

Use of a model system to study kinetics and instabilities during the drying of a polymer solution

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Keywords: Polymer solution, Drying kinetics, Instabilities, Wrinkles

Introduction

A brief resume of several works that are performed in the laboratory about the drying of polymer films is presented. The general purpose is to characterize the coupling between the drying kinetics and the final state of the film.

System

In order to get a simple and well characterized system, the solutions under study are composed of one polymer and one solvent only: Polyisobutylene/Toluene (PIB/Toluene). No polymerization or chemical reactions occur during the drying so that the dried film is obtained by evaporation of the solvent only. The glass transition temperature of PIB is -76°C (Sigma-Aldrich). The experimental temperature (ambient temperature) is far above the glass transition temperature and the system remains rubbery all along the drying, unlike in [1]. PIB was supplied by Sigma-Aldrich with $M_w=5.10^5$ and polydispersity 2.5 and Toluene was supplied by Prolabo (Chromatographic use).

System characterization

Modelling the drying kinetics from the initial dilute solution to the dry film needs to know the evolution with the solvent concentration of the saturated vapor pressure and of the mutual diffusion coefficient. In polymer solvent solutions these quantities strongly decrease in the polymer concentrated domain: for example the diffusion coefficient, D_{sp} , decreases of several orders of magnitudes when the solvent volume fraction varies from 0.3 to 0 [2]. We have measured these two quantities by series of differential sorption experiments. The experimental set-up (Hiden IGA) consists of an accurate balance coupled with a vapor chamber whose temperature and pressure are controlled. The sample is located in the chamber and changing the solvent vapor pressure allows for swelling or drying the polymer film. The evolution of the weight of the film in response to an imposed step of solvent vapor pressure gives access to the mutual diffusion coefficient (through a suitable model of the swelling kinetics). The asymptotic value reached at the end of the experiment gives the equilibrium solvent concentration in the film corresponding to the imposed solvent vapor pressure. Results obtained for PIB/Toluene in the concentrated domain are given in Figs 1a and 1b at 25°C [3].

Drying

Experiments

The PIB/Toluene solution, with an initial solvent mass fraction ranging from 85% to 98% (g/g), is poured in a dish. The dish is then put on a balance (precision 0.1 mg) that is

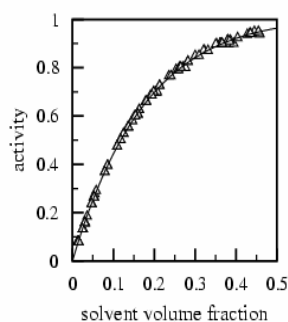


Fig 1a: Sorption isotherm

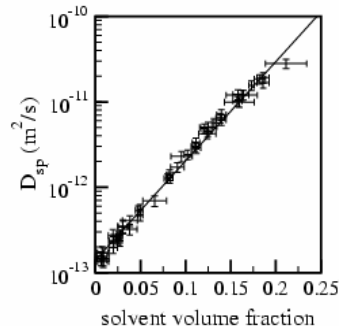


Fig 1b: Diffusion coefficient

located in an extractor hood at room temperature. Air temperature and solution weight are recorded all along the drying (60 hours). The 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 allows to record top views during drying in order to eventually detect convection (with iriodine used as a tracer) and/or the formation of wrinkles at the surface. Experiments were performed with dish diameter between 66 mm and 145 mm and initial solution thickness between 1 and 24 mm.

Drying kinetics

A typical example of experimental kinetics is given in Fig 2. Experimental configuration is: e_0 (initial thickness) = 12.7mm, $h_m=3\text{mm/s}$ 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. 2): 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 Fig 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”.

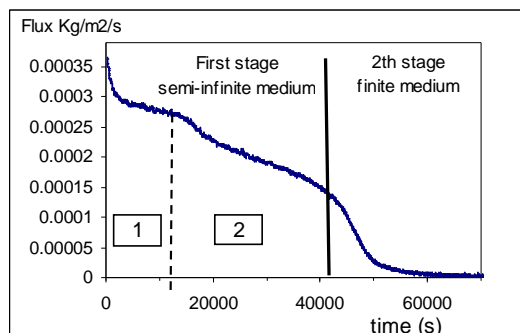


Fig 2: Typical drying kinetics
 $e_0=12.7\text{mm}$, $h_m=3\text{mm/s}$, $ws_0=0.95$

Model. The main trends of the drying kinetics can be captured by a diffusive model to describe solvent transfer in the solution. The assumptions and equations are detailed in [5]. 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 $D_{Sp}(C_S)$. Local 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 ($\text{W/m}^2\text{K}$) 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 $\text{W/m}^2\text{K}$. Using this model and the drying experiments described in the previous section an optimization procedure is under study to get $D_{Sp}(C_S)$ from drying kinetics (inverse problem): in such a global optimization, the unknown function $D_{Sp}(C_S)$ is obtained by minimization of the distance between the experimental and simulated kinetics [4].

Instabilities

Though a diffusive model for the solvent transfer in the film succeeds in reproducing the succession of the different regimes, more complex phenomena are involved during the drying.

Hydrodynamics instabilities

First, natural convection may be induced by gravity or surface tension, due to the concentration gradients and/or the temperature gradients through the film [6-8]. Indeed, due to the solvent evaporation, both the temperature and solvent concentration are smaller at the upper interface of the film than at the bottom. The density of the solution increases when the temperature decreases and when the solvent concentration decreases (the density of PIB is greater than that of Toluene). The configuration under study is then unstable. The same analysis holds for surface tension: the surface tension of the solution increases when the temperature decreases and when the solvent concentration decreases, leading again to an unstable configuration. Such instabilities have been observed at the

beginning of the drying (Fig 3). Later the viscosity of the solution strongly increases as the solvent concentration decreases, which prevents any convection when the solution becomes more concentrated.

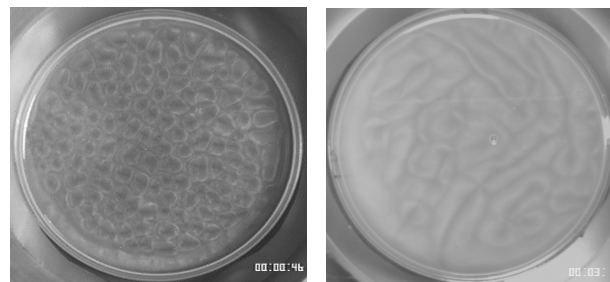


Fig 3: $h_m=3\text{mm/s}$, $ws_0=0.95$
Visualisation of convective cells (left view, $e_0=3.9\text{mm}$)
or rolls (right view, $e_0=8.7\text{mm}$)

Wrinkles

For some experimental conditions wrinkles appear at the surface of the film during the drying. They were always found to begin a little before the decrease of the evaporation flux that characterizes the transition between the first and second stage, when the solvent concentration at the bottom of the dish decreases very rapidly, and to progressively invade the sample surface in the course of the transition domain. It has also been observed that, after an undulation had formed, it remains the same as long as drying goes on and even long after (even after several months, see Fig 4). Several phenomena can be put forward to explain the wrinkles formation: they can be viewed firstly as the “signature” of local concentration variations due to convection. They could also be induced by the development of important stresses in the inner of the film while the surface is already dried and relaxed [9,10].

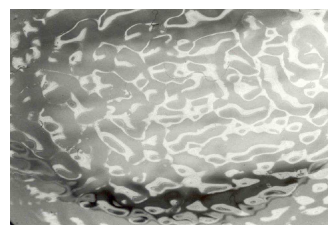


Fig 4: Wrinkled surface of the dried film.
The horizontal size of the view corresponds to about 30mm.

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