

Appendix I Two-Stage Drying Model

A two-stage model for latex drying that was originally developed by Croll¹ in terms of water concentration has been recast by Eckersley and Rudin² in terms of water mass fraction. This form is most directly applicable to gravimetric desorption experiments. The original physics of the two drying stages were described as follows:

The first stage involved evaporation from the free surface of the drying film, with percolation of water through channels comprised of the particle interstices. This water percolation process was supplied from a “wet” reservoir of uncoalesced latex below a receding drying front. Drying rates were assumed to be constant as long as this wet zone existed. Stage two, described as a “falling-rate” period, begins when the wet zone becomes depleted and the mass-transport rate of the percolation process becomes dependent upon the diminishing water concentration driving it. This second stage is assumed to end with complete water removal.

While the physics of drying in the case of waterborne latex epoxies may not precisely mirror that of the Croll model, the mathematical constructs agree very well with experimental observations. Therefore the two-stage model has been employed in this study to evaluate the effects of curing agent and surfactant segregation on latex epoxy drying, and the effect of varied environmental drying conditions.

I.1 Stage I Drying Model

The constant drying rate period can be described by:

$$\text{Equation I.1} \quad \frac{dm}{A dt} = -q$$

where m is the mass of water in the film, A is the area of the drying surface, q is the mass flux which is taken as a constant and can be referred to as the evaporation rate. When **Error! Not a valid bookmark self-reference.** is integrated from time $t=0$ when $m=m_0$ to some arbitrary time t when the water mass is m_w , the result is

$$\int_{m_0}^{m_w} dm = -Aq \int_0^t dt$$

$$\text{Equation I.2} \quad m_w - m_0 = -A q t$$

If the masses are converted to mass fractions, the result is

$$\text{Equation I.3} \quad m_w = \frac{m_p x}{1-x}$$

where m_p is the total polymer mass and x is the water mass fraction.

Substitution of Equation I.3 into

Equation I.2 yields an equation that describes the water mass fraction, as a function of time in Stage I as

$$\text{Equation I.4} \quad m_0 - \frac{xm_p}{1-x} = Aqt$$

I.2 Stage II Drying Model

The “falling-rate” period is characterized by drying dependent upon the continuously decreasing concentration of water in the film until the film is essentially dry. This process can be modeled using first order kinetics as:

$$\text{Equation I.5} \quad \frac{dm}{A dt} = -qC$$

where C is the mass concentration of water per volume of latex. This equation can be recast in terms of water mass fraction by recognizing that the mass of water in the film is

$$\text{Equation I.6} \quad m = A\rho_L l$$

where ρ_L is the latex density, and l is the latex thickness, and that

$$\text{Equation I.7} \quad C = x\rho_L$$

Using Equation I.6 and Equation I.7, Equation I.5 can be rewritten

$$\text{Equation I.8} \quad \frac{dm}{dt} = \frac{d(\rho_L l x)}{dt} = -\rho_L x q$$

Since each parameter in the differential is a function of time, the chain rule, applied to Equation I.8 yields

$$\text{Equation I.9} \quad -qx\rho_L = \rho_L x \frac{dl}{dt} + xl \frac{d\rho_L}{dt} + \rho_L l \frac{dx}{dt}$$

Equation I.9 can be recast in terms of water mass fraction x by finding relations for $l(x)$ and $\rho_L(x)$ and differentiating. The density of the latex can be written as

$$\text{Equation I.10} \quad \rho_L = x(\rho_w - \rho_p) + \rho_p$$

where ρ_w and ρ_p are the densities of water and polymer, respectively. Differentiating with respect to time yields

$$\text{Equation I.11} \quad \frac{d\rho_L}{dt} = (\rho_w - \rho_p) \frac{dx}{dt}$$

The thickness of the latex film in the Stage II drying regime can be found as a function of water mass fraction x by rearranging Equation I.6 as

$$\text{Equation I.12} \quad l = \frac{m}{Ax\rho_L}$$

and expressing the instantaneous thickness relative to the thickness at the start of the Stage II as

$$\text{Equation I.13} \quad \frac{l}{l_0} = \frac{\rho_{L0}(1-x_0)}{\rho_L(1-x)}$$

where the 0 subscripts denote the parameter at the start of the Stage II drying regime. Substituting Equation I.10 for the latex densities in Equation I.13 yields

$$\text{Equation I.14} \quad \frac{l}{l_0} = \frac{(1-x_0)(x_0(\rho_w - \rho_p) + \rho_p)}{(1-x)(x(\rho_w - \rho_p) + \rho_p)}$$

Differentiating Equation I.14 results in

$$\text{Equation I.15} \quad \frac{dl}{dt} = \left(\frac{l_0(1-x_0)}{x_0(\rho_w - \rho_p) + \rho_p} \right) \left(\frac{(\rho_w - \rho_p) - 2x(\rho_w - \rho_p) + \rho_p}{1-x^2} \right) \frac{dx}{dt}$$

The unknown l_0 can be found by recasting Equation I.6 as a mass balance from the start of Stage II drying to the point where the latex is dry:

$$\text{Equation I.16} \quad \Delta m = l A x \rho_L - l_0 A x_0 \rho_{L0} = -l_0 A x_0 \rho_{L0}$$

Since the water mass fraction $x \rightarrow 0$ asymptotically at large drying times.

Solving Equation I.16 for l_0 and substituting into Equation I.15, then substituting the differential equations Equation I.11 and Equation I.15 along with the parameter definitions from Equation I.10 and Equation I.14, into the chain rule result of Equation I.9 gives an expression in terms of unknown x and t . This result can be integrated by parts and solved for time t , resulting in

$$\text{Equation I.17} \quad t = \frac{\Delta m}{qA} \left(\frac{(1-x_0)[x_0(\rho_w - \rho_p) + \rho_p]}{\rho_w} \ln \left(\frac{[(\rho_w - \rho_p)x^2 + x\rho_p][1-x_0^2 + \rho_p x_0(x_0 - 1)]}{[(\rho_w - \rho_p)x_0^2 + \rho_p x_0][1-x^2 + \rho_p x(x-1)]} \right) + \frac{1-x_0^2 + \rho_p x_0(x_0 - 1)}{1-x^2 + \rho_p x(x-1)} - 1 \right)$$

I.3 Model Implementation

Cumulative weight loss data of the drying latex was collected by the gravimetric method described previously. The model parameters q , Δm , x_0 , m_0 , and m_p are computed from this data, while ρ_w and ρ_p are material constants and A is determined from the specimen geometry. The polymer mass m_p is simply taken to be the mass of the dry latex at long times after the weight data has reached a stable value. It is recognized that small amounts of moisture may still be present in the latex, and that as yet unreacted curing agents do not formally fit the density definition of the polymer. These deviations from the ideal account for only a relatively small error in absolute terms, and are essentially transparent in the application of the model in this work given the semi-empirical approach used to determine the model parameters. The original water mass m_0 is simply the total mass at time $t=0$ less the polymer mass m_p .

The remaining parameters q , Δm , x_0 are determined from the weight per area data by fitting a linear function to the Stage I region as shown in Figure I.1, then graphically determining the Stage I –to- Stage II transition point. This point is taken as the time where the weight loss data significantly deviates from the linear fit curve; the time (t_0) and weight per area (w_0) at this point are recognized as those corresponding to the start of Stage II drying. Each linear fit to the Stage I drying data was forced through the origin and possessed regression coefficients of greater than 0.99. The slope of the linear fit is equal to the mass flux rate q . The mass lost during Stage II, Δm , can be computed using

$$\text{Equation I.18} \quad \Delta m = (w_\infty - w_0)A$$

where w_∞ is the weight per area value at long times, when the latex is dry.

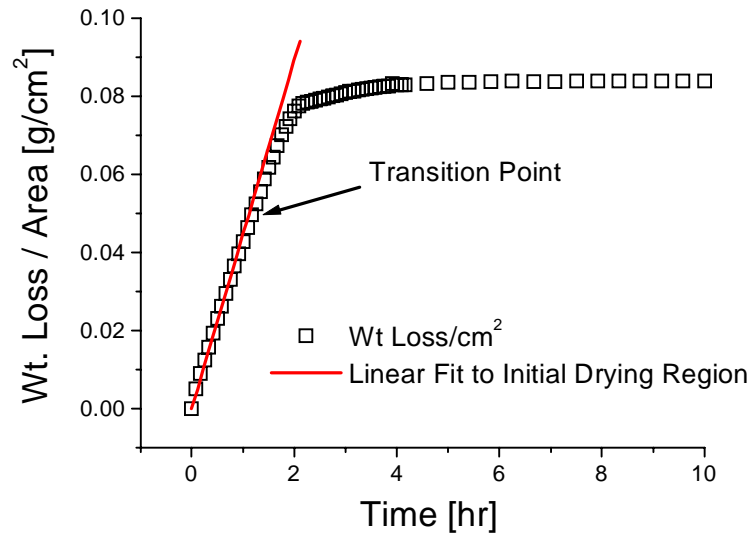


Figure I.1: Weight loss/ area vs. time plot

The water mass fraction at the start of Stage II drying, x_0 , can be computed by the mass balance

$$\text{Equation I.19} \quad x_0 = \frac{(w_i - w_0)A - m_p}{(w_i - w_0)A}$$

This value of x_0 can be checked by calculating the water mass fraction based upon the linear fit, x_{fit0} as

$$\text{Equation I.20} \quad x_{fit0} = \frac{w_i A - m_p - q A t_0}{w_i A - q A t_0}$$

If the two calculated water mass fractions of Equation I.19 and Equation I.20 disagree significantly, then the transition point has been chosen too far from the linear region, hence the weight loss curve should be reexamined to determine the proper transition point. Each data set analyzed in this study was checked by these criteria, with both x_0 and x_{fit0} found to be in good agreement.

A comparison of the model with the experimental data can be constructed using Equation I.4 and Equation I.17 for the Stage I and Stage II models, respectively, and plotting along with the experimental results, as shown in Figure I.2.

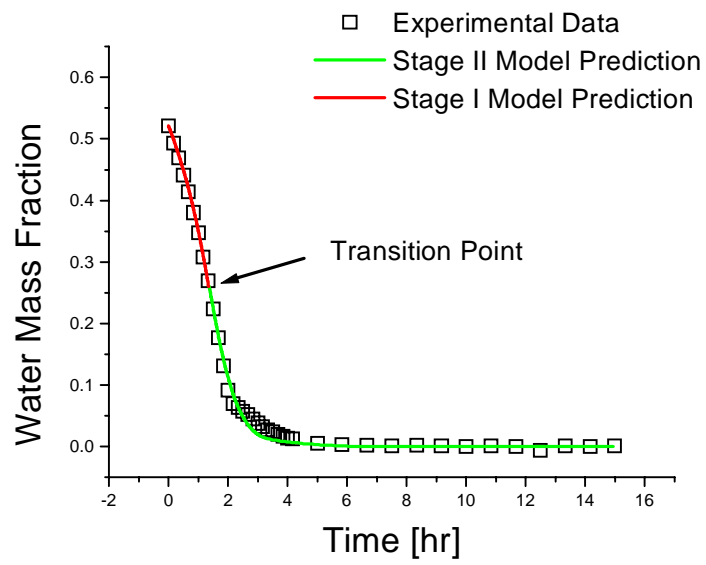


Figure I.2: Two-Stage Model Agreement with Latex Drying data

I.4 References

¹ S. G. Croll, "Drying of Latex Paint", Journal of Coatings Technology, Vol. 58, No. 734, 1986, p.41-49.

² S. T. Eckersley and A. Rudin, "Drying Behavior of Acrylic Latexes", Progress in Organic Coatings, Vol. 23, 1994, p. 387-402.