

Sorption and Transport of Water Vapor in Amphiphilic Block Copolymer Films

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ABSTRACT

Water vapor sorption in films consisting of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) amphiphilic block copolymers has been measured gravimetrically at air relative humidity in the range 38–94% at 24°C. The water sorption isotherm was obtained and compared to data for water vapor desorption (drying) for the same system. The kinetics of water vapor sorption were determined. The percentage of water gain is initially a linear function of square root of time, indicating Fickian diffusion in the block copolymer films. Diffusion models were used to fit the experimental results and to extract water diffusion coefficient values in the block copolymer film, the internal structure of which was initially semicrystalline (due to PEO) and, above ~12% water, lamellar lyotropic liquid crystalline.

Key Words: Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer; Poloxamer; Amphiphilic block copolymer; Surfactant; Hydrogel; Sorption isotherm; Kinetics; Diffusion coefficient.

1. INTRODUCTION

Water sorption and/or desorption properties are important for the characterization of polymer membranes^[1–4] and films,^[5–10] and are very relevant to the wide applications of these materials in the pharmaceutical,^[11] food,^[12–14] sensor,^[15] electronics,^[16] fuel

cell,^[4,17] and biomedical fields.^[3,8,18–20] Two properties are of most concern for these materials; (i) the equilibrium sorption/desorption, which is related to the plasticity and mechanical properties of the materials that go into the membranes or films and (ii) the kinetics of water sorption/desorption, which is related to the solvent or solute transport properties in polymer membranes or films.

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The equilibrium water content and water activity play an important role in the microbiological, enzymatic, and chemical stability of foods, and are important for selecting polymer packaging materials.^[12] The equilibrium water sorption properties are also related to the oxygen or other gas permeability of polymers, for example, contact lenses.^[3,21] The kinetics of water sorption/desorption are very important for the development and design of drug delivery vehicles. They are also important for the understanding of polymer swelling and polymer dissolution.^[22]

Block copolymers provide great structural versatility useful in both fundamental research and practical applications, and thus the water vapor sorption (or permeability) properties for several block copolymers have been well characterized.^[23] The variety of the building blocks that can be incorporated into block copolymers provides opportunities to alter the morphology and hydrophilicity of the membranes or films formed by them.^[23] The vapor sorption properties of polyurethanes and polyurethaneureas are well studied due to their applications in packaging, biomaterials, and membrane separations.^[5,23–25] Water vapor sorption has been studied for poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) homopolymers and for PPO-PEO-PPO triblock copolymers that are used as “soft” components of segmented polyurethanes to change their hydrophilicity.^[5,24,25] Water vapor sorption properties have also been characterized in other PEO-based^[1,26,27] or PPO-based block copolymers.^[28,29]

Pluronic or Poloxamer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) amphiphilic block copolymers have found numerous applications in coatings, formulations, biomaterials, and drug delivery.^[30–33] Many of their applications involve the transport of water in the block copolymer solutions and/or gels. As the solvent concentration changes, various ordered structures are formed which may affect the mechanism of block copolymer drying, swelling, or dissolution^[34]. We have recently studied the water vapor desorption (drying) properties of Pluronic hydrogels.^[35,36] The drying of Pluronic hydrogels has been shown to be mainly evaporation-limited in most of the drying course; the ordered or semi-crystalline structures that are formed by these block copolymers^[37] reduce greatly the drying rate and play a more important role in the late stage of the drying process.^[35,36] The drying rates of Pluronic block copolymers have been correlated to the PEO content in the block copolymers.^[36]

In this paper, we present experimental data on the water vapor sorption isotherm in Pluronic PEO-PPO-PEO block copolymers. The kinetics of water vapor sorption in the amphiphilic block copolymer film are also reported and water diffusion models are used to fit the

experimental data. Values for the water diffusion coefficient are thus obtained and discussed.

2. MATERIALS AND METHODS

2.1. Materials

The Pluronic P105 PEO-PPO-PEO amphiphilic block copolymer (BASF Corp.) was used as received. Pluronic P105 has a nominal molecular weight of 6500 g/mol and 50 wt% PEO, and can be represented by the formula (EO)₃₇(PO)₅₈(EO)₃₇. In order to achieve a uniform film, the neat Pluronic P105 paste was first weighted in a small Petri dish at ambient conditions, and then moved to an oven with a temperature of about 50°C. After the Pluronic block copolymer became liquid, the Petri dish was moved to ambient conditions again and the sample was cooled down slowly. The final film thickness is about 5 mm. Analytical grade lithium chloride (LiCl), sodium iodide (NaI), sodium bromide (NaBr), potassium chloride (KCl), and potassium nitrite (KNO₃) were purchased from Fisher Scientific. Saturated aqueous salt solutions were prepared by dissolving an excess amount of salt in water. Millipore-filtered water was used for all sample preparations.

2.2. Generation of Constant Water Vapor Pressure

Constant water vapor pressures can be generated by saturated aqueous salt solutions.^[38] Table 1 lists the salts that we used to generate a series of constant, known, relative humidity conditions. The %relative humidity (RH) is defined as the water vapor pressure divided by the saturated water vapor pressure at the same temperature and then multiplied by 100 [see Eq. (1)].

$$\text{RH} = 100 \frac{P}{p_0} \quad (1)$$

The Pluronic block copolymer samples were equilibrated with air of known water vapor pressure in a large sealed Petri dish (diameter $D \approx 40$ mm), with no direct contact between each Pluronic sample and the salt solutions. The saturated aqueous salt solutions and Pluronic samples were each placed in small open Petri dishes (diameter $d \approx 35$ mm). One large Petri dish contained eight small dishes, from which two dishes were Pluronic samples and the other six dishes were salt solutions to ensure that a constant vapor pressure was maintained. The Petri dishes are made from polystyrene and the sorption of water vapor by the dishes is negligible. Since the

Table 1. Relative humidity (RH) of saturated aqueous salt solutions at 24°C.

	Salt				
	LiCl	NaBr	NaI	KBr	KNO ₃
RH (%)	11.3	38.5	57.9	84.6	93.8

Note: 11.3% RH is written as 11% RH in the following text and figures for simplicity. Similar simplifications are made for other RH conditions.

dishes are sealed well and there is no disturbance except when measurements are collected, the air is still and the air velocity is not a variable in these sorption experiments.

2.3. Water Vapor Sorption Measurements

The sealed dishes with the higher RH (85% and 94%) were placed in an incubator (kept at 24°C ± 0.1°C) that maintained a surrounding RH in the range 70–90%. For the lower RH cases (38% and 58%), the sealed dishes were kept in an air-conditioned room with temperature at 24°C (±1°C) and RH ranging from 10% to 60%. In this way the disturbance caused by opening the system to take measurements was greatly shortened. The time scale shown in the results reported here is the real recording time, including the time of handling and weighing samples.

Immediately after the Pluronic block copolymer film was formed, the small dishes with samples were placed into a bigger dish and the experiment started. The amount of water vapor sorption during the film formation and sample transfer was negligible. The measurements were taken at least every 6 hr in the beginning, and longer time intervals were used when the experiment proceeded. The total time required for the water sorption ranged from about 13 days for relatively dry air conditions (38% RH) to about 90 days for very humid air conditions (94% RH) for Pluronic P105 films with initial thickness of 5 mm. A digital hygrometer (±1.5% RH accuracy, Fisher Scientific) was used to check the RH of the air in contact with the saturated aqueous salt solutions.

The Pluronic block copolymer concentration and water gain as a function of time data reported in Section 3 are the average values of two sets of experiments, conducted in parallel at the same temperature and same air RH. Very good reproducibility was observed: the errors were generally below 0.3% and the

error bars are smaller than the symbols used in the figures.

3. RESULTS AND DISCUSSION

3.1. Sorption Isotherm

The driving force for water transfer from one phase to another is a difference in water chemical potential. In our water vapor sorption study, the water chemical potential at each air RH condition examined is less negative than that in the block copolymer film, thus swelling is achieved. When the water chemical potentials in each phase become equal to each other, there is no net water transfer between the two phases and equilibrium is attained. The water chemical potential in the air, $\Delta\mu$, can be determined by the water vapor pressure:

$$\Delta\mu = RT \ln a = RT \ln \left(\frac{\text{RH}}{100} \right) \quad (2)$$

where a is the water activity. Figure 1(a) shows the variation of block copolymer concentration in the film as a function of swelling time when the film (initially water-free) was exposed to air of 38% or 85% RH. The block copolymer concentration reported here is the average value over the whole film. The block copolymer concentration decreases over time until there is no further change, indicating that equilibrium has been achieved. Results from water vapor desorption (drying) measurements^[36] are also included in this figure. The overlap of the equilibrium concentrations obtained from both the sorption and desorption experiments confirms the attainment of equilibrium.

The percentage of water gain, defined as the amount of water absorbed in the block copolymer film at time t divided by the equilibrium water sorption, is plotted in Fig. 1(b) at two RH conditions. The percentage of water loss for the same conditions and system obtained previously^[36] are also plotted in Fig. 1(b). The percentage of water loss is larger than that of water gain at the same time and RH condition, which means that water desorption is faster than water sorption. The percentage of water loss in Pluronic block copolymers is initially a linear function of time, indicating that water desorption is an evaporation-limited process.^[35,36] In the case of water desorption, the initial water content is 70 wt% or more; while in the case of water vapor sorption reported here, the much lower water content (negligible amount) and corresponding lower water diffusion coefficient in the block copolymer film leads to the slowness of water sorption process. Similar results are

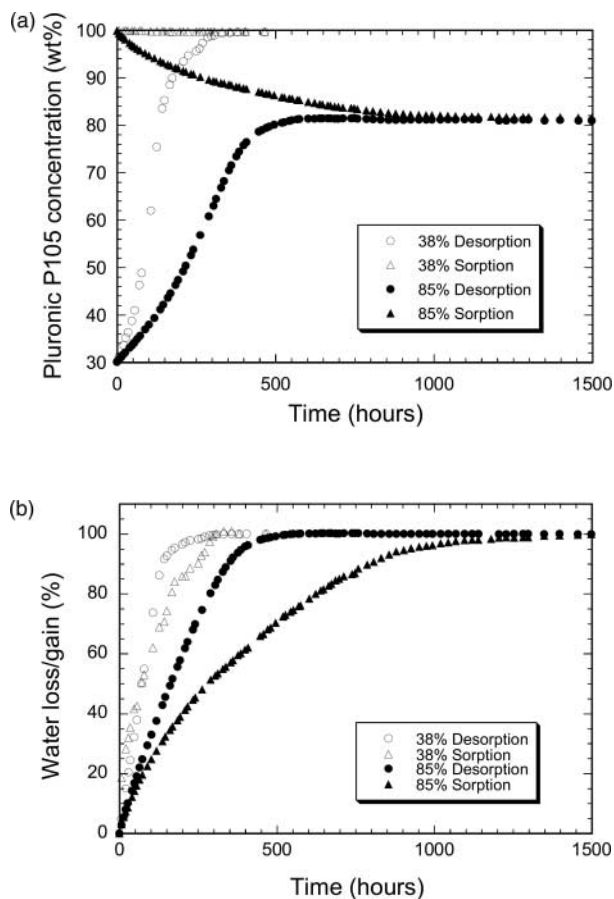


Figure 1. (a) Pluronic P105 concentration (wt%) and (b) percentage of water loss/gain as a function of time at 38% and 85% RH conditions at 24°C. The experimental data at the other conditions considered here (58% and 94% RH) show similar trends and are not presented here.

obtained for water vapor sorption of Pluronic P105 at 58% and 94% RH conditions (not shown here). For 11% RH, the adsorbed water amount is very small but bigger than the experimental error.

The equilibrium water concentration (wt%) attained by Pluronic P105 block copolymers at 24°C is plotted in Fig. 2 as a function of water activity. The water vapor desorption isotherm obtained in our previous study^[36] is also plotted in this figure. At low water activities, the amount of water vapor sorbed is relatively small. For example, the water gain is only 0.007 g/g polymer (about 0.03 H₂O molecules per EO segment) at 0.58 activity (corresponding to 58% RH). At 0.85 activity, the equilibrium water gain is 0.23 g/g polymer, about 1.1 H₂O molecules per EO segment. The results obtained from sorption measurements at higher RH (85% and 94%) are almost the same as the values obtained from desorption measurements,^[36] while at lower RH (38%

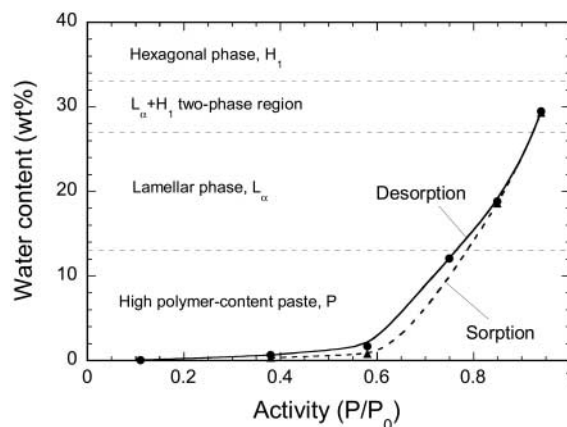


Figure 2. Equilibrium water content (wt%) in Pluronic P105 hydrogel films as a function of water activity at 24°C. The dotted lines indicate the Pluronic P105 concentration where the ordered structure changes. H₁, hexagonal phase; L_α, lamellar phase; P, high polymer-content paste.

and 58%) the values obtained from desorption measurements are relatively bigger. This difference can be better seen in the semi-logarithmic plot of moles water per EO segment vs. activity shown in Fig. 3. The difference of the equilibrium properties between water sorption and desorption is not unusual for polymer systems or other materials and has been attributed to hysteresis.^[4,39–41] There may be different causes for the hysteresis, for example, shrinkage of the materials, sorption sites that may resist water vapor when filled with gas after drying.^[39]

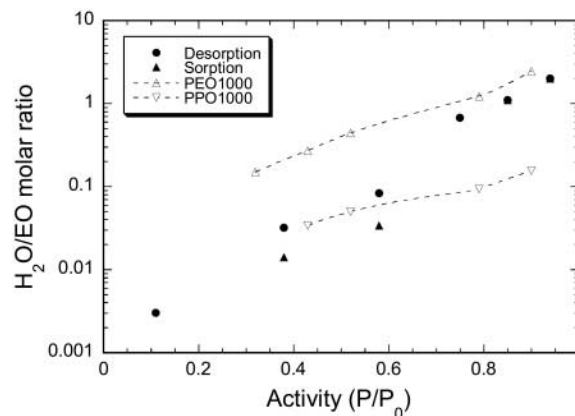


Figure 3. Equilibrium molar ratio of water to EO segment in Pluronic P105 film as a function of water activity at 24°C plotted in semi-logarithmic scale. The water sorption data for PEO1000 (MW = 995) and PPO1000 (MW = 1040) homopolymers at 23°C are from Petrik et al.^[5]

Sorption isotherms have been reported for some PEO and PPO homopolymers and PPO-PEO-PPO block copolymers.^[5] The amount of water adsorbed by the hydrophilic PEO is normally bigger than that by PPO, while the amount adsorbed by PPO-PEO-PPO block copolymers falls between them.^[5] For the Pluronic P105 block copolymers examined here, the sorption amount is close to that of PPO1000 (molecular weight = 1040) at lower RH, while close to that of PEO (molecular weight = 995) at higher RH (see Fig. 3).

The Flory–Huggins theory is widely used for describing the thermodynamics of polymer solutions.^[42] In the framework of this theory, the activity of the solvent (in our case, water) in a (homogeneous) polymer solution can be obtained from the following equation:

$$\ln(a_1) = \ln(1 - \varphi_2) + \left(1 - \frac{1}{r_2}\right)\varphi_2 + \chi_{12}\varphi_2^2 \quad (3)$$

where φ_2 is the polymer volume fraction, r_2 is the number of polymer segments, and χ_{12} is the polymer–water interaction parameter. As indicated by Gu and Alexandridis,^[43,44] the Flory–Huggins equation with constant χ_{12} is not adequate to describe the water activity of Pluronic–water systems in the whole polymer concentration range. $\chi_{12} = 0.55$ fits well water activity data in Pluronic P105–water systems up to $\varphi_2 = 0.5$.^[44] The water activities for the conditions of the sorption experiments obtained by Flory–Huggins equation using $\chi_{12} = 0.55$ are shown in Fig. 4 and the fit is not satisfactory. By fitting the Flory–Huggins equation [Eq. (3)] to the experimentally determined water activity values,

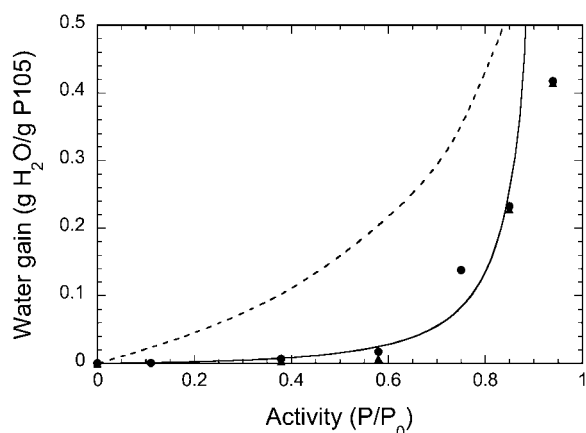


Figure 4. Equilibrium water gain (g H₂O/g P105) in Pluronic P105 hydrogel film as a function of water activity at 24°C. The solid line is fit with the multimolecular adsorption theory [Eq. (4)] the dashed line (---) is the prediction from Flory–Huggins equation [Eq. (3)] using $\chi_{12} = 0.55$.

the interaction parameter (χ_{12}) between Pluronic P105 and water has been obtained as a function of φ_2 .^[43] χ_{12} remains relatively constant and is close to 1/2 for up to $\varphi_2 = 0.7$, and then goes up to 4.2 when $\varphi_2 \approx 1$.^[43] Flory–Huggins interaction parameters between PPO-PEO-PPO block copolymers and water were also obtained and have been shown to be an increasing function of block copolymer volume fraction.^[5] The increasing function of the interaction parameters with respect to block copolymer volume fraction reported in Pluronic–water systems in our study is similar to that of systems reported by Petrik et al.^[5] and is common in many other polymer systems.^[2,10,18,20,21]

The shape of the water vapor sorption isotherm of Pluronic block copolymers shown in Fig. 2 resembles the type III isotherm as defined by Brunauer.^[45] The sorption isotherm can be modeled by a multimolecular adsorption theory for vapor adsorption on a free surface [Eq. (4)]:

$$v = \frac{v_m c p}{(p_0 - p)[1 + (c - 1)(p/p_0)]} \quad (4)$$

where c is a constant; v_m is the amount of water vapor absorbed when the entire surface is covered with a complete unimolecular layer; v is the adsorbed amount of water vapor (water gain, g H₂O/g P105) at water vapor pressure p (Pa); p_0 is the saturated water vapor pressure as defined before.

The adsorbed amounts of water vapor fitted using Eq. (4) are also shown in Fig. 4 ($v_m = 0.1$ g H₂O/g P105 and $c = 0.08$ are used in the prediction). It can be seen that Eq. (4) fits well the water sorption at low water activity conditions, while there is large deviation at high water activities between the predicted values and experimental results. The predictive ability of Eq. (4) is better than that of the Flory–Huggins equation over the low water activities (high block copolymer contents) of interest to the sorption experiments. However, it should be noted that water sorption in Pluronic block copolymers may not follow the same assumptions as the multimolecular adsorption theory, in which the molecules are assumed to be absorbed on a free surface.

3.2. Kinetics of Water Uptake

The kinetics of the water vapor sorption have been recorded and the water gain as a function of swelling time is shown in Fig. 5. The Pluronic block copolymer adsorbs only small amount of water at low RH, while appreciable amounts of water are adsorbed at high RH (Fig. 2). The swelling rate (the derivative of percentage

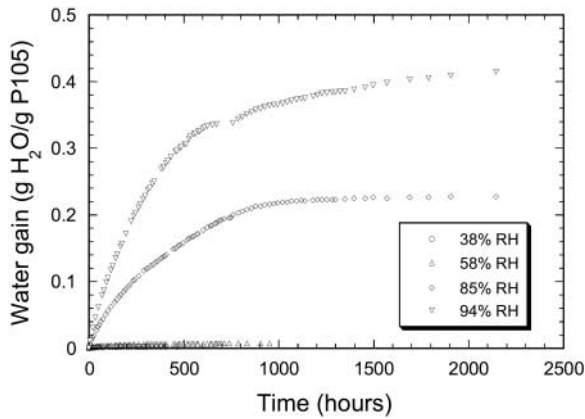


Figure 5. Water gain (g H₂O/g P105) for Pluronic P105 vs. swelling time at different RH conditions at 24°C.

of water gain with respect to time) is higher at lower RH conditions. Equilibrium was reached after 300 hr at 38% RH, while over 2000 hr were needed for equilibration at 94% RH.

For all the air RH conditions studied, the percentage of water gain is initially a linear function of square root of time, which is an indication of Fickian diffusion. However, an initial “anomalous” period can be discerned in Fig. 6 for water sorption at 85% and 94% RH, in which the percentage of water gain is not a linear function of square root of time. This initial short period has also been observed for water sorption in other polymer systems^[21] and is possibly due to the large water chemical potential difference between the air and the block copolymer film or water vapor condensation-induced temperature change.

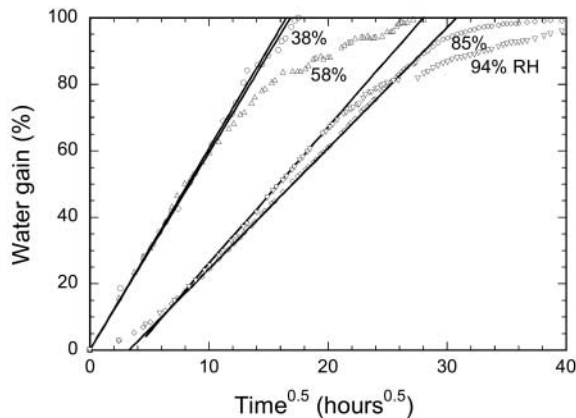


Figure 6. Percentage of water gain for Pluronic P105 as a function of square root of swelling time at different RH conditions at 24°C. The solid lines shown in the figure represent fits based on [Eq. (8)].

3.2.1. Analytical Solution

Mathematical modeling can be used to fit experimental results and to obtain optimum operating conditions for process design. Useful parameters, such as water or solute diffusion coefficient, can also be extracted from the modeling.^[46] To this end, we analyzed the water uptake vs. time data in the context of diffusion models.

The water diffusion in the block copolymer film can be described using Fick's second law:^[47]

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (5)$$

where C is the water concentration in the block copolymer film and D is the water diffusion coefficient.

In order to obtain analytical solutions for the above diffusion equation, the following assumptions are made: (1) the temperature change due to the water vapor condensation is negligible, the swelling process is isothermal; (2) water vapor sorption by block copolymer film leads to one-dimensional swelling; (3) the water diffusion coefficient is constant; and (4) the block copolymer film thickness is constant. This is a good assumption for the sorption at low RH conditions ($\leq 58\%$). However, at $\text{RH} \geq 85\%$, the water sorption amount is relatively large and the film thickness increases by much as 30% compared to the initial film thickness.

When the water concentration on the surface of block copolymer film is assumed to be the equilibrium concentration, the water gain per area (M_t , kg H₂O/m²) as a function of time can be obtained as shown below:^[46,47]

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(\frac{-D(2n+1)^2 \pi^2 t}{l^2}\right) \quad (6)$$

where M_∞ is the maximum water gain; l is the film thickness.

There are several methods to approximate Eq. (6) and to estimate the water diffusion coefficient in polymer films.^[46] The water diffusion coefficient can be estimated from the measurement of the sorption half-time ($t_{0.5}$) as shown in Eq. (7).^[46]

$$t_{0.5} = \frac{0.04919l^2}{D} \quad (7)$$

Sorption half-time ($t_{0.5}$) values at different RH conditions can be obtained by taking the half of the equilibrium sorption time from the sorption measurements, and are then used with Eq. (7) to calculate water diffusion coefficients. The water diffusion coefficient (D_h) values

thus obtained in Pluronic block copolymer films are reported in Table 2.

At short times ($M_t/M_\infty < 0.5$), Eq. (6) can be simplified as the following equation:^[46]

$$\frac{M_t}{M_\infty} = \frac{4}{l} \left(\frac{Dt}{\pi} \right)^{0.5} \quad (8)$$

The fitting results for the percentage of water gain calculated using Eq. (8) are shown in Fig. 6. The fitting values compare well with the experimental values in most of the time course, but fail at the later stage of the swelling process. The water diffusion coefficients (D_I) values used for calculating water gain with Eq. (8) are shown in Table 2. The values for water diffusion coefficients calculated based on Eq. (7) (D_h) and Eq. (8) (D_I) compare very well with each other at the same RH condition. The water diffusion coefficients remain relatively constant at lower RH ($\leq 58\%$) but decrease with the increase of air RH. The water diffusion coefficients at 85% RH are close to those at 94% RH and both values are less than half of the values at lower RH.

At long times ($M_t/M_\infty > 0.5$), Eq. (6) can be simplified as follows:^[46]

$$\ln \left(1 - \frac{M_t}{M_\infty} \right) = \ln \frac{8}{\pi^2} - \frac{\pi^2 D t}{l^2} \quad (9)$$

The values of $\ln(1 - M_t/M_\infty)$ can be plotted vs. time as shown in Fig. 7 and water diffusion coefficients (D_F) can be obtained from fitting experimental results at the later stage of the sorption process using Eq. (9) (see Table 2). When fitting the experimental results with Eq. (9) the last few data points shown in Fig. 7 are not used because they are very close to the equilibrium states. The D_F values decrease with an increase of the air RH, but remain relatively stable at high RH. The various water diffusion coefficient values obtained by all three methods [Eqs. (7)–(9)] compare very well with each other at higher RH conditions. However, at lower RH conditions

the difference is bigger between the values obtained with Eq. (9) and the values obtained with Eqs. (7) and (8). This may be due to the different polymer concentration range applied (see Fig. 7). The water diffusion coefficient in the lamellar phase (13–27 wt% H₂O) formed by Pluronic P105 in water has been reported to be 5×10^{-12} m²/sec.^[48] The diffusion coefficients obtained using the three methods above at all RH conditions studied are the same or very close to this value.

3.2.2. Numerical Solution

When using analytical equations to fit the experimental data, constant film thickness and constant water diffusion coefficients have been assumed. In reality, the film thickness increases with time, especially at high RH. Also, the water diffusion coefficient is normally a function of polymer concentration (correspondingly, water concentration). The swelling process in the case of variable film thickness and variable diffusion coefficient has been solved numerically.

If the water diffusion coefficient is assumed to be function of water content, Eq. (5) changes to:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D(C) \frac{\partial C}{\partial x} \right) \quad (10)$$

The surface condition of the block copolymer film was assumed to be evaporation. The water flux is considered a linear function of the concentration difference between the water concentration on the surface and the water concentration at infinite time (C_∞) which is in equilibrium with the outside air.^[47] When the moving boundary is accounted for, the surface condition can be written as:

$$-D \frac{\partial C}{\partial x} - C \frac{dh}{dt} = \alpha(C - C_\infty) \quad x = h(t) \quad (11)$$

where $h(t)$ is the thickness of the block copolymer film and a function of swelling time; α is a constant, which is the product of the mass transfer coefficient (k_G)

Table 2. Diffusion coefficient of water in Pluronic P105 block copolymer obtained from fitting experimental data to diffusion models with analytical solution.

	RH			
	38%	58%	85%	94%
D_h (m ² /sec)	4.8×10^{-12}	5.2×10^{-12}	1.2×10^{-12}	1.5×10^{-12}
D_I (m ² /sec)	5.0×10^{-12}	4.8×10^{-12}	1.8×10^{-12}	2.3×10^{-12}
D_F (m ² /sec)	7.3×10^{-12}	2.9×10^{-12}	2.4×10^{-12}	1.3×10^{-12}

Note: D_h , value obtained from fitting Eq. (7) to the sorption half-time ($t_{0.5}$); D_I , value obtained from fitting Eq. (8) to the sorption experimental results at shorter times; D_F , value obtained from fitting Eq. (9) to the sorption experimental results at longer times.

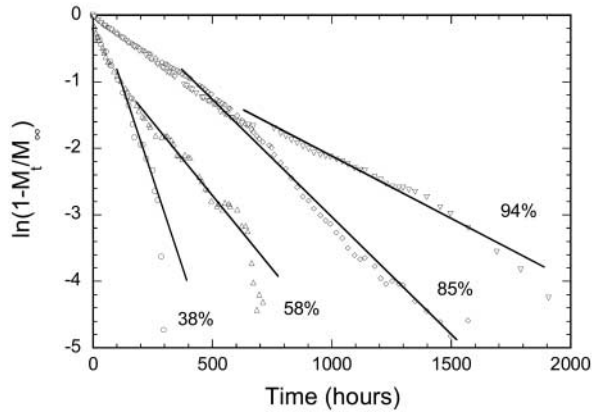


Figure 7. Values of $\ln(1 - M_t/M_\infty)$ vs. swelling time at different RH conditions at 24°C. The solid lines shown in the figure indicate fits based on Eq. (9).

between the film surface and the air and a proportionality constant (m) that represents the linear relationship between the water concentration on the film surface and the water partial pressure (p) in the air.^[36]

$$p = mC \quad (12)$$

The water gain per area is obtained by the integration of water concentration over the whole film.

$$M_t = \int_0^{h(t)} C dx \quad (13)$$

The film thickness is obtained by the following equation:

$$(1 - w_0)L_0 = (1 - w(t))h(t) \quad (14)$$

where w_0 is the initial water weight fraction, $w(t)$ is the water weight fraction at time t , and L_0 is the initial film thickness.

The density of the Pluronic hydrogel is assumed to be the density of neat Pluronic block copolymer, 1.05 g/cm³. This assumption is justified because the maximum water concentration in the hydrogel is 30 wt% under the conditions studied. The fitted results for water gain per area and the film thickness obtained from the models above are shown in Figs. 8(a) and (b). The water gain per area vs. square root of time compares well with the experimental results [see Fig. 8(a)]. The numerical model can also predict the film thickness changes as shown in Fig. 8(b). The α parameters at different relative humidities used in the fittings (see Table 3) are almost the same as the values used in the desorption (drying) studies.^[36] $D = 5.0 \times 10^{-11} \exp(0.65C')$ (m²/sec) was used in the numerical fittings, where C' is the dimensionless water concentration ($C' = C/C_\infty$).

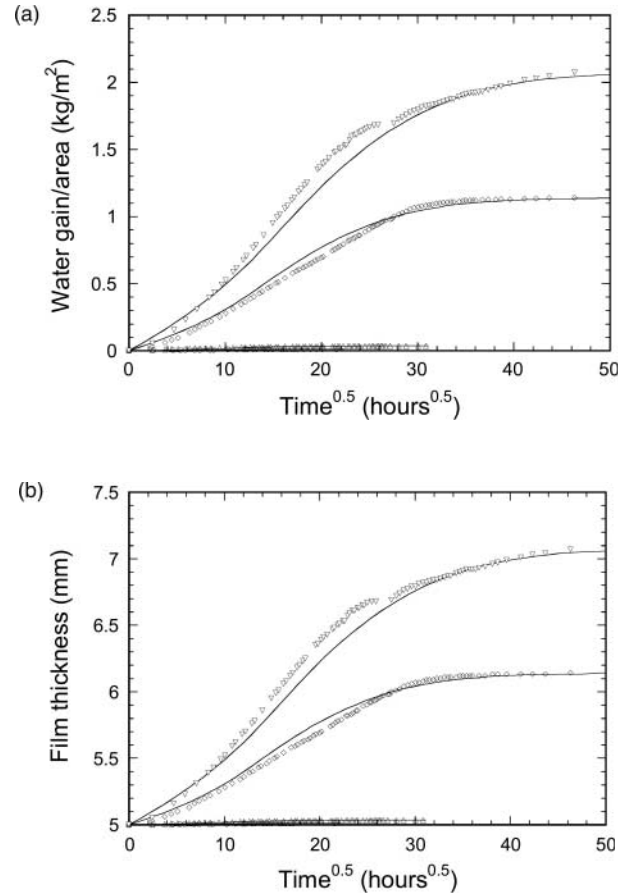


Figure 8. (a) Water gain per area and (b) film thickness of Pluronic P105 as a function of square root of swelling time at different RH conditions at 24°C. The symbols used in this figure indicate the same RH conditions as those used in Figs. 5–7. The solid lines are fitting results obtained from numerical solution of diffusion models.

The magnitude of the diffusion coefficient does not increase much in the water concentration range covered in our study, i.e., about 20% increase when the water concentration increases from 0 to about 30 wt%. The values of water diffusion coefficient obtained from the numerical fittings are normally one order of magnitude higher than the values obtained from analytical solutions as shown in Table 2. There are two possible reasons for this difference: (1) The concentration ranges considered for the analytical solution and numerical solution are different. The water diffusion coefficient used in the numerical solution is applicable for the whole concentration range covered in this study, i.e., from 0 to 30 wt% Pluronic P105, and for all the RH conditions. However, the water diffusion coefficients extracted from analytical solutions [Eqs. (7)–(9)] are only valid for that RH and for the concentration range covered in

Table 3. Constants (α) used in boundary condition [Eq. (11)] obtained from diffusion models solved numerically.

	RH (%)			
	38	58	85	94
α (m/sec)	1.8×10^{-8}	1.2×10^{-8}	5.8×10^{-9}	5.5×10^{-9}

Note: $D = 5.0 \times 10^{-11} \exp(0.65C)$ (m^2/sec) was used in the numerical fittings.

that RH condition (shown in Figs. 6 and 7). (2) The assumptions of the analytical and numerical solutions are different. For example, constant film thickness is assumed for the analytical solution, while increasing film thickness is used in the numerical solution.

As discussed in Section 3.2.1, water vapor sorption in Pluronic block copolymer films appears a diffusion-limited process. The Biot number (Bi) represents the ratio of the internal to external mass transfer resistance and can be defined as follows:^[36,49]

$$\text{Bi} = \frac{\alpha L_0}{D} \quad (15)$$

When $\text{Bi} \ll 1$, the process is mainly limited by external resistance; when $\text{Bi} \gg 1$, the process is limited by internal resistance; while when $\text{Bi} \approx 1$, both internal and external resistance matter. In water desorption from Pluronic hydrogels, initially $\text{Bi} \ll 1$ and the desorption process is mainly controlled by evaporation.^[36] In the water sorption study reported here, Bi is close to or higher than 1 when the α values shown in Table 3 and $D_0 = 5.0 \times 10^{-11} \text{m}^2/\text{sec}$ are used for calculation. This means that water diffusion in the block copolymer film is more important than evaporation on the film surface. If the water diffusion coefficient values reported in Table 2 are used in calculating the Biot number, then Bi becomes higher than 10 for all RH conditions, indicating more clearly that the water sorption in the block copolymer films is limited by diffusion. This is not contradictory to the evaporation-limited water desorption process, because there is far less water in the block copolymer film in the sorption process than in the water desorption process (70 wt% or more water exists initially in the block copolymer films).

4. CONCLUSIONS

The water vapor sorption isotherm is reported for PEO-PPO-PEO amphiphilic block copolymers. Pluronic P105 [(EO)₃₇(PO)₅₈(EO)₃₇] uptakes only a small amount of water at low water activities (less than 1 wt% H₂O at 0.58 activity), while appreciable amount of water is

adsorbed at high water activities (about 30 wt% H₂O at 0.94 activity).

Water vapor sorption kinetics were recorded. The percentage of water gain increases linearly with the square root of time in most cases, indicating that Fickian diffusion dominates the process. In water desorption experiments,^[36] the percentage of water loss has been shown to be a linear function of time initially, indicating evaporation-limited process.

Diffusion models are used to fit experimental data. Two approaches are used: one is an analytical model, which is based on constant water diffusion coefficient and constant film thickness; another is a numerical model, which accounts for variable diffusion coefficient and increasing film thickness. Both approaches gave satisfactory fitting results. The water diffusion coefficients thus obtained are compared with the values obtained from previous studies.

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