WATER ABSORPTION IN POLYMER MIXTURES – PHASE EQUILIBRIUM AND DIFFUSION KINETICS

S. Kachel, P. Scharfer, W. Schabel

Institute of Thermal Process Engineering, Thin Film Technology (TFT),
Karlsruhe Institute of Technology (KIT), Germany

Presented at the 16th International Coating Science and Technology Symposium,
September 9-12, 2012, Midtown Atlanta, GA[1]

Introduction

Polymer blends are of great interest as an immobilization matrix for active components in coatings such as proteins e.g. in biosensors. The water absorption of these mixtures is essential as water in the film can influence the properties and the performance of the active components significantly. The goal is to describe the water absorption of multi-component mixtures with a suitable model. Predicting the model parameters in polymer mixtures from measurements of pure component data would greatly facilitate simulation of water uptake in mixtures. In this work we present measured data for sorption equilibria and diffusion coefficients of water in polymer blends and propose models for their calculations from pure component data.

Experimental

Materials

The polymers polyvinylpyrrolidone (PVP) and polyvinylalcohol (PVA) were chosen to represent matrix polymers of waterborne coatings. The protein bovine serum albumin (BSA) served as model protein for the fabrication of polymer-protein films. For sorption and drying experiments the polymers were dissolved in water separately and the solutions of the two compounds were combined to yield the desired mass ratio of solids.

Water sorption in polymer blends

Water sorption isotherms for polymer-polymer and polymer-protein mixtures were measured gravimetrically. The samples were coated on aluminum trays that were stacked in sample holders and incubated in a temperature and humidity controlled climate chamber. An automated sample exchanger placed the samples on a balance in turn. The mass was recorded automatically, making opening of the incubator unnecessary. With this setup sorption isotherms of 40 samples can be measured simultaneously while weighing takes place under controlled conditions inside the climate chamber.

---

[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

Water diffusion kinetics in polymer blends

Diffusion kinetics of water in the film was studied by means of drying experiments that were analyzed with Inverse-Micro-Raman-Spectroscopy (IMRS) [1]. With this measurement setup concentrations within a film can be measured locally with a spatial resolution of 1-2 µm. Quantitative analysis of Raman spectra was done by fitting the weighting coefficients of a superposition of the pure component spectra to the measured spectra [2]. Concentrations can be obtained from the measured Raman spectra with a calibration from samples of known composition. All drying experiments were conducted in a temperature-controlled drying channel with defined air flow as shown in Figure 1.

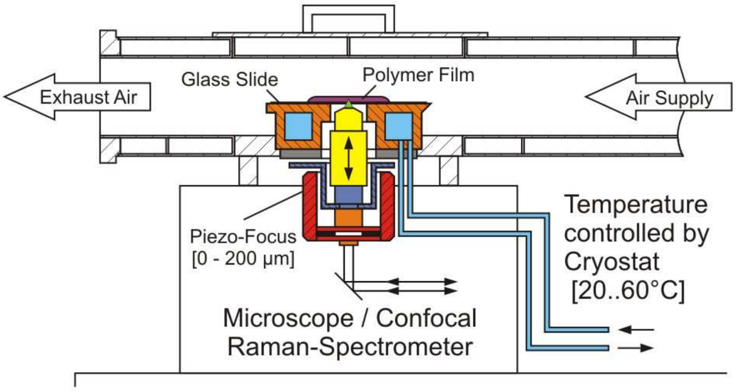

Figure 1: Inverse-Micro-Raman-Spectrometer with air flow channel for investigation of film drying.

Results and discussion

The sorption isotherms of the pure polymers and the protein were described with the Flory-Huggins model.

$$\ln a_w = \ln \frac{p_w}{p_w^*(T)} = \ln \phi_w + \left(1 - \frac{1}{r}\right) \phi_p + \chi_{wp} \phi_p^2$$

The concentration dependent interaction parameter χ_{wp} was fitted to measured data. For polymer mixtures the amount of water in the film was calculated as a weighted sum of the mass of water in the pure components as proposed by Iglesias et al. [3].

$$X_{w,mix} = \sum_{i=1}^{n} X_{w,i} \cdot x_i$$

As shown in Figure 2 the absorption behavior of binary PVP-BSA mixtures can be well described with this approach. This has also been shown for other polymer-protein and polymer-polymer mixtures.

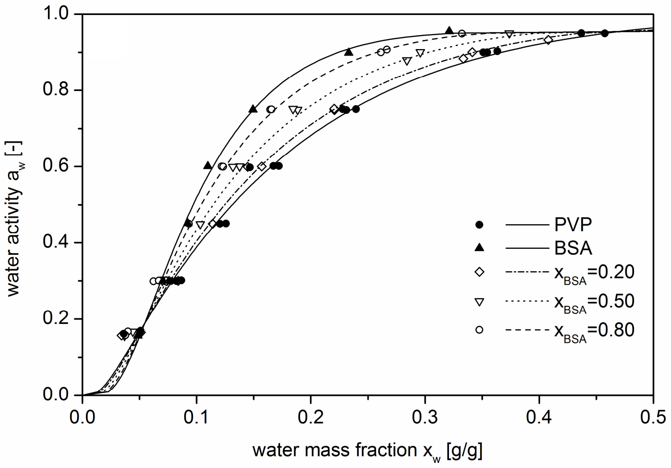

Figure 2: Measured (symbols) and calculated (lines) sorption isotherms of PVP, BSA and their binary mixtures at 40°C.

In order to determine diffusion coefficients of water in the polymer films, the drying process was simulated implementing mass transfer in the gas phase, phase equilibrium and diffusion in the film. A detailed description of the equations for the simulation can be found elsewhere [4]. An exponential approach was used to describe the dependency of the diffusion coefficient on the water content in the film.

$$D_{1S} = exp\left(-\frac{A + B \cdot X_1}{1 + C \cdot X_1} \right)$$

The parameters A, B and C were fitted to experimental data. Simulation was done using an in-house numerical simulation program. The implemented FORTRAN solver is specialized in solving the non-linear differential equations occurring in heat and mass transfer problems in thin films. In polymer blends the diffusion was considered quasi-binary, i.e. diffusion of water through a homogeneous polymer matrix.

On the left hand side of Figure 3 a drying experiment of a PVP-BSA blend with measured and simulated water concentration profiles in the film is shown. The decrease in water content and the shrinking of the film can be well described with the proposed model. For this system only small concentration gradients were measured indicating a rather high diffusion coefficient of water in the film even at low solvent contents.

On the right hand side of Figure 3 the curves for the diffusion coefficients obtained through fitting to the measurements are shown. The diffusion coefficients of water in PVP and BSA are compared to the one in the mixtures. As expected the curve for the mixture lies between the ones for the pure components. At low water concentrations in the film the diffusion coefficient is still above $10^{-12}\ \frac{m^2}{s}$ which is rather high and supports the observation from the drying experiment.

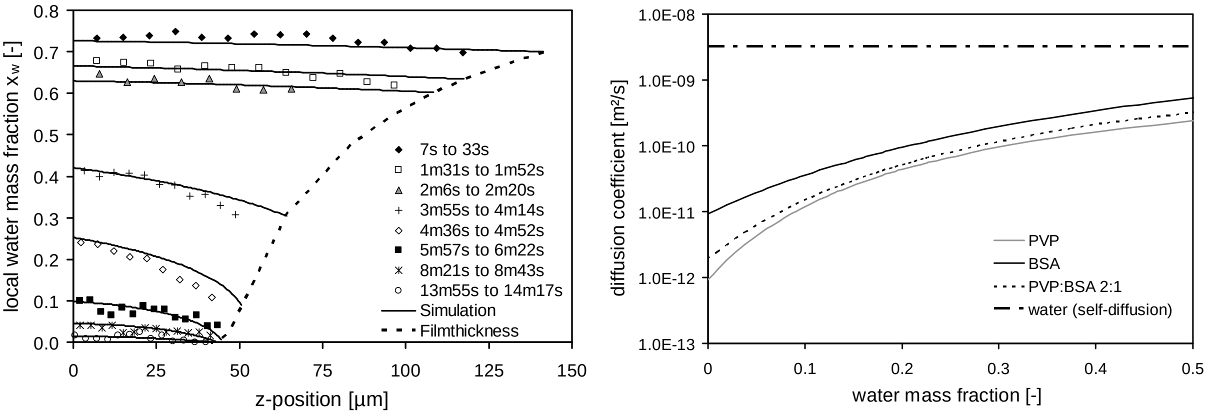

Figure 3: Diffusion kinetics in PVP-BSA blends at 40°C. Left: Concentration profiles of water in a PVP-BSA blend at a mass ratio polymer/protein of 2 during drying with 0.4 m/s air velocity. Measurements are shown as symbols, lines represents simulations. Right: Diffusion coefficient of water in PVP, BSA and its mixture with a polymer/protein ratio of 2. The self-diffusion coefficient of water is shown for reference.

The results show that for the system PVP-BSA-water the quasi-binary simulation approach is valid and may be used to obtain diffusion coefficients of water in the polymer-protein matrix. In the future deriving concentration dependent diffusion coefficients of solvents in mixtures from their values in the pure components would be a next step reducing the number of experiments for the determination of diffusion coefficients in polymer blends.

With the knowledge of phase equilibrium and kinetics of water diffusion in polymeric mixtures we are now able to predict the process of water absorption in these systems. This will improve the development of matrices for protein immobilization.

Acknowledgements

The authors would like to thank Jonas Hettler for his contributions to this work within the scope of his diploma thesis.

References

[1] W. Schabel, I. Ludwig, M. Kind, Measurements of concentration profiles in polymeric solvent coatings by means of an inverse confocal micro Raman spectrometer - initial results, Drying Technology 22 (1-2) (2004) 285–294.

[2] P. Scharfer, W. Schabel, M. Kind, Mass transport measurements in membranes by means of in situ Raman spectroscopy - first results of methanol and water profiles in fuel cell membranes, J. Membr. Sci. 303 (2007) 37–42.

[3] H. A. Iglesias, J. Chirife, R. Boquet, Prediction of water sorption isotherms of food models from knowledge of components sorption behavior, J. Food Sci. 45 (3) (1980) 450–452.

[4] R. Saure, G. Wagner, E.-U. Schlünder, Drying of solvent-borne polymeric coatings: I. modeling the drying process, Surf. Coat. Technol. 99 (3) (1998) 253 – 256.