Experimental and numerical observations of surface deformation during drying of polymer solutions due to Marangoni phenomena

S. G. Yiantsios,¹ S. K.Serpetsi,¹ F. Doumenc,² S. Mergui,² and B. Guerrier²

¹Department of Chemical Engineering, Aristotle University of Thessaloniki, Univ. Box 453, GR 541 24, Thessaloniki, Greece, yiantsio@auth.gr ²Univ Paris-Sud, Univ Paris 06, CNRS, Lab FAST, Bât 502, Orsay, F-91405, France, doumenc@fast.u-psud.fr

Experimental observations [1, 2] on the drying of polymer solution films under conditions of controlled evaporation of the volatile solvent are analyzed. The physicochemical and transport properties of the solutions are strongly dependent on polymer concentration, most notably the solution viscosity which increases by several orders of magnitude over the course of the experiments. Over a range of conditions, namely for relatively, yet not overly, small initial film thicknesses and evaporation rates, the dynamics is dominated by solutocapillary driving forces and wrinkling of the films takes place during a final stage. During this stage the interfacial polymer concentration approaches a certain threshold marking a significant reduction in the evaporation rate and the cessation of fluid motion. It has been observed qualitatively that the final dried films are accordingly patterned. The objective of the study is to find out the involved mechanisms for the selection of wavelengths and pattern amplitudes, through in-situ observation of the free surface deformation during drying (see FIG. 1) and through numerical simulations. Numerical simulations of the solutocapillary phenomena are performed taking into account the variability of the transport properties and the deformation of the film interface [3]. The simulations suggest that at relatively low Marangoni numbers the mechanism of Overdiep [4] may be responsible for the final film wrinkling, whereas at sufficiently high Marangoni numbers the fine cellular structure of the Pearson mechanism dominates [5, 6] but interfacial deformation is inhibited by strong capillary pressure forces. Yet, this mechanism results in nonuniform distribution of the solute along the thin film. Hence, the numerical simulations corroborate the analysis of the experimental observations in the suggestion that the cellular instability is responsible for the uneven distribution of the solute and for the uneven profile of the dried polymeric deposit.



FIG. 1. Visualisation of the free surface deformation using a Schlieren method [7, 8]. Image corresponding to the end of drying for a PIB/toluene solution, with initial conditions $h_0 = 1.1$ mm, $\Phi_{P0} = 0.05 \Delta h_{max}$ (red to dark blue colors)~ 40 μ m.

- [1] F. Doumenc, E. Chénier, B. Trouette, T. Boeck, C. Delcarte, B. Guerrier, M. Rossi, *Free convection in drying binary mixtures: solutal versus thermal instabilities*, IJHMT, **63**, 336-350 (2013).
- [2] N. Bassou, Y. Rharbi, *Role of Bénard-Marangoni Instabilities during Solvent Evaporation in Polymer Surface Corrugations*, Langmuir, **25**, 624-632 (2009).
- [3] S. K. Serpetsi, S. G. Yiantsios, *Stability characteristics of solutocapillary Marangoni motion in evaporating thin films*, POF, **24** (2012).
- [4] W. S. Overdiep, The leveling of paints, Prog. Org. Coatings, 14, 159-175 (1986).
- [5] J. R. A. Pearson, On convection cells induced by surface tension, J. Fluid Mech., 4, 489-500 (1958).
- [6] P. G. de Gennes, *Instabilities during the evaporation of a film: Non-glassy polymer+ volatile solvent*, Eur. Phys. J. E, **6**, 421 (2001).
- [7] F. Moisy, M. Rabaud, K. Salsac, A Synthetic Schlieren method for the measurement of the topography of a *liquid interface*, Exp. Fluids, **46(6)**, 1021-1036 (2009).
- [8] P. Cavadini, J. Krenn, P. Scharfer, W. Schabel, *Investigation of surface deformation during drying of thin polymer films due to Marangoni convection*, Chem. Eng. Proc., **64**, 24-30 (2013).