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Research paper

The effect of humidity on the CO_2/N_2 separation performance of copolymers based on hard polyimide segments and soft polyether chains: Experimental and modeling

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Abstract

In this work, we studied two copolymers formed by segments of a rubbery polyether (PPO or PEO) and of a glassy polyimide (BPDA-ODA or BKDA-ODA) suitable for gas separation and CO_2 capture. Firstly, we assessed the absorption of water vapor in the materials, as a function of relative humidity (R.H.), finding that the humidity uptake of the copolymers lies between that of the corresponding pure homopolymers values. Furthermore, we studied the effect of humidity on CO_2 and N_2 permeability, as well as on CO_2/N_2 selectivity, up to R.H. of 75%. The permeability decreases with increasing humidity, while the ideal selectivity remains approximately constant in the entire range of water activity investigated. The humidity-induced decrease of permeability in the copolymers is much smaller than the one observed in polyimides such as Matrimid® confirming the positive effect of the polyether phase on the membrane performance.

Finally, we modeled the humidity-induced decrease of gas solubility, diffusivity and, consequently, permeability, using a suitable approach that considers the free volume theory for diffusion and LF model for solubility. Such model allows estimating the extent of competition that the gases undergo with water during sorption in the membranes, as a function of the relative humidity, as well as the expected reduction of free volume by means of water molecules occupation and consequent reduction of diffusivity.

Keywords: CO_2 capture; Humid gas permeation; Transport properties in polymeric membranes; Water vapor sorption; Modeling

1. Introduction

Glassy polyimides represent an important class of materials tested for gas separation and CO_2 capture [1,2], due to their high temperature and chemical resistance and highly tunable gas selectivity [3]. Due to their glassy state at room temperature, as reported by many authors [4–8], they are affected by physical aging, which makes them less attractive for membrane separation systems. In addition polyimides are sensitive to plasticization, which leads to increase of permeability along with a rapid decrease of process selectivity [9]. Moreover polyimides are hydrophobic or weakly hydrophilic [1]. On a practical point, it is well known that condensable components, in particular water, present in the gaseous mixture, undergo competitive sorption with CO_2 in hydrophobic membrane. The higher condensability promotes H_2O in the competition with other penetrants for sorption in the

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microvoids of the material. The CO_2 and CH_4 permeabilities are reported to decrease up to 60% in 6FDA-TMPDA and Matrimid® polyimides increasing the water activity of the feed stream [10,11]. Ansaloni et al. [12] extensively studied the effect of water on the permeation of He, N_2, CH_4 and CO_2 in Matrimid®, observing that permeability decreases with relative humidity (R.H.) in a similar way for all gases. It was hypothesized that behavior is due to the fact that sorbed water molecules partially occupy the polymer free volume, thus making it unavailable for gas diffusion and reducing the diffusivity of gases with respect to dry conditions. Such mechanism was also confirmed qualitatively and quantitatively by modeling analysis [12].

Finally, polyimides possess an extraordinary ability to separate complex mixtures of gases in many applications, due to their tunable free volume cavities. Usually, these materials have high selectivity to CO_2 but have moderate permeability [1]. In order to increase permeability without compromising permselectivity, one of the possible approaches is the introduction of CO_2-phylic moieties able to interact with the targeted gas [13−15].

Okamoto et al. [16] synthesized poly(ethylene oxide) (PEO) containing poly(ether imide) copolymers with microphase-separated structures, consisting of microdomains of rubbery polyether segments and of glassy polyimide segments. It was observed that the permeation occurred through PEO domains while the glassy phase contributed to film formation and mechanical properties [16]. In these materials, high CO_2 solubility in the polyether phase guaranteed high separation performance both in terms of productivity and separation efficiency. In particular, for the different polyimides considered, both CO_2 permeability and CO_2/N_2 selectivity increased by increasing PEO content in the copolymers, which was attributed to the solubility selectivity surpassing the diffusivity selectivity. It was also observed that the CO_2 permeability increases with increasing the polyether chain length, due to improved phase segregation in the membranes.

After the work of Okamoto, many researchers have intensively investigated PEO-containing poly(ether imide) copolymers membranes for CO_2 separation applications. In recent years, Tena et al. [14] have found direct relationship between permeability and phase segregation, which increases with thermal treatment of copolymers. It has been observed that permeability increases when polyether content increases in the material, without substantial effect on ideal permselectivity, and similar results have been obtained also for copoly(ether imides) obtained from the polyimide derived from 3,3′,4,4′-bypheniltetracarboxyilic dianhydride (BPDA) and 4,4′-oxydianiline (ODA) (BPDA-ODA) and polypropylene oxide [13]. Another positive aspect is the relative low temperature necessary for the complete imidization of copolymers, compared with those temperatures, above 300 °C, needed to achieve complete imidization of polyimides. Finally, these copoly(ether imides) are CO_2 − selective, due to high affinity of polyether with carbon dioxide, which guarantees high solubility selectivity.

One can also see the incorporation of rubbery phase into glassy phase as a strategy to reduce or avoid the physical aging typical of glassy materials. Furthermore, the hydrophilic nature of polyethers such as PEO or poly(propylene oxide) (PPO) segments may reduce the drawbacks observed during humid gas permeation in polyimides. Indeed, previous works which investigated the gas separation performance of polymers and copolymers based on different polyethers, indicate a good stability of the performance of those membranes in humid conditions [17,18].

2. Experimental

2.1. Materials

In this work, two copolymers have been characterized. In particular the first material, BPDA-PPO4000-ODA 2/1, is made by 3,3′,4,4′-bypheniltetracarboxyilic dianhydride (BPDA), 4,4′-oxydianiline (ODA) and bis(2-aminopropyl) poly(propylene oxide) (PPO) with nominal molecular weight of 4000 g/mol. It contains 43.50 wt% of polyether PPO [13]. The second copolymer, BKDA-PEO6000-ODA 4/1, is made by 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BKDA), 4-4′oxydianiline (ODA) and α,ω-Diamine poly(ethylene oxide) (PEO) with nominal molecular weight of 6000, and it contains 60.40 wt% of PEO [14].

Polymers were synthesized by mixing polyether diamine with aromatic diamine in appropriate ratio in N,N′-dimethylacetamide (DMAc). Reaction mixture thus obtained was cooled down to 0 °C and dianhydride was added. Subsequently, the reaction was stirred overnight at room temperature obtaining high viscosity solution, which was diluted in DMAc to the appropriate viscosity for casting. For more details we refer to previous works [13,14], and we report chemical structures of monomers in Fig. 1.

As observed in a previous work [19] from volumetric data, and testified by experimental and modeling sorption results,

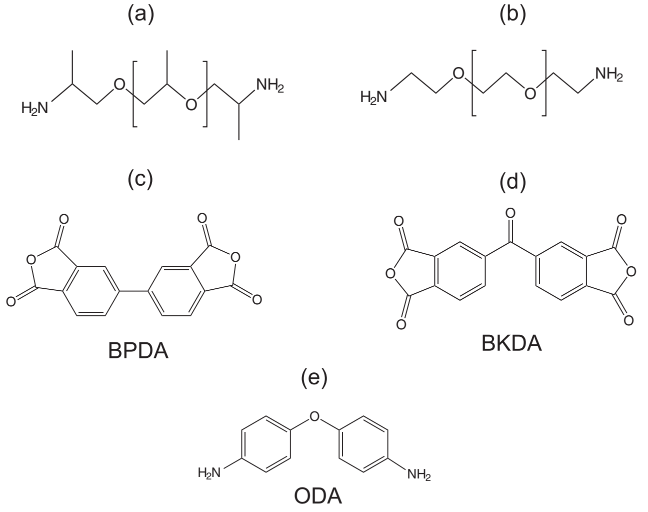

Fig. 1. Structure of (a) diamino-terminated PPO, (b) diamino-terminated PEO, (c) BPDA, (d) BKDA and (e) ODA [13,14].

these materials show negative mixing volume, which can be attributed to glassy free volume reduction due to partial occupation of rubbery phase during copolymerization reaction.

2.2. Water sorption experiments

Water vapor sorption experiments have been carried out in a quartz spring microbalance (QSM), already described in previous papers [20–23] on the copolymer membranes at 30 °C. The system is characterized by a quartz spring (Deerslayer, sensitivity of 1 mm/mg and maximum hold of 100 mg) housed inside a water jacketed glass column for temperature control, which is connected by means of stainless steel tubing and valves to a vacuum pump and to a water reservoir in which the pressure is measured with a capacitive transducer (Full Scale 1000 mbar). The specimen is attached to the end of the spring, whose elongation during sorption steps is monitored by a CCD camera.

Water sorption uptake during time can be calculated according to Hooke's law as follows:

$$M(t) = k(x - x_0) + F_b \tag{1}$$

where k is the constant of the spring, x and x_0 are current and initial spring extension and F_b is the buoyancy contribution, which is quite negligible in the present study, due to low pressure of water vapor.

Liquid water sorption measurements were carried out with a simple blot and weigh method, where the membrane sample is immersed into liquid deionized water at 30 °C and then rapidly removed and weighed at regular time intervals until equilibrium is reached.

2.3. Permeation experiments

The effect of the presence of water vapor on the mass transport properties of BPDA-PPO-ODA 2/1 has been characterized investigating the permeability of N_2 and CO_2 at 30 °C, and relative humidities ranging between 0 and 90%, with upstream pressure of 1 bar and vacuum on the downstream side.

Gas permeability tests were carried out in a closed volume, variable pressure apparatus, described in previous works and equipped with vacuum Swagelok VCR fittings [12,22–25]. Leak tests were performed prior to each permeation experiment, revealing that leakages are negligible compared to the gas fluxes due to permeation across the membrane. In these experiments, the concentration of humidity in the membrane is kept constant during the permeation test, so that the only species diffusing across the membrane is the gas. In particular the permeability, P_i, can be calculated in the same fashion as in the case of pure gases, from the derivative of the downstream pressure p_i^{down} at steady state (ss), the donstream volume V_d, the surface of the membrane A, the temperature held constant T, the membrane thickness l, and the partial pressure difference of component i across the membrane $(p_i^{up} - p_i^{down})$:

$$P_i = \left.\frac{dp_i^{down}}{dt}\right|_{ss} \frac{V_d}{RTA} \frac{l}{(p_i^{up} - p_i^{down})} \tag{2}$$

3. Theoretical background

3.1. Modeling fluid solubility in rubbery-glassy copolymers

First of all, we modeled competitive sorption effects between the gases and water in the membrane.

We assumed that the rubbery and glassy phases of the membrane are randomly distributed, and the system is like a composite material where the properties are a simple combination of the properties of the two phases. Rubbery and glassy states have different thermodynamic behavior: the rubbery phase is in equilibrium and its density can be calculated from an Equation of State (EoS); the sorption in such phase can be modeled with an Equation of State model, like the Lattice Fluid one [26].

The glassy phase is in a pseudoequilibrium state where the density of the solid has a lower value than the equilibrium one. An extension of the EoS model valid for glassy polymers, is the Non Equilibrium Theory for Glassy Polymers (NET-GP) approach, that adopts an additional state variable to univocally define the state of the glassy systems and of its mixtures, namely the polymer density. A non equilibrium version has been proposed for the LF EoS models for polymers, generating the NE-LF model, that adopts the same set of parameters proposed by the original theory [27–29].

The LF models require knowledge of the pure components characteristic parameters, T^*, p^*, ρ^* of polymers and penetrants, which can be obtained from best fit of LF EoS with vapor-liquid equilibrium data for gases and PVT data for polymers.

We report in the Supplementary Information the main equations and parameters of lattice fluid models. The models also contain a binary gas-polymer interaction parameter, k_{ij}, which affects the characteristic pressure of the gas-polymer mixture and can be adjusted on pure gases solubility data.

In general, in the case of a rubbery polymer the solubility of fluid i is calculated by solving the phase equilibrium condition between gas (G) and solid (S) phase, together with the equation of state for the density of polymeric mixture:

$$\mu_i^{(G)}\left(T, p, \underline{y}\right) = \mu_i^{(S)}(T, p, \underline{\omega}) \tag{3}$$

For the glassy phase, the polymeric mixture (polymer + gas dissolved) density is provided to the model from experimental data, or adjusted on solubility data:

$$\mu_i^{(G)}\left(T, p, \underline{y}\right) = \mu_i^{(S)}(T, p, \rho_{POL}, \underline{\omega}) \tag{4}$$

In general, for gases like CO_2 the density of the polymeric mixture changes with gas pressure due to swelling; however, authors agree on the fact polymer density decreases linearly with increasing gas pressure, and thus only one additional parameter is required to account for swelling, namely the swelling coefficient k_{sw}, which is the ratio between relative polymer volume increase and gas pressure.

For a copolymer membrane formed by a glassy (G) and rubbery (R) phase, with a rubbery weight fraction equal to w_R, we recently proposed a simple model for gas solubility in the copolymer, c_{copol}, that invokes the additivity of solubility in the rubbery and glassy phase, c_R and c_G, respectively (equation (5)), as well as the semi-additivity of specific volumes of homopolymers, labeled in a similar fashion (equation (6)) [19]:

$$c_{copol} = w_R c_R + (1 - w_R) c_G \tag{5}$$

$$\widehat{v}_{copol} = w_R \widehat{v}_R^0 + (1 - w_R) \widehat{v}_G \tag{6}$$

In particular, in this approach we consider that both phases contribute to sorption according to their mass fraction in the copolymer (equation (5)): the sorption in the rubbery and glassy phase are estimated using the LF and NELF model, respectively, at each gas pressure. We assume (equation (6)) that the specific volume of the rubbery phase is equal to its pure homopolymer value, indicated by the apex 0, while the glassy phase volume is different from the corresponding value of the pure copolyimide, and is estimated using equation (6) and experimental values for the copolymer specific volume. Previous studies indeed indicate that the rubbery phase occupies part of the glassy phase excess free volume, and thus motivate the choice made for the assumption of the model [19].

Once pure components parameters and adjustable parameters for CO_2-homopolymer mixture were known, the model allowed the completely predictive calculation of CO_2 solubility in the copolymer mixtures, well describing the transition between glassy to rubbery sorption behavior. In Table 1 we report LF-EOS characteristic parameters for pure homopolymers and penetrants considered in this work.

The extension to the mixed gas case, required to calculate the sorption of gases in the copolymers in the presence of water, does not require any particular variation of the model, apart from the estimation of fluid–fluid binary interaction parameters, that has been reported in the following sections.

Table 1
LF EoS pure components parameters.

Component	T^*	p^*	ρ^*	Reference
	K	MPa	g/cm^3	
PPO	542	420	1.096	[19]
PEO	590	620	1.218	[19]
BPDA-ODA	570	480	1.610	[19]
BKDA-ODA	670	600	1.530	[19]
CO_2	300	630	1.515	[27]
N_2	145	160	0.943	[28]
H_2O	670	2400	1.050	[30]

Table 2
Van der Waals volumes for pure homopolymers [32].

Polymer	Van der Waals volume cm^3/g
PPO	0.592
PEO	0.673
BPDA-ODA	0.495
BKDA-ODA	0.490

Also the swelling of the polymeric matrix can be estimated with a simple additive rule as reported in previous works [29].

3.2. Gas diffusivity in presence of humidity

In our permeation tests, the gas diffuses through the membrane in result of a concentration gradient with a prefixed, constant concentration of water molecules absorbed in it. In hydrophobic polymers, water does not swell significantly the matrix, but simply occupies part of the original membrane free volume that is no longer available for the diffusing gas molecules, which partly explains the reduced permeability. To account for such reduction, we used the model proposed by Ansaloni et al. [12]. Such model estimates the reduction of the free volume due to partial occupation by the water vapor molecules, assuming no swelling is induced by water vapor. This assumption leads to the estimation of fractional free volume (FFV) at a certain relative humidity, $FFV_{humid}\,(a_{H_2O})$ as follows:

$$\begin{aligned} FFV_{humid}(a_{H_2O}) &= \frac{\widehat{v}_{pol} - \widehat{v}_{pol}^{occ}}{\widehat{v}_{pol}} - \frac{\widehat{v}_{H_2O}^{occ} \Omega_{H_2O}(a_{H_2O})}{\widehat{v}_{pol}} \\ &= \frac{\widehat{v}_{pol} - 1.3\widehat{v}_{pol}^{VdW} - 1.3\widehat{v}_{H_2O}^{VdW} \Omega_{H_2O}(a_{H_2O})}{\widehat{v}_{pol}} \end{aligned} \tag{7}$$

where the occupied volume of polymer and water, $\widehat{v}_{pol}^{occ}$ and $\widehat{v}_{H_2O}^{occ}$, are estimated using Bondi's rule using the respective Van der Waals volumes, $\widehat{v}_{pol}^{VdW}$ and $\widehat{v}_{H_2O}^{VdW}$. Ω_{H_2O} is the amount of water vapor in the membrane, expressed as grams of water per grams of polymer.

In the case of aromatic-aliphatic copolyetherimides, materials formed by two randomly distributed phases, the dry free fractional volume was estimated with an additive rule as follows [31]:

$$\begin{aligned} FFV_{copol} &= \frac{\widehat{v}_{copol} - \widehat{v}_{copol}^{occ}}{\widehat{v}_{copol}} \\ &= \frac{\widehat{v}_{copol} - 1.3\left(w_R \widehat{v}_R^{VdW} + (1 - w_R)\widehat{v}_G^{VdW}\right)}{\widehat{v}_{copol}} \end{aligned} \tag{8}$$

where $\widehat{v}_R^{VdW}$ and $\widehat{v}_G^{VdW}$ are the van der Waals volume of rubbery and glassy pure homopolymers, respectively, estimated according to the group contributions reported in ref. [32] and reported in Table 2.

In such a way the humid free volume and the diffusion coefficient in humid conditions can be represented by equations (9) and (10) respectively:

$$FFV_{copolhumid}(a_{H_2O}) = \frac{\hat{v}_{copol} - 1.3\left(w_R\hat{v}_R^{VdW} + (1-w_R)\hat{v}_G^{VdW}\right) - 1.3\hat{v}_{H_2O}^{VdW}\Omega_{H_2O}(a_{H_2O})}{\hat{v}_{copol}} \tag{9}$$

$$D_i = A_i \exp\left(-B_i/FFV_{copolhumid}(a_{H_2O})\right) \tag{10}$$

where the constant A_i and B_i depend on the particular penetrant considered. The constant A_i depends on the system temperature and the gas molecular volume and shape, and B_i, while originally labeled as a material constant was later found to depend on the gas kinetic diameter [33–35]. In general, for a fixed gas and chemical class of polymers considered, the value of B_i can also depend on the polymer initial free volume, being smaller for high free volume polymers and larger for low free volume polymers. Indeed, for instance for CO_2 (N_2), a value of B equal to 0.54 (1.44) has been reported in a high free volume polymer like PIM-1, and a value of 3.5 (4.3) in lower free volume matrices based on polysulfone [36]. In this work, due to unavailability of pre-existing data on similar polymers, we used the value of B_i as an adjustable parameter on permeability data.

3.3. Gas permeability in presence of humidity

By combining the previous equations which represent the effect of the presence of humidity in the membrane on the gas solubility coefficient S_i, due to multicomponent sorption, and on the gas diffusivity due to free volume reduction, we obtain a simple, solution-diffusion based [37], equation for the permeability variation as a function of humidity (or water activity a_{H_2O}) as follows:

$$\begin{aligned} P_i(a_{H_2O}) &= D_i(a_{H_2O})\cdot S_i(a_{H_2O}) \\ &= A_i \exp\left(-B_i/FFV_{copolhumid}(a_{H_2O})\right)\cdot S_i(a_{H_2O}) \end{aligned} \tag{11}$$

where A_i and B_i must be adjusted on gas permeability data for each penetrant. In the case of the present work, such procedure can seem poorly predictive as a limited set of permeability data is available for adjusting the values of A_i and B_i, however the model proved successfully also in representing the data at different temperatures with constant values of such parameters [12,23].

4. Experimental results

4.1. Water vapor solubility

The solubility of water vapor has been studied for two samples, BPDA-PPO-ODA 2/1 and BKDA-PEO-ODA 4/1: those materials were picked from a set of materials with different compositions obtained in a previous work because they have a rubbery/glassy ratio that is close to 50/50 and can possibly show more clearly an hybrid behavior. The first material contains 43.50 wt% of PPO, and the second one contains 60.40 wt% of PEO [13,14]. The water vapor solubility isotherms are reported at 30 °C in Figs. 2 and 3, together with the values measured in the corresponding pure homopolymers and taken from the literature. The Figure also reports data relative to the liquid water sorption in BPDA-PPO-ODA 2/1 membrane, which are in line with those relative to water vapor. For the PEO-based copolymer the amount of liquid water sorbed, and the consequent swelling produced, is extremely large and the determination of liquid water sorption with the simple blot and weigh method is inhibited.

Such studies reveal that pure PEO and pure PPO have a similar sorption isotherm [38], while high differences can be observed for the two polyimides, and in particular BKDA-ODA shows solubility which is 50% higher than the solubility of BPDA-ODA at high water activity [39,40]. This aspect was explained by Han et al. [41] considering that BKDA dianhydride shows higher affinity to water than BPDA, due to additional carbonyl group present in the backbone.

When considering the water uptake in the two copolyimides (Fig. 2), one sees that the PEO-based copolymer is characterized by a higher vapor uptake than the PPO-based one, due to its higher content in polyether (60 wt% vs 44 wt % of polyether phase in the copolymer), and also to the higher hydrophilicity of PEO when compared to PPO.

The trends of Fig. 3 indicate that the water uptake in the copolymer, at fixed humidity, lies in between the values of the corresponding pure polyimide and polyether. In the Figures we

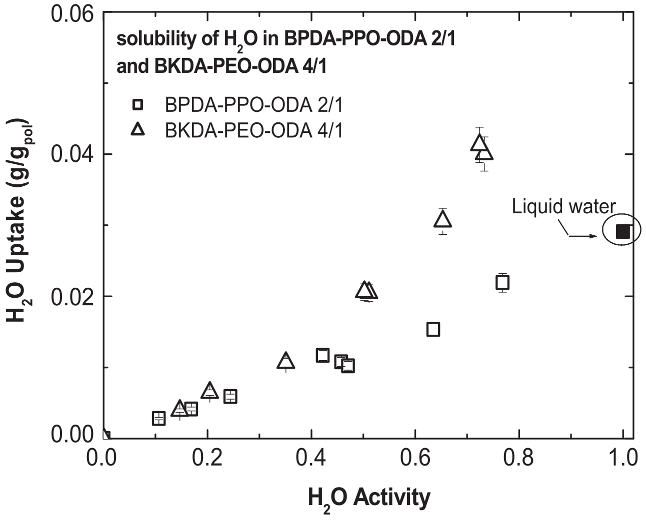

Fig. 2. Solubility of water vapor in BPDA-PPO-ODA 2/1 and BKDA-PEO-ODA 4/1 copolymers at 30 °C.

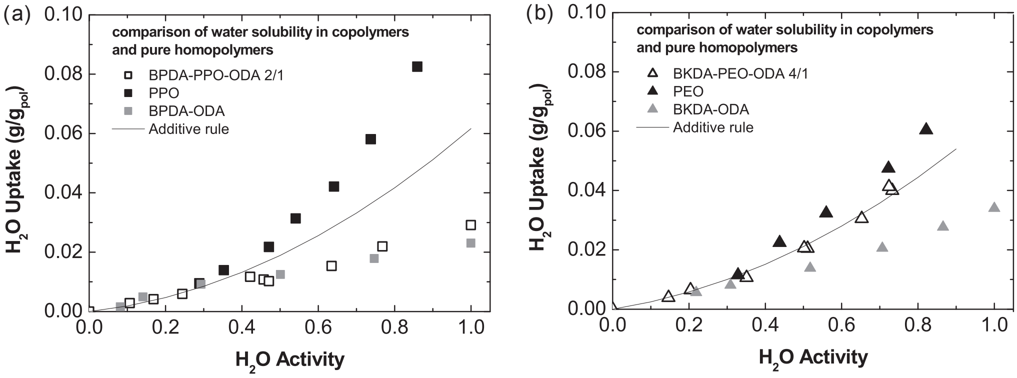

Fig. 3. Comparison of water vapor solubility in BPDA-PPO-ODA 2/1 (a) and BKDA-PEO-ODA 4/1 (b) and corresponding homopolymers PPO, PEO [38], BPDA-ODA [39] and BKDA-ODA [40]. Lines are additive rule.

also report a line representing an additive rule combining the solubility of water vapor in the corresponding homopolymers: the data lie on this line in the case of the PEO-based copolymer, and below the line for the PPO-based one, which is thus less hydrophilic than expected.

In conclusion of this section it is worthwhile to notice that, even if limited, the water molar solubility is higher than gas solubility in the same pressure and temperature conditions. For CO_2, which in general is more soluble than N_2, the solubility is around 5 cm^3(STP)/cm^3 in BPDA-PPO-ODA 2/1 and 2 cm^3(STP)/cm^3 for BKDA-PEO-ODA at 30 °C and 1 bar [16], which correspond respectively to about 8% and 3% of the maximum value obtained for water in the present work (i.e. 64 cm^3(STP)/cm^3 in BKDA-PEO-ODA film). Therefore, there is a relatively higher amount of water molecules than gas molecules in the membrane during gas permeation, and this aspect can explain the observed permeation behaviors, as discussed in the following.

4.2. Gas permeability versus relative humidity

The effect of water vapor uptake on gas permeability has been monitored with humid permeation experiments with CO_2 and N_2 for BPDA-PPO-ODA 2/1 sample at 30 °C and 1 bar upstream pressure, up to 75% relative humidity, as reported in Figs. 4 and 5. In dry conditions, it can be said that, due to higher condensability and smaller kinetic diameter, CO_2 has higher permeability than N_2, 30.1 vs. 1.3 Barrer. As expected and already reported [13], the material is CO_2-selective and its ideal selectivity is equal to 23. The presence of water causes a decrease of the permeability with respect to pure gases values. However, if compared to the reduction of permeability observed in glassy polyimides [10,12], such copolymers show slighter decreases of permeability with relative humidity, as reported in Fig. 7. In particular the permeability decrease with respect to dry gases values is around 12% and 17% for N_2 and CO_2, respectively, at 70% relative humidity and it is a limited reduction compared with 50% reduction of dry gas permeability observed in Matrimid® films.

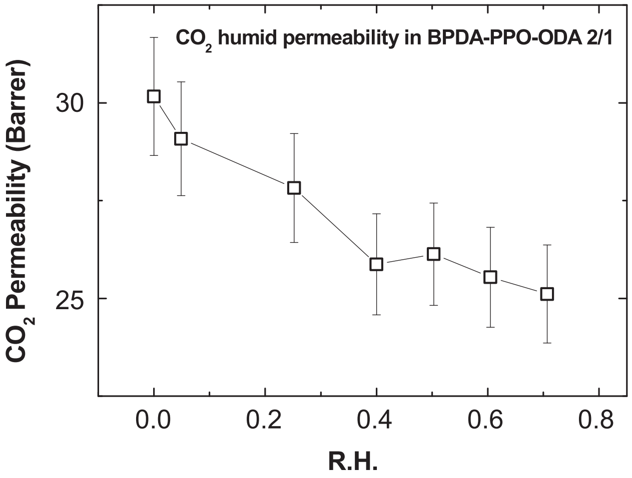

Fig. 4. The effect of relative humidity on CO_2 permeability at 30 °C and 1 bar upstream pressure in BPDA-PPO4000-ODA 2/1 copolymer.

The permeability decrease of the gases considered is similar, as shown in Fig. 6, thus the humidity seem not to impact much the selectivity. The data relative to gas permeability decrease in Matrimid® [11] are reported for comparison.

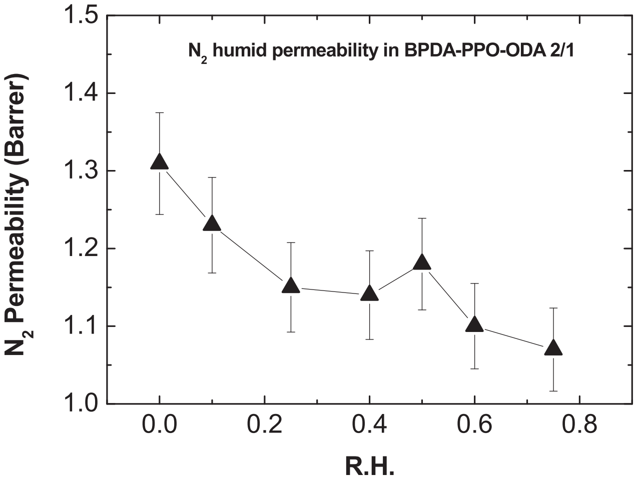

Fig. 5. The effect of relative humidity on N_2 permeability at 30 °C and 1 bar upstream pressure in BPDA-PPO4000-ODA 2/1 copolymer.

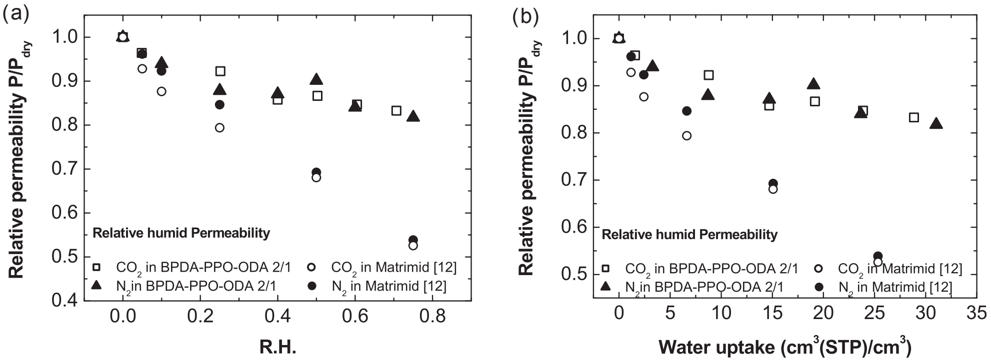

Fig. 6. The effect of relative humidity on BPDA-PPO4000-ODA 2/1 permeability: comparison between CO_2 and N_2 relative permeability variation versus relative humidity (a) and water concentration in the membrane (b).

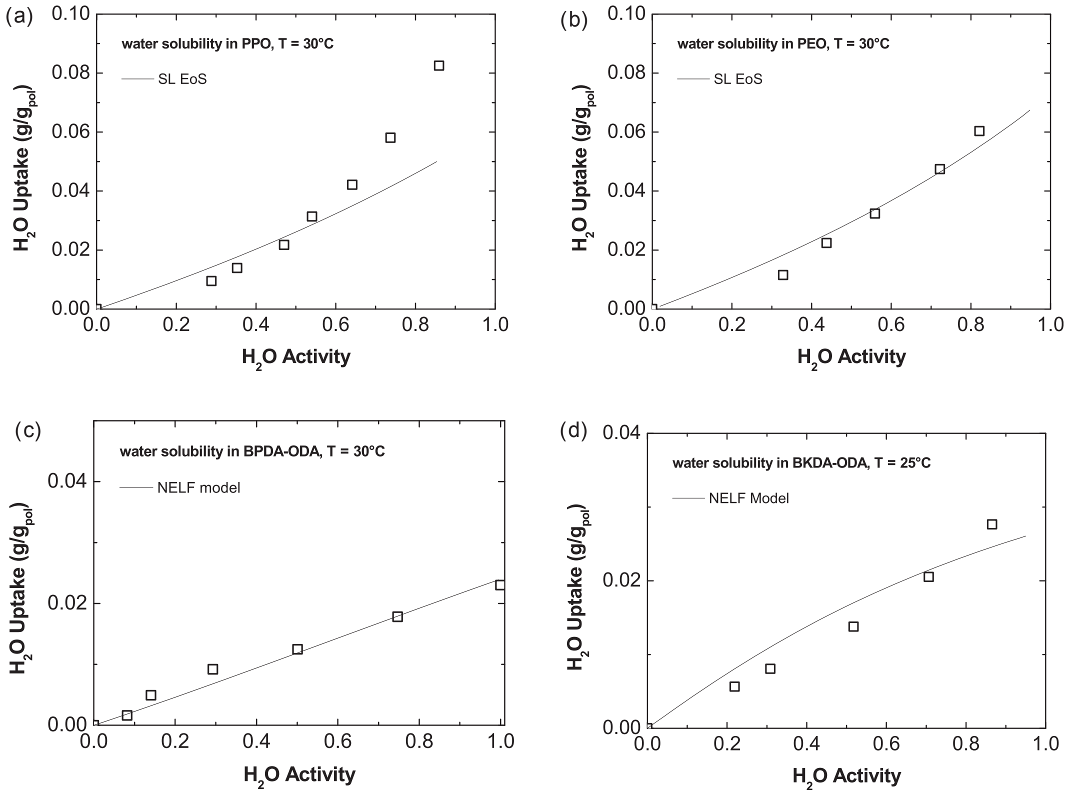

Fig. 7. Modeling of the solubility of water in (a) PPO, (b) PEO, taken from ref. [38] (c) BPDA-ODA taken from ref. [39], (d) BKDA-ODA taken from ref. [40] with LF models.

5. Modeling

5.1. Determination of the binary parameters for solubility modeling in presence of humidity

When we deal with multicomponent sorption, it is important to take into account gas–gas interactions, especially when we consider a system containing CO_2 and water. Interaction parameters for the gas–gas couple considered in this work are reported in Table 3 and they were fitted with LF EoS, for the water-CO_2 mixture, on binary vapor liquid equilibrium experimental data in the temperature range 383–533 K taken from ref. [42] and CO_2 absorption experimental data at 303 K taken from ref. [43]. The interaction water-nitrogen has been obtained from the modeling of nitrogen solubility data at 303 K taken from ref. [43] with LF EoS.

The binary interaction parameters k_{ij} and swelling coefficient k_{sw} for the fluid-polymer pairs have been calculated from literature data of water sorption using LF EoS for PPO [38] and PEO [38] and NELF model for polyimides BPDA-ODA [39] and BKDA-ODA [40]. Results are reported in Fig. 7 while adjustable parameters for water sorption in rubbery

Table 3
Gas-water interaction parameters used in this work.

Components	k_{ij}	Reference	Experimental data source
CO_2–H_2O	−0.117	This work	VLE data 385–533 K from [42], absorption data at 303 K from [43]
N_2–H_2O	0	This work	Solubility data at 303 K from [43]

and glassy phases are reported in Table 4. It has to be noted that for all the homopolymers the interaction parameter k_{ij} is a large negative number, resulting in an unexpected higher solubility due to favorable interaction between water and polymers. The very large values are due to the fact that the LF model was not conceived for polar or associating substances like water and oxygen moieties of polyethers, and a large correction of the model estimate of the energetic interactions is required. In addition the swelling coefficient is null for both glassy polyimides considered, as for the case of carbon dioxide and nitrogen sorption [19], due to their high rigidity and low tendency to swell in presence of fluid sorption.

The results of the modeling of water vapor solubility in BPDA-PPO-ODA 2/1 and BKDA-PEO-ODA 4/1 are reported in Fig. 8 together with the comparison with the experimental data. As for the case of CO_2 sorption [16] it can be observed that the model allows to reproduce accurately experimental data, confirming the validity of the model even in the case of water vapor.

5.2. Calculation of gas solubility in the presence of humidity

In Fig. 9 the relative solubility coefficients of CO_2 and N_2 are reported with respect to dry gas solubility calculation, in the pure homopolymers and in the copolymers considered in this work. It can be observed that the solubility of CO_2 in neat PPO slightly increases in the presence of water, while the solubility of the same gas in the pure glassy homopolymer BPDA-ODA and in the copolyimide decreases with increasing humidity, due to the prevalence of competitive sorption effects. Nitrogen solubility is lower in the presence of water, in all the polymer inspected (PPO, BPDA-ODA and BPDA-PPO4000-ODA 2/1) due to competition effects for the sorption in the matrix. The highest decrease can be observed for nitrogen, which is less soluble in both the copolymeric matrix and water. In particular, solubility decreases of around 20% for CO_2 and 25% for N_2 in the polyimide, due to competition effects. In pure PPO, the CO_2 solubility increases up to 2.5% at 75% R.H., due to favorable interactions between absorbed water and carbon dioxide, for nitrogen the solubility decay is less pronounced than in the glassy polyimide, around 10% at 75% R.H. Such results indicate the important and negative effect that the humidity has on the solubility of gases in the membrane, which, together with the reduction of free volume reported, can justify and explain the observed trends of permeability with humidity.

Table 4
Binary water-polymer parameters for LF model.

Homopolymer	k_{ij}	k_{sw} MPa^{-1}	Reference	Source of experimental water solubility data
PPO	−0.250	–	This work	[38]
PEO	−0.125	–	This work	[38]
BPDA-ODA	−0.125	0	This work	[39]
BKDA-ODA	−0.078	0	This work	[40]

Similar qualitative trends can be observed for BKDA-PEO-ODA 4/1 and relative homopolymers. In particular due to higher content of hydrophilic polyether phase we have a slight increase of CO_2 humid solubility, around 1% with respect to dry conditions. As for the previous case considered, N_2 solubility decreases around 10% at 75% R.H., but the behavior of the copolymer is very comparable to the polyether phase, due to high rubbery phase content in the material.

5.3. Calculation of gas permeability in presence of humidity

Humid permeability data have been modeled with equation (11), by taking into account the effect of water on gas solubility, and the results are reported in Fig. 10. The model results for the impact that water has on fractional free volume and diffusivity is reported in the Supplementary Information. The two adjustable parameters are listed in Table 5, and it can be observed how *A* seems to scale with kinetic diameter, increasing with it, being CO_2 kinetic diameter 3.3 and N_2 one 3.64 [44]. On the contrary, the parameter *B* is the same for CO_2 and N_2 in this kind of material.

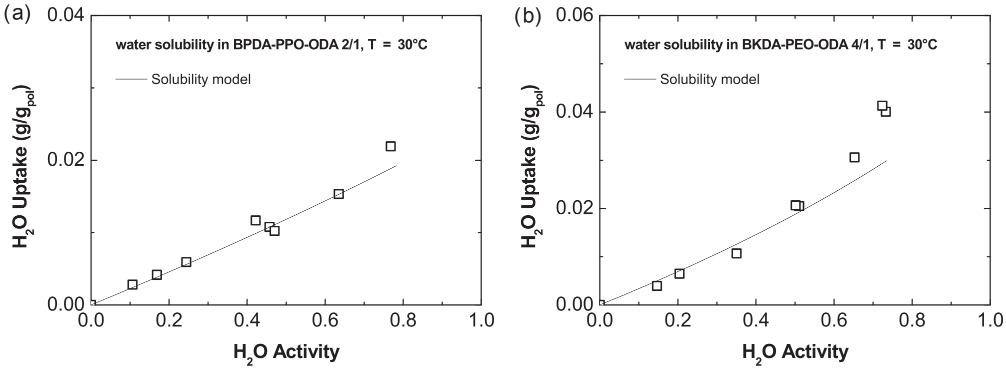

Fig. 8. Solubility modeling of water in (a) BPDA-PPO4000-ODA 2/1 and (b) BKDA-PEO6000-ODA 4/1 at 30 °C and different water activities.

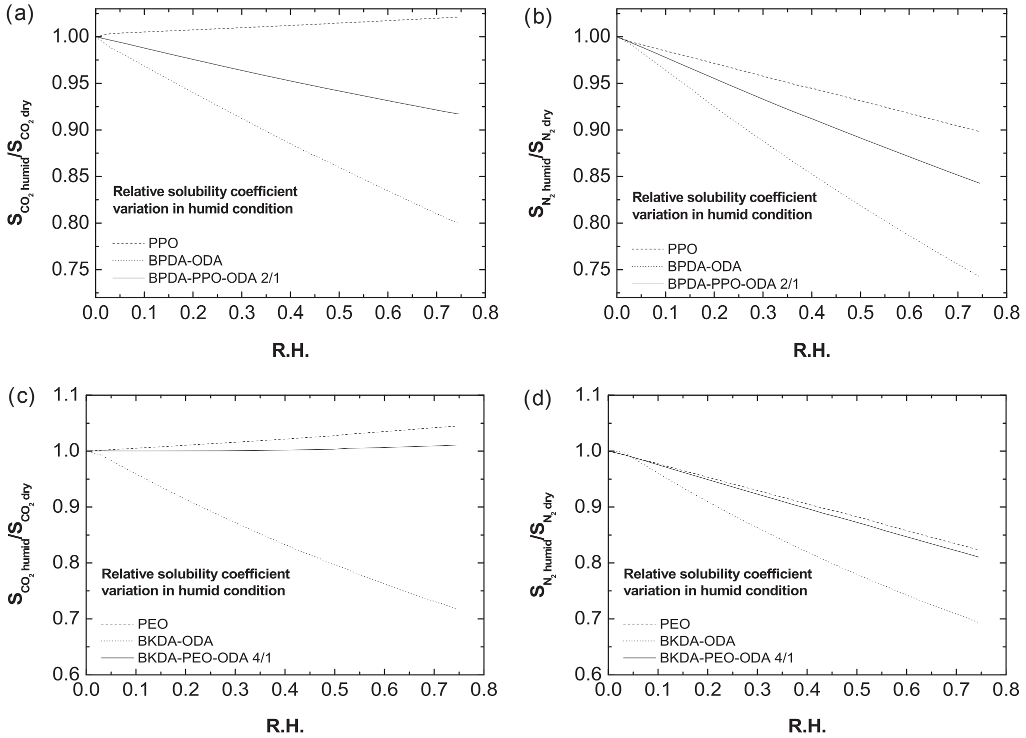

Fig. 9. Relative variation of the solubility coefficients of (a) CO_2 and (b) N_2 in PPO, BPDA-ODA and BPDA-PPO4000-ODA 2/1 and (c) CO_2 and (d) N_2 in PEO, BKDA-ODA and BKDA-PEO6000-ODA 4/1 at 30 °C.

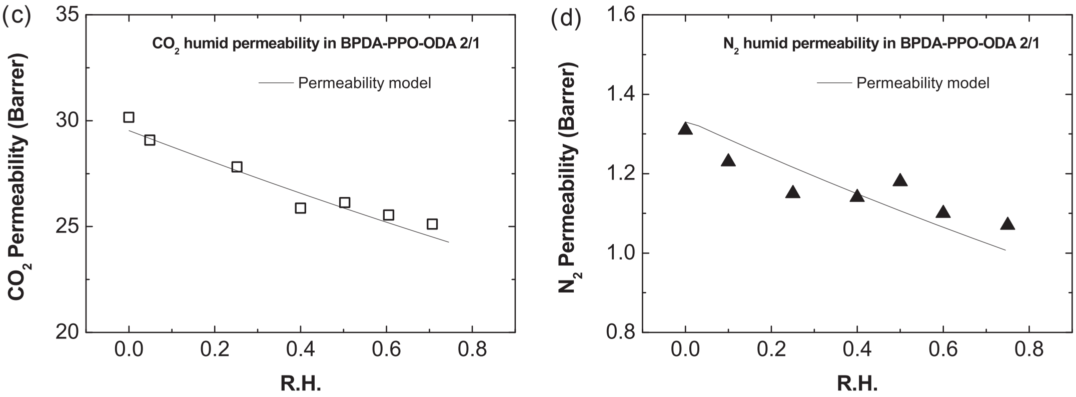

Fig. 10. Modeling the variation of various quantities of copolymer BPDA-PPO4000-ODA 2/1 as a function of relative humidity: (a) fractional free volume; (b) gas diffusivity; (c) CO_2 permeability; (d) N_2 permeability at 30 °C. ((a), (b) in the Supplementary Information).

Table 5
Free volume theory adjustable parameters.

Gas	A_i cm^2/s	B_i
CO_2	$2.80 \cdot 10^{-6}$	0.45
N_2	$2.10 \cdot 10^{-6}$	0.45

6. Conclusions

In this work, the effect of humidity on copolyetherimides formed by rubbery and glassy phases, BPDA-PPO-ODA 2/1 and BKDA-PEO-ODA 4/1, has been studied through dedicated water vapor sorption and humid CO_2, N_2 permeation tests. Indeed it is known that gas permeability in hydrophobic polyimides decreases strongly with increasing relative humidity, and that the extent of such phenomenon is a function of the amount of water absorbed by the membrane. A possible explanation lies in the fact that water undergoes competitive sorption with the permeating gases and occupies free volume available for diffusion, thus lowering the gas solubility and diffusivity in the membrane.

The moisture sorption tests indicate that the amount of humidity sorbed by the copolymers is intermediate between the values absorbed by the two homopolymers, at fixed humidity. The copolymer formed by PEO is the more hydrophilic one, due to higher percentage of polyether present, and also to the increased accessibility of ether moieties and to the higher hydrophilicity of the polyimide BKDA-ODA with respect to BPDA-ODA. The CO_2 and N_2 permeability values were studied in the less hydrophilic polymer, namely BPDA-PPO-ODA 2/1, that shows a percentage decrease of permeability equal to − 12% and −17% for N_2 and CO_2, respectively, at 70% relative humidity: such reduction is small if compared with the −50% reduction observed in Matrimid® films. The selectivity, being the permeability decrease similar for both penetrants, is not strongly affected.

A simple model, based on the solution-diffusion mechanism, free volume theory and LF models represents accurately permeability data in humid conditions, using the idea that water occupies part of the free volume available for gas diffusion and that undergoes competitive sorption with the diffusing gases. A precise quantitative analysis of the effect that the presence of water has CO_2 and N_2 solubility and diffusivity in the membrane was carried out and reasonable values of the adjustable parameters of the model were obtained.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.gee.2016.09.002.

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