Non-Fickian Drying Behavior of Binary Polymer Solution Coatings

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Fick's law of diffusion, which states that the flux of a diffusing species at a location equals the product of diffusion coefficient and its concentration gradient there, describes mass transfer is solids, liquids and gases quite accurately. Transport of solvent in polymer solvent systems is no exception. In these systems, diffusion coefficient is a strong function of concentration and temperature. Free volume theory (1977a, b) predicts this function accurately for many polymer solvent systems.

Fick's law has been used extensively to describe solvent transport during its sorption and desorption in polymer solvent systems. During sorption, Fick's law predicts that the solvent mass uptake varies as time to the exponent of one-half. During drying of coatings cast from a polymer solution, the solvent leaves the top of the coating but the polymer does not because it is practically non-volatile under conditions used for drying. At the top, the diffusion coefficient falls several decades because of low solvent concentration. Consequently, a steep concentration gradient of the solvent develops so that the internal transport matches the external one described by a mass transfer coefficient.

When polymer solvent systems go through glass transition, Fick's law may be inadequate to describe solvent mass transport. During sorption of methanol in poly (methyl methacrylate) sheets anomalous transport was reported by Thomas and Windle (1978, 1981); they showed that the solvent mass uptake varied linearly with time instead of an exponent of one-half. Cairncross and Durning (1996) modeled drying of viscoelastic coatings by including contribution due to in-plane stress gradients. In-plane stress develops when a polymer solvent system goes through glass transition and, it relaxes with time. This

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relaxation was described by Maxwell's model for viscoelastic materials with a single relaxation time. Edwards (1998) modeled drying of coatings using viscoelastic theory and showed that when coatings are dried at higher air flows more solvent is retained in the coating. Vinjamur and Cairncross (2002) followed the viscoelasctic drying model of Cairncross and Durning (1996) and applied it to poly (methyl methacrylate)-acetone system and showed that more acetone is retained in coating dried at high air flows— an anomalous drying behavior.

Vinjamur and Cairncross (2002) also showed that the concentration profiles predicted by their model, which includes contribution of stress and concentration gradients to solvent transport is phenomenologically different from those that neglect stress gradients. They showed that the concentration profile is sigmoidal in shape. It is flat near the substrate and falls steeply inside the coating and is flat again near the top. Fick's law does not predict the flat profile near the top and, flux due to stress gradients makes the profile flat.

In this work, poly (styrene)-*p*-xylene and other systems have been considered because they pass through glass transition during drying. Binary solutions containing 17 wt% poly (styrene)-83 wt% *p*-xylene were prepared by dissolving precise amounts of the polymers in the solvents. The solutions were allowed to equilibrate for few days. A known amount of poly (styrene) solution was injected into a stainless steel sample holder of 15 mm diameter and 500 microns thickness. This solution was dried at room temperature of $33^{o}C$ for 50 minutes. Depth profiling of the dried coatings was done using an oil immersion objective of 100 X magnification. The objective was procured from Olympus, Tokyo, Japan. The refractive index of the oil used was about 1.516, which matches closely with that of the polymer solution (about 1.50). This ensures that the depth of penetration is within two microns of the set depth. Surface of stainless steel was located and the spectra were taken at several depths from the surface till the spectra contained characteristic peak only of the oil and not of the solvent and the polymer.

Figure 1 shows measured depth profiles of *p*-xylene and Figure 2 shows those of poly (styrene). Profiles of the solvent and the polymer are sigmoidal in shape with a flat profile near the top. Poly (styrene) has a glass transition temperature of about $100^{o}C$ and, hence, the region near the top, which becomes dry during drying, is expected to go through glass transition. When this happens, in-plane stress develops near the top and stress gradient there also aids in solvent transport from inside of the coating to the top. This leads to a flat profile near the top (Vinjamur and Cairncross, 2002). Near the end of this flat profile, a steep

gradient forms and the profile becomes flat again. The concentration of the polymer is high near the top and low deeper in the coating with a steep gradient in between.

The results reported here are promising and few more polymer solvent systems that become glassy during drying should be tested for non-Fickian behavior.
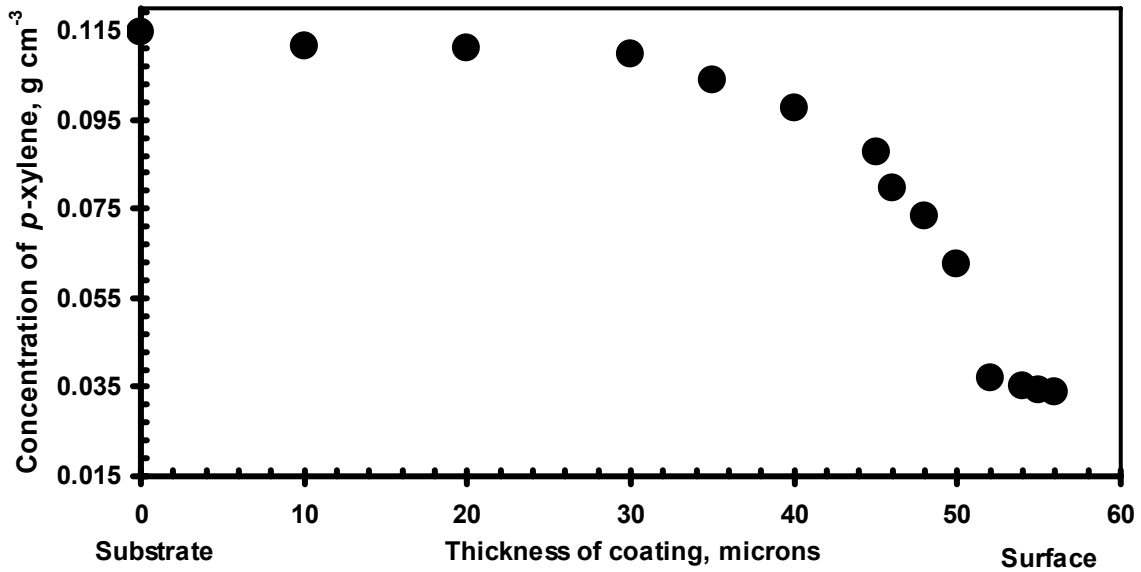

Figure 1: Concentration of *p*-xylene in poly (styrene)-*p*-xylene coating dried at 29ºC under natural convection conditions. Initial concentration of poly (styrene) and *p*-xylene were 0.151, 0.737 g/cc, respectively. Initial thickness of coating was 466 microns and it was dried for 1 hour.
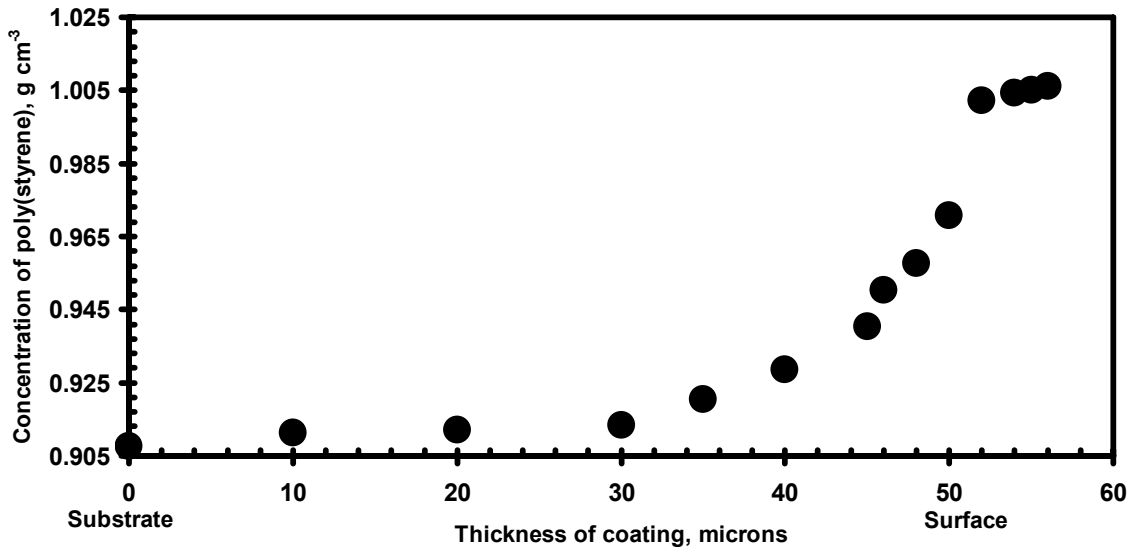
Figure 2: Concentration of poly (styrene) in poly (styrene)-*p*-xylene coating dried at 29ºC under natural convection conditions. Initial concentration of poly (styrene) and *p*-xylene were 0.151, 0.737 g/cc, respectively. Initial thickness of coating was 466 microns and it was dried for 1 hour.

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