Surface structures during thin film-drying caused by Marangoni convection

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Presented at the 14th International Coating Science and Technology Symposium,
September 7-10, 2008, Marina del Rey, California[1]

Introduction

For thin coated products, surface homogeneity is an important quality characteristic, e.g. for LCD-foils or polarization foils the requirements are under 1 μm deviation in surface roughness. Different heat conductivities of the substrate (e.g. reparation with a different material) or non uniform heat supply or air flow in the dryer can cause lateral temperature gradients in the drying polymer solution leading to different drying rates and thus lateral solvent concentration gradients. The emerging surface tension gradients are driving forces for interfacial dynamic instabilities – called Marangoni instabilities – which result in various structures of the thin film surface. To inhibit the appearance of unintentional surface structures, the drying process has to be investigated and the influence of surface tension and viscosity as antagonists of the interfacial convection has to be described theoretically.

Experimental setup

The measurement technique to observe the appearances of surface structures during drying of thin films is based on the analysis of the refracted images of a dot pattern through the surface of transparent fluid shown by Moisy, Rabaud and Salsac [1]. A schema of the measurement technique is shown in figure 1. A CCD-camera perpendicular above the film is used to take sequences of images during the drying of the

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polymer solution. The polymer film is casted on a thin glass substrate with a dot pattern on its bottom side. To induce lateral temperature gradients on the glass substrate during the drying process a plate with different thermal conductivities ($\kappa_1 > \kappa_2$; for the shown experiments aluminum / Teflon) is placed between the heating plate and the glass substrate (see figure 1 left).

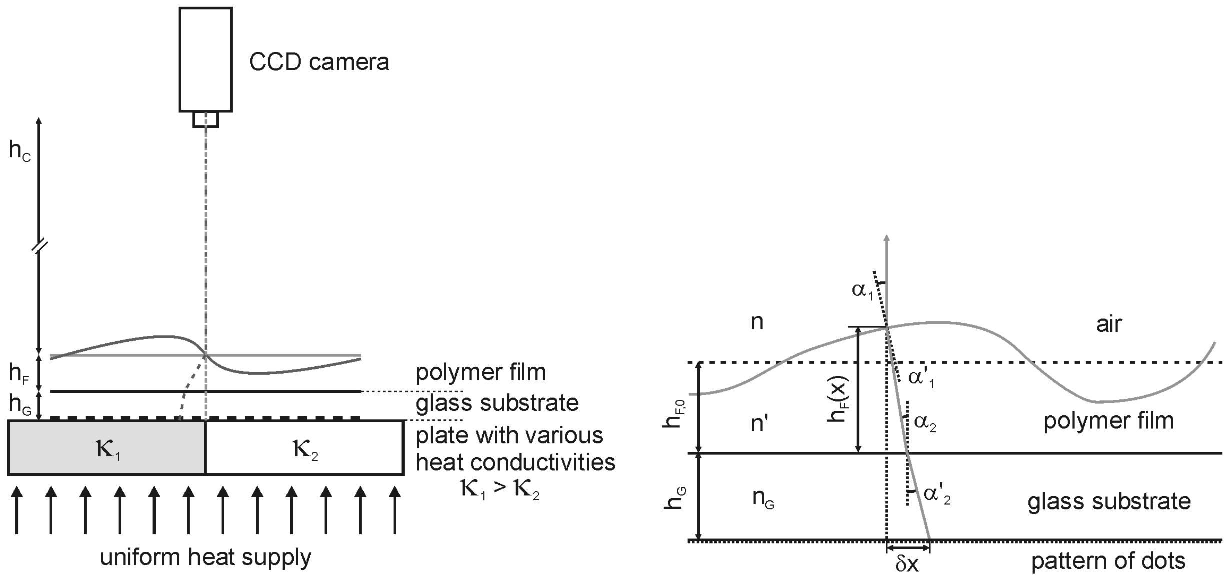

Figure 1: Schematic principle of the measurement technique and the optical path through the polymer film and the glass substrate.

If the optical properties of the system (i.e. refraction index of the polymer solution and the glass substrate) are known, the instantaneous deformation of the polymer film can be reconstructed from the displacement field ($\delta x, \delta y$) between the refracted image of the deformed surface and the reference image obtained at planar surface (see figure 1 right). The mathematical equations for this nonlinear 2D problem are very difficult to solve. Moisy, Rabaud and Salsac [1] recently published different approaches for linearizing the problem with respect to the geometry of the arising structures. For thin films, shrinking during drying, there are some additional difficulties which have to be taken into account. First of all, the dots of the pattern must be very small, so that the resolution is good enough to detect the slight deformations of the thin film surface. A second problem for the reconstruction is that the theoretical height of the planar surface has to be known for every time step. For the initial results presented in this contribution, this height is calculated from the well known drying behavior of the polymeric system at the constant temperature above the plate with the higher thermal conductivity (isothermal drying). First measurements are shown in the next section.

Results and Discussion

To perform first experiments, a polymer solution of poly(vinyl acetate) (PVAc) with methanol as solvent was used. For this polymer system the drying process is well known from former works [2]. The polymer solution is prepared with an initial solvent content of $X_0 = 2\,\frac{\text{g (methanol)}}{\text{g (PVAc)}}$ and then casted on the temperature-controlled glass substrate. During the drying process a sequence of images is taken and the local height of the polymeric film h_F is calculated for every time step. Some results of the calculations are shown in figure 2.

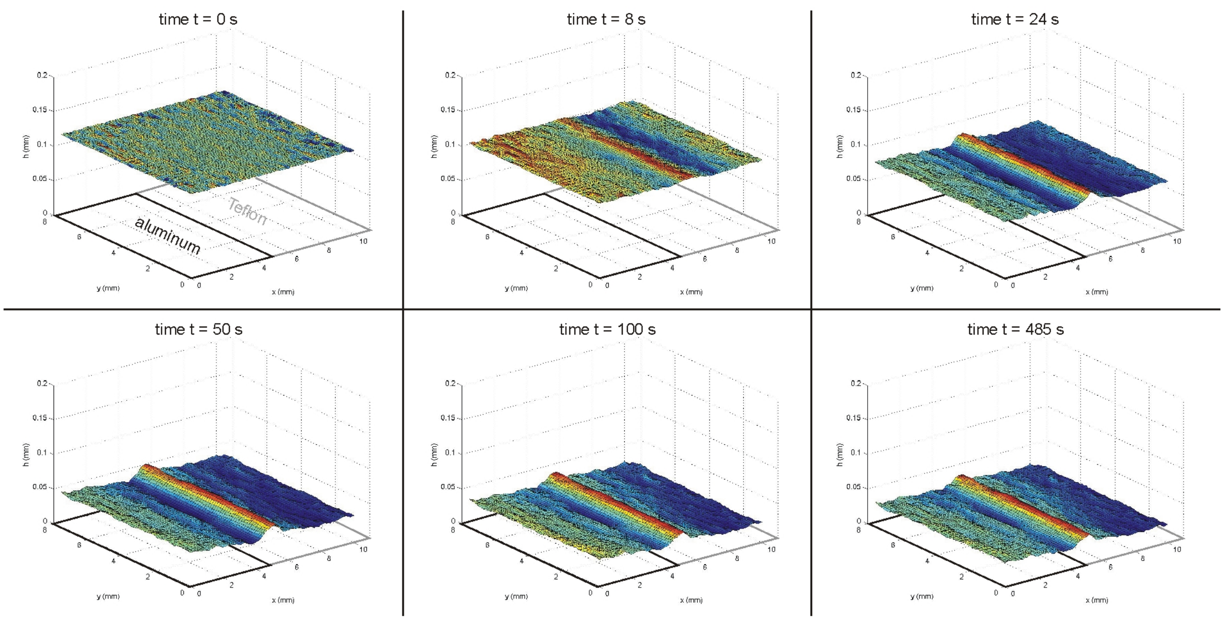

Figure 2: Perspective view of the drying polymer film ($X_0 = 2\,\frac{\text{g (methanol)}}{\text{g (PVAc)}}$, $h_{F,0} \approx 125\mu m$ *) at different time steps.*

Due to the evaporation of the methanol the film shrinks. Above the Teflon block the film cools down due to evaporation cooling and the low thermal conductivity of the Teflon. The temperature drops and the drying rate slows down and a lateral solvent concentration gradient between the aluminum and the Teflon supported side of the glass substrate occurs. The surface tension is a strong function of the solvent concentration and the surface tension above the Teflon gets lower than above the aluminum and a resulting driving force induces a convective flow (Marangoni convection) of the polymer solution. This polymer flow leads to a wave along the border between Teflon and aluminum. At a certain solvent content, the surface structures “freeze” due to the increasing viscosity of the polymer solution.

A comparison between a cross section of the dry film measured with a contact profiler and the calculated height (see last image in figure 2) shows, that the measured profile of the film is represented qualitatively very well by the new optical method. Solely the shape of the wave along the border differs and the local measured height is on the aluminum side a little lower than represented by the optical method.

Conclusion and Prospect

The results in this contribution show, that the presented optical measurement technique is suited well to investigate the development of surface structures during the drying of thin films. At the present point of this work, the results are qualitatively in good agreement with mechanically measured surface profiles. For a quantitative evaluation, the measurement technique – especially the dot pattern – has to be improved and the linearization of the mathematical solution of the 2D problem has to be analyzed.

Measuring the development of surface structures during thin film drying is a necessary step to validate future CFD simulation results of Marangoni convection flows. For a simulation, a profound knowledge of the dependence of surface tension and viscosity on the solvent content in the polymeric systems is necessary; obtaining these data will be the next important step.

Acknowledgement

The authors would like to thank Mr. Rabaud for the support and the idea for the measurement technique at ECS 2007 and the DFG (German Research Foundation) for initial funding the screening investigations to prepare a full DFG proposal.

References

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