In-situ polymerized Pebax®/polydopamine blend membranes with high CO_2/N_2 selectivity

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Abstract

The objective of this work was to produce Pebax®/polydopamine (PDA) blends and apply these blends to produce membranes for gas separation. Flat sheet membranes were tested for gas permeation, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), wide angle x-ray diffraction (WAXD), scanning electron microscopy (SEM) and fourier transformed infrared spectroscopy (FTIR). The results show an optimal concentration of dopamine hydrochloride that produces the best results (α=100, P=114 Barrer). DSC and WAXD results indicate that polydopamine influences the crystallization of Pebax®, reducing the melting and crystallization temperatures of PA blocks and increasing the melting temperature of PEO blocks. The incorporation of PDA decreases gas permeability and increases gas selectivity. The decrease in permeability indicates that the presence of polydopamine reduces the diffusion coefficient of Pebax® by reducing the segmental mobility of PEO blocks and possibly the fraction free volume. Compared to the trade-off, Pebax®/PDA membranes surpasses the upperbound for CO_2/N_2 separation.

Keywords: *Pebax, polydopamine (PDA), in-situ polymerization, CO_2 separation, polymer blends.*

1. Introduction

Gas separation membranes have been successfully applied for carbon capture processes to separate CO_2 from N_2[1]. For carbon capture, CO_2/N_2 can be separated by different mechanisms which include solution-diffusion polymer membranes[2], facilitated transport membranes[3], mixed matrix membranes[4] and membrane contactors[1]. The separation based on the solution-diffusion mechanism is strongly dependent on the polymer chemical structure, especially the flexibility of the polymer backbone and the fraction free volume of the membrane[5]. Although these membranes can be very efficient for different separations, their properties are subjected to the trade-off between permeability and selectivity which limits the applications for gas separation[5]. Facilitated transport membranes are produced using carriers that interact selectively and reversibly with the gases that need to be separated[6-8]. Carriers can be fixed or mobile and the transport mechanism depends on the type of carrier. Among different carriers, amine-based substances are very efficient to improve CO_2 separation from different gas mixtures including natural gas and flue gas[6,7,9]. Amines react with CO_2 to form either carbamate ions or bicarbonate ions, depending on the characteristics of the amine group, and facilitates the transport of CO_2 which is transported by the carrier itself for mobile carriers or by a hoping mechanism for fixed carriers[10,11]. The type of ion that is formed depends on whether the amine is hindered or unhindered. Unhindered amines form the stabler carbamate ion that reduces the amount of CO_2 that can react with the carrier[10]. Hindered amines produce bicarbonate increasing the maximum amount of CO_2 that reacts with the carrier[10-12]. Hindered amines are primary amines in which the amino group is attached to a tertiary carbon atom or a secondary amine in which the amino group is attached to at least one secondary or tertiary carbon[11]. Hindered amines have been studied as carriers in facilitated transport membranes with promising results that depend on the degree of hindrance[6,7,9,12]. Besides amines, other chemical groups have been used to improve the permeability and selectivity of polymer membranes towards CO_2. Poly(ethylene oxide) groups have excellent interaction with CO_2 which increases the permeability and selectivity of CO_2 in gas separation membranes[13]. Among different polymers that contain PEO groups, Pebax® a copolymer of poly(ethylene) oxide and poly(amide) 6 has been studied in gas separation membrane applications. In Pebax®, the presence of PEO blocks increases CO_2 permeability and ideal gas selectivity especially CO_2/N_2[14-19]. Several authors have modified Pebax® to improve gas permeability and selectivity. Polyethylene glycol[20], 2,4-toluylene diisocyanate, quaternary ammonium moieties[21], triglycerides[15] and ionic liquids[18,22,23] have been used to modify Pebax®. Another substance that can be used to improve the properties of polymer membranes in polydopamine. Polydopamine is a

natural substance that can be synthesized by the oxidation of dopamine hydrochloride in alkaline conditions[24]. Although the chemical structure of polydopamine has been the subject of intense debate[24-26], there is evidence that polydopamine is a mixture of dihydroindole and indole moieties and open chain aminoethyl compounds[27] that are linked by covalent bonds. The analysis of polydopamine reaction was realized by introducing a dopamine hydrochloride solution in HPLC. The work identified the self-assembled (dopamine) 2 /DHI physical complexes during polydopamine preparation[27]. Other results have provided strong and direct evidence of supramolecular organization in both natural and synthetic eumelanins[28]. Using low voltage–high resolution transmission electron microscopy (LVHRTEM) it has been shown that sheets of protomolecules stack to form onion-like nanostructures. The inter-sheet spacings within these structures are between 3.7 and 4.0 Å consistent with non-covalent $\pi - \pi$ stacking in heteroaromatic systems[28]. Yu et al.[24] have identified a similar stacked structure by the pyrolysis of polydopamine. According to the authors the distance between the nanodisks in the graphite-like structure of pyrolyzed polydopamine is 3.4 Å which is consistent with the work of Watt et al. [27]. Liebscher et al.[23] have established that indole groups are linked by covalent bonds and that the supramolecular structure is the result of charge transfer interactions between polydopamine molecules. Because of the indole and amino groups, polydopamine can interact with CO_2 and improve solubility selectivity of polymer membranes.

The indole groups of polydopamine can interact with CO_2 via dipole–π interactions with great potential to improve CO_2/N_2 selectivity as shown by Xu et al.[28] and Chang et al. [29]. Recent work shows that indole based microporous organic polymers have enhanced uptake for CO_2 due to local dipole–π interactions with CO_2/CH_4 selectivity of 32 and CO_2/N_2 selectivity of 15. Chang et al.[29]. have used DFT to calculate the binding energy of CO_2 with formamide and indole groups. The results show that both groups have high binding energies with CO_2 and that amide groups can capture CO_2 molecules that desorb from indole groups. In another work, Lee et al.[30] have calculated the binding energy of several multi-N-containing superbases and heteroaromatic ring systems with CO_2. The results show that substances like melanine and indoles have stronger binding energies when compared to other substances. Polydopamine has been added to Pebax® to improve CO_2/CH_4 selectivity with good results that depend on polydopamine concentration[31]. C_3H_6/N_2 selectivity was also improved with the incorporation of polydopamine which was explained by the difference in the adsorption of each gas in polydopamine. The results have shown that polydopamine adsorbs C_3H_6 but not N_2[32]. Both works incorporate polydopamine particles in Pebax® but only a few works have synthesized polydopamine inside a polymer solution. In most cases the objective of *in-situ* polymerization was to produce fluorescent polydopamine by conjugation with substances like amine- or thiol-containing organic species that eliminate the stacking interaction of PDA and prevents cyclization reactions and disrupts the stacking of PDA by reducing π-π interactions[33].

Considering the importance of CO_2 capture, the advantages of both Pebax® and amine-based additives in CO_2 separation and the limited adsorption of N_2 by polydopamine (PDA),

this work applies an *in-situ* polymerization method to produce Pebax®/PDA blends and shows the properties of the membranes prepared from the blends. *In-situ* polymerization was performed using green solvents (ethanol/water mixture). Gas permeability of Pebax® was reduced while CO_2/N_2 selectivity increased with the incorporation of polydopamine. The results suggest that there is an optimal concentration of dopamine hydrochloride that produces the membranes with better CO_2/N_2 selectivity and that the presence of polydopamine reduces the diffusion coefficient of Pebax® which reduces the permeability.

2. Background and Theory

Polymer membranes can separate gases by two general mechanisms, solution diffusion and facilitated transport. Solution-diffusion is characteristic of both glassy and rubbery materials that do not possess specific chemical groups that react with the gases to be separated[5]. Facilitated transport takes place when specific chemical groups react reversibly with one of the gases, usually CO_2, and promote the selective transport of this gas through the membrane. There are two mechanisms for facilitated transport depending on the carrier. For fixed carriers, the hopping mechanism takes place while for mobile carriers the carrier itself moves through the structure of the membrane transporting the gas molecule[7,8]. Polydopamine, which has indole and amine groups that are CO_2-philic could result in facilitated transport.

The solution diffusion model states that the permeability (P) is the product of the solubility (S) and the diffusion coefficient (D) (Equation 1).

$$P = D.S \quad (1)$$

Based on Equation 1, the ideal selectivity is the product of the diffusion selectivity and the solubility selectivity (Equation 2).

$$\alpha = \frac{P_A}{P_B} = \frac{D_A}{D_B}\frac{S_A}{S_B} \quad (2)$$

For most materials, the diffusion selectivity that depends on chain flexibility and the relative sizes of the molecules is responsible for separation. It is also the easiest to control and modify. Solubility selectivity can be improved by the incorporation of specific chemical groups that interact selectively with the gas molecules that form the mixture to be separated but very often these groups can change the flexibility and fraction free volume of the polymer and affects the diffusion coefficient.

3. Experimental Section

3.1 Materials

Polyether-b-amide copolymer Pebax MH-1657® from Arkema Brazil was used as matrix to produce the membranes. Ethanol PA (98.5%) was used as co-solvent with distilled water. Dopamine hydrochloride (MW=189,64 g/mol, 98%) from Sigma Aldrich and sodium hydroxide (97%) were used for polydopamine synthesis.

3.2 Synthesis of polydopamine nanoparticles

Polydopamine nanoparticles were synthesized by dissolving dopamine hydrochloride (DA) in ethanol/water mixtures with different ratios, 70/30, 50/50 and 30/70 w/w. After dissolution, a 0.1 mol.L^{-1} NaOH solution was added as the oxidant agent. The concentration of dopamine hydrochloride was fixed in 1 mg.mL^{-1} and NaOH/DA ratio was 2:3. The mixture was agitated for 24 h, and the nanoparticles were separated by centrifugation in a Edutec digital centrifuge. The nanoparticles were washed with distilled water, centrifuged, and dried in a Labstore convection oven at 100 °C for 24 h.

3.3 In-situ polymerization

The *in-situ* polymerization method was performed by preparing Pebax solutions different ethanol/water mixtures (70/30, 50/50 and 30/70) and heating at 80 °C for 2 h under reflux and N₂ stream. After complete dissolution of Pebax®, dopamine hydrochloride and the sodium hydroxide solution were added to the Pebax® solution and stirred for 24 h with an IKA C-MAG HS7 magnetic stirrer. Three concentrations of dopamine hydrochloride were used 0.5, 1.0 and 1.5 mg.mL^{-1} and a NaOH/DA ratio of 2:3. The samples were named Pebax®/PDA$_{x,y}$ where x represents the dopamine hydrochloride concentration and y represents ethanol concentration in solvent mixture (70, 50, 30).

3.4 Membrane preparation

Pebax® and Pebax®/PDA membranes were prepared by solvent evaporation. After the dissolution of Pebax®, the solution was poured in Teflon petri dishes and the membrane was formed by evaporation of the solvent mixture in a vacuum oven at 50 °C for 24 h. Pebax®/PDA membranes were prepared using the same conditions except for the fact that the solution was obtained direct from *in-situ* polymerization. After membrane formation all membranes were heated for another 24 h at 30 °C to remove residual solvent. Membrane thicknesses were in the range of 70-80 μm.

3.5 Characterization

The characterization protocols used in the work are presented in detail in the Supplementary Material.

4. Results

4.1 Effect of solvent mixture on PDA morphology and particle size

Polydopamine particles are prepared by the oxidation of dopamine hydrochloride in basic medium. The kinetics of the reaction is influenced by different process conditions including the properties of the solvents. Based on Hansen's theory of solubility, PDA has more affinity for solvent mixtures with higher water content. Nevertheless, Pebax® membranes are usually produced using ethanol/water mixtures with higher ethanol content. To evaluate the effect of the solvent mixtures on PDA morphology, the particles were synthesized with different solvent mixtures. Figure 2 (Supplementary Material) shows the morphology of polydopamine nanoparticles synthesized using different

ethanol/water ratios. The results indicate that the ratio between ethanol and water influences the particle size. The diameter decreases with the increase of water content that increases the solvent power of the solvent mixture. Yue et al.[33] have attributed the increase in polydopamine particle size to the decrease in nucleation rate due to the increase in ethanol concentration. Table 1 (Supplementary Material) shows the average diameter.

The results suggest that using higher water concentration favors the formation of smaller particles. Moreover, washing PDA particles to remove unreacted substances influences the particle size and shape.

4.2 Identification of PDA nanoparticles in Pebax®/PDA blends

Pebax®/PDA membranes were prepared by *in-situ* polymerization of PDA inside Pebax® solutions. As shown in Figure 3 (Supplementary Material), the characterization of the membranes by FTIR did not help to identify the presence of PDA. FTIR spectra for Pebax® show the presence of the band at 3298 cm^{-1} that represents -N-H, 1729 cm^{-1} related to O-C=O, 1638 cm^{-1} stretching vibration of C=O, 1537 cm^{-1} bending vibration of -NH- and 1096 cm^{-1} symmetric vibrations of C-O-C. Some authors attribute peaks at 844 cm^{-1} to OH stretching vibrations. For PDA, the characteristic bands are 3396 cm^{-1} for N-H and O-H stretching vibrations, 2914 cm^{-1} for C-H stretching vibration, 1645,2 cm^{-1} for N-H scissoring bending stretching, 1502 cm^{-1} C=C stretching vibrations in benzene, 1276 cm^{-1} C-O-H stretching vibrations and 1026 cm^{-1} for C-N stretching[34-37].

Comparing Pebax® with Pebax®/PDA blends it is possible to observe small changes in the format and width of some bands. The band at 1262 cm^{-1} becomes wider for C_{DA} = 1.5 mg.mL^{-1}. The band at 844 cm^{-1} is also changed for C_{DA} = 1.5 mg.mL^{-1}. The differences in FTIR spectra are minimal which could be explained by the fact that the characteristic bands for PDA coincide with the bands of Pebax®. Moreover, as reported by other authors PDA can react with Pebax® to form a single polymer which would explain why FTIR results do not show any specific band of PDA. Visual inspection of the membranes could be considered an indicative of the formation of PDA during in-situ polymerization. The formation of PDA particles usually results in a dark solution. During in-situ polymerization, Pebax®/PDA mixtures became dark over time, and the final membranes were darker than neat Pebax®. Figure 4 (Supplementary Material) shows the appearance of Pebax® and Pebax®/PDA membranes. The images show that Pebax® membranes are white and Pebax®/PDA membranes are dark. The membranes become darker as the concentration of dopamine hydrochloride increases. The fact that Pebax®/PDA membranes are dark indicate that polydopamine was formed inside de membranes.

4.3 Morphology of Pebax®/PDA membranes

SEM analyses were conducted to determine the effect of PDA on the morphology of Pebax®. The morphology of polymer membranes is direct related to composition and crystallization kinetics. Figures 5 and 6 (Supplementary Material) show the morphology of neat Pebax® membranes

and Pebax®/PDA membranes, respectively. The morphology of Pebax® is not affected by the solvent mixture although roughness can be observed in Figure 5c which could be explained by the fracture protocol. With the addition of PDA, the morphology chances significantly and seems to depend on the solvent mixture. As shown in Figures 6a and 6b (Supplementary Material), the sample prepared with the 70/30 solvent mixture has layers with some orientation on the surface of the membrane. For the 50/50 solvent mixture a very smooth morphology with a few small pores was observed and for the 30/70 mixture the morphology is smooth and dense with some dark spots on the surface. The results indicate that the incorporation of PDA influences the final morphology of Pebax® (Figure 6) (Supplementary Material). Liu et al.[38] have produce Pebax/PDA mixed matrix membranes by incorporating PDA microspheres in Pebax. The morphology of the membranes was different from the morphology observed in this work. The membranes produced by Liu et al.[38] shows a rough fracture surface and indications of agglomeration of PDA particles at high PDA loadings (10 wt%). Moreover, the layered structure observed in Figures 6a and 6b (Supplementary Material) was not observed in Liu et al.'s[39] work. Furthermore, Figure 6 shows that Pebax and PDA form a homogenous morphology which favors gas transport and separation. According to Wu and Chung[39] and Nilouyal et al.[40], membranes with a homogenous supramolecular structure prepared by the incorporation of specific organic compounds in PBI result in gas permeability and selectivity that surpasses the upperbound and the properties of ordinary polymer membranes.

4.4 Wide angle X-ray diffraction

Figure 7 shows XRD curves for Pebax®/PDA membranes. Pebax® has two characteristic peaks at $2\theta=20.5°$ (d= 4.3 Å) and $2\theta=24°$ (d= 3.7 Å) that are related to the crystalline structure of PA groups[41-43]. In Figure 7 (Supplementary Material) the second peak has high intensity while the former appears as a low intensity shoulder. For sample Pebax®/PDA$_{0,50}$ and Pebax®/PDA$_{1,50}$ (Figure 7b) (Supplementary Material) both peaks have the same intensity, and both are broad. Increasing C_{DA} makes the peak at $2\theta=24°$ more intense and narrower. The incorporation of PDA does not affect the peaks related to PA groups except for sample Pebax®/PDA$_{1,5,50}$. Moreover, for the samples Pebax®/PDA$_{x,70}$, it is possible to observe a peak at $2\theta=32°$ (d= 2.8 Å) that could be associated with the PEO segments[42] indicating that PDA helps the crystallization of PEO blocks. The appearance of the peak at $2\theta=32°$ can be considered and indicative that the incorporation of PDA affects the distance between PEO segments which would increase intermolecular interactions and affect the flexibility of the polymer and the diffusion of gas molecules.

4.5 Thermal stability (TGA)

Figure 8 (Supplementary Material) shows TGA thermograms of Pebax® and Pebax®/PDA membranes. Pebax® has three transitions, the first with onset at 50 °C, the second at 683 K and the third at 873 K. The total weight loss of Pebax® is almost 100% at 973 K. PDA has three transitions at 348 K, 523 K and 773 K. The total weight loss of PDA at 1173 K is 60% which shows the high thermal

stability of PDA nanoparticles. Pebax®/PDA blends have a similar behavior than Pebax® with the same thermal transitions at 323 K, 683 K and 873 K. Compared to neat Pebax®, the blends have higher weight loss at 323 K and higher residual mass after 873 K. In immiscible polymer blends and mixed matrix membranes, TGA can indicate the presence of a second phase by a thermal transition in a different temperature compared to the new polymer. The fact that Pebax®/PDA blends do not show additional thermal transitions when compared to Pebax® indicates that the blends form a homogenous structure confirming what was observed in SEM analysis. The absence of new thermal transitions can also be an indicative of the polymerization of PDA. As shown by Wu et al.[14] the incorporation of low molecular weight triglycerides influences the thermal stability of Pebax® with the appearance of new transitions at low temperatures.

4.6 Thermal properties and crystallization (DSC)

Figure 9 (Supplementary Material) shows the results of DSC first heat for the membranes. The first heat shows the actual properties of the membranes. The second heat is performed in the materials that have been melted and crystallized from the melt and shows the influence of polydopamine in the crystallization process. From the results in Figure 9 (Supplementary Material), it is evident that the composition of the solvent mixture influences the crystallization of Pebax® and Pebax®/PDA blends. The decrease in ethanol concentration affects the width and height of PA melting peak and in the case of the sample prepared from 30 wt% ethanol mixture a new peak appears at low temperatures. PDA has two effects in Figure 9 (Supplementary Material), it reduces melting temperature of PA blocks and increases the melting temperature of PEO blocks. It also reduces the height of the PA melting peak and in the specific case of the sample Pebax®/PDA$_{1,70}$ a second melting peak for PA blocks appears at low temperatures. The other samples have shoulders in this temperature range but not a clear peak. As shown in Tables 2, 3 and 4 (Supplementary Material) the incorporation of PDA reduces crystallization and melting temperature which indicates that PDA hinders PA segments crystallization and reduces the interactions between them. This is evidenced by the decrease in PA crystallinity degree. The influence of PDA on Pebax® thermal properties could be indicative of the interactions between PDA and the amide blocks which could hinder molecular mobility and affect crystallization. The influence of the incorporation of ionic liquids on Pebax® crystallization was studied by Bai et al.[43] and could be an indicative of the effects of PDA on Pebax®. The results show that the incorporation of ionic liquid [bmim]PF$_6$ on Pebax® reduces the crystallization temperature and broadens the melting peak. The study of non-isothermal crystallization kinetics revealed that the ionic liquid reduces the percentage of primary crystallinity but induces a secondary crystallization that produces a less ordered structure. Higher ionic liquid concentrations lead to an increase in crystallization temperature due to the higher molecular mobility of PEO groups. The results of second heating confirm the effect of PDA on the crystallization of Pebax®. The melting temperature of PEO blocks increases and the melting temperature of PA block decreases with the

presence of PDA. The most important difference is that the second melting peak of PA is absent which indicates that the effect of PDA in Pebax® depends on whether it is crystallized from solution or from the melt. The results indicate that the incorporation of PDA weakens the hydrogen bonding between amide blocks in Pebax® reducing the melting temperature. It also decreases the crystallinity of Pebax® but increases the interactions between PEO blocks which is evidenced by the increase in melting temperature.

4.7 Transport properties and selectivity

Gas permeability of polymer membranes is an important property for several separation processes such as carbon capture, natural gas, and biogas purification. The separation of CO_2 from N_2 is an important process for flue gas treatment and CO_2 capture from air, while the separation of CO_2 from CH_4 is applicable for biogas and natural gas treatment. As shown in Figures 10 and 11 (Supplementary Material), the influence of PDA depends on the concentration of dopamine hydrochloride (C_{DA}). For N_2 and CH_4 the increase in C_{DA} reduces the permeability for all gases but when C_{DA} = 1.5 mg.mL^{-1} the permeability increases and is equal to the permeability of neat Pebax®. For CO_2, the effect of C_{DA} depends on the solvent mixture used to prepare the solutions. For ethanol concentration ($C_{ETHANOL}$) of 50% and 30 wt% the effect of C_{DA} is similar to the effect on other gases except for the smaller increase in permeability when C_{DA} = 1.5 mg.mL^{-1}. For $C_{ETHANOL}$ = 70 wt% CO_2 permeability decreases systematically with the increase in C_{DA}. In terms of selectivity, the results show that the best selectivities are obtained when C_{DA} = 1.0 mg.mL^{-1}. Moreover, the best solvent mixture is 70/30 ethanol/water. The greatest selectivity is 100 for CO_2/N_2 which represents an increase of 50% compared to Pebax®.

Polydopamine has been used to produce multilayer composite membranes for CO_2 separation. Polydopamine membranes were grown on top of polysulfone supports. The results show that increasing the thickness of polydopamine membrane decreases CO_2 permeability and increases CO_2/N_2 selectivity[44]. Polydopamine nanoparticles have been introduced in Pebax® to produce mixed matrix membranes for CO_2 separation[32]. The results show that CO_2 permeability and CO_2/CH_4 selectivity depend on PDA content. Both properties increase for low concentrations of polydopamine (up to 5%) but decrease for higher concentrations. Polydopamine has also been applied to prepare supported membranes for propylene/nitrogen separation. Gas uptake shows that polydopamine does not absorb significant amounts of nitrogen which contributes to the membrane selectivity[33]. Dong et al.[45] have produced polydopamine submicrospheres of polydopamine (PDASS) and incorporated them in PIM-1. PDASS particles reduced the permeability of PIM-1 and increased the selectivity in a similar manner as observed for *in-situ* polymerized PDA in Pebax® of this work. The decrease in permeability was explained by the decrease in diffusion coefficient, due to interactions between PDASS and PIM-1, that surpassed the increase in solubility.

Compared to the upperbound (Figure 12 of Supplementary Material) the properties of the membrane Pebax®/PDA$_{1,70}$ surpasses the CO_2/N_2 upperbound limit for both

pressures tested. The increase in pressure improves the properties of the membranes and favors CO_2/N_2 separation. Compared to neat Pebax®, the sample Pebax®/PDA$_{1,70}$ has a superior set of properties for CO_2/N_2 separation. For the other membranes, the incorporation of PDA reduces the ability of Pebax® to separate CO_2 from N_2.

5. Discussion

Considering the high pressures applied, it is unlikely that the transport of gas molecules in Pebax/PDA membranes takes place by facilitated transport because the functional groups of polydopamine are probably saturated at 1 and 1.5 MPa. Based on the solution-diffusion mechanism, the permeability (P) is the product of the solubility (S) of gas molecules in the polymer and the diffusion coefficient (D) – Equation 1.

CO_2 solubility is expected to increase with the incorporation of polydopamine due to strong interaction of indole groups and melanine with CO_2 molecules. Moreover, indole and melanine groups do not interact with N_2 and CH_4 so the incorporation of PDA decreases their solubility in Pebax®. Therefore, the incorporation of PDA should increase CO_2 permeability and decrease CH_4 and N_2 permeabilities. Furthermore, the ideal selectivity should increase due to the increase in solubility selectivity (Equations 2 and 3). The decrease in N_2 and CH_4 permeability is consistent with the idea of reduced solubility but the decrease in CO_2 permeability indicates that solubility is not the main effect on Pebax®/PDA membranes.

If the solubility is not the main effect influencing the permeability of Pebax®/PDA membranes, the results should be explained by the diffusion coefficient. The diffusion process depends on the fraction free volume, chain flexibility and polymer crystallinity. Overall, the crystallinity of Pebax® is reduced by the incorporation of PDA which should increase the diffusion coefficient and the permeability. Fraction free volume can be reduced by the presence of PDA between Pebax® polymer chains and chain flexibility can be reduced by the interactions between Pebax® and PDA. Although there is no evidence of crosslinking, it is plausible that PDA interacts with the amide blocks of Pebax® forming hydrogen bonding which would reduce chain flexibility and decrease the diffusion coefficient and gas permeability. Based on DSC results, the incorporation of PDA also increases the intermolecular interactions in PEO which reflects on the increase in the melting temperature. Based on the results, it is plausible to state that the decrease in gas permeability (especially CO_2) is due to the influence of PDA in the diffusion coefficient that results from the interactions between Pebax® intermolecular forces and from the interactions between Pebax® and PDA. The decrease in fraction free volume can also explain the decrease in gas permeability.

The decrease in the concentration of ethanol in the solvent mixture ($C_{ethanol}$) tends to reduce the permeability of all gases in the Pebax®/PDA membranes and increase all membrane selectivities except for C_{DA} = 1.0 mg.mL^{-1}. In this case, there is an optimal selectivity for $C_{ethanol}$ = 70%. Although the results indicate a close relation between these variables and the properties of the membranes, it is not possible to

establish a direct structure-property relationship based on the results presented. The synthesis of PDA with different ethanol concentrations indicates that the decrease of $C_{ethanol}$ reduces particle size due to the increase in nucleation rate. Moreover, the increase in C_{DA} can influence the size and the interactions between PDA molecules which affects CT interactions of PDA and its stacked morphology. *In-situ* polymerization or conjugation has been used to control particle size and generate fluorescence of PDA. While the presence of radicals controls de size of PDA, conjugation reduces intra- and intermolecular coupling of PDA generating fluorescence. The greater the concentration of the conjugated polymer, the smallest is PDA particle, and the weakest is the interaction between PDA molecules.

Therefore, the effect of $C_{ethanol}$ and C_{DA} could be related to particle size and intramolecular forces between PDA particles in Pebax®. Decreasing $C_{ethanol}$ will decrease particle size which favors the interactions between Pebax® and PDA. Increasing C_{DA} could decrease the interactions between Pebax® and PDA because of the decrease of Pebax® concentration during *in-situ* polymerization. In summary, there seems to exist a suitable combination between $C_{ethanol}$ and C_{DA} that results in the best properties. The effect of these two variables might result from their influence in particle size and intermolecular interactions of polydopamine that will influence the interactions between polydopamine and Pebax®. Figure 13 (Supplementary Material) illustrates a proposed effect that PDA could have in Pebax® and its properties. After in-situ polymerization, PDA molecules would interact with PA blocks and increase the distance between them which reflects in the decrease of melting temperature. Simultaneously, PEO blocks would be closer which increases the melting temperature. The presence of PDA could decrease in fraction free volume because PDA molecules occupies the space between PA blocks.

6. Conclusions

Pebax®/polydopamine blend membranes were prepared by *in-situ* polymerization and the presence of polydopamine was determined by vision inspection of the membranes. The presence of polydopamine reduces gas permeability for all gases compositions except for high C_{DA}. Ideal gas selectivity depends on C_{DA} and on the composition of the solvent mixture. An optimal selectivity was obtained for $C_{DA}= 1mg/mL$. The results of DSC and XRD confirm that PDA affects the crystallization of Pebax® and creates a structure that has higher d-spacing which influences gas transport and separation. The morphology of the samples with higher selectivity is clearly different than the other membranes which supports the idea that PDA affects crystallization of Pebax®. The effect of PDA on membrane permeability and selectivity can be explained by a decrease in diffusion coefficient, due to the decrease in polymer flexibility and fraction free volume, that has more influence on gas permeability and selectivity than the increase in gas solubility that is expected especially for CO_2. The results show that incorporation of polydopamine can be successfully applied to modify polymer membranes and improve their separation capacity.

7. Author's Contribution

- **Conceptualization –** Ariele dos Santos Pirola; Daniel Eiras.
- **Data curation –** Daniel Eiras; Sônia Faria Zawadski.
- **Formal analysis –** Ariele dos Santos Pirola; Daniel Eiras.
- **Funding acquisition** – Daniel Eiras.
- **Investigation** – Ariele dos Santos Pirola; Daniel Eiras; Sônia Faria Zawadski; Paula Sacchelli Pacheco.
- **Methodology** – Ariele dos Santos Pirola; Paula Sacchelli Pacheco.
- **Project administration** – Daniel Eiras.
- **Resources** - Daniel Eiras; Sônia Faria Zawadski.
- **Software** – NA.
- **Supervision** – Daniel Eiras.
- **Validation** – Daniel Eiras; Sônia Faria Zawadski.
- **Visualization** – NA.
- **Writing – original draft** – Daniel Eiras.
- **Writing – review & editing** – Daniel Eiras; Sônia Faria Zawadski.

8. Acknowledgements

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Supplementary Material

Supplementary material accompanies this paper.

Table 1. Mean diameters of PDA nanoparticles as a function of methanol concentration and washing protocol.

Table 2. Thermal properties of Pebax® and Pebax®/PDA blends determined by DSC. 70%

Table 3. Thermal properties of Pebax® and Pebax®/PDA blends determined by DSC. 50%

Table 4. Thermal properties of Pebax® and Pebax®/PDA blends determined by DSC. 30%

Figure 1. Schematic representation of the permeation cell used in this work. 1- Gas Cylinder; 2-Manometer; 3- Oven; 4- Gas reservoir; 5- Permeation cell; 6- Temperature Control; 7- Permeate; 8- Flowmeter; 9- Retentate.

Figure 2. Polydopamine nanoparticles synthesized with different water/ethanol concentrations (a) and (b) 30/70, (c) and (d) 50/50, (e) and (f) 70/30. And the effect of washing protocol on the morphology of the particles (a), (c) and (e) centrifuge, washing and drying; (b), (d) and (f) centrifuge and drying.

Figure 3. FTIR spectra of Pebax® and Pebax®/PDA membranes.

Figure 4. Pictures of Pebax® and Pebax®/PDA membranes.

Figure 5. Morphology of Pebax® membranes cross-section with different ethanol/water concentrations . (a) Pebax® 70/30, (b) Pebax® 50/50, (c) Pebax® 30/70.

Figure 6. Morphology of Pebax®/PDA membranes. Cross sections: (a) Pebax®/PDA$_{1,70}$, (b) Pebax®/PDA$_{1,50}$, (c) Pebax®/PDA$_{1,30}$. Surfaces: (d) Pebax®/PDA$_{1,70}$, (e) Pebax®/PDA$_{1,50}$, (f) Pebax®/PDA$_{1,30}$.

Figure 7. XRD diffractograms of Pebax® and Pebax®/PDA membranes. (a) Pebax®/PDA$_{x,70}$, (b)Pebax®/PDA$_{x,50}$, Pebax®/PDA$_{x,30}$.

Figure 8. TGA thermograms of Pebax®, PDA and Pebax®/PDA blends.

Figure 9. DSC thermograms of Pebax®/PDA blends. First Heating. a) Pebax®/PDA$_{x,70}$, b) Pebax®/PDA$_{x,50}$ and c) Pebax®/PDA$_{x,30}$

Figure 10. Gas permeability (upper graphic) and ideal selectivity (lower graphic) of Pebax®/PDA membranes at 1 MPa. 1 Barrer = 10^{10} cm³(STP).cm.cm^{-2}.s^{-1}.cmHg^{-1} = 7.518x10^5 m³(STP).m.m^{-2}.s^{-1}.MPa^{-1}.

Figure 11. Gas permeability (upper graphic) and ideal selectivity (lower graphic) of Pebax®/PDA membranes at 1.5 MPa. 1 Barrer = 10^{10} cm³(STP).cm.cm^{-2}.s^{-1}.cmHg^{-1} = 7.518x10^5 m³(STP).m.m^{-2}.s^{-1}.MPa^{-1}.

Figure 12. Pebax®/PDA properties compared to the Robeson's upperbound at 1 and 1.5 MPa. a) Pebax®/PDA$_{x,70}$, b) Pebax®/PDA$_{x,50}$ and c) Pebax®/PDA$_{x,30}$

Figure 13. Proposed effect of PDA molecules in fraction free volume, and interactions between Pebax® molecules.

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