

CONDUCTIVITY ANALYSIS OF ASYMMETRIC POLYSULFONE MEMBRANES FOR CO₂

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Abstract:

Membrane technologies are currently one of the promising strategies to face the continuously increasing CO₂ accumulation in the atmosphere and the associated environmental impact. They have become an alternative for separating and absorbing CO₂ due to their low cost and relatively more straightforward preparation. Polysulfone (PSf) is one of the most common polymers for its commercial availability, processing, and favourable selectivity-permeability characteristics. PSf were blended with a commercial hyperbranched polyethyleneimine Lupasol, modified with benzoyl chloride or phenyl isocyanate with several percentages to improve their performance in terms of direct CO₂ capture. All the membranes were prepared by phase inversion precipitation. The morphology, thermal properties, molecular motion, and conductivity were analyzed. The blended membranes show differences in the microstructure, and the presence of urea and amide groups promoted a considerable increment in the efficiency of the CO₂ capture process compared to the neat membrane due to the enhancement in hydrophilicity and chemical stability. In composite membranes, the absorption capacity is controlled by the conductivity, chemical affinity to CO₂, and morphology of the membranes. The phenyl isocyanate improves the motions of hyperbranched polyethyleneimine in blended membranes facilitating CO₂ direct air capture.

Keywords:

CO₂ air absorption, Asymmetric Polysulfone/hyperbranched polyethyleneimine membranes, morphological, thermal, dielectric, and conductivity analysis.

1. Introduction

Since the beginning of the 21st century, global Greenhouse gas (GHG) emissions have been increasing. GHG traps heat and makes the planet warmer. Human activities such as burning fossil fuels for electricity, heat, and transportation are responsible for almost all of the increase in GHG in the atmosphere over the last 150 years. The Emission Database for Global Atmospheric Research indicated that in only two decades, the global emissions from carbon dioxide have been increasing, rising by approximately 50% of emissions to the atmosphere. If carbon dioxide emissions are not drastically reduced, the increase in temperature is accelerating and is projected to be at the 1.5 °C level within 15 to 20 years. The United Nations International Panel on Climate Change (IPCC) indicated that exceeding a 1.5 °C temperature increase will be catastrophic with consequences of unprecedented flooding, drought, rising sea level, heat waves, and famine [1-2].

There is no single solution to remove carbon dioxide from the air and reduce GHG; no technology is enough to avoid the effects of climate change. Between them, capturing and storing carbon dioxide and its subsequent use may be a possible solution. Nevertheless, this implies that the carbon dioxide must first be captured at atmospheric pressure and stored efficiently.

An interesting technology is a membrane separation-based CO₂ capture system. It uses permeable and semipermeable materials that selectively transport and separate CO₂ from other components in the gas

stream. This separation process is efficient because it does not involve a phase change, leading to low energy consumption. Other advantages over other capture technologies are their compact design and simplicity since adding chemical agents is unnecessary. However, this method also presents disadvantages; it must resist impurities and harden ageing. Recently, a new hybrid technique has been developed; it combines membrane separation and solvent absorption processes with an effective CO₂ absorption in a contactor device. It is also a tiny modular system that can be easily assembled and integrated into other devices [3-6].

Currently, amines are the most efficient and cost-effective materials for carbon dioxide capture. It is commonly mentioned that primary amines are more reactive toward CO₂. However, the basicity of amines is the most critical factor affecting CO₂ capture performance due to the acid/base reaction between CO₂ and amines. Therefore, capturing CO₂ using solid polymeric adsorbents, such as polyamines, is a promising alternative to avoid the problems associated with aqueous amine adsorbents. Amines and aminic compounds have found wide applications as CO₂-removing agents due to the reversible reaction between aminic groups (basic) and CO₂ (acidic). Other commercial options are used Polysulfone (PSf) as basic material because have remarkable hydrolytic stability that sets them apart from other thermoplastics. In addition, it is a high-performance thermoplastic polymer with excellent physical properties at high temperatures. Their characteristics are rigidity, excellent thermal, mechanical, and oxidation resistance, and a high glass transition temperature [6].

This paper aims to increase the performance of Polysulfone membrane contactors by blending commercial PSf with a commercial, hyperbranched polyethylene imine, specifically. Lupasol G20 is a water-soluble polymer; this could prevent membrane preparation from a water coagulation bath as previously described for neat PSf and membrane stability in contact with the storing aqueous. The presence of the basic nitrogen atoms should increase the membrane affinity for carbon dioxide, thus improving its capture and permeability concerning PSf. On the other hand, hyperbranched polyethyleneimine Lupasol G20 is, modified with benzoyl chloride or phenyl isocyanate to enhance the molecular motion and facilitated CO₂ direct air capture. Broadband dielectric spectroscopy (BDS), through the analysis of the molecular motions and the dielectric conductivity, is a suitable technique to determine the reorientation of the permanent dipoles present on the side chains and on the backbone of polymeric materials, which might provide insights into the mobility of the CO₂ in the membranes and tuning the suitable composition of benzoyl chloride or phenyl isocyanate in the blend.

2. Materials and Methods

2.1. Materials and membrane preparation

The used materials are:

Polysulfone (PSf), with a molecular weight of 35,000 Da, was purchased from Sigma-Aldrich.

Lupasol G20, provided by BASF, has a molecular weight of 1300 Da.

Additive 1 is a chemically modifying Lupasol G20 with benzoyl chloride.

Additive 2 is Lupasol G20 chemically modified with phenyl isocyanate.

A phase inversion process at ambient conditions prepared all polysulfone-based membranes. 1-Methyl-2-pyrrolidone (NMP), purchased from Sigma-Aldrich, was used to dissolve 20 g of PSf/G20 mixture (1 and 2, distinctly) so that the total polymer concentration was set at 20% by weight concerning the total weight of the polymer solution. The polymer mixtures were stirred for 48 h. The polymer solutions were then cast on glass support using a 250 µm thick castor blade. Immediately afterward, they were placed in a coagulation bath containing non-solvent water, where the membranes were precipitated by the exchange between the solvent (NMP) and the non-solvent. The resulting flat membranes were removed from the coagulation bath, washed with distilled water, and air-dried overnight [7].

In this way, five different membranes were prepared, one of pure Polysulfone M0, two membranes with 2% and 10% of additive 1 (M1-2%; M1-10%), and two membranes with 2% and 10% of additive 2 (M2-2%; M2-10%).

2.2. Field Emission Scanning Electron Microscopy (FE-SEM)

The surface of the prepared membranes was evaluated through Field Emission Scanning Electron Microscopy (FE-SEM). The membranes, previously vacuum dried, was platinum sputter-coated for 10 s using a Leica EM MED020 coater. Surface electronic micrographs were taken in a Zeiss Ultra 55 at 295 K with a 1 kV voltage.

2.3. Differential scanning calorimetry (DSC)

The surface of the prepared membranes was evaluated through Field Emission Scanning Electron Microscopy (FE-SEM). The membranes, previously vacuum dried, was platinum sputter-coated for 10 s using a Leica EM MED020 coater. Surface electronic micrographs were taken in a Zeiss Ultra 55 at 295 K with a 1 kV voltage.

2.4. Broadband Dielectric Spectroscopy (BDS)

The impedance measurements were conducted using a Novocontrol Broadband Dielectric Impedance Spectrometer (BDS) connected to a Novocontrol Alfa-A Frequency Response Analyzer. All the measurements were obtained under isothermal conditions by increasing in steps by 10 K. The sample electrode assembly (SEA) consisted of two stainless steel electrodes filled with the sample and was directly placed in the cell.

The dielectric spectra were analyzed in terms of the complex permittivity (ϵ^*) using as many Havriliak-Negami (HN) functions as needed. All the characteristic parameters of each relaxation process were determined as shown in Equation 1:

$$\epsilon^* = \epsilon_{\infty} + \frac{\Delta\epsilon}{(1 + (i\omega\tau)^a)^b} \quad (\text{Eq. 1})$$

Where:

τ is the Havriliak-Negami relaxation time. The a and b parameters correspond to the width and asymmetry of the relaxation peak. $\Delta\epsilon$ is the value of the relaxation strength [8-10].

The conductivity response to an applied electric field of a polymer consists mainly of frequency-dependent and frequency-independent components. The former is ascribed to the DC conductivity and shows a frequency independent plateau. In contrast, the latter is attributed to the AC conductivity and is characterized by a high dispersion at higher frequencies. This behaviour can be modelled by the universal dynamic response model, as shown in Equation 2.

$$\sigma(\omega) = \sigma_{DC} + A\omega^n \quad (\text{Eq. 2})$$

3. Results and Discussion

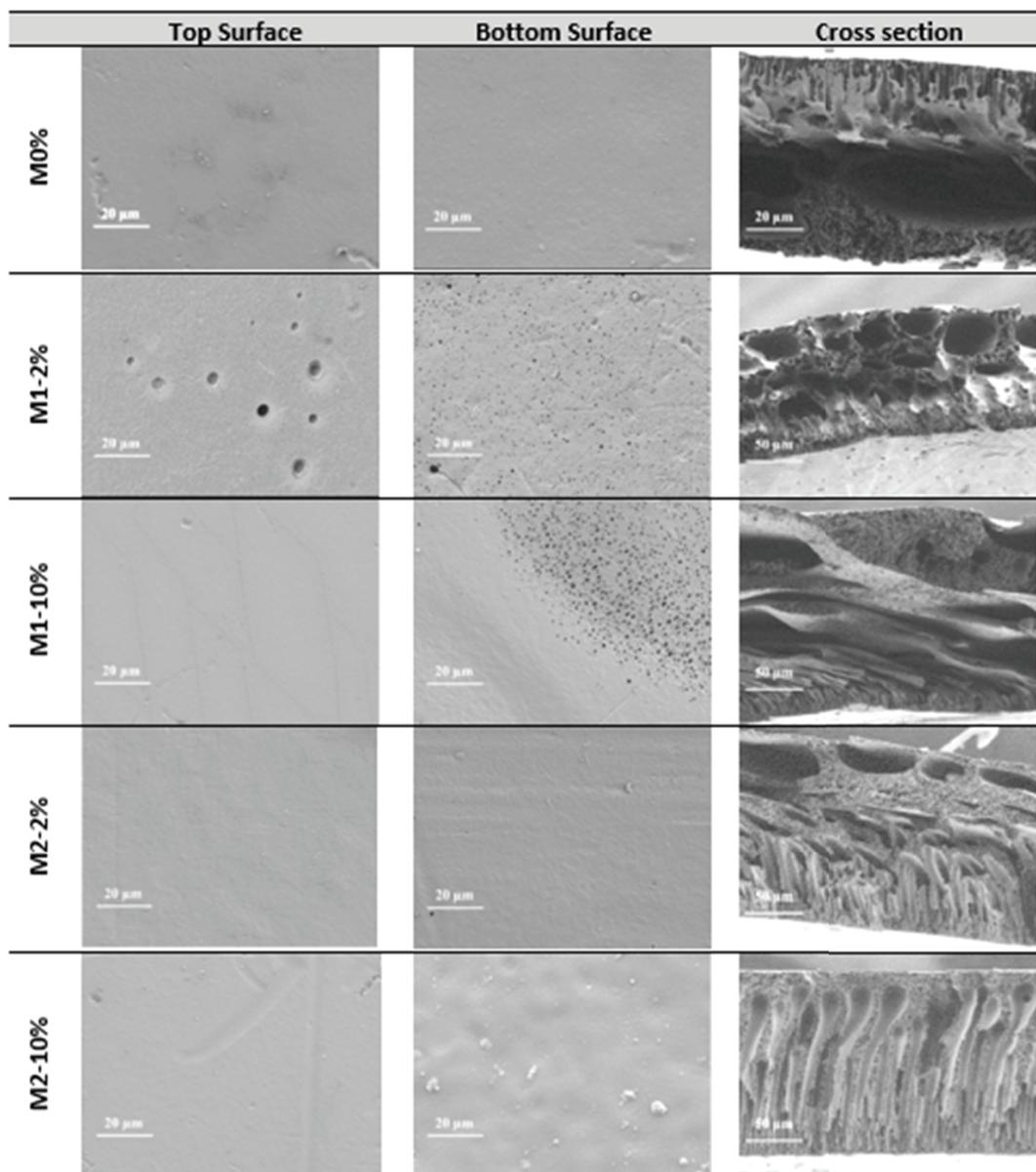
3.1. Morphology

The surface of the samples was analyzed at a microscopic level. Table 1 displays these results. All the membranes present a smooth appearance, with minor roughness marks that could be due to the phase inversion process. The membrane M1-2% shows an active layer with small holes. The back layer of the pure membrane without additive, M0, and the M2-2% membrane, the surface is practically smooth, without any defects. However, the M2-10% membrane presents minor flaws. In contrast, tiny pores are observed along all or part of the surface in membranes with additive 1, M1-2%, and M2-2%.

The cross-section shows that the pure membrane without additive, M0, presents a channel-shaped structure on a porous and dense matrix. In contrast, the channel-shaped structure disappears in the M1-2% membrane, only observing that porous matrix. On the other hand, by increasing the amount of modified Lupasol additive, the morphology of the membrane changes, with the M1-10% membrane showing an evident spongy layer with a much denser layer.

Therefore, it can be affirmed that the morphology of the membrane becomes denser with a higher content of additive 1. The precipitation rate during the phase inversion process predominantly affects the membrane morphology.

Table 1.
Superficial morphology of blended polysulfone membranes



Rapid precipitation is determined by the rapid penetration of the non-solvent into the polymer solution and gives rise to highly asymmetric structures with channel-shaped macrovoids; a slower penetration of the coagulant, and consequently slower precipitation, produce spongy and more symmetrical structures. Thus, the more closely related the polymer and coagulant are, the slower the precipitation and the more symmetrical structures can be expected. The modified Lupasol additive is a relatively hydrophilic and polar polymer; when mixed with PSf, it decreases the polymer solution's precipitation rate [7].

Regarding the samples with additive 2, it can be observed that the M2-2% membrane presents a morphology very similar to the pure sample, M0, with a structure of finger-shaped channels and a dense porous layer. By increasing the additive content, M2-10%, it can be seen that the porous matrix disappears, leaving only the finger-shaped structure for the pores. The number of microvoids remains the same as the modified Lupasol content increases. The membrane's rapid precipitation can explain the pores' internal

structure during phase inversion. This internal structure is due to the rapid penetration of water, as a non-solvent, into the solvent-containing polymer solution.

Consequently, the morphology of the membrane is an asymmetric structure with finger-shaped pores. Since modified M2-10% is a hydrophilic polymer, it should contribute to faster precipitation of PSf-based membranes and leads to a more porous structure, which may enhance CO₂ absorption. Nevertheless, the additive structure and composition favour the interaction and absorption of CO₂.

3.2. Thermal properties

Table 2 presents the glass transition temperatures obtained from the corresponding thermogram in the different heating and cooling scans.

Table 2.
Glass transition temperature values of membranes (M0, M1-2%, M1-10%, M2-2%, and M2-10%).

	1 st Heating	Cooling	2 nd Heating
	T _g (K)	T _g (K)	T _g (K)
M0	475	452	474
M1-2%	469	437	465
M1-10%	473	446	469
M2-2%	471	444	469
M2-10%	476	447	475

The first heat shows the material with this thermal history. The cooling step imposes a standard thermal trace on the material, so the second heat makes it possible to compare the materials directly. Table 2 shows that glass transition values in the second heating are lower than in the first heating and more uniform among themselves. Considering the DSC curves corresponding to the second heating cycle, it can be observed that the glass transition temperature of the pure membrane without additives, M0, is higher than blended membranes. However, the glass transition temperature increases again as the additive increases. In both cases, the additives have a. Nevertheless, the hyperbranched polyethyleneimine might block the movement of the main chain and reduce the plasticizing effect.

3.3. Analysis of the dielectric spectra

The dielectric relaxation spectrum of each of the membranes (M0, M1-2%, M1-10%, M2-2%, and M2-10%) was studied in terms of loss tangent (tan δ), the real and imaginary part of the complex dielectric permittivity (ε'), (ε'') respectively as a function of frequency and temperature. Figure 1 shows the values of (ε') increase when the temperature increases and the frequency decreases in all the membranes. However, the dielectric spectrum is more complex in the blended membranes due to the motions of hyperbranched polyethyleneimine together with polysulfone chains. It is especially relevant for lower frequencies because the relaxation of both components is more separated.

Figure 2 presents the isothermal dielectric relaxation spectrum in terms of the loss tangent as a function of frequency. Since all isothermal curves are represented on the same scale, the M0 membrane without additive shows higher loss tangent values than M1-2%, M1-10%, and M2-2% additive membranes. Specifically, the loss tangent values are very similar at low temperatures for all the membranes studied. In contrast, the isothermal curves that present the most similar behaviour at high temperatures correspond to the membranes M0, M1-2%, and M1-10%.

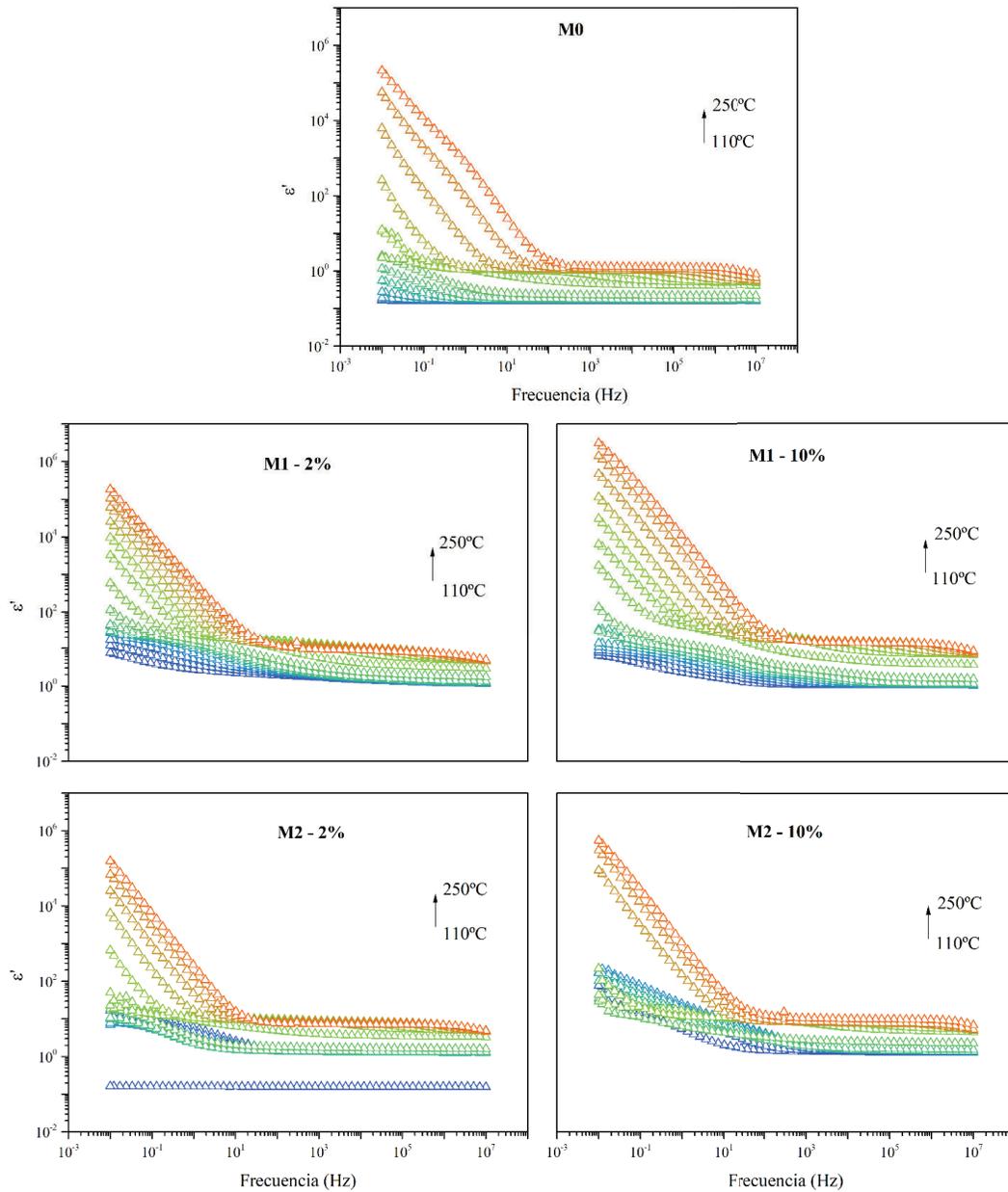


Figure 1. Isothermal curves in terms of the real part (ϵ') of the complex dielectric permittivity (ϵ^*) for the membranes (M0, M1-2%, M1-10%, M2-2%, and M2-10%).

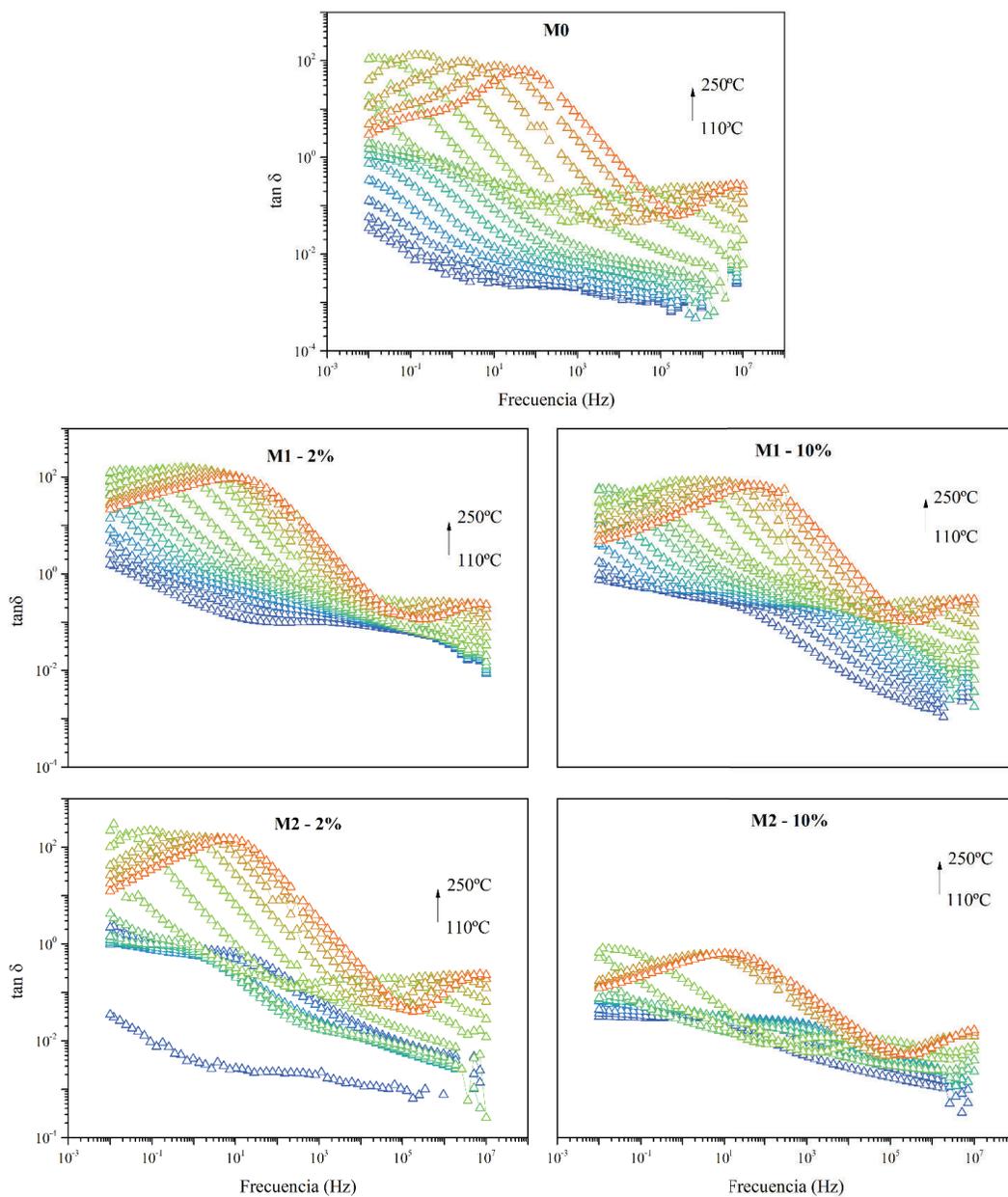


Figure 2. Isothermal curves in terms of the loss tangent ($\tan \delta$) for the membranes (M0, M1-2%, M1-10%, M2-2%, and M2-10%).

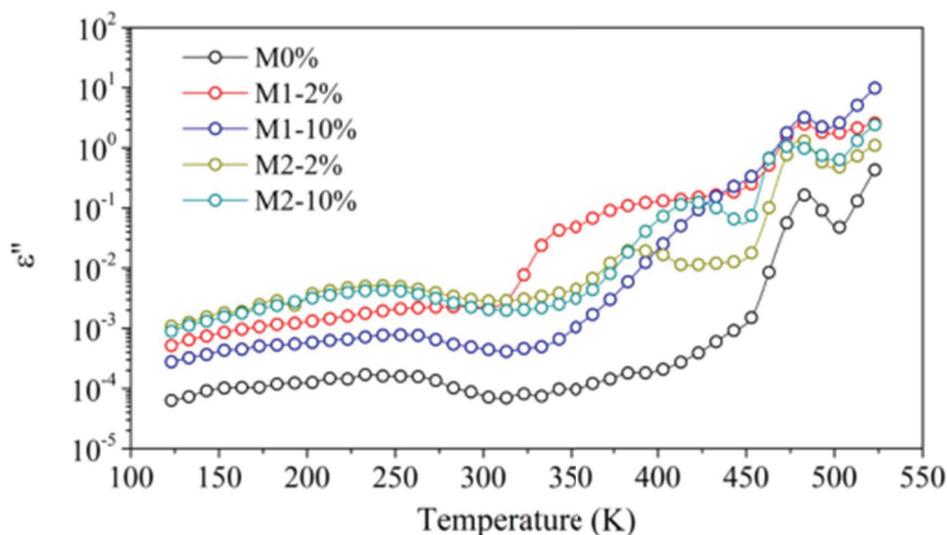


Figure 3. Isochronal curves of the imaginary part (ϵ'') of the complex permittivity (ϵ^*) of the pure (M0) and blended membranes (M1-2%, M1-10%, M2-2%, M2-10%) at 10 Hz.

Figure 3 presents the dielectric spectrum of the M0 no blended membrane in terms of the imaginary part of the complex permittivity at 10 Hz. Three dielectric relaxation zones γ , β , and α , with increasing temperature order, are observed to consist of three dielectric relaxations that might be ascribed to motions of local groups and the glass transition of polysulfone (PSf). However, the dielectric spectra of the blended membranes are more complex. Dielectric relaxations corresponding to molecular motions of local and segmental origin of the hyperbranched polyethyleneimine (HPEI) emerge together with the (γ , β_{PSf} , and α_{PSf}) dielectric relaxations (transition of polysulfone PSf. The loss factor is higher for the M2-2% and M2-10% membranes than M0, indicating greater mobility of the molecular chains of the mixed membranes.

In order increasing temperature, γ relaxation zone appears between 125K and 223K, and it seems that the loss tangent is independent of the additive concentration in M2-2% and 10%. At higher temperatures, between 393K and 523K, the most prominent relaxations, α_{PEI} , and α_{PSf} arise from the motion of the main chains produced by the glass transition of PSU and PEI, respectively. The temperature of α_{PSf} relaxation peak around 483K slightly decreases with the additive concentration, whereas the most remarkable differences appear in the α_{PEI} relaxation. These results confirm the plasticizing effect of hyperbranched polyethyleneimine modified with benzoyl chloride or phenyl isocyanate. The additive imposes fewer steric restrictions on molecular movement. Still, it simultaneously increases the number of chains that can move by plasticizing effect, therefore facilitating the ability of the membrane to diffuse CO_2 .

3.4. Analysis of the dielectric spectra

Jonscher's model (Equation 2) quantified the electric conductivity. Table 3 presents the electrical modulus of conductivity, which increases as the temperature increases. Regarding M0, the n -parameter in both regions is equal to 1 and, therefore, is considered the ideal case where long-range pathways for ion transfer are available. Concerning the blended membranes, a more significant dispersion is found regarding the n -parameter.

M1-2% displays the lowest values that are not equal or less than 0.5, which would suggest a high degree of tortuosity, but it reflects that the landscape for ion transfer might not be as favourable as in the case of M1-10%, M2-2%, and M2-10%.

The membranes with phenyl isocyanate additive have the highest values. Note that in this region, the conductivity is higher for the membranes blended with phenyl isocyanate are more polar than benzoyl chloride.

Table 3.
Jonscher's parameters of the pure (M0) and the blended (M1-2%, M1-10%, M2-2%, M2-10%).

	T (K)	$\sigma_{DC} \times 10^{15}$ (S·cm ⁻¹)	A · 10 ¹³	n	R ²
M0%	443	1.7 × 10 ¹	6.9 × 10 ¹	1	0.99
	463	1.6 × 10 ²	4.3 × 10 ¹	1	0.99
	503	2.9 × 10 ⁵	3.8 × 10 ¹	1	0.99
	513	1.5 × 10 ⁶	3.2 × 10 ¹	1	0.99
M1-2%	373	4.4 × 10 ¹	1.5 × 10 ²	0.86	0.99
	393	2.8 × 10 ²	1.7 × 10 ²	0.86	0.99
	503	1.1 × 10 ⁷	6.6 × 10 ³	0.83	0.99
	513	1.8 × 10 ⁷	2.3 × 10 ³	0.89	0.99
M1-10%	373	3.3 × 10 ³	1.3 × 10 ¹	0.95	0.99
	393	1.3 × 10 ⁴	1.7 × 10 ¹	0.95	0.99
	503	2.5 × 10 ⁷	1.2 × 10 ⁴	0.83	0.99
	513	5.8 × 10 ⁷	5.4 × 10 ³	0.89	0.99
M2-2%	373	1.1 × 10 ³	4.5 × 10 ¹	0.96	0.99
	393	1.3 × 10 ⁴	4.9 × 10 ¹	0.96	0.99
	503	4.3 × 10 ⁶	1.0 × 10 ³	0.94	0.99
	513	8.0 × 10 ⁶	1.3 × 10 ³	0.93	0.99
M2-10%	373	5.2 × 10 ⁴	4.9 × 10 ¹	0.96	0.99
	393	3.9 × 10 ⁵	6.2 × 10 ¹	0.95	0.99
	503	6.0 × 10 ⁶	1.1 × 10 ³	0.94	0.99
	513	1.4 × 10 ⁷	1.1 × 10 ³	0.94	0.99

The dielectric relaxation spectrum demonstrated that the molecular chain motions of blended membranes are higher than polysulphone membranes. The additive has a plasticizing effect and decreases the glass transition, but this temperature increases as the phenyl isocyanate and benzoyl chloride amount increases. These results agree with the direct air capture CO₂ absorption test carried out in a gas-liquid membrane contactor with the homemade module, as described elsewhere.

Briefly, the prepared membranes were placed in the module, where the top surface was exposed to ambient air by holes in the side of the module. The bottom surface of the flat sheet membrane is in contact with 100 mL of 0.64 M KOH solution as a liquid absorbent in a different flow rate range from 40 to 340 mL/min at room conditions (25 °C and 1.013 × 10⁵ Pa). After one hour, samples were collected, and the absorbed CO₂ amount was determined through a carbon dioxide ion-selective electrode (Hanna HI4105 connected with Thermo Scientific Orion Dual Star pH/ISE Benchtop meter, Thermo Scientific, Waltham, Massachusetts, USA) [11-12].

The CO₂ solubility increases with the addition of modified hyperbranched polyethyleneimine. It is regardless of the additive used (benzoyl chloride or phenyl isocyanate), according to the high affinity of the additive to carbon dioxide. The presence of basic nitrogen enhances the interaction between both molecules. Nevertheless, phenyl isocyanate exhibits higher CO₂ solubility concerning benzoyl chloride. The hyperbranched polyethyleneimine and phenyl isocyanate reaction produce urea groups with more affinities to CO₂. This has been validated through a CO₂ capture device, where a remarkable improvement in comparison with neat PSf (30%) is found. Overall, additive 2 determined better characteristics in terms of CO₂ permeability and capture when compared with additive 1. This information is unpublished (pol.20220773), and the authors are preparing a patent application for the absorption device.

4. Conclusions

Asymmetric polysulfone membranes blending with hyperbranched Lupasol G20 grafted with benzoyl chloride or phenyl isocyanate with 2% and 10%wt were prepared via phase-inversion precipitation to increase their ability for carbon dioxide capture at ambient pressure.

The resulting morphology of the blended membrane presents finger-like macropores together with meso- and micropores and a dense layer, which increases as the additive amount increases. The phenyl isocyanate awards a suitable morphology to improve CO₂ permeability and capture.

The glass transition temperature decreases with the addition of a lower amount of modified hyperbranched polyethyleneimine due to plasticizing effect of the additive. However, this temperature increases as the additive percentage increases.

The dielectric relaxation spectrum demonstrated additives' plasticizing effect and improved the molecular chain motions of blended membranes. The membranes with phenyl isocyanate additive have the highest values of conductivity.

All these results, in turn, indicate the importance of considering all these factors to find the most suitable composition to prepare polysulfone membranes which could favour gas permeation of CO₂.

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