

# NOTE

## Experimental Investigations of Trapping Skinning

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### INTRODUCTION

Coatings are produced by spreading a polymer solution (polymer dissolved in a solvent) on a substrate and then removing the solvent in drying ovens. Photographic films, audio tapes, and video tapes are a few examples of coated products. Industrial dryers consist of several zones with each zone being operated at a specified gas flow rate and temperature for drying to produce a coating with the desired specifications. Drying is accomplished by blowing jets of hot air at a high velocity to increase the rate of evaporation of the solvent and to increase the rate of production of coatings. Improper drying can impact the quality of the final coating product due to formation of defects<sup>1</sup> such as blisters, “starry night” phenomena, delamination, and so forth. Coatings with high residual solvent are also unacceptable. The goals of minimizing the residual solvent and avoiding defects often conflict, resulting in optimal drying conditions at an intermediate gas temperature and flow rate for drying. This note presents the effect of the operating conditions on the residual solvent content (RSC) of dried coatings.

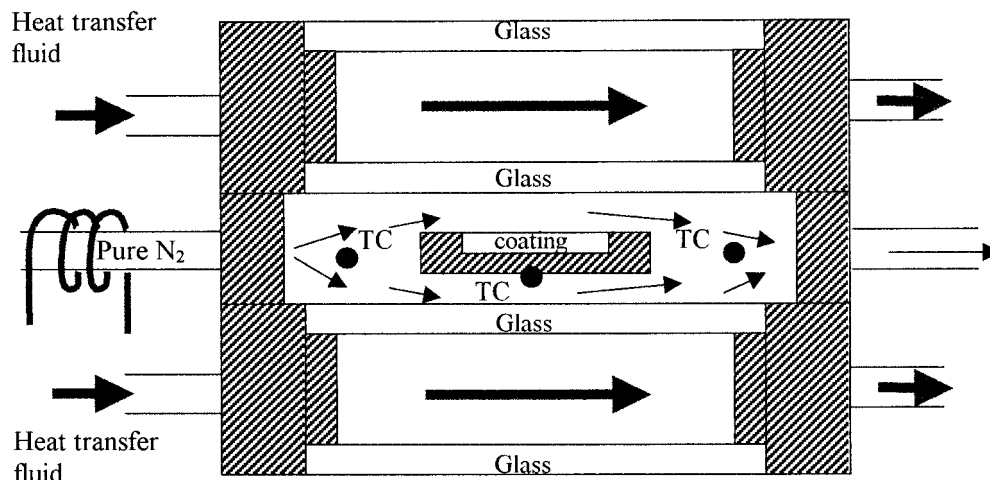
Coatings are often reported<sup>2</sup> to exhibit *trapping skinning* behavior. This behavior occurs when more solvent is trapped inside the coating dried at higher gas temperatures and/or flow rates of drying gas and is often attributed to diffusion coefficients that are a strong function of the solvent concentration. Thus, for coatings that show trapping skinning behavior, a low gas temperature or flow rate of drying gas needs to be used to meet residual solvent specifications.

Crank and Park<sup>3,4</sup> noted anomalous drying behavior reported in the British patent literature. They showed that Fick’s law of diffusion cannot explain this behavior and compared drying when the concentration of the solvent at the surface falls to 10% of its initial value and when it falls to zero. In both cases the amount of residual solvent is more or less the same. Crank and Park claim that the fall in concentration of the solvent at the surface, and thus the concentration dependent diffusion coefficient  $[D(c)]$ , is compensated by very steep concentration gradients at the surface  $(\partial c/\partial x)$ , such that the product  $D(c)(\partial c/\partial x)$  for a surface solvent concentration of zero is higher than for an initial surface solvent concentration of 10%. Vrentas and Vrentas<sup>5</sup> analyzed drying with various functional forms of the  $D$  and showed that the  $D(c)$  cannot explain trapping skinning behavior. Cairncross et al.<sup>2</sup> argued by steady-state diffusion through a film that Fick’s law of diffusion cannot capture trapping skinning. If trapping skinning occurs, then other mechanisms such as the glass-transition, phase-separation, or curing reactions must be responsible and need to be investigated.

There are very few modeling<sup>6</sup> and experimental investigations on trapping skinning. Edwards<sup>7</sup> modeled trapping skinning by including viscoelastic stress driven diffusion in mass conservation equations. He showed that at higher mass transfer coefficients the accumulated flux through the coating gas boundary decreases, although the flux increases with the mass transfer coefficient during the earlier stages of drying. Cairncross and Durning<sup>8</sup> described drying of viscoelastic coatings and showed that the coating thickness goes through a minimum as the diffusional Deborah number ( $De$ ), the ratio of the characteristic relaxation time to the characteristic diffusion time, is varied. They argue that the  $De$  can be increased by increasing the temperature and thus present an indirect argument that trapping skinning occurs at higher temperatures. Powers and Collier<sup>9</sup> studied a poly(methyl methacrylate)

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**Figure 1** The three layered drying chamber of the high air flow drying experimental setup. The top and bottom layers are identical and heat transfer fluid is passed through them to maintain the drying of the gas at the desired temperature. Glass is provided to visually inspect the coating during drying. Nitrogen gas is blown through the middle layer across the coated slide. TC, thermocouple.

(PMMA)/toluene system using a thermogravimetric analyzer and showed that the amount of toluene trapped in the coating dried at 366 K is higher than that in the coating dried at 347 K. The initial coating weight that was dried at 366 K was 44% higher than that of the coating dried at 347 K and the increase in the residual toluene was only marginal. Thus, their results are not conclusive if trapping skinning occurs in that system and our experiments were unable to verify their results. This note presents some experimental measurements of trapping skinning for the PMMA/acetone system.

## EXPERIMENTAL

A high air flow drying experimental setup (HADES) with a drying chamber that simulates industrial dryers was constructed<sup>10</sup> to study the drying behavior of various polymer–solvent systems. The HADES was shown to simulate industrial drying conditions by measuring heat transfer coefficients and comparing them with values typical of industrial dryers. It allows controlled gas flow rates for drying, a controlled gas temperature and solvent partial pressure for drying, and measurement of the temperature and evaporation from a small ( $0.6 \times 0.6$  in.) coating sample.

The drying chamber, which was built in-house, is shown in Figure 1. A stack of three aluminum layers comprise the chamber. The top layer is provided with glass windows on the top and bottom for visual inspection of the coating during drying. The bottom layer is identical to the top layer. The HADES achieves conditions similar to industrial drying by blowing nitrogen

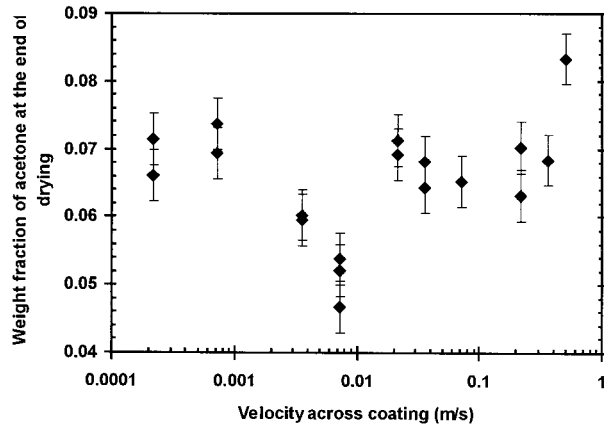
across the sample through a narrow gap between the walls of the drying chamber and the sample. Heat transfer fluid is continuously pumped through the top and bottom layers by a heating circulator, thereby maintaining the drying chamber at the desired temperature. The middle layer of the chamber is equipped with a door for insertion of a coated slide and with three thermocouple ports. Gas temperatures upstream and downstream of the coating and the coating temperature are measured and recorded. A total hydrocarbon analyzer obtained from Gow-Mac Instrument Co. measures the solvent concentration in the gas using a flame ionization detector (FID). The FID measures solvent concentrations from 20 to 20,000 ppm.

The RSC for all experiments is determined gravimetrically by weighing the sample holder without a sample ( $W_1$ ), after drying in the HADES ( $W_2$ ), and after baking in an oven at a temperature higher than the glass-transition temperature ( $T_g$ ) of the pure polymer ( $W_3$ ). The RSC, which is the weight fraction of solvent at the end of drying, is obtained by the ratio

$$\text{RSC} = \frac{W_2 - W_3}{W_2 - W_1} \quad (1)$$

## RESULTS AND DISCUSSION

Figure 2 displays the variation in the residual acetone with the gas velocity for drying at a gas temperature of 323 K for a coating with a 15- $\mu\text{m}$  dry PMMA thickness. The PMMA used in the experiments is obtained from Aldrich Chemical Company and has an average molec-



**Figure 2** The effect of the velocity across the coating on the residual solvent for the poly(methyl methacrylate)/acetone system at 323 K. The system shows anomalous behavior at velocities exceeding 0.0072 m/s.

ular weight of 120,000. At low gas flow rates (from 0.000216 to 0.0072 m/s) the residual acetone decreases from 7.1 to 5.4%. External mass transfer in the drying gas controls the drying process at low gas velocities and short times, and the residual solvent decreases as the gas velocity increases. At higher gas velocities the internal mass transfer in the coating should control the drying process. For mass transfer by Fickian diffusion the residual solvent should plateau as the gas velocity increases. However, Figure 2 shows that at higher gas velocities (from 0.0072 to 0.50 m/s) the residual acetone increases from 5.4 to 8.3%. These results disagree with Fickian diffusion and are indicative of trapping skinning.

The RSC data show some scatter, but the RSC at intermediate flow rates is significantly larger than experimental uncertainty. The uncertainty in the RSC is determined by

$$E = \sqrt{\sum_{i=1}^3 \left\{ \left[ \frac{\partial(\text{RSC})}{\partial W_i} \right] \Delta W_i \right\}^2} \quad (2)$$

where  $E$  is the predicted uncertainty in the RSC at any run, the RSC is calculated from eq. (1), and  $\Delta W_i$  is the accuracy of the weight measurement. The accuracy of the Mettler H542 analytical balance used for weight measurements is 0.01 mg. The error is estimated at every run, and the average error for all runs is a  $3.8 \times 10^{-3}$  weight fraction. The results in Figure 2 indicate a clear increase in the weight fraction of acetone at the end of drying at higher drying gas velocities. The reproducibility studies at various gas velocities show a maximum variation of 10% in the RSC, a clear minimum in the RSC at an intermediate gas velocity, and an increase at higher gas velocities.

In the sorption experiments PMMA was shown to exhibit anomalous behavior where the solvent mass uptake by the polymer varies linearly with time instead of with an exponent of one-half.<sup>11</sup> This behavior is attributed to the finite relaxation rates of the polymer chains that occur during the glass transition. During drying of the coatings the layers of coating near the coating–gas interface can go through the glass transition because of depleted solvent levels. The relaxation and diffusion rates can be on the same order during the glass transition. Vrentas et al.<sup>12</sup> defined a  $De$  to characterize the solvent mass transport:

$$De = \frac{\theta_{\text{relax}}}{\theta_{\text{diffusion}}} \quad (3)$$

where  $\theta_{\text{relax}}$  and  $\theta_{\text{diffusion}}$  are the characteristic relaxation and diffusion times of the polymer, respectively. The  $\theta_{\text{relax}}$  can be estimated<sup>13</sup> from the variation of the polymer self-diffusion coefficient ( $D_2$ ) with the concentration and temperature:

$$\theta_{\text{relax}} = \tau_0 \frac{D_2(T_0)}{D_2(T, w_1)} \quad (4)$$

where  $\tau_0$  is the relaxation time at the reference temperature  $T_0$  for the polymer melt and  $w_1$  is the mass fraction of the solvent. Employing the Vrentas and Duda<sup>14</sup> free volume expression for the  $D_2$ ,

$$\theta_{\text{relax}} = \tau_0 \frac{\exp\left[-\frac{\gamma \hat{V}_1^*}{\hat{V}_{\text{FH}}}\right]}{\exp\left[-\frac{w_1 \hat{V}_1^* + w_2 \hat{V}_2^* \xi}{\xi \hat{V}_{\text{FH}}/\gamma}\right]} \quad (5)$$

where  $\gamma$  is an overlap factor;  $\xi$  is the ratio of the molar volume of the solvent to that of the polymer jumping unit;  $w_2$  is the mass fraction of the polymer;  $\hat{V}_1^*$  and  $\hat{V}_2^*$  are the specific free hole (FH) volumes of the solvent and the polymer, respectively, that are required for a diffusion jump. The FH volume is

$$\frac{\hat{V}_{\text{FH}}}{\gamma} = \frac{K_{11}}{\gamma} w_1 (K_{21} - T_{g1} + T) + \frac{K_{12}}{\gamma} w_2 (K_{22} - T_{g2} + T) \quad (6)$$

where  $K_{11}/\gamma$  and  $K_{21} - T_{g1}$  are the solvent free volume parameters and  $K_{12}/\gamma$  and  $K_{22} - T_{g2}$  are the polymer free volume parameters.

The  $\theta_{\text{diffusion}}$  is

$$\theta_{\text{diffusion}} = \frac{L^2}{D} \quad (7)$$

**Table I Solvent and Polymer Parameters to Estimate Diffusion Deborah Number ( $De$ )**

Solvent Parameters	Acetone	Butyl Benzene	Polymer Parameters	Poly(methyl methacrylate)
$D_0$ (cm <sup>2</sup> /s)	$3.6 \times 10^{-4}$	$1.48 \times 10^{-4}$	$K_{21}/\gamma$ (cm <sup>3</sup> /g/K)	$3.05 \times 10^{-4}$
$K_{11}/\gamma$ (cm <sup>3</sup> /g/K)	$1.86 \times 10^{-3}$	$2.28 \times 10^{-3}$	$K_{22} - T_{g2}$ (K)	-301
$K_{21} - T_{g1}$ (K)	-53.33	-126.45	$\hat{V}_2^*$ (cm <sup>3</sup> )	0.788
$\hat{V}_1^*$ (cm <sup>3</sup> )	0.943	0.944	$\tau_0$ (s)	140
$\chi$	0.4	0.4	$T_0$ (K)	463
$\xi$	0.375	0.73		

where  $L$  is the thickness of the dry polymer and  $D$  is the mutual diffusion coefficient described by the Vrentas and Duda free volume theory<sup>14</sup>:

$$D = D_0(1 - \Phi_1)^2 \times (1 - 2\chi\Phi_1)\exp\left(-\frac{E}{RT}\right)\exp\left[-\frac{w_1\hat{V}_1^* + w_2\hat{V}_2^*\xi}{\hat{V}_{FH}/\gamma}\right] \quad (8)$$

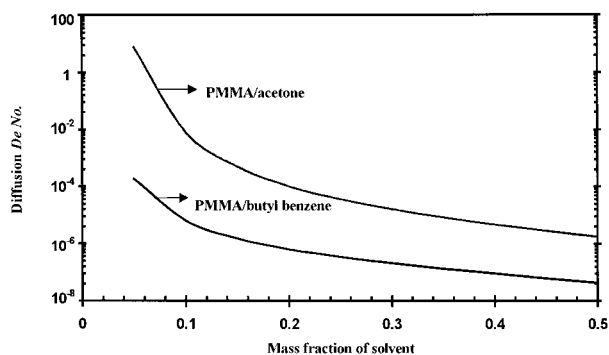
where  $D_0$  is the preexponential factor,  $\Phi_1$  is the volume fraction of the solvent,  $\chi$  is the polymer–solvent interaction parameter that can be determined from the Flory–Huggins theory,<sup>15</sup>  $E$  is the activation energy,  $R$  is a gas constant, and  $T$  is the temperature. Combining eqs. (3)–(8) produces

$$De = \tau_0 \frac{D_0}{L^2} (1 - \Phi_1)^2 (1 - 2\chi\Phi_1) \exp\left(-\frac{E}{RT}\right) \times \exp\left[-\frac{\hat{V}_1^*\left(w_1 - \frac{w_1}{\xi}\right) + \hat{V}_2^*[1 - (1 - w_1)(1 - \xi)]}{\hat{V}_{FH}/\gamma}\right] \quad (9)$$

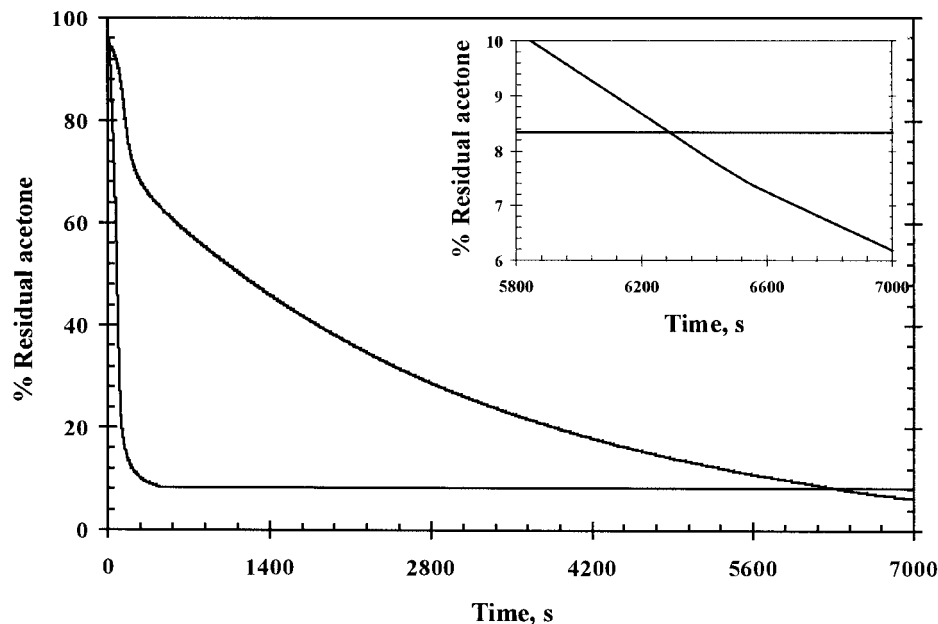
The  $De$  characterizes the solvent mass transport in the coating and determines if the relaxation rate of the polymer chains in the coating influences the solvent mass transport in the coating. If the  $De$  remains very low or very high during the whole drying process, then the concentration gradients drive the solvent mass transport and Fickian diffusion accurately describes the drying process. At a  $De$  near a value of one the relaxation and diffusion times are comparable and the solvent mass transport cannot be described as being due to concentration gradients only. Layers of coatings near the coating–gas boundary go through a glass transition because of a low solvent concentration and stresses that develop at the surface. Stress and concentration gradients<sup>7</sup> drive diffusion, and Fickian diffusion is inadequate to describe the solvent mass transfer in the coating. We postulate that trapping skinning occurs when the  $De$ , which is a function of the solvent concentration, the temperature of the coating, and the thickness of the polymer film, becomes on the order of one during drying.

Hong<sup>16</sup> provides all the parameters needed to evaluate the mutual diffusion coefficient and self-diffusion coefficient of the polymer. Fuchs et al.<sup>17</sup> report the relaxation time of PMMA for several different molecular weights. Table I lists all parameters used to compute the  $De$  for two different polymer–solvent systems. Figure 3 shows that the  $De$  for a dry polymer thickness of 15  $\mu\text{m}$  for the PMMA/acetone system is on the order of one at low mass fractions of acetone, indicating that this system may exhibit trapping skinning. For PMMA/butyl benzene coatings at the same dry polymer thickness, the  $De$  is below one, even at low mass fractions of butyl benzene, which indicates that this system may not exhibit trapping skinning.

Figure 4 displays the measured residual acetone versus the time in the coating at two different velocities. At a high gas velocity for drying (0.50 m/s) the drying is initially rapid and faster than that at a low velocity (0.0072 m/s). However, the drying rate at high velocity shuts off at 450 s and the residual acetone remains virtually the same for the remainder of the drying period. On the other hand, the drying rate at low velocity remains finite for a longer time and the residual solvent at the end of drying is less than that at high



**Figure 3** The diffusion Deborah number ( $De$ ) as a function of the mass fraction for two different combinations of polymer and solvents at 323 K and a dry polymer thickness of 15  $\mu\text{m}$ . The polymer–solvent systems are expected to exhibit anomalous behavior at a  $De$  on the order of  $\sim 1$ .



**Figure 4** The residual acetone in the coating at 0.0072 m/s for the low gas velocity and 0.50 m/s for the high gas velocity. The crossover of the two curves indicates trapping skinning.

velocity. The crossover of the two curves indicates trapping skinning.

## CONCLUSIONS

Trapping skinning is an anomalous drying behavior shown by some polymer-solvent systems where residual solvent rises as drying conditions become more intense. Our experiments on drying of PMMA/acetone show evidence of trapping skinning at higher flow rates. As PMMA passes through a glass transition during drying it is likely that non-Fickian diffusion is responsible for the anomalous behavior. The hypothesis developed in this article will be applied to other polymer-solvent systems to test its applicability.

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