

EXPERIMENTAL AND NUMERICAL INVESTIGATION OF MULTI-SOLVENT MASS TRANSPORT DURING THIN FILM DRYING

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Introduction

Many high technological industrial coatings require polymer solutions with more than two solvents to achieve certain properties of the final film. To predict the drying process and the influence of the solvents on the properties of the coating, a detailed understanding of the multi-solvent mass transport during thin film drying has to be established. Although this topic is not new and of great interest for many industrial applications, there are no experimentally verified approaches for a theoretical description. This is mainly due to a lack of experimental data, since it has been almost impossible to determine the local mass fractions of the distinct solvents within the drying film with sufficient accuracy.

In this work, the drying of quaternary solutions of polyvinyl acetate (PVAc) with three different solvents was investigated for the first time by means of Inverse-Micro-Raman-Spectroscopy (IMRS). The IMRS measurement technique gives the opportunity to measure the solvent concentration profiles of all three solvents quantitatively during the drying process with a high spatial resolution. The influence of different drying conditions (e. g. drying temperature, air flow rate, initial solvent composition) will be shown and first approaches for a numerical simulation will be discussed.

Experimental

To investigate the drying of multi-solvent coatings, thin films of a multi-solvent solution are cast on a temperature-controlled flat plate in laminar flow within a double-jacket drying channel. To investigate the influence of the boundary conditions on the mass transport of the solvents, the air velocity and the isothermal drying temperature were varied. To avoid any influences on the air flow across the polymer sample, the measuring technique is injected “inversely” (from the bottom) into the drying channel. Fig. 1 shows the flow channel with measuring technique.

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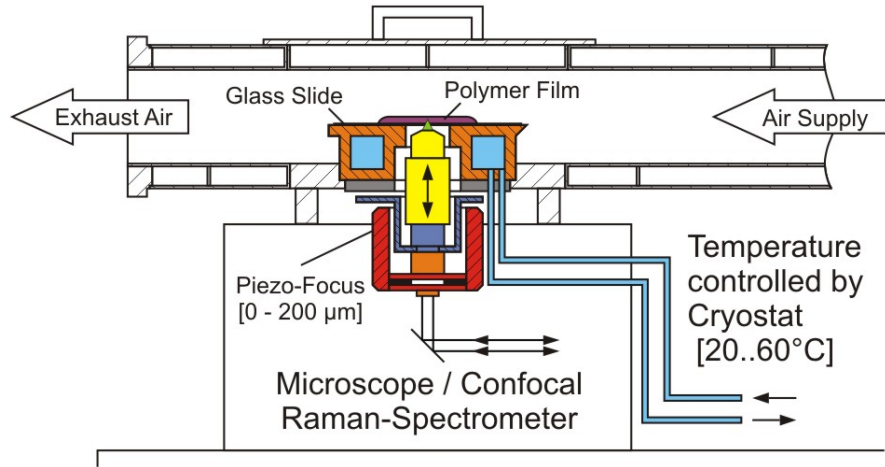


Fig. 1: Drying channel with flat plate in laminar flow and IMRS measuring technique.

The measuring technique consists of a Raman spectrometer and an inverse microscope with confocal optics. An oil-immersion objective is used to obtain a high spatial resolution of 1-2 μm . To determine the solvent concentration profiles during drying, Raman spectra are recorded at different positions within the drying film. The Raman spectra contain the information about the local composition of the sample and by combining the single spectra of a certain depth scan the solvent concentration profiles are obtained.

To quantitatively analyse the signals recorded at different positions within the drying film, the multi-component Raman spectra of the mixture are represented as superposition of the weighted pure components spectra by means of a least squares method [1]. The weighting factors α_i correlate with the components relative intensity I_i/I_{Polymer} which linearly corresponds to the solvent content X_i (mass component i / polymer mass).

$$\frac{I_i}{I_{\text{Polymer}}} = \frac{\alpha_i}{\alpha_{\text{Polymer}}} = K_i \cdot X_i \quad (1)$$

The calibration constant K_i can be determined experimentally by analysing samples with known composition.

Results and discussion

As basis for model calculations, the influence of different drying conditions (e. g. drying temperature, air flow rate, initial solvent composition) was investigated for the multi-solvent model system methanol-ethanol-toluene-PVAc. Fig. 2 exemplarily shows the integral drying curves for the three different solvents at 30°C and an air flow velocity of 0.4 m/s. Plotted is the solvent loading X_i vs. the drying time.

As expected, the low boiling methanol evaporates first and after three minutes no methanol is present in the film anymore. The methanol drying rate is almost constant; there is no significant mass transport resistance for methanol in the film. Ethanol, whose vapor pressure is clearly below methanol, shows a constant drying rate only at the beginning of the experiment. With increasing drying time the evaporation rate significantly slows down due to an increasing mass

transport resistance in the film. After ethanol is completely evaporated, the high boiling toluene is trapped within the film due to a significant diffusive mass transport resistance which is already known from our past work [2, 3]. It is noteworthy, that with gravimetric drying experiments only the overall solvent content could have been measured and no information about the single solvents would have been obtained.

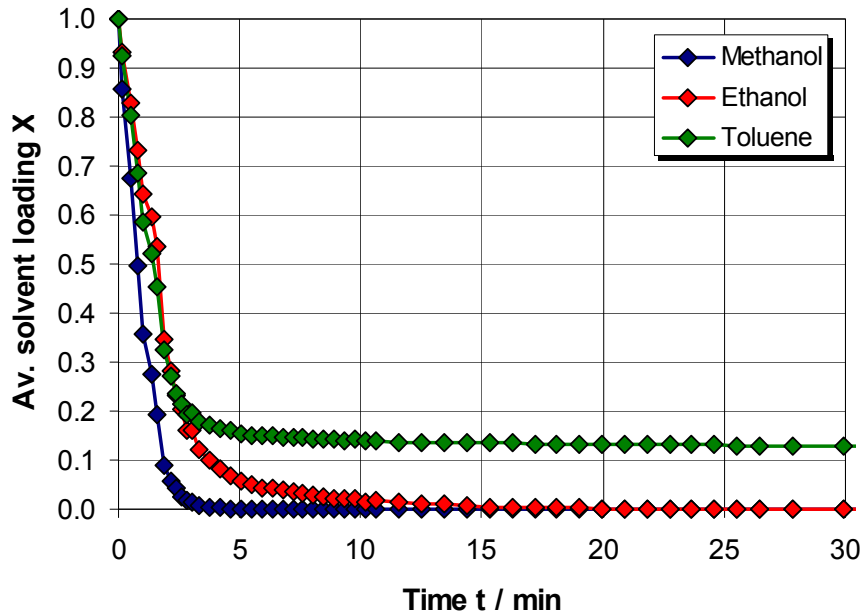


Fig. 2: Integral drying curves for methanol-ethanol-toluene-PVAc. $T = 30^{\circ}\text{C}$, $u = 0.4 \text{ m/s}$, $h_{dry} = 42 \mu\text{m}$.

Even so, integral drying curves of the single components are often insufficient to precisely verify model calculations. Apart from the complicated description of the multi-component mass transport within the film, there are several uncertainties regarding the phase equilibrium and the local mass transport in the gas phase, especially in the case of a quaternary system. Since generally some of the unknown model parameters are fitted to the experimental data (mostly the diffusion coefficient), an incorrect description of any other parameter significantly affects the quality of the fit. E.g. in the case of gravimetric drying experiments, the effect of a moving drying front due to decreasing mass transport coefficients in the gas phase in flow direction along the film is often misinterpreted as diffusive mass transport resistance in the film, which results in much too low values for the solvent diffusion coefficient.

To overcome these well-known problems, the IMRS measuring technique delivers not only the integral drying curves but also provides detailed information about the solvent concentration profiles in the film (Fig. 3). By fitting model calculations to the measured solvent content profiles, a significant improvement can be obtained.

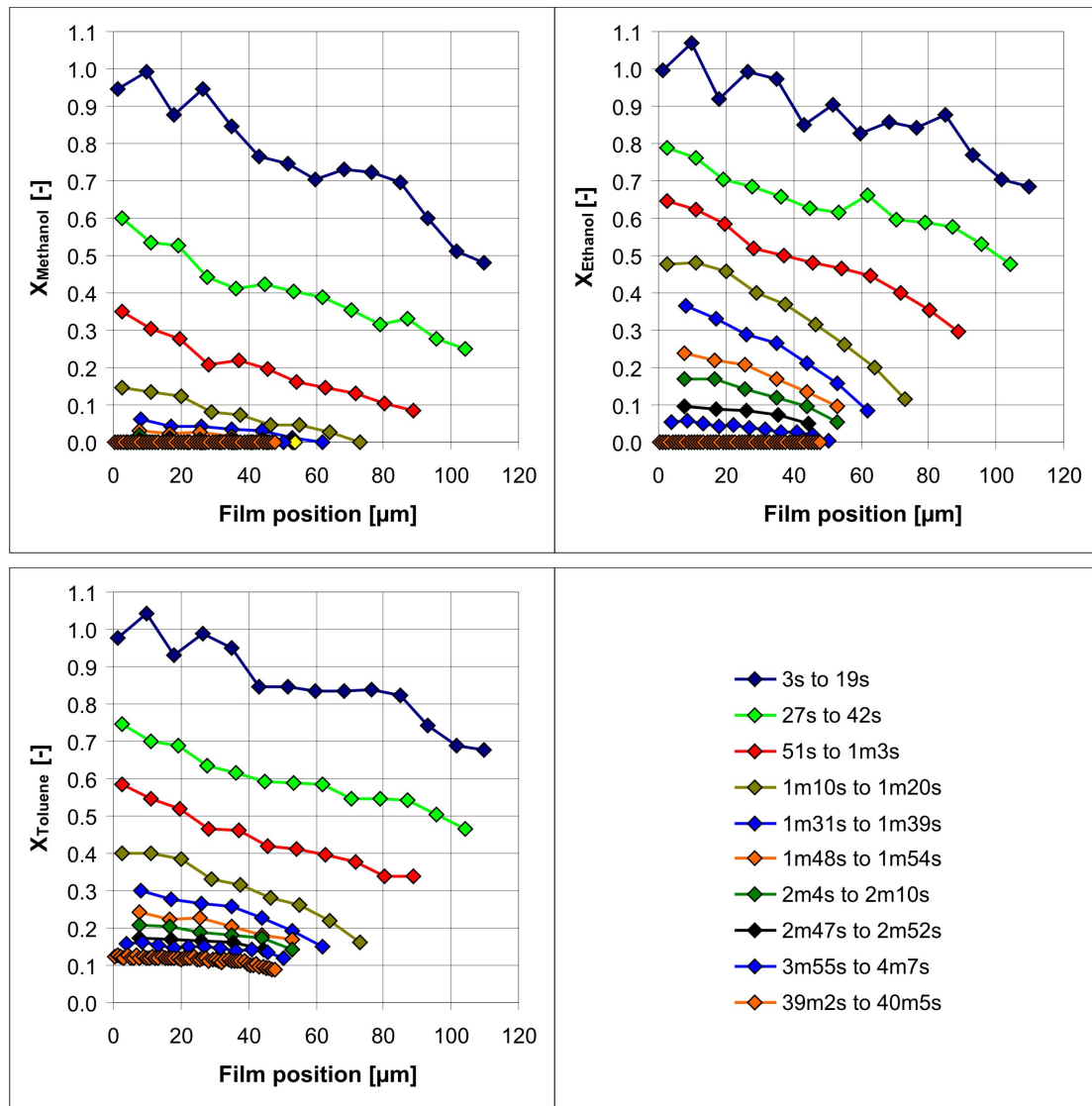


Fig. 3: Local solvent loading profiles during drying. $T = 30^\circ\text{C}$, $u = 0.4 \text{ m/s}$, $h_{\text{dry}} = 42 \mu\text{m}$.

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