

By Orders of Magnitude Decelerated Solvent Transport in Polymer Nanolayers

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Introduction

The fabrication of organic electronic devices by liquid deposition features a number of advantages compared to vacuum deposition such as reduced material loss, better suitability for polymer deposition and the increased feasibility of scale-up using continuous roll-to-roll coating processes for reaching commercial scale. In this context, mass transport in polymer nanolayers is of high interest regarding the drying, solvent residues, solvent vapor annealing and layer intermixing. In this talk the decreased mass transport in polymer nanolayers is addressed experimentally and by proposing a numerically underpinned diffusion coefficient model.

Experimental

Materials

As model system polyvinyl acetate is used with methanol as solvent. For this chemical system all the necessary data for concentration-dependent diffusion coefficients and phase equilibria in micrometer layers have been measured, validated and published by our institute [1,2].

Methods

We established an ultra-precise sorption apparatus utilizing a quartz crystal microbalance in order to perform sorption experiments on polymer nanolayers with thicknesses between 20 nm and 500 nm. The experimental setup allows for the distinct determination of concentration- and thickness-dependent sorption equilibria and kinetics.

Modeling

The kinetic sorption data have been evaluated by fitting 1D mass transport simulations utilizing an analytic solution of the Second Fick's law under realistic boundary conditions [3]. In addition to this complete solution (CS) we determined the solvent diffusion coefficient for small times (ST) and for long times (LT). Especially the determination using short time fitting is very common in literature. The comparison of the diffusion coefficients D revealed that $D_{ST} > D_{CS} > D_{LT}$ and that all determined diffusion coefficients for polymer layers below 200 nm are significantly smaller than literature data for micrometer scale layer thicknesses. This leads to the hypothesis of a substrate-near

boundary layer with a diffusion coefficient that is by orders of magnitude lower than the diffusion coefficient determined for micrometer-scale layers [4]. By this 2-layer-model the experiments are simulated in order to tune the model parameters which are the thickness of the substrate near boundary layer and the diffusion coefficient in this layer (see Figure 1).

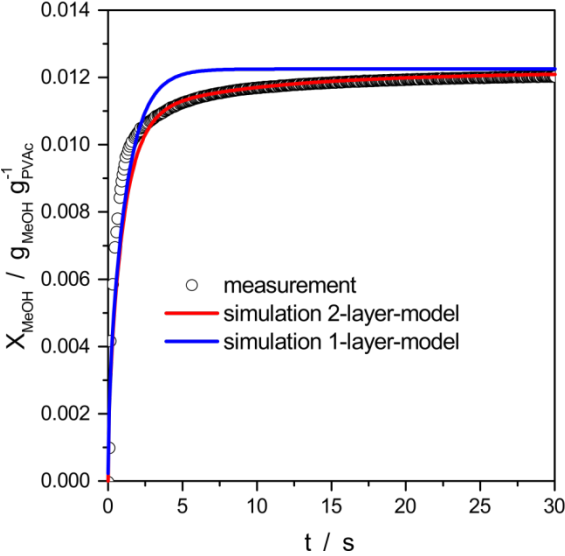


Figure 1: Exemplary sorption curve with the best fit of the 1-layer-model and the 2-layer-model. Film thickness: 488 nm, temperature: 40 °C, methanol activity in gas phase: 0.16.

Results and discussion

Using the 2-layer-model we are able to reproduce the experimental solvent sorption curves of polymer nanolayers. The model is not only capable of reproducing the experimental data but also physically plausible since the mobility of polymer chains may be limited by the substrate which leads to a decreased solvent diffusion coefficient. Drying curves can be simulated using the 2-layer-model. As shown in Figure 2, the impact of the substrate near boundary layer is significant for the solvent concentration profile in nanolayers and is therefore of high importance for example for the production of organic electronics by liquid deposition.

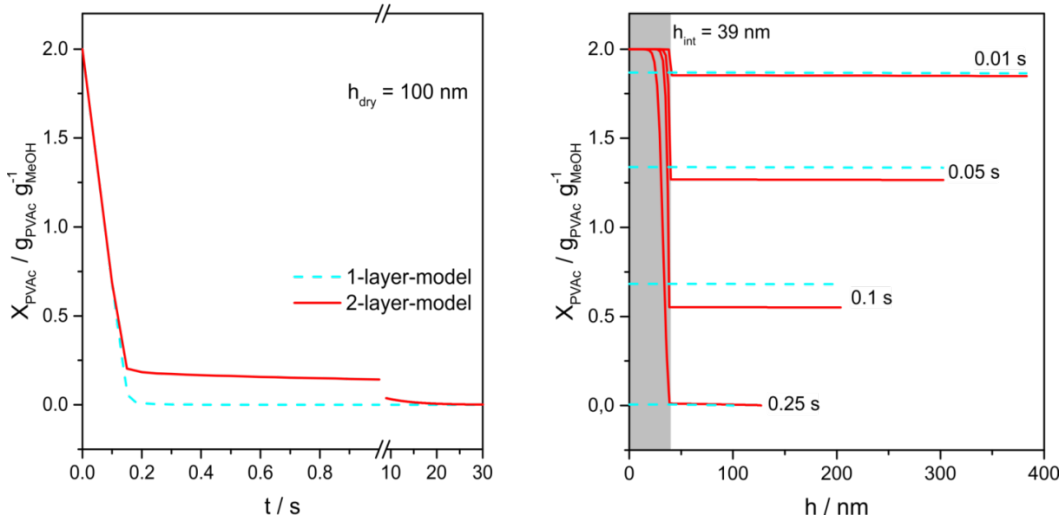


Figure 2: Comparison of the integral drying curve (left) and concentration profiles (right) for the 1-layer-model and the 2-layer-model simulating the drying a polymer nanolayer

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