

# Non-Fickian Drying of Polymeric Coatings

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**Abstract**-Concentration profiles in two binary polymeric coatings - poly (styrene) – p-xylene and poly (methyl methacrylate) – ethylbenzene, have been measured using confocal laser Raman spectroscopy. Measured profiles are very different from as shown earlier for rubbery coatings. Sigmoidal profiles are observed in these polymeric coatings during the course of drying because they went through the glass transition temperature. Fick's law of diffusion is inadequate to explain such type of diffusion.

**Index Terms:** Confocal Raman Spectroscopy, Non-Fickian Drying, Rubbery Coating, Glass Coatings, Binary Coatings, Thin Films



## 1.Introduction

Several polymer coatings such as adhesives, magnetic media, audio and video tapes are made by applying a polymer solution, made by dissolving a polymer in a solvent(s), on a moving substrate and then drying it. The aim of drying is to remove solvent(s) from a wet coating to desired levels without inducing any defects such as blisters, cracking and blush. Drying is usually accomplished in multi-zone dryers where in each zone hot air is blown over the coating. Figure 1 shows a schematic of a multi-zone dryer in which the air impinges on the coating from the top side and bottom sides. They are manipulated to achieve two goals: one is to remove the solvent(s) quickly and the other is dry the coatings without creating defects such as blisters. Drying is the last and quality controlling step in the production of polymer coatings; hence, coatings with defects lead to production losses. Due to poor choice of operating conditions, defects could be induced in the coatings: internal gradients could develop, blister could

form, coatings could crack, phase separate etc. Many other dryer configurations exist in practice, which have been characterized by the heat transfer coefficient obtained in them [1]. In few configurations, the air flows only on the top side and parallel to the coating. The air temperature and its flow rate constitute important operating conditions of a dryer. The conditions could change from one zone to the other to achieve the drying goals. Improper choice of the conditions could generate defects in the coatings during drying and lead to production losses. Price and Cairncross [2] studied the effect of operating conditions on blister formation during drying in a single-zone dryer. They defined bubble point temperature as the temperature at which the solvent partial pressure becomes equal to the ambient pressure. The bubble point temperature falls from the top of the coating to its bottom because the solvent concentration and, hence, its activity rises in that direction. They stated that whenever the coating temperature exceeds the bubble point temperature, blisters are induced.

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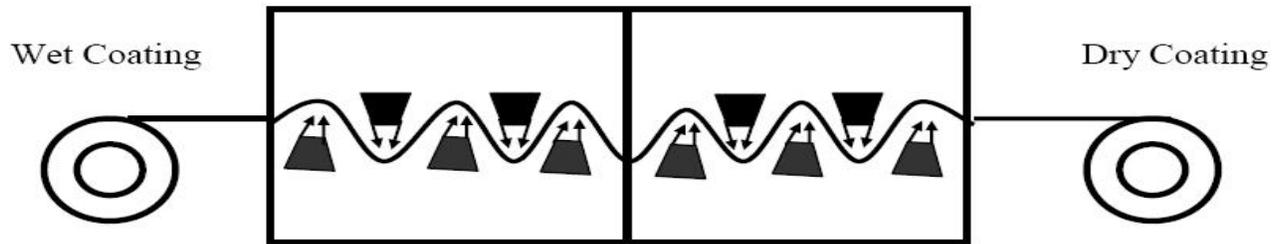


Figure 1 . Schematic of an industrial two zone dryer. Wet coating enters at one end, passes through both the zones and emerges as dry coating. Hot air is blown over the coating and it supplies heat to the coating from the top and bottom sides.

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 the mass transfer in solids, liquids and gases quite accurately. Transport of solvent in polymer solvent systems is no exception. It is complicated by the fact that the diffusion coefficient is a strong function of concentration and temperature. Free volume theory [3,4] predicts this function accurately for many polymer solvent systems. The theory combines thermodynamics and self-diffusion coefficient to predict mutual diffusion coefficient. Self-diffusion coefficient depends on free volume available for diffusion and the volume required for diffusion. The theory predicts these two volumes as a function of concentration, temperature and other properties of polymer-solvent system.

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 the 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 the conditions used for drying. There 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.

Figure 2 shows the concentration profile of p-xylene at several times during drying of a poly (styrene) -p-xylene coating on a substrate using simulation. As mentioned in the preceding paragraph, steep profile develops at the surface; diffusion flattens the profile inside the coating. The steep profile develops after long time (2000 s) because of low drying temperature and low mass and heat transfer coefficients. When these are raised, steep profile forms earlier.

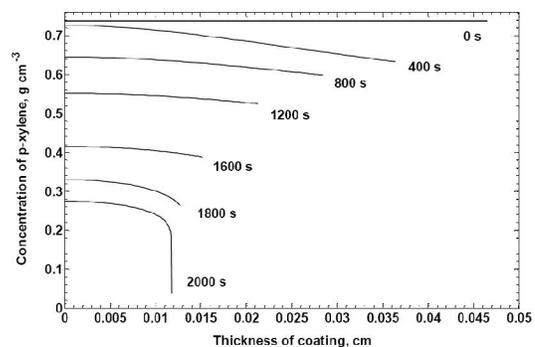


Figure 2 Concentration profile of p-xylene in poly (styrene) -p-xylene system. Concentration of poly (styrene) and p-xylene were 0.151, 0.737  $g\ cm^{-3}$  respectively, thickness of coating was: 466 micrometers, coating temperature of coating: 23.5°C and coating side heat transfer coefficient was: 8.36  $W\ m^{-2}\ ^\circ C^{-1}$ .

Schabel et al. [5,6] reported depth profiling of solvent concentration with confocal Raman spectroscopy during drying of binary system. They showed the effect of drying temperature and air flow rate on the solvent concentration and good agreement between the predictions of a drying model and measurements. The instrument has been used for a variety of researches in drying of thin film polymer coatings [5-8].

When polymer solvent systems go through glass transition, Fick's law may be inadequate to describe solvent mass transport. Thomas and Windle [9,10] reported anomalous transport during sorption of methanol in poly (methyl methacrylate) sheets. They showed that the solvent mass uptake varied linearly with time instead of an exponent of one-half. Barr-Howell and Gordon [11] also showed this behaviour.

Cairncross and Durning [12] 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 relaxation was described by Maxwell's model for viscoelastic materials with a single relaxation time. Edwards [13] modeled drying of coatings using viscoelastic theory and showed that at when coatings are dried at higher air flows more solvent is retained in the coating. Vinjamur and Cairncross [14] followed the viscoelastic drying model of Cairncross and Durning [12] 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 [14] 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, falls steeply inside the coating, and is flat again near the top. The flux due to stress gradients makes the profile flat near the top.

Glass transition of polymer solvent system depends on temperature and the solvent concentration. Solvent depresses the glass transition temperature. As a coating dries and solvent depletes in region near the top, the region could go through glass transition. In fact, Romdhane et al. [15] showed that the glassy layer begins near the top and grows gradually toward the substrate.

In this paper, poly (styrene)-*p*-xylene and poly (methyl methacrylate)-ethylbenzene systems have been considered because they pass through glass transition during drying. The concentration profiles of *p*-xylene and ethylbenzene were measured in dried coatings using confocal laser Raman spectroscopy equipped with an oil immersion objective. In confocal Raman spectroscopy a laser beam is focused through a pinhole arrangement at a location inside a sample. The scattered light is captured by a detector and its spectra are recorded in an attached computer. The spectrum is reported as intensity (in some arbitrary units) versus wave number ( $\text{cm}^{-1}$ ). Ternary and binary polymer solvent systems should be chosen in such a way that the polymer and the solvents should be distinguished by having characteristic peak at some different wave numbers. The ratio of the intensity of the polymer to that of the solvent is calibrated against known ratio of concentration of the polymer to that of the solvent.

## 2. Materials and Methods

In this work, two binary polymer solvent systems, poly (styrene)-*p*-xylene and poly (methyl methacrylate)-ethylbenzene have been studied. Suppliers of these materials are listed in Table I. Each of the systems show distinct

characteristic peaks for the polymer and the solvent so that their concentration in the solution can be obtained from the calibration plots. Figures 3 and 4 show calibration plots for poly (styrene)-*p*-xylene and poly (methyl methacrylate)-ethylbenzene systems respectively. Binary solutions containing 17 wt% poly (styrene)-83 wt% *p*-xylene and 9.1 wt% poly (methyl methacrylate)-90.9 wt% ethylbenzene were prepared by dissolving precise amounts of the polymers in the solvents. The solutions were allowed to equilibrate for few days.

Table 1  
Specifications of materials used.

Name of Chemical	Supplier	Molecular Weight, $g\ mol^{-1}$	Density $g\ cm^{-3}$	Refractive Index
Poly (styrene)	Sigma Aldrich, Germany	230000	1.047	1.46
Poly (methyl methacrylate)	Sigma Aldrich, Germany	120000	1.188	1.497
Tetrahydrofuran	Qualigens Fine Chemicals, India	72.11	0.886	1.407
Ethylbenzene	Spectrochem Pvt. Ltd., India	106.17	0.886	1.495
<i>p</i> -Xylene	S.D.Fine-Chem Ltd., India	106.17	0.861	1.4950

100 micro liters 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°C for 50 minutes. In another experiment, poly (styrene) solution was dried for 1 h 32 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 depth of focus was moved gradually up till spectra contains characteristic peak only of the oil and not of the solvent and the polymer. For poly (methyl methacrylate) solution, 90 micro liters were injected into the holder, it was dried for 52 minutes and the above procedure for depth profiling was followed. It was checked through independent experiments that neither poly (styrene) nor poly (methyl methacrylate) dissolve in the oil used for depth profiling.

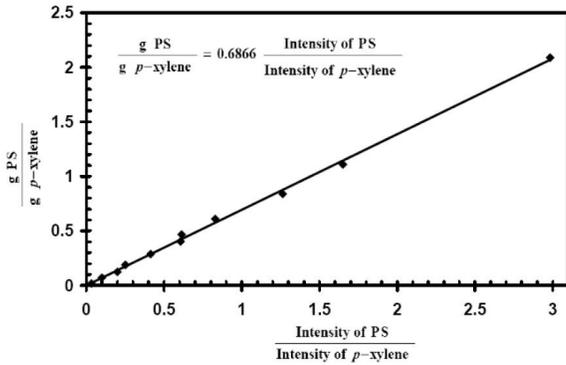


Figure 3 Calibration plot for poly (styrene) – p-xylene system.

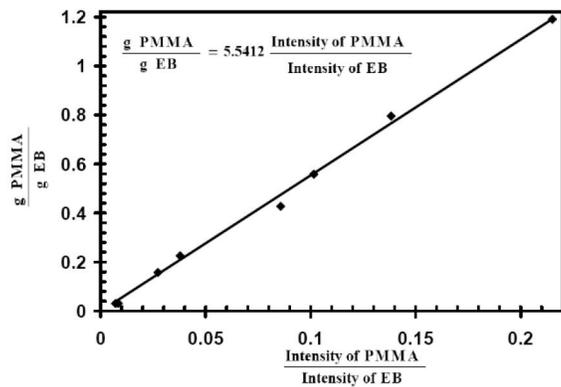


Figure 4 Calibration plot for poly (methyl methacrylate) – ethylbenzene system.

### 3. Results and Discussion

Figure 5 shows two depth profiles of p-xylene and Figure 6 shows those of poly (styrene). The two curves in each Figure are from different experiments; in one of them, the poly (styrene) solution was dried for 50 minutes and in another for 1h 32 minutes. Figure 7 shows depth profile of ethylbenzene and Figure 8 that of poly (methyl methacrylate). Profiles of the solvents and the polymers, for both the systems, are sigmoidal in shape with a flat profile near the top. Poly (styrene) and poly (methyl methacrylate) have glass transition temperatures of about 100oC and 110oC, respectively. Hence, the region near the top is expected to go through glass transition during drying. When this happens, in-plane stress develops near the top and they also aid in solvent transport from inside of the coating to the top. This leads to a flat profile near the top [14]. 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.

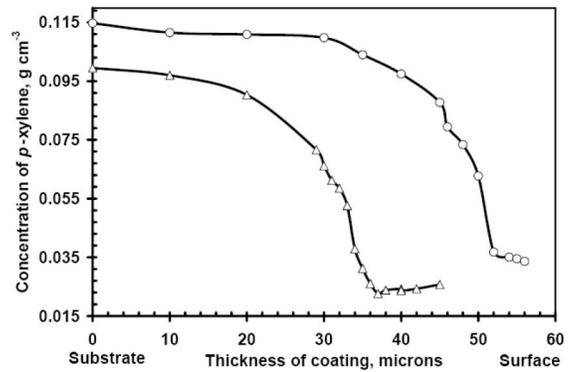


Figure 5 Concentration of p-xylene in poly (styrene)-p-xylene coating dried at 29°C under natural convection condition. Concentration of poly (styrene) and p-xylene were 0.151, 0.737  $g\ cm^{-3}$  respectively. In case 1( $\Delta$ ), initial thickness of coating was: 487 microns and dried for 3hrs. In case 2( $\circ$ ), initial thickness of coating was: 466 microns and dried for 1 hour. Coating side heat transfer coefficient for both the cases was: 8.36  $W\ m^{-2}\ ^\circ C^{-1}$ .

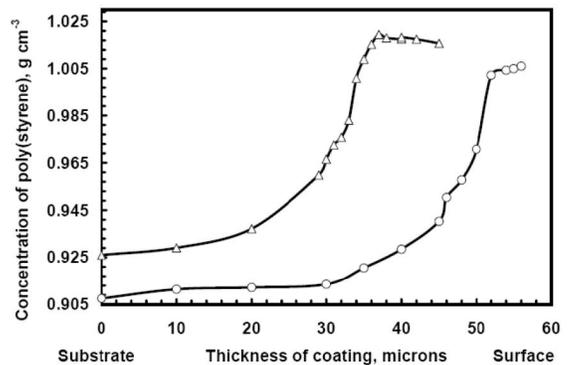


Figure 6 Concentration of poly(styrene) in poly (styrene)-p-xylene coating dried at 29°C under natural convection condition. Concentration of poly (styrene) and p-xylene were 0.151, 0.737  $g\ cm^{-3}$  respectively. In case 1( $\Delta$ ), initial thickness of coating was: 466 microns and dried for 3hrs. In case 2( $\circ$ ), initial thickness of coating was: 487 microns and dried for 1 hour. Coating side heat transfer coefficient for both the cases was: 8.36  $W\ m^{-2}\ ^\circ C^{-1}$ .

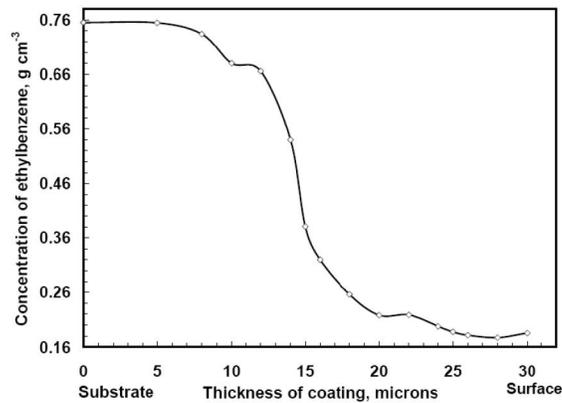


Figure 7 Concentration of ethylbenzene in poly (methyl methacrylate)-ethylbenzene coating dried at 29°C under natural convection condition. Concentration of poly (methyl methacrylate) and ethylbenzene were 0.081, 0.807  $g\ cm^{-3}$  respectively and initial coating thickness: 429 microns and dried for 31 minutes. Coating side heat transfer coefficient was: 8.36  $W\ m^{-2}\ ^\circ C^{-1}$ .

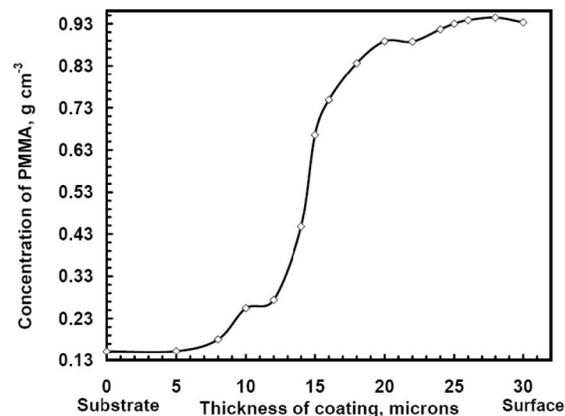


Figure 8 Concentration of PMMA in poly (methyl methacrylate)-ethylbenzene coating dried at 29°C under natural convection condition. Concentration of poly (methyl methacrylate) and ethylbenzene were 0.081, 0.807  $g\ cm^{-3}$  respectively and initial coating thickness: 429 microns and dried for 31 minutes. Coating side heat transfer coefficient was: 8.36  $W\ m^{-2}\ ^\circ C^{-1}$ .

Vinjamur and Cairncross [14] showed such sigmoidal profiles in their modeling studies of viscoelastic coatings. They mentioned that the in-plane stress begins to develop near the top and it starts to relax there. A region of flat and low concentration develops at the top in contrast to a steep gradient there predicted by Fick's law of diffusion. The flat profile is followed by a steep concentration gradient and a flat profile again. The region near the top grows in size and the front

(steep gradient) moves toward the substrate as drying proceeds. Depth profiles of p-xylene shown in Figure 5 exhibit this behaviour with thicker region of low concentration in coatings dried for 1 h 32 minutes than that dried for 50 minutes.

Schabel et al. [5,6] measured depth profiles of toluene during drying of poly (vinyl acetate)-toluene coatings at different temperatures and air flow rates. Their measurements show a steep gradient at the top and not a flat one as reported here. Poly (vinyl acetate) has a glass transition temperature of about 32°C and is expected to be rubbery throughout drying period.

The results reported here are promising for polymer solvent systems that become glassy during drying.

#### 4. Conclusions

Depth profiling of two dried binary coatings, poly (styrene)-p-xylene and poly (methyl methacrylate)-ethylbenzene was conducted using confocal laser Raman spectroscopy with an oil immersion objective. Both the systems are expected to go through glass transition during drying and they do show phenomenologically different behavior from those remain rubbery. The measured profiles of p-xylene and ethylbenzene were sigmoidal in shape with a flat region near the top followed by a steep gradient and a flat profile. Fick's law predicts steep gradient of solvent near the top and not flat profile. It has been shown in the literature that by augmenting Fick's law with contribution of stress gradients to solvent transport, the sigmoidal shape can be predicted.

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