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Gas Separation Performance of Polycarbonate Membranes Modified With Multifunctional Low Molecular-Weight Additives

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Abstract: The gas permeation performances and various physical properties of dense polycarbonate (PC) membranes containing low molecular-weight additives (LMWA) with functional groups were evaluated. The selected LMWAs were *p*-nitroaniline, 4-amino 3-nitro phenol, catechol and 2-hydroxy 5-methyl aniline, and LMWA concentration in the membrane was changed between 1 and 10% (w/w). The PC/LMWA membranes had higher ideal selectivities but lower permeabilities than pure PC membrane. The most effective LMWA which provided the highest selectivity and the lowest permeability in membranes was *p*-nitroaniline and the least effective one was catechol. The selected LMWAs antiplasticized the PC matrix and improved the separation performances even at low concentrations. The glass transition temperature (T_g) of PC/LMWA membranes was lower than that of pure PC membrane. Reduction of T_gs as a function of *p*-nitroaniline concentration obeyed to Gordon-Taylor model which indicates antiplasticization type interaction. FTIR spectra of pure and blend membranes also demonstrated the existence of interaction.

Keywords: Gas separation, polycarbonate, low molecular-weight additive, antiplasticization, glass transition temperature

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INTRODUCTION

The Robeson upper bound curve (1) shows a performance trade-off between permeability and ideal selectivity for polymeric membranes. The theoretical explanation of this upper bound curve (2, 3) suggests that homogenous membranes produced from classical polymers have a limited performance. Modifications in the physical and chemical structures of polymeric membranes have been carried out to overcome this limitation, thus to achieve better separation characteristics (2–5). The incorporation of low molecular-weight additives (LMWA) into polymer matrix has been examined as a promising way to modify membrane performance (6–11).

A polymer/LMWA blend membrane is desired to have a homogenous morphology with nonporous and dense structure, since it is the simplest and most suitable structure to investigate permselective properties of different polymers and the effect of type and concentration of LMWA (9–12). In addition to provision of miscibility of additive and polymer, systematic evaluation of the additive is also carried out at the same time. Interaction capability of additives with polymers should also be considered for compatibility between selected compounds (9–12).

A number of studies have been conducted to investigate the effects of different additives on the structure and performance of polymeric membranes. Usually long aliphatic and polyaromatic based compounds are incorporated into glassy polymers to prepare high performance membrane blends (6–13). These additives generally have a rigid and planar structure and they contain polar atoms such as halogens, nitrogen and oxygen (9, 12, 13).

Maeda and Paul (7) prepared dense and homogenous polysulfone, (PSF), and poly(phenylene oxide), (PPO), membranes by introducing sebacate-, phthalate-, phosphate- and sulfone- based compounds as additives. Their concentrations in the membrane ranged between 10 and 30% by weight. Although additives decreased the permeabilities, the selectivities of membranes for helium over methane and carbon dioxide increased significantly. The change in membrane performance was explained by antiplasticization effect of additives on polymer matrices. Antiplasticization was described as increasing stiffening of polymer with the addition of a low molecular-weight compound due to reduced rate of segmental motions in the polymer chain (7). Ruiz-Treviño and Paul (9) examined the effect of various naphthalene-, bisphenol- and fluorene based additives on the performance of PSF membranes. The antiplasticization effect of those additives was related to the free volume reduction in polymer, which restricted the diffusion of gas molecules through modified PSF membranes. Larocca and Pessan (11) prepared polyetherimide membranes containing 5 to 40% by mol halogen containing polyaromatic additives. They also observed the antiplasticization effect of those additives, which decreased both the glass transition temperature and gas permeabilities of the polymer. The extent of antiplasticization depended on the degree of interaction between the additive and the polymer as well as the concentration of additive in the matrix.

The aforementioned studies imply that the incorporation of additives into a polymer may improve permselective properties of gas separation membranes if polymer-additive pair is selected judiciously (7, 9, 11). Moderately high molecular-weight additives are introduced to modify the polymer at concentrations of 10–30% by weight. The interaction between polymer and additive seems to be an important factor in the preparation of high performance membrane blends.

Objective of this study is the systematic evaluation of the effect of low molecular- weight additives with multifunctional groups on physical, permselective, and structural properties of polymeric gas separation membranes. Additives with multifunctional groups that are capable of interacting with polymer can be more efficient to improve performance of polymeric membranes. Multifunctionality of the additives may allow them to be introduced at small concentrations into membrane blends, and this may lead them to be real additives instead of being a major component of the membrane.

To achieve this, the effect of low molecular-weight additives, containing nitro, amine, and/or hydroxyl functional groups on the structure and performance of polycarbonate (PC) gas separation membranes was investigated. As PC provides the necessary backbone rigidity for good thermal resistance ($T_g = 150°C$, $T_{degradation} = 450°C$) and mechanical behavior while allowing relatively fast gas permeation rates, it was chosen as the matrix polymer (14–16). A number of low molecular-weight compounds were selected as additives by considering their interaction capability toward PC with their multifunctional groups. Their molecular-weight were much smaller and they were used in lower amounts, 1 to 10% (w/w), compared to those employed in the studies mentioned above.

EXPERIMENTAL

Materials

The polymer used for membrane preparation was reagent grade polybisphenol-A-carbonate (PC, Aldrich), with a weight-average molecular-weight of 64,000. Dichloromethane (DCM, Aldrich), which has the normal boiling point of 40°C, was used as solvent. The LMWAs were *p*-nitroaniline (pNA), 4-amino 3-nitro phenol (ANP), 2-hydroxyphenol (catechol) and 2-hydroxy 5-methyl aniline (HMA). They were bought from Aldrich. All LMWAs were reagent grade and used as purchased without any treatment.

Single gas permeability measurements were performed with N_2, H_2, O_2 and CO_2. The gases were obtained from local companies and their purities were higher than 99%.

Determination of Solubilities of LMWAs

The solubility of a LMWA in DCM was determined at room temperature. A small amount of LMWA was vigorously mixed in 10 ml DCM by a magnetic stirrer for at least 3 h. If a clear solution was obtained, more LMWA was put in and mixed for another 3 h. The amount of LMWA was gradually increased until it was not dissolved any more. This amount was noted as the saturation concentration and the solubility of that LMWA.

Membrane Preparation Methodology

Membranes were prepared by solvent-evaporation method developed previously (15, 17–19). A small amount of LMWA was dissolved in DCM, and then PC was added into this solution. The mixture was stirred until PC dissolved completely. The concentration of PC in DCM was kept constant at 7% (w/v) based on the previous study with dense homogenous PC membranes (15). The LMWA/PC ratio was varied between 1 and 10% (w/w) on solvent-free basis as shown in Table 1.

The solution was drop cast on a glass petri dish with a diameter of 10 cm at room temperature and dried at 55°C and 0.9 bar for 45 min in nitrogen. The membrane that was detached from the petri dish was annealed at 55°C for 24 h. Evaporation and annealing temperature and period were also determined previously (15) to prepare dense and homogenous PC membranes by using the same solvent.

Membrane Characterization

Thermal characterization of membranes was carried out by differential scanning calorimeter (DSC, DuPont 910S, TA Instrument). A small piece of membrane was heated at a heating rate of 5°C/min from room temperature to 200°C in nitrogen with a flow rate of 50 cm^3/min. The sample was then cooled to room temperature and heated again to 200°C with the same

Table 1. LMWA/PC ratios in the membrane preparation solution

Membrane	LMWA/PC ratio (w/w%)
pNA/PC	1, 2, 5, 10
ANP/PC	1
HMA/PC	1
Catechol/PC	1

procedure for second scan. The second scan thermogram was used to determine T_g of the membrane. In addition a few membranes were scanned from −100°C to 200°C to be sure about the existence of only one T_g, which was taken as a proof of homogenous, single phase structure of membrane.

The T_g of each LMWA was also determined by DSC. A small amount of powder LMWA was heated to 10°C above its melting point at a rate of 20°C/min; held there for 5 min and quenched to −150°C in liquid nitrogen, and then a second heating scan was carried out.

IR spectra of membranes and LMWAs were obtained by using FTIR spectrophotometer (Equinox 55 model, Brucker Optics Inc.). Membranes were analyzed in the film form, and powder LMWAs were prepared as KBr pellet. The measurements were performed against air in the mid-infrared region. The SEM pictures of membranes were taken by scanning electron microscopy (JSM-6400, JEOL) at an accelarating voltage of 20 kV after coating the samples with gold.

Single Gas Permeability Measurements

Single gas permeabilities through membranes were measured by constant volume variable pressure technique at 25°C using a permeation cell, set-up and methodology which were described previously in detail (15–18). The feed side pressure was initially set to 3.7 bar and kept constant. Before each measurement, both feed and permeate sides were evacuated to less than 0.1 bar and kept in vacuum for 2 h.

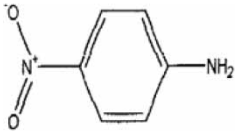
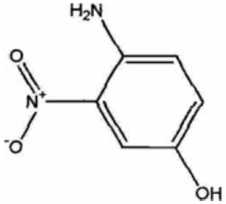
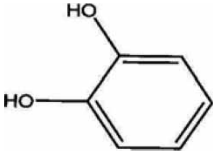
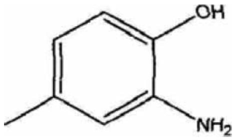
For each LMWA and composition two identical membranes were prepared and the permeability of the gases through each membrane was measured at least twice. The average of all measurements was reported as the permeability. The permeabilities are expressed in a unit of Barrer (1 Barrer = 10^{-10} cm^3(STP) cm/cm^2 s cmHg). Ideal selectivity was defined as the ratio of permeabilities of single gases.

RESULTS AND DISCUSSION

Selection of LMWAs

Table 2 shows the chemical structure and physical properties of the selected LMWAs. The additives with functional groups were selected to increase the probability of interaction between PC and the additive. In their selection the main factor was their possession of amine, nitro, and hydroxyl functional groups. Since amine and hydroxyl groups may interact with carbonyl groups of polycarbonate through hydrogen bonding, as reported by Yong et al. (21) in the preparation of polyimide membranes with 2,4,6-triaminopyrimidine and

Table 2. Physical properties of selected LMWAs

Acronym & Chemical formula	Structure	Molecular weight (20)	Melting point (°C) (20)	Maximum solubility in DCM at room temperature (this study)	Glass transition temperature (°C) (this study)
pNA $C_6H_6N_2O_2$		138.1	148.5	2 w/v %	−72
ANP $C_6H_6N_2O_3$		154.1	154.0	0.25 w/v %	−93
Catechol $C_6H_6O_2$		110.1	105.0	3 w/v %	−54
HMA C_7H_9NO		123.1	137.0	1 w/v%	−86

by Garcia et al. (12) in the preparation of polyamide membranes with hydroxyl containing additives. Besides, nitro being directive and activating group may extend hydrogen bonding capability of LMWAs with PC, by increasing the polarity of hydroxyl and amine bonds (13, 22).

Another important factor to consider when they are used as additives was their solubility in DCM. They all have sufficient solubility in DCM to prepare homogenous membrane casting solutions in this study. In addition to these conditions, their melting points are higher than the annealing temperature of the membranes so that they are expected to be solid in the membrane at room temperature and form stable blends with PC (12, 21). Many low molecular-weight compounds other than those listed in Table 2 were also examined based on these criteria but due to their lack of sufficient solubility in DCM they could not be used as additives.

Table 2 also shows the experimentally determined T_g values of each additive. All additives have T_gs appreciably lower than 0°C. Among them, catechol has the highest, and ANP has the lowest glass transition temperature.

Membrane Characterization

The morphology of membranes was determined from cross-sectional and surface SEM images. In Fig. 1a, the cross-sectional SEM image of a 5% (w/w) pNA/PC membrane was shown. No difference was observed between the cross-sectional and surface views of the membrane, which has a dense and homogeneous structure. A similar morphology was also observed in the membranes prepared with 1 and 2% (w/w) pNA and with other LMWAs at 1% (w/w) concentration. Thicknesses of all membranes were in the range of 40–45 μm based on the SEM measurements.

When visually inspected all membranes were uniform and transparent except the one with 10% (w/w) pNA, which consisted of small yellow-colored regions in addition to transparent regions. The cross-sectional and surface SEM images of a yellow-colored region were shown in Fig. 1b and 1c, respectively. The membrane had a thickness of approximately 80 μm. The bright tracks on the image are likely to be pNA agglomerates. As solvent evaporated some of the pNA was probably phase separated, leading to agglomerates. This suggests that maximum pNA concentration in a homogenous pNA/PC blend should be less than 10% (w/w), therefore higher pNA concentrations were not attempted. The inspection of transparent regions by SEM showed a homogeneous structure, therefore further characterization of 10% (w/w) membranes was performed on transparent regions.

Figure 2 shows the FTIR spectra of pure PC and pNA besides pNA/PC membranes. The FTIR spectra of pure pNA showed amine stretching peaks at 3484 cm^{-1} and at 3360 cm^{-1}, and an amine bending peak at 1634 cm^{-1} (23). As the concentration of pNA increased, those peaks appeared strongly, however, the amine stretching peaks shifted to the higher frequencies, and

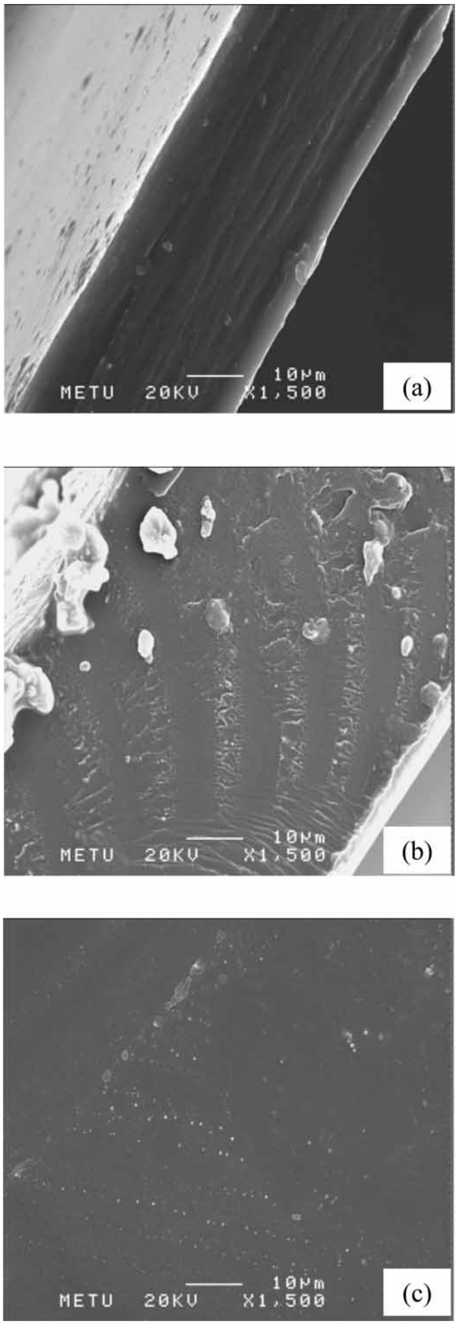


Figure 1. Cross-sectional SEM micrographs of (a) pNA/PC (5 w/w%); (b) pNA/PC (10 w/w%) and surface SEM micrograph of (c) pNA/PC (10 w/w%).

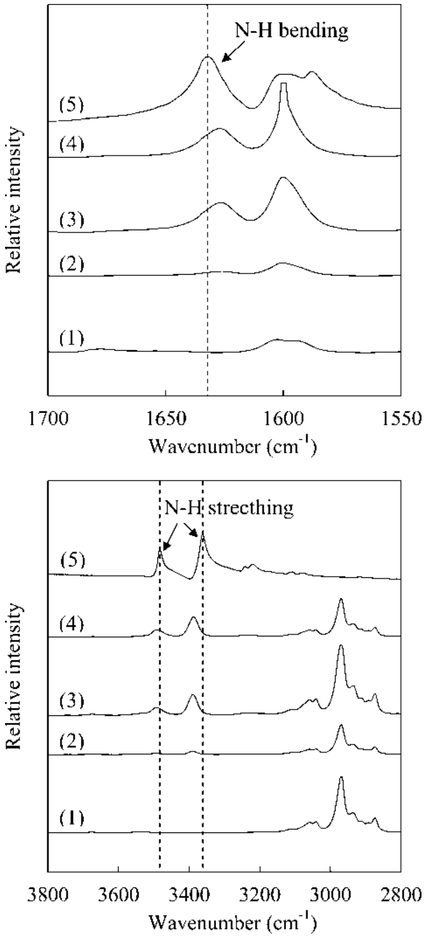


Figure 2. FTIR spectra of pNA powder, pure PC membrane and pNA/PC blend membranes at (a) 1700–1550 cm^{-1} and (b) 3800–2800 cm^{-1} wavenumber regions: (1) PC; (2) pNA/PC (2 w/w%); (3) pNA/PC (5 w/w%); (4) pNA/PC (10 w/w%); (5) pNA powder.

the amine bending peak shifted to the lower frequencies and broadened. The shift and broadening of amine peaks of pNA can be attributed to an interaction between pNA and PC matrix. Yong et al. (21) also observed similar shifts in amine stretching and bending peaks of 2,4,6-triaminopyrimidine (TAP) in polyimide matrix and proposed that these shifts indicate a hydrogen bond between the carbonyl group of polymer and the amine group of TAP.

A typical DSC thermogram of a pNA/PC blend membrane is depicted in Fig. 3. For all membranes, in the selected concentration range, a distinctive single T_g was observed. In addition, for some selected membranes the DSC

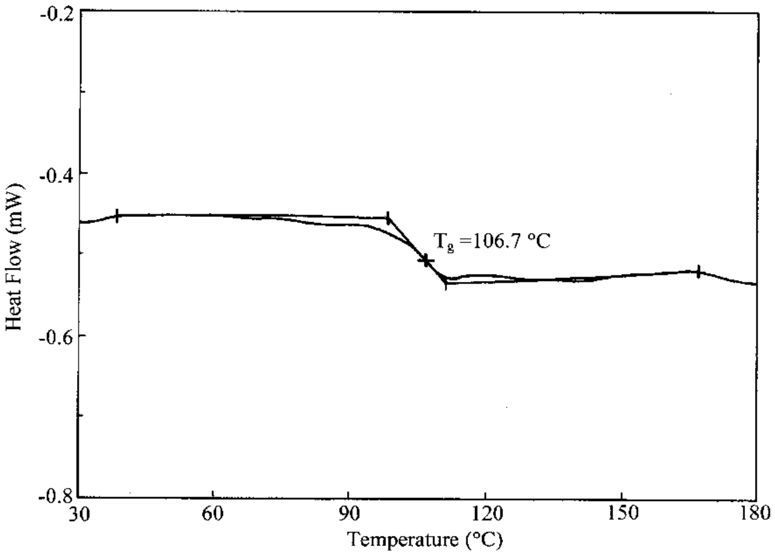


Figure 3. The DSC thermogram of a pNA/PC (5 w/w%) blend membrane.

thermograms obtained in wide temperature region, −100°C to 200°C, were indicated a presence of only one T_g demonstrating the formation of homogenous single phase blends (12, 24, 25).

The T_g of membranes decreased with increasing concentration of pNA in membrane formulation (Fig. 4) and they were related to the pNA

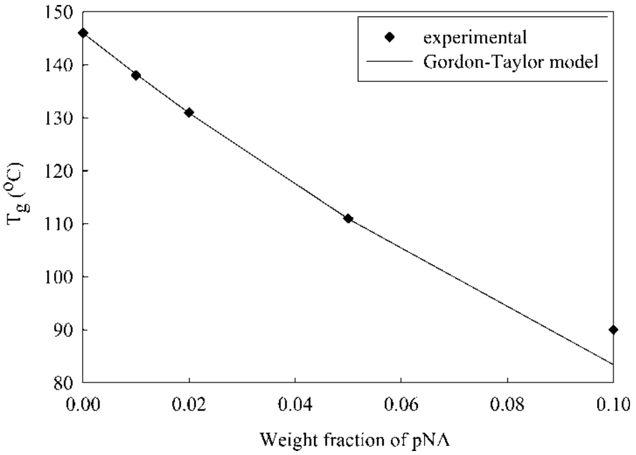


Figure 4. Effect of pNA concentration on glass transition temperature of PC membranes.

concentration by the Gordon-Taylor model (Eqn. 1) (9, 10). In this model, K is an adjustable parameter that depends on the types of the polymer and LMWA and the extent of interaction between them.

$$T_g = \frac{w_a T_{ga} + K w_p T_{gp}}{w_a + K w_p} \tag{1}$$

where subscripts a and p stand for LMWA and polymer, respectively, and w is the weight fraction of the species in the membrane.

Gordon-Taylor equation is a model relating the T_g of a blend to the weight fraction and T_gs of pure components when antiplasticization occurs (9–12). As it fits well with the measured T_gs of pNA/PC membranes, except for the membrane with 10% (w/w) pNA, we may speculate that an antiplasticization type interaction occurs between pNA and PC. For the membrane with 10% (w/w) pNA, the homogeneous region probably had a lower concentration than 10% (w/w), hence it deviated from the model.

The value of K for pNA/PC membranes was found as 0.28 by nonlinear regression analysis, which is similar to the K values reported for PSF-naphthalene membranes, where PSF matrix was antiplasticized by naphthalene (9).

The effect of different low molecular-weight additives on T_g of PC was determined by preparing membranes with 1% (w/w) LMWA (Table 3). All LMWA containing membranes had lower T_g than pure PC had. The largest shift from the T_g of pure PC was observed for catechol/PC membrane despite cathecol has the highest pure substance T_g (Table 2). Similarly ANP, with the lowest pure substance T_g, gave rise to the smallest shift.

The extent of shift from the T_g of pure PC depends on both the T_g of pure LMWA and the degree of interaction between LMWA and PC. Ruiz-Treviño and Paul (9) observed that the extent of shift increased as the T_g of pure additive decreased. However, Larocca and Pessan (11) showed that the shift can be smaller for an additive with a higher T_g if the polymer and additive interact strongly. This suggests that the higher the T_g of LMWA/PC membrane is, the stronger the interaction possibility. Thus, pNA, HMA and ANP had stronger impact on PC matrix than cathecol.

Table 3. Glass transition temperature (T_g) of PC membranes prepared with different LMWAs (LMWA/PC = 1 w/w%)

Membrane	T_g (°C)
PC	146
ANP/PC	140
pNA/PC	138
HMA/PC	136
Catechol/PC	130

Membrane Performance

A series of reproducibility experiments were carried out with PC/LMWA membranes by measuring the permeability of each gas through a particular membrane at least twice. The standard deviations between successive runs were in between 0.4 and 2.4%. Two membranes, which were prepared in different times with similar conditions, were also tested. The standard deviation between single gas permeabilities of those membranes was less than 5.7%, which confirms the reproducibility of membrane preparation and test methods followed in the present study.

Permeabilities and selectivities of pNA/PC membranes are presented in Table 4. Single gas permeabilities through pNA/PC membranes were lower than those of pure PC membrane. The largest decrease was observed in N_2 permeability. Its permeability decreased from 0.27 Barrer to 0.13 Barrer even with the addition of 1% (w/w) pNA. In contrast the smallest decrease was observed in H_2 permeability. As opposed to the permeabilities, selectivities of pNA/PC membranes for H_2, O_2 and CO_2 over N_2 were higher than the selectivities of pure PC membranes. A significant improvement in selectivities was achieved by adding a very small amount of pNA into the membrane formulation. Selectivity improvement is especially noticeable for H_2/N_2 system. Since hydrogen has the smallest kinetic diameter, its permeability may be influenced to a lesser degree from reduction of free volume or from motion restrictions due to stiffening caused by the antiplasticization (7).

In order to investigate the effect of the chemical structure of LMWA on the performance of PC membrane, membranes were prepared at a LMWA/PC ratio of 1% (w/w). The nitrogen permeabilities of PC/LMWA membranes are shown in Fig. 5 and the selectivities are reported in Table 5. All LMWAs decreased the permeability of nitrogen and increased the selectivities of H_2/N_2, O_2/N_2 and CO_2/N_2, yet the permeabilities and selectivities of PC/LMWA membranes were similar with each other although their chemical structures are very different. Adding low molecular-weight compounds with

Table 4. Permeabilities and selectivities of pNA/PC membranes at different pNA weight percentages (measured at 25°C, feed side pressure was 3.7 bar)

% Weight of pNA	Permeability (Barrer)[a]				Selectivity		
	N_2	H_2	O_2	CO_2	H_2/N_2	O_2/N_2	CO_2/N_2
0	0.27	11.5	1.5	5.5	42.6	5.6	20.4
1	0.13	10.8	1.2	4.8	83.1	9.2	36.9
2	0.10	9.6	1.0	3.6	96.0	10.0	36.0
5	0.07	7.6	0.9	3.5	108.6	12.9	50.0
10	0.04	5.5	0.4	1.4	137.5	10.0	35.0

[a] 1 Barrer = 1×10^{-10} cm^3 (STP) cm/cm^2 s cmHg.

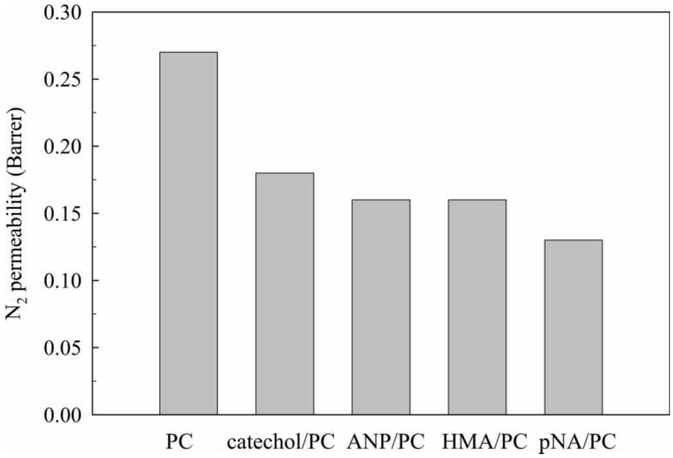


Figure 5. N_2 permeabilities of PC membranes prepared with different LMWAs. (LMWA/PC= 1 w/w%).

functional groups (even at low amounts) into PC membrane formulation decreased the permeabilities of all gases, and increased the selectivities with respect to nitrogen. Therefore, our data showed that all of the LMWAs we used may stiffen the polymer matrix, which associates with a decrease in free volume and restricts the diffusion of gas molecules through the membrane, so that gas permeabilities decrease.

Antiplasticization also influences the T_g of PC, thus the decrease in permeabilities can be correlated with the depression of T_gs. The largest change in T_g was observed for catechol/PC membrane that has the lowest decrease in permeability. On the other hand, the lowest T_g reduction corresponded to the highest reduction in permeability as in the case of pNA/PC membrane.

The separation performance of the PC membrane blends prepared at different concentrations of pNA additive was plotted on upper bound trade-off curve for H_2/N_2 and O_2/N_2 gas pairs in Fig. 6 and Fig. 7,

Table 5. Selectivity results of PC membranes prepared with different LMWAs (LMWA/PC = 1 w/w%)

	Selectivity		
Membrane	H_2/N_2	O_2/N_2	CO_2/N_2
Pure PC	42.6	5.4	20.2
pNA/PC	82.8	9.3	36.8
ANP/PC	71.3	9.4	36.3
HMA/PC	75.0	8.8	38.1
Catechol/PC	68.3	8.9	36.7

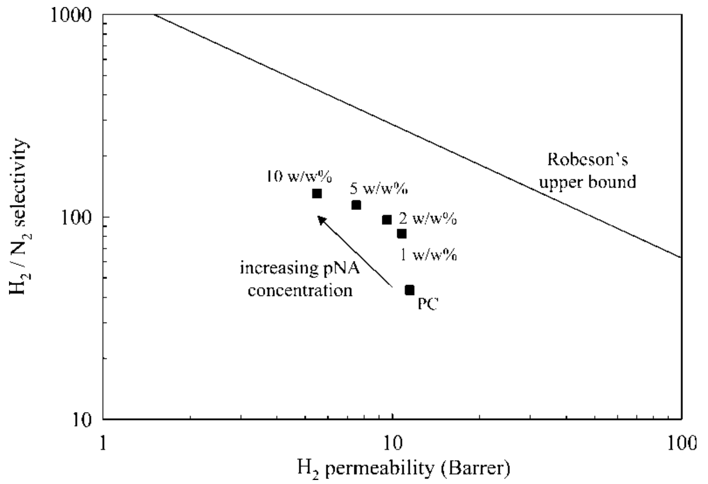


Figure 6. H_2/N_2 selectivity and H_2 permeability of pNA/PC blend membranes on Robeson's upper bound trade off curve.

respectively. The region of improved trade-off was defined as the above or to the right of the upper bound line (1). The improvement in separation performance is apparent for the O_2/N_2 pair with increasing pNA concentration. It is remarkable to point out that this performance improvement was achieved by adding small amounts of our LMWA. On the other hand, for the H_2/N_2 gas pair an abrupt improvement in performance was observed

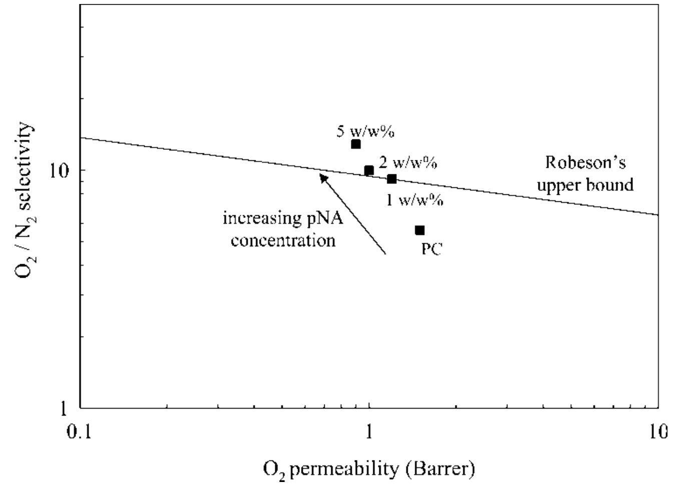


Figure 7. O_2/N_2 selectivity and O_2 permeability of pNA/PC blend membranes on Robeson's upper bound trade off curve.

initially, then it leveled off near to the upper bound line and left parallel to the left side of the line.

Apparently, the addition of pNA into PC membrane matrix results in a better trade-off between permeability and selectivity than the pure PC membrane. Similar improvement was also observed with the other additives studied, although they were used at a concentration of 1% (w/w) in PC matrix.

CONCLUSIONS

Dense and homogenous polycarbonate membranes containing low molecular-weight compounds with multifunctional groups were prepared. An improvement in the gas separation performance of the membranes was achieved with the addition of even a very small amount of LMWA into membrane formulation.

Despite the different functional groups of LMWAs, their effect on the PC membrane performance was similar. They all decreased the permeabilities and increased the selectivities of PC membrane due to their antiplasticization effect on PC. In addition to this, the LMWA containing membranes had a lower T_g than pure PC. Thus, the characterization and performance results of the membranes indicated a strong interaction between PC and additives.

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