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Surface Undulations Formed during Polymer Solution Drying

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Introduction

The drying kinetics of a polymer/solvent solution depends both on the physico-chemical properties of the solution and on the external exchange conditions. The concentration range spanned during an experiment is very large, the polymer volume fraction increasing from a few percents to 100% at the end of drying. This results in a change of several orders of magnitude of the mutual diffusion coefficient and of the viscosity. Solvent evaporation gives rise to a concentration gradient in the film whose amplitude and time evolutions depend on the film characteristics and on the exchange with the surroundings. For some experimental conditions, permanent undulations are observed at the film surface. We present in this paper some results on the relation between the undulations formation and the drying kinetics.

Experimental

Materials. The polymer/solvent solution used in this study is PIB/Toluene. PIB (Polyisobutylene) was supplied by Aldrich with M_w=5.10^5 and polydispersity 2.5. Toluene was supplied by Prolabo

Experimental set-up. The solution, with an initial solvent mass fraction ranging between 85% to 98% (g/g), is poured in a dish. The dish is put on a balance (precision 0.1 mg) that is located in an extractor hood at room temperature. Air temperature and solution weight are recorded all along the drying (60 hours). Evaporation flux used in the following is obtained by derivation of weight measurements. The air velocity above the film can be changed by opening more or less the hood air inlet. A camera located above the solution gives information on the evolution of the surface morphology during drying in order to detect when the undulations appear and how the surface is overrun. Experiments were performed with dish diameter between 66 mm and 145 mm and initial solution thickness between 1 and 24 mm. Let us note that the glass transition temperature of PIB is -76°C. Experiments are then performed well above the glass transition and the system remains rubbery all along the drying.

Drying kinetics

Model. Drying kinetics show several domains that can be qualitatively analyzed using a diffusive model to describe solvent transfer in the solution. The assumptions and equations are detailed in [1] and we only recall the main features of the model. The model is 1D (direction z perpendicular to the dish). The state variables are the local solvent concentration in the solution, $C_S(z,t)$, the solution temperature T(t) and thickness e(t). External inputs are the ambient air temperature and air velocity above the sample. Solvent flux in the solution is described by the Fick law, with a variable mutual diffusion coefficient D(Cs). Thermodynamical equilibrium is assumed and the saturating vapor pressure P_{VS} at the interface is given by the Flory-Huggins model. Temperature is obtained by writing the system heat balance. Exchanges between the solution and the hood air depend on the air velocity in the hood. They are characterized by two exchange coefficients, h_{th} the thermal exchange coefficient (W/m^{2}K) and h_m the mass exchange coefficient (m/s). Depending on the air velocity, h_m can be changed from 2.6 to 12.5 mm/s and h_{th} from 10 to 100 W/m^{2}K.

Kinetics. A typical example of experimental kinetics is given in Figure 1. Experimental configuration is: e_o (initial thickness) =12.7mm, h_m=3mm/s and w_{S0} (initial solvent mass fraction)=95%. In a first stage, the inner of the solution is still at the initial concentration, i.e. the concentration gradient has not reached the sample bottom. The behavior is then similar to that of a semi-infinite medium. A transition is observed when the perturbation reaches the bottom of the dish (finite medium): the evaporative flux strongly decreases and the end of the drying is characterized by a very weak evaporative flux, due to the strong decrease of the mutual diffusion coefficient when the solvent concentration decreases.

Moreover, it is possible to characterize the first stage (semi-infinite medium) by the succession of different regimes that involve different phenomena. First, the evaporation is similar to the evaporation of pure solvent since the activity of polymer solutions is close to one at high solvent concentration. The flux is controlled by the heat and mass exchange coefficients with the hood air (domain 1 in Fig.ure 1): After a rapid thermal transient regime, the solution temperature reaches an equilibrium value and the flux is nearly constant ("plateau" domain). Then, when the solvent mass fraction at the interface becomes less than about 0.4, the activity decreases and a new regime appears, characterized by a weak decrease of the evaporative flux (domain 2 in Figure 1). Detailed analysis of the equations shows that this regime depends mainly on the initial concentration of the solution and on the value of the diffusion coefficient for high solvent concentration. That is why experiments with different h_m and initial thicknesses gather around the same master curve, as shown in Figure 2. Let us note that the duration of this regime depends on the initial thickness and exchange coefficient h_m. It may disappear if the finite medium stage occurs before the end of the "plateau".

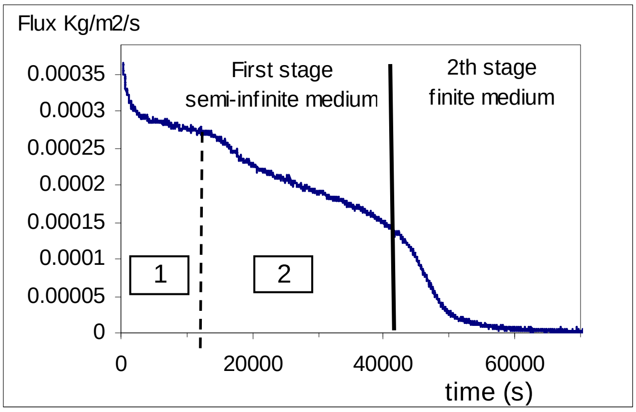

Figure 1. Typical drying kinetics - e_o=12.7mm, h_m=3mm/s , ws_0=0.95

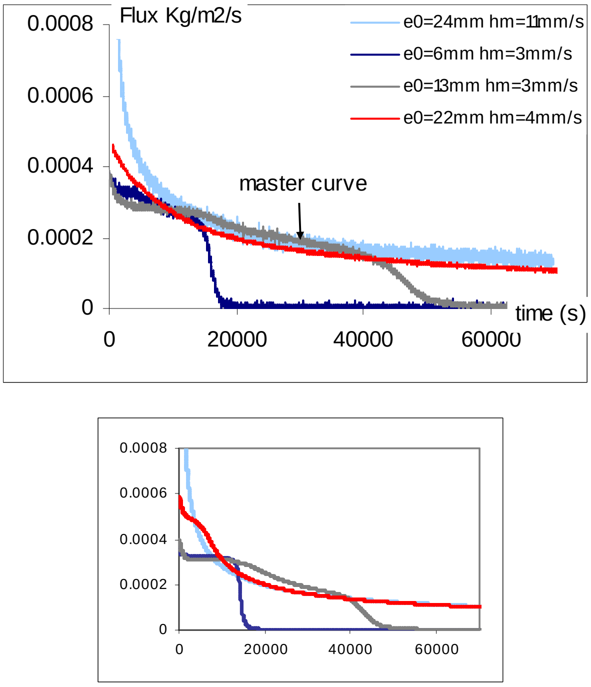

Figure 2. Solvent evaporation flux for different e_0 and h_m, w_{S0}=95% Top: Experiments – Bottom: Simulation

Instabilities

The main trends of drying kinetics are captured by a diffusive model, but drying involves more complex phenomena as hydrodynamical and mechanical instabilities that may result in the development of undulations at the film surface, as illustrated in Figure 4. In the following we give some first results on the possible origins of these phenomena and correlate experimental observations with the kinetics stages described in the previous section.

Figure 4. Wavy surface; the dish diameter is 116mm.

Hydrodynamic instabilities. These instabilities come from the differences between the densities and the surface tensions of the solvent and polymer [2]. Indeed, the evaporation induces a decrease of the temperature and of the solvent concentration at the upper surface that, for the physicochemical system investigated here, leads to an unstable situation [3,4]. The instabilities were observed by using iriodine particles as a tracer. Typical convection cells appear at the beginning of the drying (Figure 5). Later the convective cells cannot be observed anymore. A complete stability analysis is very difficult in this free boundary system, since viscosity and diffusion coefficient strongly depend on the solvent concentration that is not uniform through the film and that changes during drying (transient regime) [5]. Recent study has shown the importance of surface tension gradients on the development of instabilities [6].

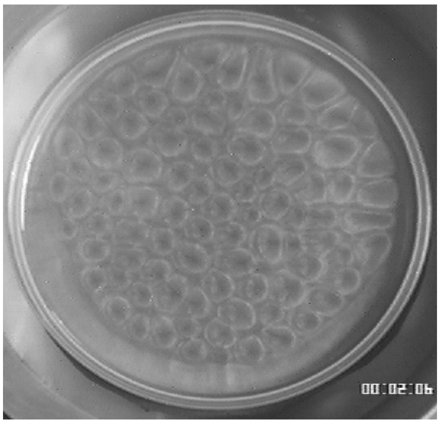

Figure 5. Convective cells; the dish diameter is 116 mm.

Undulations. For some experimental configurations, undulations appear at the surface of the film which can be totally or partially overrun. Exhaustive characterization of the parameters that influence their occurrence is not yet achieved, but preliminary analysis show the following results: except some small radial wrinkles (about a few mm) in the meniscus that are not taken into account in the following, no undulations appear for initial solvent concentration equal or less than 90%, that corresponds to an initial viscosity of 339mPa.s. Results obtained for initial concentration equal to 95% show the following trends (initial viscosity=21mPa.s) [7]: no undulations appear if the initial thickness is greater than about 15mm or if the exchange coefficient h_m is smaller than 0.5 mm/s. The surface is totally wavy for small thicknesses (<8mm) and small h_m (<4mm/s) and only partially wavy if h_m increases. These observations show that this phenomenon may depend on the solution rheology but is also strongly coupled with the drying kinetics and cannot be studied independently of the development of the concentration gradient in the solution during the drying. That is why visualization by a camera was performed to correlate the evolution of the surface and the kinetics. For all the experiments, undulation was found to begin a little before the decreasing of evaporation flux that characterizes the transition between the semi-infinite and finite media. For totally wavy surfaces, the undulations overrun the surface during the transition between the two stages and then are frozen until the end of the drying. For partially wavy surface, the behavior is similar except than the phenomenon stops before the end of the flux decrease. Figure 6 gives the example of two experiments with small thicknesses, so that the transition between semi-infinite and finite media occurs before the end of the first "plateau" regime.

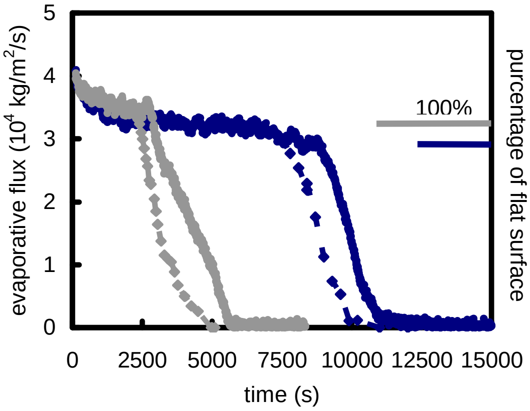

Figure 6: Evaporative flux (continuous lines) and percentage of flat surface (dotted lines),
grey: e_0=1.8mm - h_m=2.5mm/s, dark blue: e_0=3.9mm h_m=2.7mm/s.

Conclusion

Surface undulations formation during the drying of polymer films is a complex problem that is coupled with the evolution of the concentration in the film. Some authors analyze this instability as the consequence of the convective instabilities that appear at the beginning of the drying [8]. It may also be due to mechanical instability (buckling) due to the stresses in the « crust » (the domain near the surface which is highly concentrated in polymer). The present analysis have shown that undulations appear a little before the transition between the semi-infinite to finite medium. Further experiments are actually performed to go deeper in the understanding of the observed phenomena.

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