU spectrum and there was no occurrence of new bands and/or wavenumber changes with the addition of GO or RGO. The addition of these materials did not interfere with the chemical bonds of the polymeric film, which indicates the occurrence of bonds and interactions of a physical nature between the polymer and the additives used.

Thermogravimetric analysis

The TGA analysis was carried out to verify the thermal stability of the produced membranes. The obtained TGA curves are shown in Figure 5.

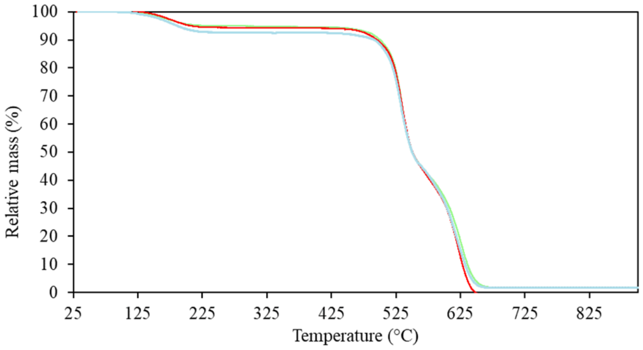

Figure 5. TGA analysis of PSU (green line), PSU/GO (red line), and PSU/RGO (blue line) membranes.

The curve of mass loss as a function of temperature was very similar for the three membranes and all of them showed two main peaks where the greatest mass losses occurred. These peaks occurred around temperatures of 170 °C and 555 °C. More detailed data relative to the TGA curves are shown in Table 1.

Table 1. TGA curve data for the PSU, PSU/GO, and PSU/ RGO membranes.

Membrane	T1* (°C)	First mass loss (%)	T_2** (°C)	Second mass loss (%)	Residual mass*** (%)
PSU	166.7	4.9	552.3	48.3	2.40
PSU/GO	170.9	6.1	557.3	52.1	0.01
PSU/RGO	170.5	7.3	554.7	49.9	2.00

* Temperature at which the first mass loss occurred. ** Temperature at which the second mass loss occurred. *** At 900 °C.

Close to 100 °C, there was a small loss of mass probably related to the evaporated water that was physically adsorbed on the surface of the membranes. The first considerable mass loss (T ≈ 170 °C) may have been the result of thermolysis of the bonds of the sulfonic groups, which occur in this temperature range [27]. The second mass loss occurred at approx. 555 °C and may have resulted from the decomposition of the rest of the polymer structure, such as the depolymerization of the phenolic/benzene groups in the samples. Thus, the main polymer chain started to degrade at 510 – 515 °C, and the maximum degradation rates occurred in the temperature range of 575 – 585 °C for the three membranes, respectively.

Lima et al. [27] reported a similar behavior for PSU membranes. According to the authors, up to 132 °C there was a loss of water that was physically adsorbed on the membranes; from 132 °C to approx. 230 °C, there was the loss of mass attributed to the breaking of the bonds involving the sulfonic groups, and, at approximately 500 °C, the degradation of the main polymer chain began [27-29].

According to Ansari et al. [30], who studied the incorporation of GO and RGO in PSU membranes, an increase in the thermal stability of the hybrid membranes would be expected if the additives were well distributed. As partial agglomeration of GO and RGO occurred on the membranes, the thermal effects of the additives were not pronounced. In addition, it is important to highlight that the amount of material to be added significantly interferes with the effect on the polymer. Even if well distributed, the amount of additive used was small (0.5 wt.%), and the effect on the stability thermal effect of the membranes would not be very strong.

Membrane thickness and pressure test

The average thickness values of the produced membranes are shown in Table 2.

Table 2. Membrane thickness values for the PSU, PSU/GO, and PSU/RGO membranes developed in this study.

Membrane	Average thickness (µm)
PSU	45.0±1.6^a
PSU/GO	45.2±2.0^a
PSU/RGO	34.4±1.6^b

Means followed by the same lowercase letter do not differ by Tukey's test at a 5 % probability error.

The results for the thicknesses of PSU/RGO membranes are consistent with the fact that, as RGO is not soluble in the solvent used (chloroform), there was a reduction in the interaction between the polymer chains, reducing its viscosity. Thus, the thickness of the PSU/RGO membranes was smaller than those of pure PSU. However, PSU/GO membranes have functional groups in their structure, allowing interactions between GO and the polymer to take place, maintaining, or increasing the interactions with the polymeric chain and, consequently, increasing membrane thickness [14].

Membrane thickness is an important parameter since it is linked to greater resistance to mass transfer as the thickness increases [1,3]. Thus, the PSU/RGO membrane, with a smaller average thickness, may present less resistance to the permeating molecules, facilitating the mass transfer. However, it is very important to observe that the chemical affinity between the components of the feed and the membrane is one of the most important factors regarding separation performance, especially for dense membranes, such as those used in gas permeation [1,4].

The prepared membranes were submitted to the pressure test, and all of them withstood the maximum pressure of the system (6.0 bar). Thus, the presence of the additives in the polymer matrix had no deleterious effect on the mechanical strength of the membranes. The regions of accumulation of GO and RGO in the PSU membranes, according to Maraschin [18], are critical points that negatively influence the mechanical resistance, and the accumulation of additives may have caused the mechanical failure (rupture) of the membranes.

One of the factors that influence the resistance of the prepared membranes is the dense morphology obtained. This can be explained by the high degree of chemical affinity between PSU and chloroform, which allows for good interaction between the polymeric chains in the curing stage, generating a structure with a higher degree of intermolecular interactions in the matrix. This was also reported by Souza [31] when preparing PSU membranes using chloroform as solvent.

The dense morphology is also a result of the conditions and method of preparing the membranes. According to Ismail and Lai [32], the polymer and solvent concentration, the shear rate, the coagulation bath temperature, and the evaporation time are the main parameters to be controlled to obtain a dense selective layer free of defects. Considering that the membranes were produced by the phase inversion process by evaporation and by immersion, it can be stated that the dense morphology obtained in the membrane is closely related to these two aspects, mainly to the solvent evaporation process during the phase inversion. The mass transfer rate between the solvent and the non-solvent was the main parameter that influenced the morphology observed in the produced membranes, regardless of the presence of GO and RGO [33].

Permeability test

The permeability tests for the PSU, PSU/GO, and PSU/RGO membranes were performed using a gas permeation system, with synthetic air as the feed, whose molecules have an effective mean diameter of 3.4 Å (0.34 nm). The results obtained are shown in Table 3.

According to the data presented in Table 3, it can be observed that the PSU membrane did not present permeate flux and the PSU/RGO membrane presented almost zero permeate flux when subjected to the maximum pressure supported by the system (6 bar). On the other hand, the PSU/GO membrane showed a considerable permeate flux starting from 0.5 bar.

Table 3. Results of the permeability test for the PSU, PSU/GO, and PSU/ RGO membranes using synthetic air as feed.

Pressure (bar)	Permeate flow rate ($L\cdot h^{-1}$)		
	PSU	PSU/GO	PSU/RGO
0.5	-	6.98 ± 0.09^{l}	-
1.0	-	9.57 ± 0.08^{k}	-
1.5	-	12.08 ± 0.10^{j}	-
2.0	-	14.63 ± 0.09^{i}	-
2.5	-	17.63 ± 0.07^{h}	-
3.0	-	20.18 ± 0.07^{g}	-
3.5	-	23.10 ± 0.09^{f}	-
4.0	-	25.93 ± 0.06^{e}	-
4.5	-	28.47 ± 0.09^{d}	-
5.0	-	32.07 ± 0.09^{c}	-
5.5	-	33.51 ± 0.12^{b}	-
6.0	-	34.95 ± 0.09^{a}	0.0014^{*}

* Results obtained after 1 h of permeation. Means followed by the same lowercase letter do not differ by Tukey's test at a 5 % probability error.

The pure PSU dense membrane showed no permeate in the pressure range from 0.5 bar to 6.0 bar, which is a characteristic behavior of this type of membrane. PSU is a highly resistant polymer, characterized as being of high performance in its applications [9]. Since chloroform has a good interaction with PSU, strengthening the binding forces and making the membrane more resistant and denser, there was an impediment to mass transfer through the membrane. For there to be airflow at the tested pressures, it would be necessary to modify the method of preparing the membranes, such as the temperature of the precipitation bath and the time of solvent evaporation. This would cause changes in the membrane morphology to occur, allowing mass transfer [32].

The PSU/RGO membrane showed little airflow, which was detected and measured only at a pressure of 6 bar and 1 h of permeation. Fryczkowska et al. [34], studying membranes based on polyacrylonitrile (PAN) with the addition of RGO, reported an increase in permeate flux using water as feed. Considering that water is a polar substance, the increase in permeate flux could indicate that substances of non-polar nature, such as nitrogen and oxygen gases, the main components of synthetic air, would have their permeability reduced with the addition of RGO to PSU membranes.

Permeate formation occurred in the PSU membranes with the addition of 0.5 wt.% GO. As shown in Figure 6, the flow was directly proportional to the increase in pressure, i.e., the behavior was linear. This behavior was also found by Zhao et al. [13] in the synthesis of poly(ethylene oxide-b-amide-6) hybrid membranes with GO. The regression equation, whose angular coefficient corresponds to the gas permeability through the PSU/GO membrane, and the coefficient of determination (R^2) are also shown in Figure 6.

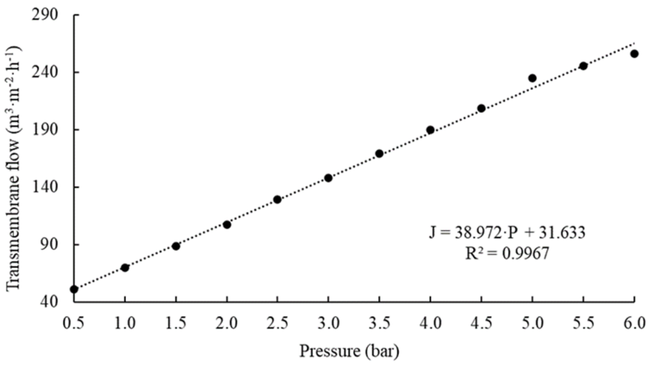

Figure 6. Transmembrane airflow through the PSU/GO membrane as a function of system pressure.

According to the results obtained, the addition of GO in the PSU membranes allowed for the permeation of synthetic air through the membranes. As analyzed by SEM, GO was accumulated in parts of the polymeric matrix, and this may have created a preferential path for the passage of gases. However, there was also an accumulation of RGO on the PSU/RGO membranes. If the permeation mechanism were the same, a similar result would be expected in both hybrid membranes. Another hypothesis to explain the passage of air is that, as GO has functional groups in its structure, it becomes more soluble and more stable in aqueous media than RGO. This may have favored its dispersion by the PSU and generated some kind of interaction with the polymer, which allowed air permeation [35].

Yoon et al. [36], who also studied the addition of GO and RGO in PSU membranes at concentrations of 0.01, 0.05, 0.10, and 0.15 wt.%, noted that membranes produced with GO had better performance regarding membrane permeability when compared to membranes synthesized with RGO. However, the same authors highlighted that membranes containing graphene and derivatives have their performance improved up to a certain amount of additive added. Above that, pore-clogging, formation of aggregates, and decreased performance may occur.

Comparing the addition of GO and RGO in the membranes, the difference in the permeate flux was noticeable. As the main driving force in the permeation of gases is the concentration gradient, maybe the gas does not have an affinity with the material of the synthesized membrane (PSU and PSU/RGO), which is why there was no flow in the mentioned membranes [21].

Conclusion

There was an agglomeration of the additives in the PSU membranes, indicating that the sonication dispersion performed was not fully effective. From the FTIR spectra, it can be concluded that only physical interactions occurred between the polymer and the GO/RGO. Due to the presence of polar moieties in GO and PSU, the polymer/additive interactions probably are from dipoles, while the RGO/PSU interactions probably are between aromatic moieties, as hydrophobic interactions. The TGA curves were similar for all membranes, i.e., there was no change in thermal stability with the presence of the additives. All membranes supported the maximum pressure of the system (6 bar), so the presence of materials in the polymer matrix had no negative effect on the mechanical properties of the membranes. In addition, considering that gas permeation implies the use of high transmembrane pressures (> 10 bar), adequate mechanical strength is necessary for the membrane to be usable. In the permeability test, the difference in the flow of the membranes was noticeable, and the PSU/GO was the only one that presented a considerable flow. This may have happened since the functional groups present in GO may have generated some kind of interaction with the PSU, which allowed air permeation. Thus, the use of GO as an additive in hybrid PSU membranes can be interesting for gas permeation and other membrane separation processes, aiming to ally the properties of graphene and its derivatives with the intrinsic properties of engineering polymers, to obtain more efficient and robust hybrid membranes.

Authors Contribution

L. G. Tosin: Conceptualization, Investigation, Writing–original draft; W. P. Silvestre: Methodology, Formal analysis, Investigation, Writing; review and editing, Visualization; C. Baldasso: Conceptualization, Methodology, Writing; review and editing, Supervision, Project administration. All authors have approved the final version of the manuscript.

Conflicts of Interest

The authors have declare no conflicts of interest.

References

[1] A. C. Habert, C. P. Borges, R. Nobrega, Membrane separation processes, Rio de Janeiro: E-Papers, 2006.

[2] J. C. C. Petrus, I. C. Tessaro, Membrane separation processes, in: C. C. Tadini, V. R. N. Telis, A. J. A. Meirelles, P. A. Pessoa Filho (Eds.), Unit Operations in the Food Industry. LTC, Rio de Janeiro, 2016, pp. 251-300.

[3] S. L. Wee, C. T. Tye, S. Bhatia, Membrane separation process: pervaporation through zeolite membrane. Separation and Purification Technology, vol 63, pp. 500-516, 2008. DOI:10.1016/j.seppur.2008.07.010.

[4] A. E. L. Silva, Influence of GO and RGO dispersion in polyurethane nanocomposites in gas permeation membrane applications and in API 5L X80 steel coatings, Master's thesis, State University of Rio de Janeiro, Rio de Janeiro, 2019.

[5] S. P. Nunes, K. V. Peinemann, Membrane technology in the chemical industry. Weinheim: Wiley-Vch, 2001.

[6] D. E. S. L. L. Silva, A. C. Habert, M. E. Sena, Development of hybrid polymeric membranes of poly (ether imide) with organofunctionalized silica as an alternative in fuel cell systems, Proceedings of the 22nd Brazilian Congress of Engineering and Materials Science, pp 9565-9577, 2016.

[7] C. Rodrigues, Preparation of new membranes with MOF's and ionic liquids for application in CO2 capture processes, Master's thesis, New Lisbon University, Lisbon, 2013.

[8] V. M. Trentin, Application of polymeric membrane technology for biogas purification, Master's thesis, University of Caxias do Sul, Caxias do Sul, 2017.

[9] B. A. Araujo, R. A. Dias, V. N. Medeiros, K. M. Medeiros, E.M. Araújo, Polysulfone membranes with titanium dioxide obtained using the phase inversion technique for the treatment of textile effluents. Research, Society and Development, vol 10, e210101119605, 2021. DOI:10.33448/rsd-v10i11.19605.

[10] J. Lyu, X. Wen, U. Kumar, Y. You, V. Chen, R.K. Joshi, Separation and purification using GO and r-GO membranes, RSC Advances, vol 8, pp. 23130-23151, 2018. DOI:10.1039/c8ra03156h.

[11] B. C. Maini, Hybrid polymeric membranes containing functionalized inorganic nanoparticles for gas separation, Master's thesis, Federal University of Rio de Janeiro, Rio de Janeiro, 2018.

[12] L. He, L. F. Dumée, C. Feng, L. Velleman, R. Reis, F. She, W. Gao, L. Kong, Promoted water transport across graphene oxide–poly(amide) thin film composite membranes and their antibacterial activity. Desalination, vol 365, pp. 126-135, 2015. DOI:10.1016/j.desal.2015.02.032.

[13] D. Zhao, J. Ren, Y. Qiu, H. Li. K. Hua, X. Li, M. Deng, Effect of graphene oxide on the behavior of poly(amide-6-b-ethylene oxide)/graphene oxide mixed-matrix membranes in the permeation process. Journal of Applied Polymer Science, vol 132, 42624, 2015. DOI:10.1002/app.42624.

[14] A. Razaq, F. Bibi, X. Zheng, R. Papadakis, S. H. M. Jafri, H. Li, Review on graphene-, graphene oxide-, reduced graphene oxide-based flexible composites: from fabrication to applications. Materials. 15, 1012, 2022. DOI:10.3390/ma15031012.

[15] M. Herrera-Alonso, A. A. Abdala, M. J. McAllister, I. A. Aksay, R. K. Prud'homme, Intercalation and stitching of graphite oxide with diaminoalkanes. Langmuir, vol 23, pp. 10644-10649, 2007. DOI:10.1021/la0633839.

[16] D. Favero, Obtaining micro and nanocellulose for the preparation of polymeric membranes as a selective barrier, Master's thesis, University of Caxias do Sul, Caxias do Sul, Brazil, 2014.

[17] M. E. A. Ali, L. Wang, X. Wang, X. Feng, Thin film composite membranes embedded with graphene oxide for water desalination. Desalination, vol 386, pp. 67-76, 2016. DOI:10.1016/j.desal.2016.02.034.

[18] T. G. Maraschin, Preparation of graphene oxide and reduced graphene oxide and dispersion in a biodegradable polymeric matrix, Master's thesis, Pontifical Catholic University of Rio Grande do Sul, Porto Alegre, 2016.

[19] R. M. Bueno, The influence of graphene oxide and colloidal silica on the chemical and mechanical properties of cementitious matrices. Master's thesis, São Judas Tadeu University, São Paulo, Brazil, 2020.

[20] S. H. Aboutalebi, A. T. Chidembo, M. Salari, K. Konstantinov, D. Wexler, H.K. Liu, S.X. Dou, Comparison of GO, composite GO/MWCNTs and MWCNTs as potential electrode materials for supercapacitors. Energy and Environment Science, vol 4, pp. 1855-1865, 2011. DOI:10.1039/c1ee01039e.

[21] A. T. Lawal, Recent progress in graphene-based polymer nanocomposites. Cogent Chemistry, vol 6, 1833476, 2020. DOI:10.1080/23312009.2020.1833476.

[22] R. M. Silverstein, F. X. Webster, Spectrometric identification of organic compounds, 6th ed. New York: John Wiley & Sons, 1996.

[23] H. Lobo, J.W. Bonilla, Handbook of plastics analysis, 1st Ed. New York: CRC Press, 2003.

[24] S. Indherjith, S. Karthikeyan, J. H. R. Monica, K. K. Kumar, Graphene oxide and reduced graphene oxide polysulfone nanocomposite pellets: an alternative adsorbent of antibiotic pollutant-ciprofloxacin. Separation Science and Technology, vol 54, pp. 667-674, 2019. DOI:10.1080/01496395.2018.1518986.

[25]M. Najafi, M. Sadeghu, A. A. Shamsabadi, M. Dinari, M. Soroush, Polysulfone membranes incorporated with reduced graphene oxide nanoparticles for enhanced olefin/paraffin separation. Chemistry Select, vol 5, pp. 3675-3681, 2020. DOI:10.1002/slct.202000240.

[26] N. Bogoni Junior, Preparation and characterization of polysulfone-polyurethane membranes for water recovery from simulated industrial textile processes, Ph.D. dissertation, University of Caxias do Sul, Caxias do Sul, Brazil, 2020.

[27]A. P. Lima, A. V. Tirone, A. C. F. Batista, L. C. Morais, P. P. Souza, M. V. F. Duarte, D. Pasquini, Production, characterization and use of sulfonated polystyrene and polysulfone membranes as catalysts in the esterification reaction of oleic acid, Revista Virtual de Química, vol 10, pp. 124-141, 2018. DOI:10.21577/1984-6835.20180012.

[28] V. A. Amorim, F. Muller, M. A. Hocevar, B. Hansen, L. O. Meneguzzi, C.A. Ferreira, Heterogeneous anion membranes developed from ion exchange resin and polysulfone matrix for application in electrodialysis, Proceedings of the 22nd Brazilian Congress of Engineering and Materials Science, 2016. Natal, RN, Brazil. Natal, CBECiMat (2016) pp. 8007-8016.

[29] G. A. Lando, Polysulfone films superficially modified by UV-assisted irradiation for evaluation of biodegradation by microorganisms, Master's thesis, Federal University of Rio Grande do Sul, Porto Alegre, 2016.

[30] S. Ansari, A. Kelarakis, L. Estevez, E. P. Giannelis, Oriented arrays of graphene in a polymer matrix by in situ reduction of graphite oxide nanosheets. Small, vol 6, pp. 205-209, 2010. DOI:10.1002/smll.200900765.

[31] J. F. Souza, Development of polysulfone membranes for lipase immobilization, Master's thesis, University of Caxias do Sul, Caxias do Sul, 2006.

[32] A. F. Ismail, P. Y. Lai, Effects of phase inversion and rheological factors on formation of defect-free and ultrathin-skinned asymmetric polysulfone membranes for gas separation. Separation and Purification Technology, vol 33, pp. 127-143, 2003. http://dx.doi.org/10.1016/s1383-5866(02)00201-0.

[33] M. A. Aroon, A. F. Ismail, M. M. Montazer-Rahmati, T. Matsuura, Morphology and permeation properties of polysulfone membranes for gas separation: effects of non-solvent additives and co-solvent. Separation and Purification Technology, vol 72, pp. 194-202, 2010. DOI:10.1016/j.seppur.2010.02.009.

[34] B. Fryczkowska, A. Machnicka, D. Binias, C. Slusarczyk, J. Fabia, The influence of graphene addition on the properties of composite rGO/PAN membranes and their potential application for water disinfection. Membranes, vol 10, 58, 2020. DOI:10.3390/membranes10040058.

[35] A. Bakshi, H. Bustamante, X. Sui, R. Joshi, Structure dependent on water transport in membranes based on two -dimensional materials. Industrial and Engineering Chemistry Research, vol 60, pp. 10917-10959, 2021. DOI:10.1021/acs.iecr.1c01919.

[36] Y. Yoon, H. Kye, W. S. Yang, J. W. Kang, Comparing graphene oxide and reduced graphene oxide as blending materials for polysulfone and polyvinylidene difluoride membranes. Applied Science, vol 10, 2015, 2010. DOI:10.3390/app10062015