Depth Profiling of Multicomponent Coatings to Test Theories of Diffusion

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Prediction of drying behavior by mathematical modeling is important for solvent(s) based polymer coatings because accurate experiments that mimic conditions of industrial driers are difficult to perform, especially at high air flows. For ternary systems consisting of a polymer and two solvents, the equations that describe the change in solvents' concentration are:

$$\frac{\partial c_1}{\partial t} = \frac{\partial}{\partial x}\left(D_{11} \frac{\partial c_1}{\partial x} \right) + \frac{\partial}{\partial x}\left(D_{12} \frac{\partial c_2}{\partial x} \right)$$

$$\frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x}\left(D_{21} \frac{\partial c_1}{\partial x} \right) + \frac{\partial}{\partial x}\left(D_{22} \frac{\partial c_2}{\partial x} \right)$$

c_1 and c_2 are concentrations of the solvents, D_{11} and D_{22} are main term diffusion coefficients, D_{12} and D_{21} are cross term diffusion coefficients. Free volume theory has been used to estimate the self diffusion coefficients and Bearman's friction based theory to relate them to the main term and cross term coefficients. Making suitable assumptions in the development, several

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theories have been proposed by Alsoy and Duda (1999), Zielinski and Hanley (2001) to predict the diffusion coefficients. Price and Romdhane (2003) analyzed the theories showed some of their shortcomings and unified them by deriving a generalized theory.

The aim of this work is to compare predictions of the evolution of concentration of solvents in a drying coating made from two solvents and a polymer with measurements by confocal laser Raman spectroscopy. This is an indirect way of testing the theories; direct way would be to measure the diffusion coefficients and compare them with those predicted by the theories.

Two coatings made from poly styrene/tetrahydrofuran/*p*-xylene and poly (methyl methacrylate)/ethylbenzene/tetrahydrofuran were dried at ambient conditions and the concentrations of the three components in each coating were measured at several depths at several times. Free volume theory requires many parameters out of which four, as suggested by Price et al (1999), should be estimated because they cannot be determined from the pure component properties. We estimated the parameters for binary coatings of above polymers and solvents by minimizing the difference between measured and predicted weight loss. These parameters, indicated in the Figure captions, were used in the ternary model to predict evolution of concentrations.

Figure 1 shows comparison of *p*-xylene concentrations predicted by the theories and those measured by Raman spectroscopy at 400, 300 and 200 microns from the base of the coating. Concentration of *p*-xylene rises with time, because tetrahydrofuran departs the coating quickly. Eventually, it falls everywhere in the coating. The theories seem to predict the experimental trends well, especially during the initial stages of drying, but there is a quantitative mismatch. It is not clear why the discrepancy exists between the model predictions and the experiments.

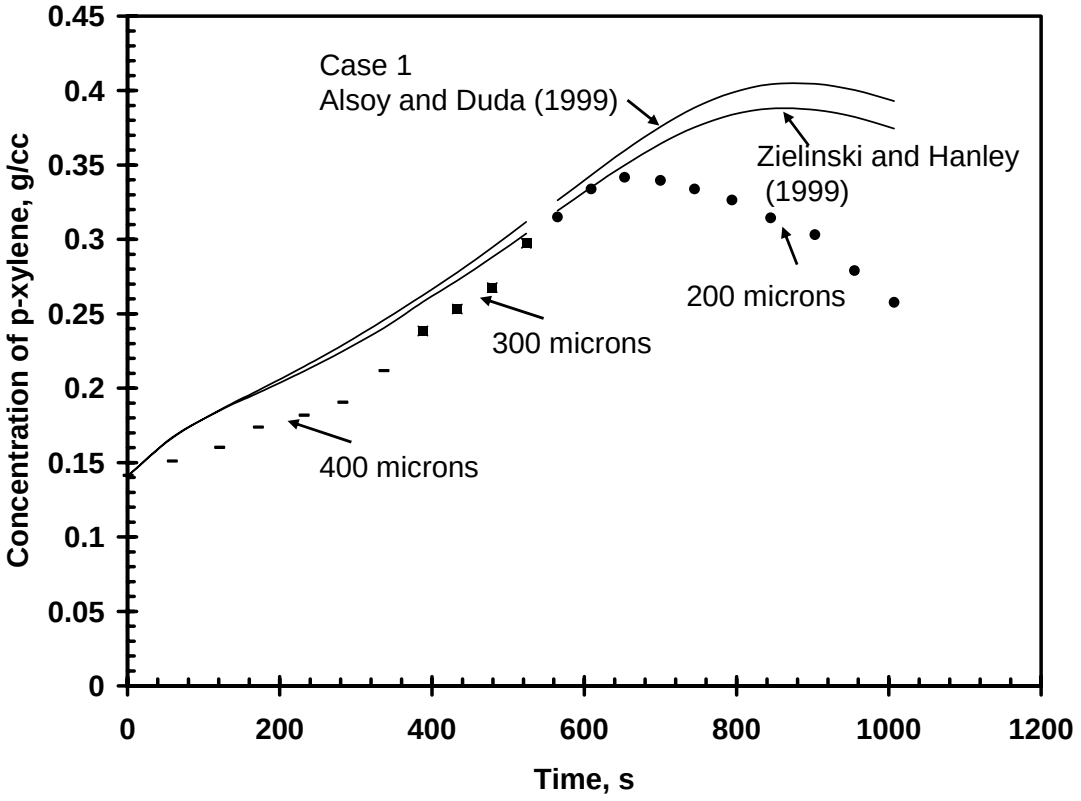

Figure 1: Comparison of concentration of *p*-xylene at 400, 300 and 200 microns from the base of coating made from 15% poly styrene/70% tetrahydrofuran/15% *p*-xylene. Initial coating thickness is about 1000 microns; drying temperature is 23°C. The four diffusion parameters estimated were $D_o = 7.84 \times 10^{-3}$ cm^2/s , $\xi = 0.45$, $K_{12}/\gamma = 2.89 \times 10^{-4}$ cm^3/(g K) and $K_{22}-T_{g2} = -326.4$ K. Dashes, squares and circles represent concentrations of *p*-xylene at 400, 300 and 200 microns from the base of the coating.

Figure 2 shows reasonable comparison for concentration of tetrahydrofuran. Unlike concentration of *p*-xylene, concentration of tetrahydrofuran falls everywhere in the coating as drying progresses. The theories predict a gradual fall in concentration whereas the experiments show somewhat steep fall in the middle stages of drying. Predictions of other cases of Alsoy and Duda (1999) and generalized model match the trends qualitatively but not quantitatively.

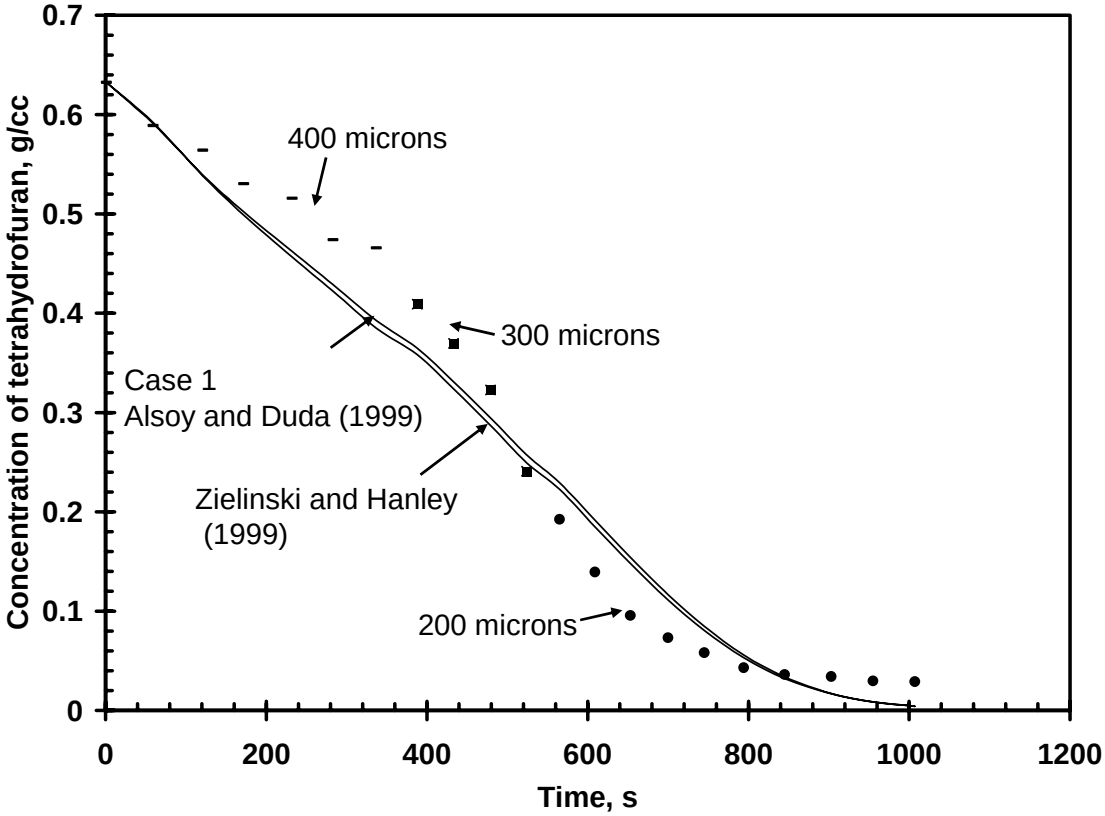

Figure 2: Comparison of concentration of *p*-xylene at 400, 300 and 200 microns from the base of coating made from 15% poly styrene/70% tetrahydrofuran/15% *p*-xylene. Initial coating thickness is about 1000 microns; drying temperature is 23°C. The four diffusion parameters estimated were $D_o = 9.8 \times 10^{-3}$ cm^2/s, $\xi = 0.38$, $K_{12}/\gamma = 2.89 \times 10^{-4}$ cm^3/(g K) and $K_{22}-T_{g2} = -326.4$ K. Dashes, squares and circles represent concentrations of tetrahydrofuran at 400, 300 and 200 microns from the base of the coating.

References

Alsoy, S. and Duda, J. L., 1999, "Modeling of multicomponent drying of polymer films," AIChE J, 45, 896.

Price, P. E. and Romdhane, I. H., 2003, "Multicomponent diffusion theory and its applications to polymer-solvent systems," AIChE J, 49, 309.

Price, P. E., Wang, S. and Romdhane, I. H., 1997, "Extracting effective diffusion parameters from drying experiments," AIChE J, 43, 1925.

Zielinski, J. M. and Hanley, B. F., 1999, "Practical friction-based approach to modeling multicomponent diffusion," AIChE J, 45, 1.