

## Drying of Aqueous Surfactant Solutions

Paschalis Alexandridis\* & Zhiyong Gu

Department of Chemical and Biological Engineering, University at Buffalo,  
The State University of New York (SUNY), Buffalo, NY 14260-4200

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### Introduction

Film formation is frequently encountered in applications of polymer solutions and/or gels, e.g., paints and coatings, papers and inks, surface cleaning solutions, foods, and personal care products [1,2]. The removal of solvent from such systems (drying) is important in the film formation process. Solvent removal may alter the structure of polymers, e.g., from random coils to crystalline or liquid crystalline. Few studies exist on the drying of crystalline (semi-crystalline) polymers or gels with ordered structures [3,4] despite several studies on the drying of disordered polymer solutions [5-7].

We are interested in the thermodynamic and transport properties of hydrated Pluronic or Poloxamer poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-PPO-PEO) amphiphilic block copolymers that exhibit ordered nanostructure due to self-assembly [8-12]. The ordered structure undergoes a transition from micellar cubic (spherical assemblies) to hexagonal (cylinders) and to lamellar (planar) as the water concentration in the hydrogel decreases [13,14]. Crystallization of the PEO blocks may also occur when the water concentration is very low. These ordered structures may affect the drying mechanism of the hydrogels. Such amphiphilic block copolymers find numerous applications in coatings and personal care formulations, and also in the area of biomaterials and drug delivery [15]. Many of their applications involve the transport of solvent (water) in the amphiphile solutions and/or gels.

We highlight here results from studies where we probed the time evolution of water loss from PEO-PPO-PEO block copolymer hydrogels when brought in contact with air of different relative humidities (RH) [11,12]. These data allow us to access whether it is the ordered nanostructure formed by block copolymer self-assembly or the solvation level in the hydrogel that primarily affects the drying rate. Our studies not only improve

the understanding of formation and drying of films based on amphiphilic block copolymer hydrogels, but are also relevant to other applications of surfactant-containing films.

## Results and Discussion

*Equilibrium Adsorption Isotherm:* The equilibrium concentrations of Pluronic solutions and hydrogels are different depending on the RH (see Figure 1), and correspond to different ordered structures [10,13]. The values close to the data points are the hydration level ( $\text{H}_2\text{O}/\text{EO}$  molar ratio) at different RH values. During the drying process various ordered structures form. In the case of Pluronic P105 ( $(\text{EO})_{37}(\text{PO})_{58}(\text{EO})_{37}$ ) shown in Figure 1, the micellar cubic, hexagonal and lamellar lyotropic liquid crystalline phases will successively form during the drying course when the initial concentration of the hydrogel is 30 wt% (dotted lines in Figure 1 indicate the phase boundaries at different compositions). At low RH ( $\leq 58\%$ ), the block copolymer hydrogel retains very low water content at equilibrium ( $\leq 2$  wt%), and thus contains crystalline PEO (as attested by the opacity of the film). For example, when the RH is 58%, the water content is about 1.7 wt% ( $\text{H}_2\text{O}/\text{EO}$  molar ratio = 0.083, corresponding to the high polymer-content paste region in the phase diagram). When the RH increases to 85% or higher, the equilibrium water content in the Pluronic P105 hydrogel increases to 81.2 wt% ( $\text{H}_2\text{O}/\text{EO}$  molar ratio is 1.1, corresponding to the lamellar phase).

*Surface Evaporation vs. Diffusion inside Film:* The water weight loss from Pluronic hydrogels is recorded as a function of drying time. The percentage of water loss (defined as water weight loss at time  $t$  divided by water weight loss at infinite time) from the film initially increases linearly with the drying time (constant rate region, stage I); a nonlinear behavior is then observed (falling rate region, stage II, see Figure 2) leading to a plateau. Higher RH increased the time needed for the water weight loss, but in all the air RH conditions examined, the percentage of water loss increased linearly with the time initially. The linear region and nonlinear region in the water loss vs. time curves (Figure 2) follow the two-stage mechanism for the drying process observed by many researchers [2,16,17]. Although polymer entanglement and water hydration in the block copolymer hydrogels is expected to hinder the water transport in the hydrogel, the water content in the hydrogel is very high initially (70 wt%  $\text{H}_2\text{O}$ ) and water can move relatively freely. So the drying process in stage I is limited by the water evaporation at the film surface. When the time proceeds and the water concentration becomes low, polymer

structure (entanglement or crystallinity) and hydration are expected to play a more important role and both surface evaporation and water transport in the structured hydrogel will affect the drying rate. This corresponds to stage II of drying.

*Self-assembled Nanostructure vs. Degree of Hydration:* It has been reported that gas permeability or molecule diffusion is affected by the complex or ordered structures formed by block copolymers [18-20]. It may thus be reasonable to assume that the ordered structures present in the systems examined here may also affect the drying mechanism and time-course. The drying of Pluronic F127 ((EO)<sub>100</sub>(PO)<sub>70</sub>(EO)<sub>100</sub>) Pluronic L64 ((EO)<sub>13</sub>(PO)<sub>30</sub>(EO)<sub>13</sub>), and homopolymer polyethylene glycols (PEG) of molecular weights 4000 and 20000 is reported in [11,12]; representative drying rate vs. water content curves for the different polymers considered are shown in Figure 3 for 85% RH. Initially (high water contents), the drying rate is relatively constant for all the polymers. However, the drying rate drops with the decrease of solvent content and the change of drying rate is different depending on the polymer. The drying rate is found lower when the PEO content of the polymer is higher: L64 (40 wt% PEO) > P105 (50 wt% PEO) > F127 (70 wt% PEO) > PEG (100% PEO). For the drying of PEG4000 and PEG20000, the drying rate is very similar to each other at most of the time course, however, the trend of the drying rate of PEG20000 changed at the later stage of drying process, which may be due to the formation of crystalline structure by PEG.

It has been established that the intermolecular interactions in Pluronic hydrogels are mainly attributed to interactions between PEO and water [10], so it is reasonable to assume that the diffusion of water in the hydrogels is mainly affected by the interactions between PEO and water. Based on this supposition, the drying rate vs. water content curve was re-plotted based on the “corrected” water content (H<sub>2</sub>O wt%\*) defined below:

$$H_2O \text{ wt}\%^* = \frac{H_2O \text{ wt}\%}{(100 - H_2O \text{ wt}\%) \times PEO \text{ wt}\% + H_2O \text{ wt}\%}$$

where H<sub>2</sub>O wt% is the water content in Pluronic-water system and PEO wt% is the PEO content of the Pluronic molecule, for example, PEO wt% = 50 for Pluronic P105. The “corrected” water content represents the hydration level at different block copolymer concentrations. The drying rate vs. the “corrected” water content (H<sub>2</sub>O wt%\*) data are shown in Figure 4 for 85% RH. When plotted against the “corrected” water content, the drying rates of different Pluronic block copolymers overlap fairly well in most regions of the drying curves. Moreover, the drying rates of Pluronic hydrogels compare very well

with these of PEG solutions when the water content is high (when there is no crystallinity). This indicates that the hydration level, rather than the type of ordered structure, plays a more important role in the drying process of Pluronic hydrogels.

### Conclusions

The drying of films formed by Pluronic amphiphilic block copolymer hydrogels has been investigated at various air RH conditions covering the range from 11% to 94%. Two regimes can be distinguished in the drying process, constant drying rate (stage I) and falling drying rate (stage II). The drying rate in stage I increases linearly with a decrease of the RH. The results indicate that the hydration level in Pluronic hydrogels play an important role in determining the drying rate, while the type of self-assembled nanostructure formed by Pluronic block copolymers may not have appreciable effect on the drying rate. Semicrystalline structures formed by PEO blocks at low water contents affect significantly the stage II drying.

A model for one-dimensional water diffusion has been used [12] to fit the experimental drying results at different RH, initial film thickness, and initial water content conditions. The model accounts for the shrinkage of the film during drying and for a water diffusion coefficient that is a function of the water concentration in the film. For the experimental conditions considered in our studies [11,12] the Biot number is less than unity and the drying is mainly limited by evaporation at the film surface. The diffusion model has been used to obtain information for cases where  $Bi > 1$  [12].

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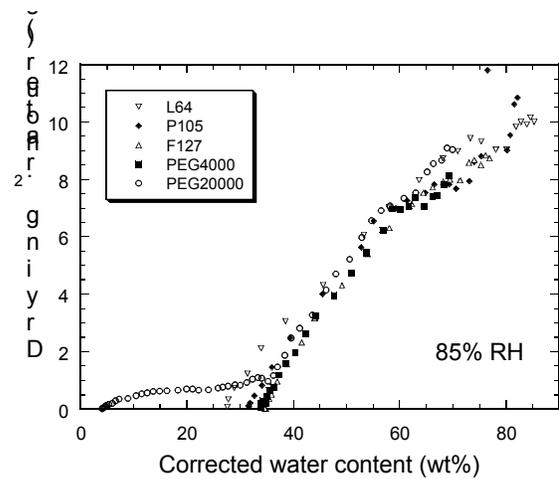
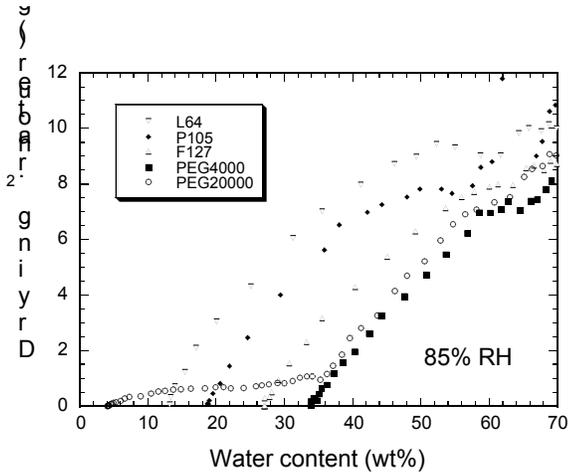
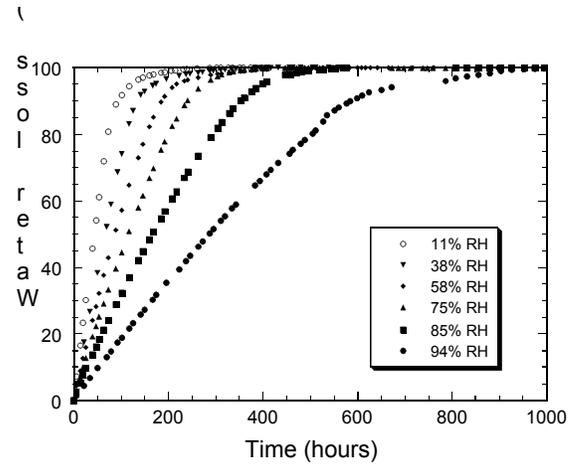
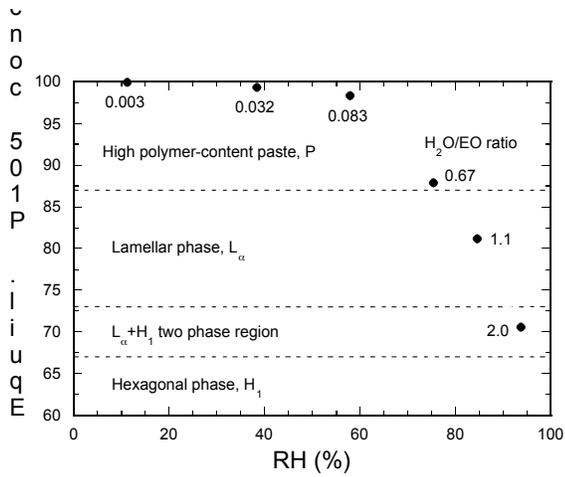


Figure 1: Equilibrium concentration of Pluronic P105 in the hydrogel film as a function of RH. The dotted lines indicate the concentration where the ordered structure changes.

Figure 2: Percentage of water loss vs. drying time at different RH (for Pluronic P105).

Figure 3: Drying rate vs. water content curves for different polymers (RH=85%).

Figure 4: Drying rate vs. "corrected" water content curves for the data of Figure 3.