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Regression of Thermal, Thermodynamic, and Transport Properties for the Optimization of Multi-Component Polymer-Solvent Drying Processes

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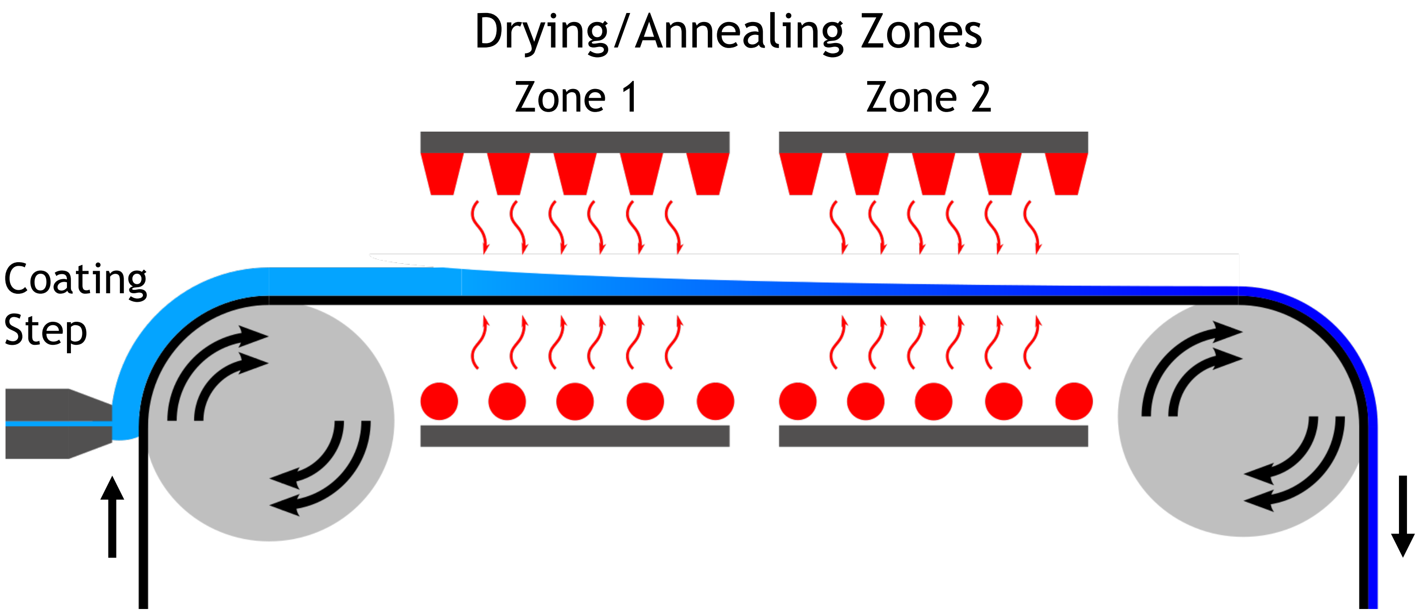
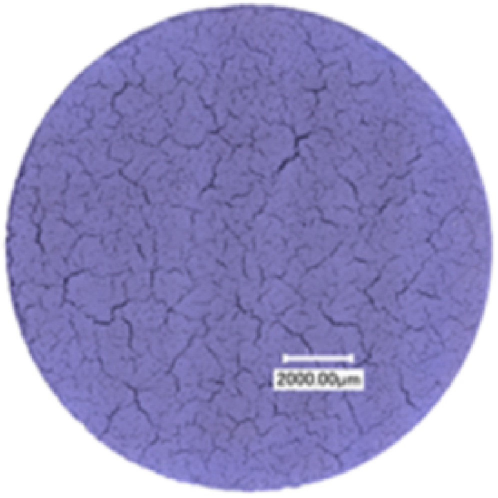
Challenges in high-throughput drying processes



Dried Cathode Slurry



Sahore et. al, ACS Sustain. Chem. Eng., 2020. 8, 3162

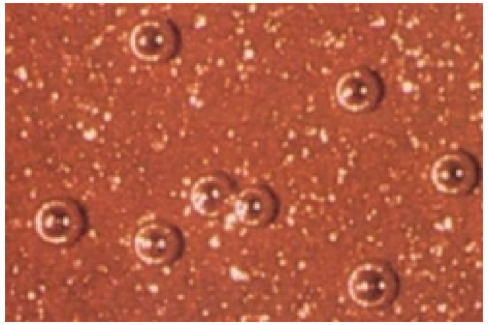
- Coating and drying conditions often determine product cost and quality (e.g., efficiency, durability, etc.)
- Coating and drying at high speeds increases the risk of defects and comes with significant capital and energy costs
- Opportunities to reduce these costs and mitigate defects via optimization of process conditions and coating formulation

Fundamentals of Defect Formation in Drying Coatings

Cracking

fitzsatlas.com

Blistering



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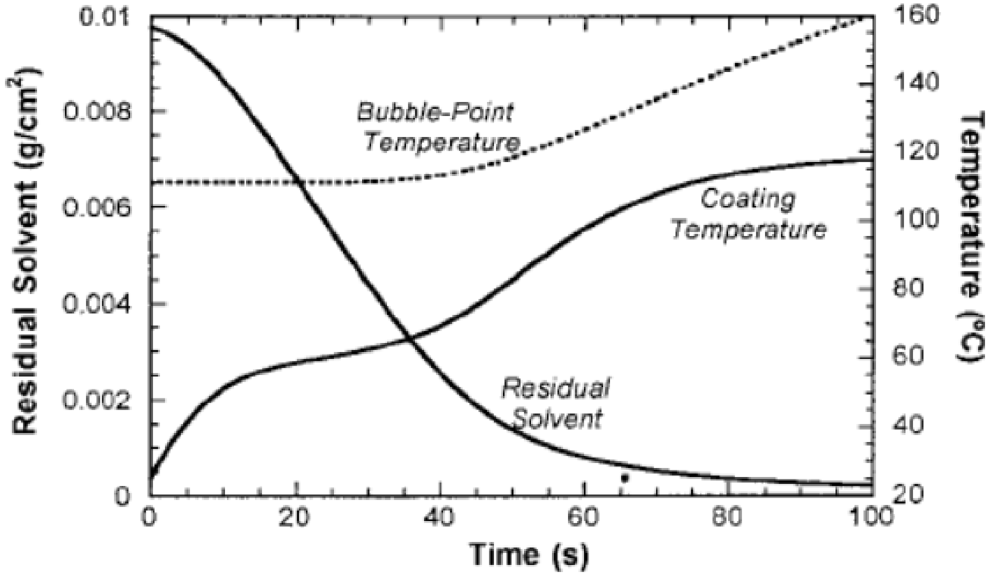
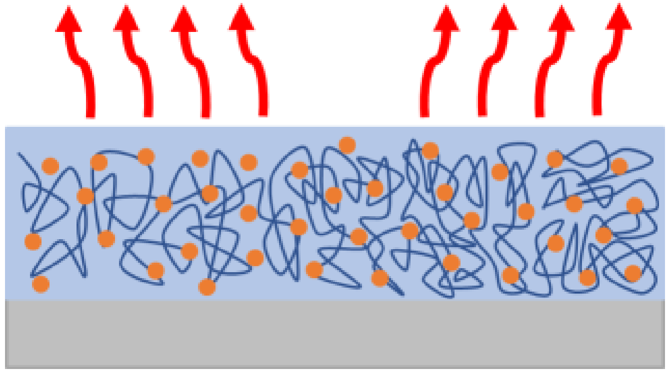


Price Jr. & Cairncross, J. Appl. Polym. Sci. 2000. 78, 149

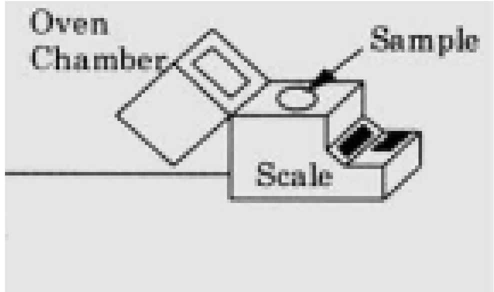
- Improper choice of drying conditions can lead to various defects
  - Wet coating at dryer exit
  - Boiling, cracking, delamination of coating
  - Deformation of substrate
- Drying conditions must yield appropriate drying rates to avoid defects
- Two important phenomena that affect overall drying rate:
  - External heat and mass transfer
  - Diffusion of solvent through coating



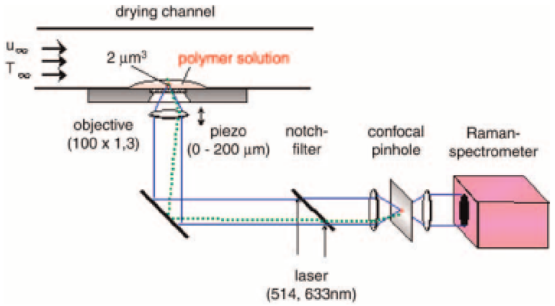
Prior Work on Benchtop Dryer Design Tools

Prior Work

Drying and Sorption Experiments

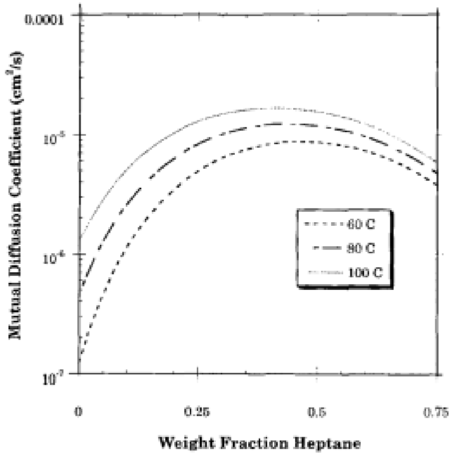


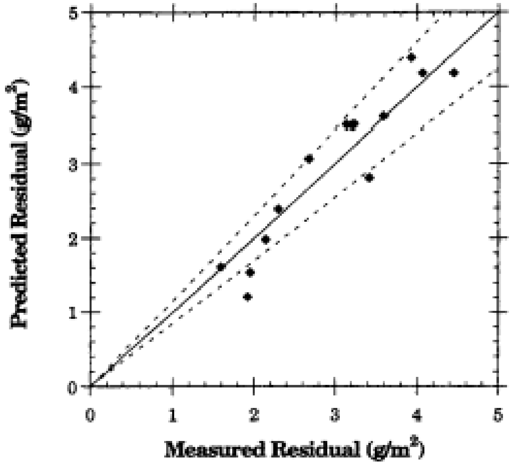
Price Jr. et al. AIChE J. 1997. 43, 1925



Schabel et al. Dry. Technol. 2004. 22, 285

Drying Process Predictions

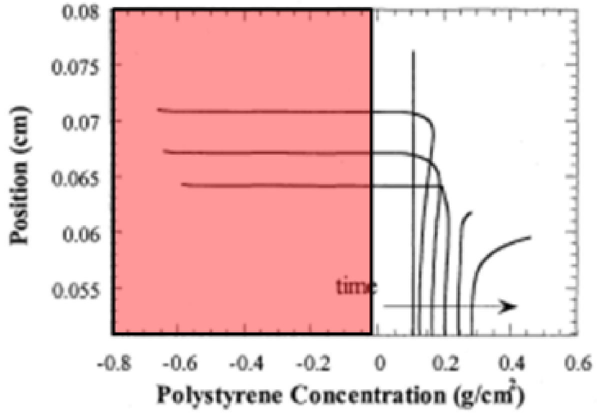




Price Jr. et al. AIChE J. 1997. 43, 1925

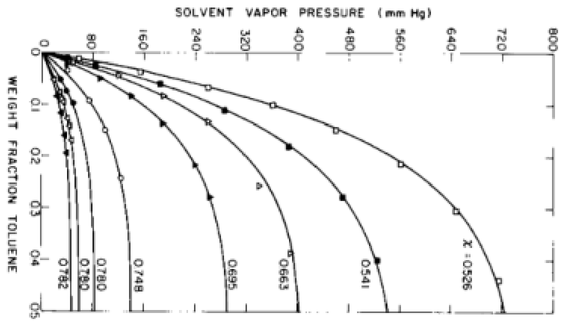
Challenges

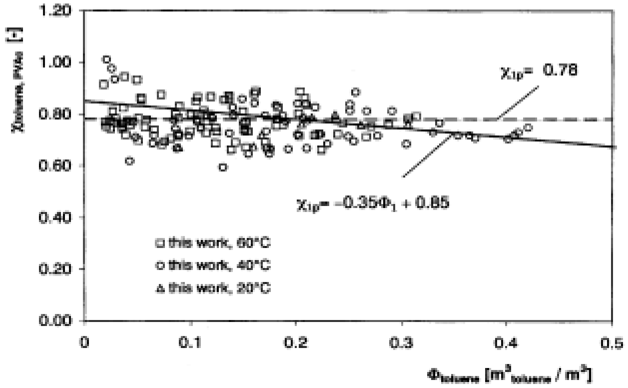
Ill-Posed Diffusivity Models



Price Jr. & Romdhane. AIChE J. 2003. 49, 309

Inconsistency in Thermodynamic Parameters



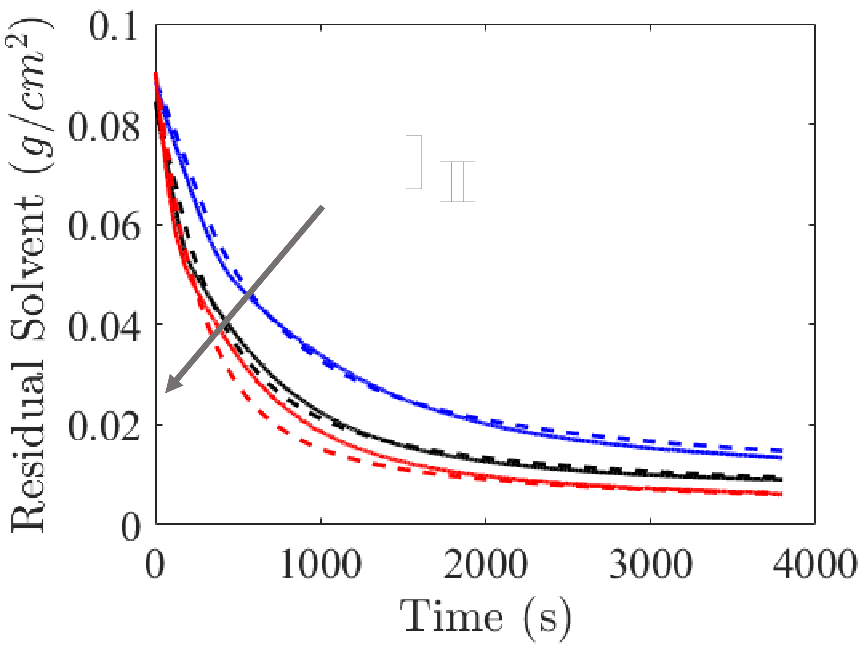


Vrentas et al. J. Polym. Sci. B. 1985. 23, 289 Mamaliga et al.. Chem. Eng. Process. 2004. 43, 753

Design Tool for Drying Processes

Moisture Balance

- Provide a cheap, benchtop tool to regress model parameters from gravimetric drying data
- Use model parameters to predict residual solvent during drying process
- Provide estimates for optimal dryer conditions for given inks/coatings



Free-volume diffusivity

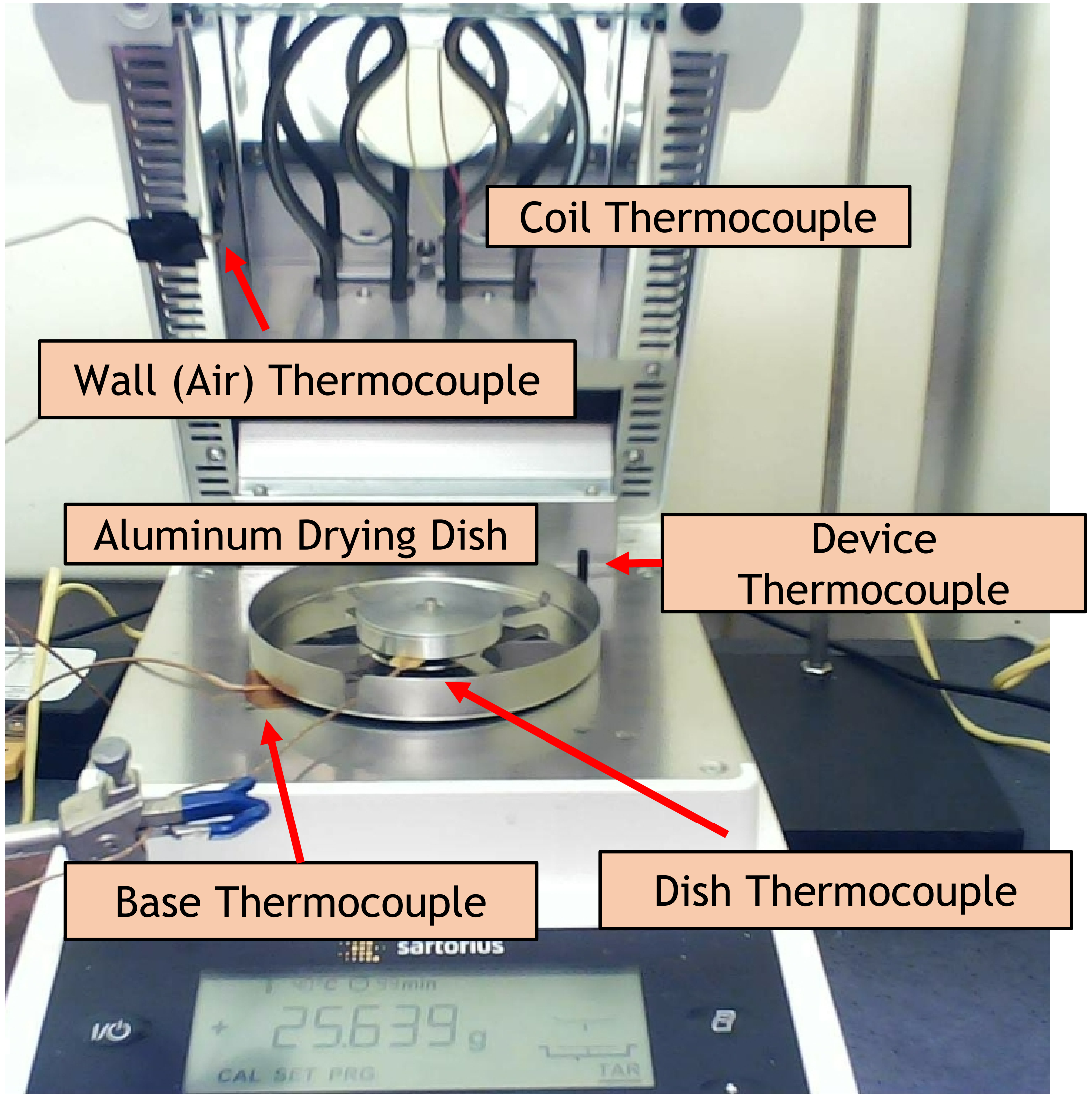
$$D_{ik} = D_i\left(\frac{c_i}{RT}\frac{\partial\mu_i}{\partial c_k}\right) - \sum_{j=1}^{N-1} D_j c_i \hat{V}_j\left(1 - \frac{D_N\hat{V}_N M_N}{D_j\hat{V}_j M_j}\right)\left(\frac{c_j}{RT}\frac{\partial\mu_j}{\partial c_k}\right)$$

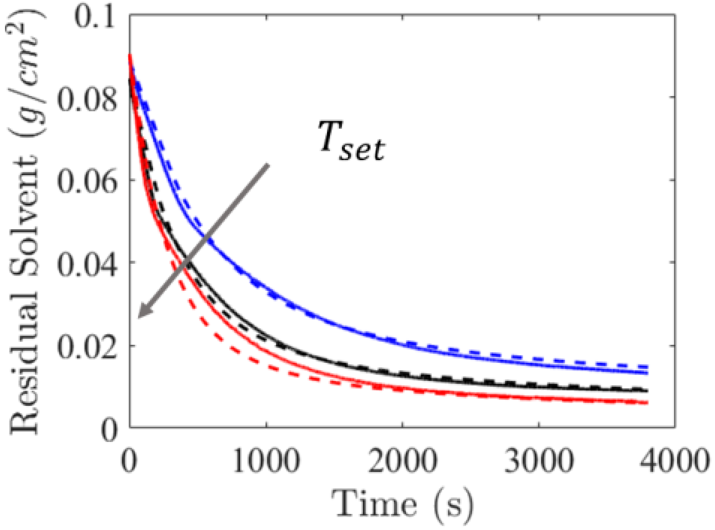
$$D_i = D_{0,i}\exp\left(\frac{-\gamma\sum_{j=1}^{N}\left(\omega_j\,\hat{V}_j^*\,\frac{\xi_{iN}}{\xi_{jN}}\right)}{\hat{V}_{FH}}\right)$$

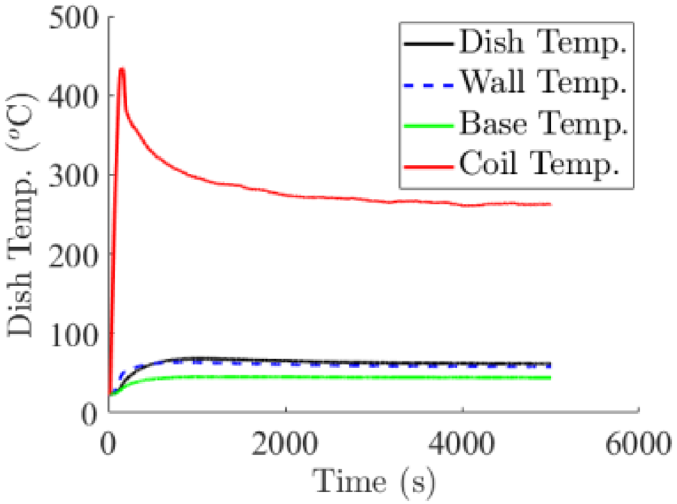
$$\frac{\hat{V}_{FH}}{\gamma} = \sum_{j=1}^{N}\frac{K_{1i}}{\gamma}\omega_i\left(K_{2i} - T_{gi} + T\right)$$

Price Jr. & Romdhane. AIChE J. 2003. 49, 309

Experimental Setup







Drying Model for Multicomponent Polymer-Solvent Coatings

Heat Transfer B.C.: Liquid-Air Interface

$$\kappa \frac{\partial T}{\partial y} = \epsilon\sigma(T_{coil}^4 - T^4) + h_{air}(T - T_r) + \sum_{i=1}^{N_{solv}} \Delta H_{vap} k_i (P_i^v - P_{0,i})$$

Species Transport: Diffusion

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial y}\left(\sum_{j=1}^{N-1} D_{ij}(\underline{c},T)\frac{\partial c_j}{\partial y}\right)$$

$D_{ij}(\underline{c},T)$ from Price (2004)

Heat Transfer: Liquid

$$\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial y}\left(\kappa \frac{\partial T}{\partial y}\right)$$

Drying Flux for solvent i

$$\sum_{j=1}^{N_{solv}} D_{ij}\frac{\partial c_j}{\partial y} + c_i \frac{\partial H}{\partial t} = -k_i(P_i^v - P_{0,i})$$

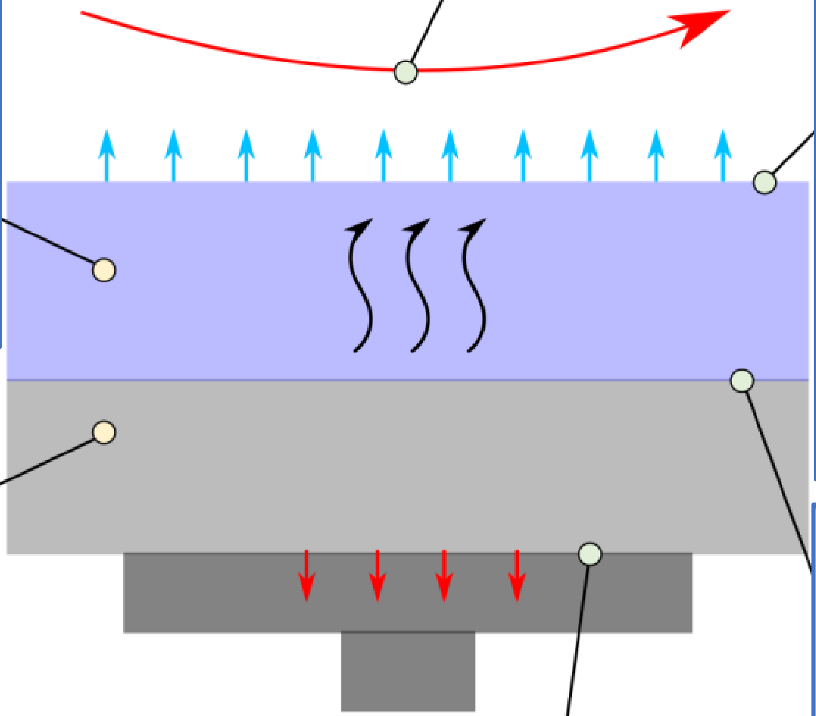
Vapor-Pressure: Flory Huggins

$$P_i^v(\underline{c},T) = \phi_i(\underline{c})\cdot\gamma_i(\underline{c})\cdot\tilde{P}_i^v(T)$$

$$\tilde{P}_i^v(T) = \exp\left(A_i - \frac{B_i}{T+C_i}\right)$$

$$\ln\gamma_i(\underline{c}) = \sum_{k=1}^{N}\left(\frac{\bar{v}_i}{\bar{v}_k}\right)(\delta_{ki}-\phi_k) \ldots$$

$$\ldots + \sum_{k=2}^{N}\sum_{j=1}^{k-1}\left[\delta_{ij}\phi_k\chi_{jk} + \phi_j\left(\frac{\bar{v}_i}{\bar{v}_j}\right)(\delta_{ki}-\phi_k)\chi_{jk}\right]$$



Heat Transfer: Substrate

$$\frac{\partial T_s}{\partial t} = \frac{\kappa_s}{\rho_s C_{p,s}}\frac{\partial^2 T_s}{\partial y^2}$$

No-Flux B.C. for solvent i

$$\sum_{j=1}^{N_{solv}} D_{ij}\frac{\partial c_j}{\partial y} = 0$$

Heat Transfer B.C.

$$\kappa_s \frac{\partial T_s}{\partial y} = \kappa\frac{\partial T}{\partial y}$$

$$T_s(0^+,t) = T(0^-,t)$$

Heat Transfer Boundary Condition

$$\kappa_s\frac{\partial T_s}{\partial y} = h_{base}(T_s - T_b)$$

Drying Model: Key Device and Material Properties

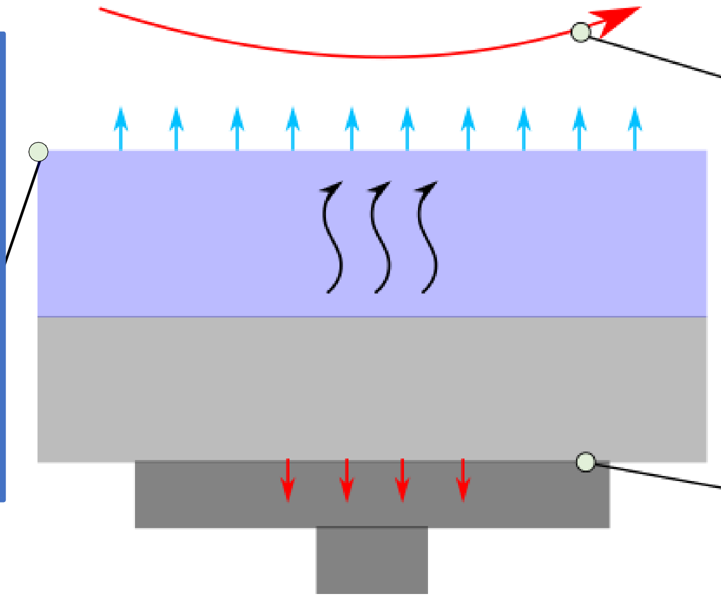
Drying Flux for solvent i

$$c_i \frac{\partial H}{\partial t} + \sum_{j=1}^{N_{solv}} D_{ij} \frac{\partial c_j}{\partial y} = -k_i \left(P_i^v - P_{0,i}\right)$$

Activity Coefficient: Flory-Huggins

$$\ln \gamma_i(\underline{c}) = \sum_{k=1}^{N} \left(\frac{\bar{v}_i}{\bar{v}_k}\right)(\delta_{ki} - \phi_k) + \sum_{k=2}^{N} \sum_{j=1}^{k-1} \left[\delta_{ij} \phi_k \chi_{jk} + \phi_j \left(\frac{\bar{v}_i}{\bar{v}_j}\right)(\delta_{ki} - \phi_k) \chi_{jk}\right]$$

$$\chi_{jk} = \chi_{r,jk} \cdot \frac{273.15K}{T}$$



Heat Transfer B.C.: Liquid-Air Interface

$$\kappa \frac{\partial T}{\partial y} = \underbrace{\epsilon \sigma \left(T_{coil}^4 - T^4\right)}_{\text{radiation}} + \underbrace{h_{air}\left(T - T_{wall}\right)}_{\text{convection}} + \underbrace{\sum_{i=1}^{N_{solv}} \Delta H_{vap} k_i \left(P_i^v - P_{0,i}\right)}_{\text{evaporative cooling}}$$

Heat Transfer B.C.: Dish Base

$$\kappa_s \frac{\partial T_s}{\partial y} = \underbrace{h_{base}\left(T_s - T_{base}\right)}_{\text{conduction}}$$

Ambient conditions and known properties

T_{coil}: coil temperature

T_r: reference temperature for air-side heat transfer

T_b: base temperature

ΔH_{vap}: specific heat of vaporization

σ: Stefan-Boltzmann constant

κ: thermal conductivity

Heat transfer boundary conditions

h_{air}: heat transfer coefficient to air

ϵ: emissivity for radiation modeling

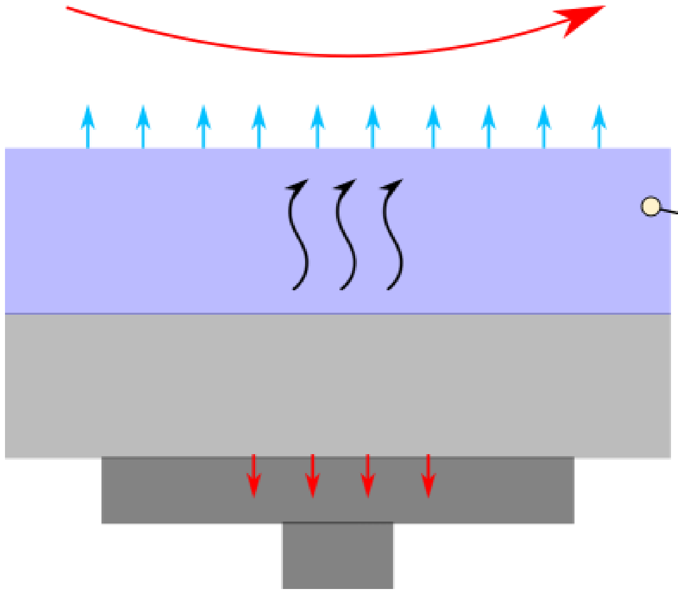
h_{base}: heat transfer coefficient to base

Mass transfer: drying and evaporative cooling

k_i: mass transfer coefficient of component i

χ_{ij}: FH binary interaction parameter

Drying Model: Solvent Diffusivity



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Price Jr. & Romdhane. AIChE J. 2003. 49, 309

Free-volume parameters

$D_{0,i}$: infinite-dilution diffusion coefficient

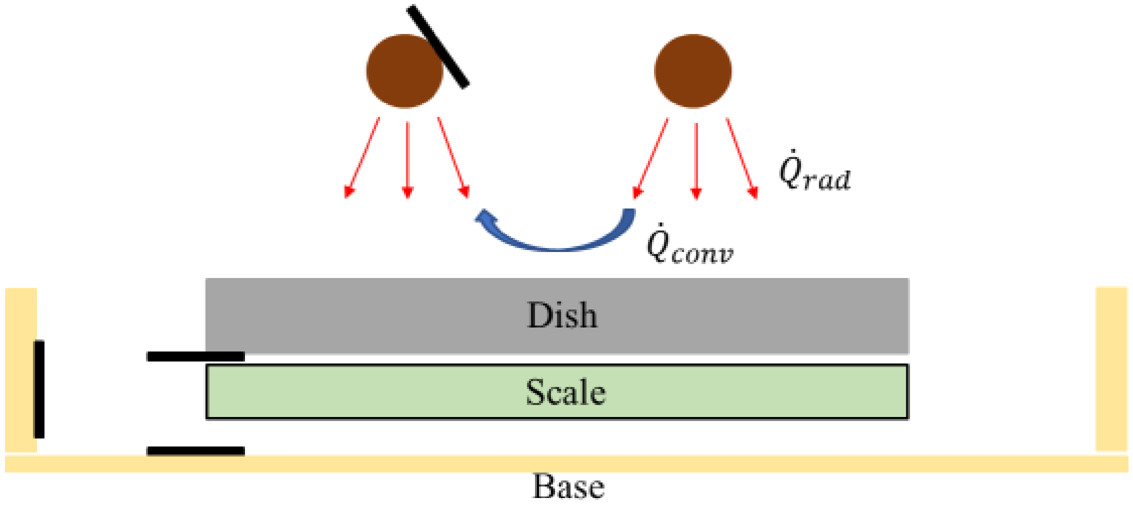
ξ_{iN}: solvent i to polymer N jumping unit ratio

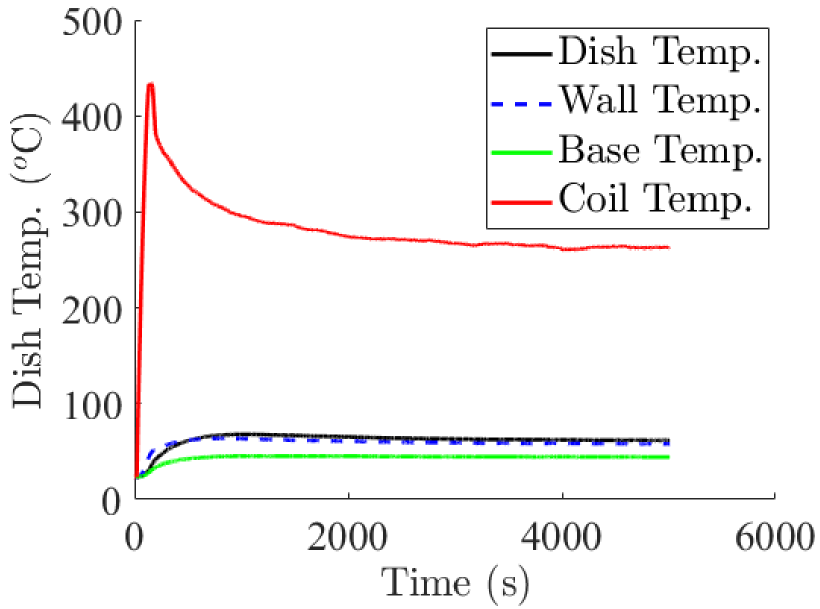
$\hat{V}_i^*$: critical hole volume of component i

K_{1i}/γ: solvent free-volume params.

$K_{2i} - T_{gi}$: polymer free-volume params.

Example Parameter Regression: Heat Transfer Parameters





Total Energy Balance for polymer and dish

$$\left(m_{poly}\, c_{p,poly} + m_{dish}\, c_{p,dish}\right)\frac{dT_{dish}}{dt} =$$

$$\ldots - \boldsymbol{h_{air}}(A + A_s)(T_{dish} - T_{wall}) \ldots$$

$$\ldots + \boldsymbol{\epsilon}\sigma A\left(T_{coil}^4 - T_{dish}^4\right) \ldots$$

$$\ldots - h_{base} A(T_{dish} - T_{base})$$

h_{air}: heat transfer coefficient (wall)

h_{base} : heat transfer coefficient (base)

ϵ: emissivity for radiation modeling

m: dish mass

c_p: dish heat capacity

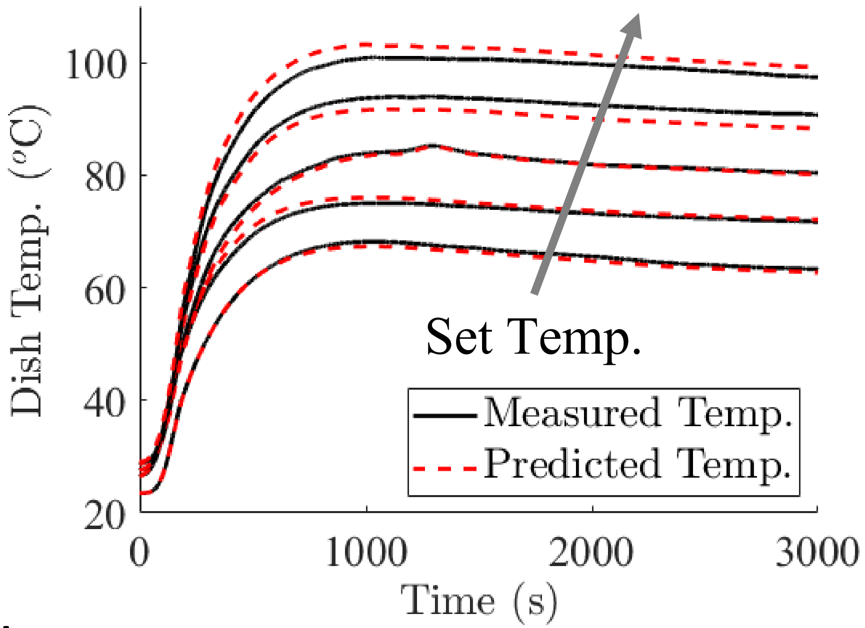
σ: Stefan-Boltzmann constant

A: area of top/bottom dish surfaces

A_s: area of dish side

Example Parameter Regression: Heat Transfer Parameters

h_{air} $(cal/s\ cm^2\ K)$	1.78×10^{-4}
ϵ_{PVAc} $(unitless)$	0.1222
h_{base} $(cal/s\ cm^2\ K)$	5.76×10^{-4}



Total Energy Balance for polymer and dish

$$\left(m_{poly}\, c_{p,poly} + m_{dish}\, c_{p,dish}\right)\frac{dT_{dish}}{dt} =$$

$$\ldots - h_{air}(A + A_s)(T_{dish} - T_{wall}) \ldots$$

$$\ldots + \epsilon\sigma A\left(T_{coil}^4 - T_{dish}^4\right) \ldots$$

$$\ldots - h_{base}A(T_{dish} - T_{base})$$

h_{air}: heat transfer coefficient (wall)

h_{base} : heat transfer coefficient (base)

ϵ: emissivity for radiation modeling

m: dish mass

c_p: dish heat capacity

σ: Stefan-Boltzmann constant

A: area of top/bottom dish surfaces

A_s: area of dish side

Regression Method for Diffusion and Flory-Huggins Params.

Measured Residual Solvent

$$r_{i,exp} = \frac{m_{coating}(t_i) - m_{poly}}{A}$$

Predicted Residual Solvent

$$r_{i,pred} = \int_{x=0}^{x=h(t)} c_i\,(x, t_i)dx$$

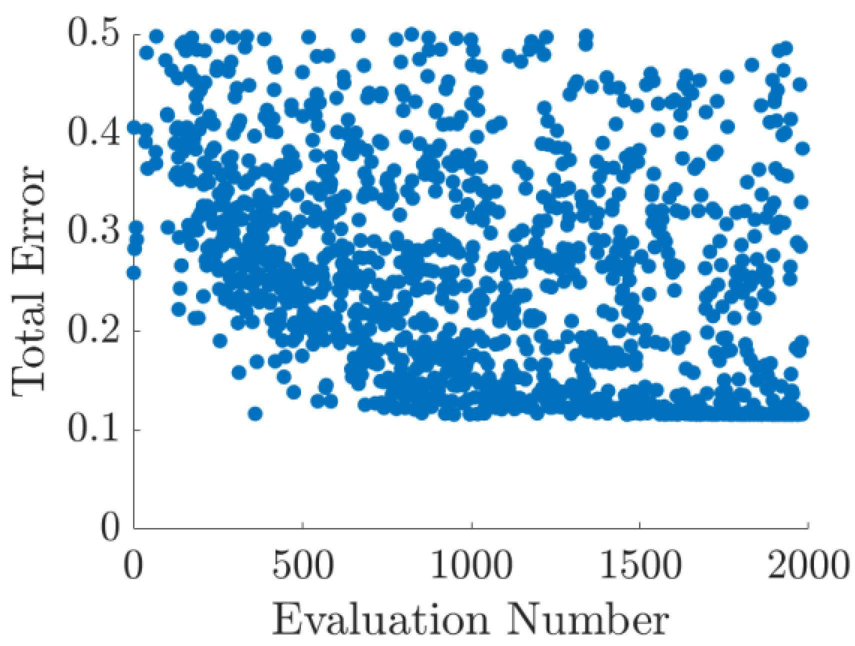
Individual Experimental Error

$$e_1^k = \sum_{j=1}^{N_{pts}} \sqrt{\frac{\left(1 - \frac{r_{i,pred}}{r_{i,exp}}\right)^2}{N_{pts}}}$$

$$e_2^k = \sum_{j=1}^{N_{pts}} \sqrt{\frac{1}{100}\left(\frac{r_{i,exp} - r_{i,pred}}{r_{i,exp}(t_{end}) - r_{i,exp}(0)}\right)^2}$$

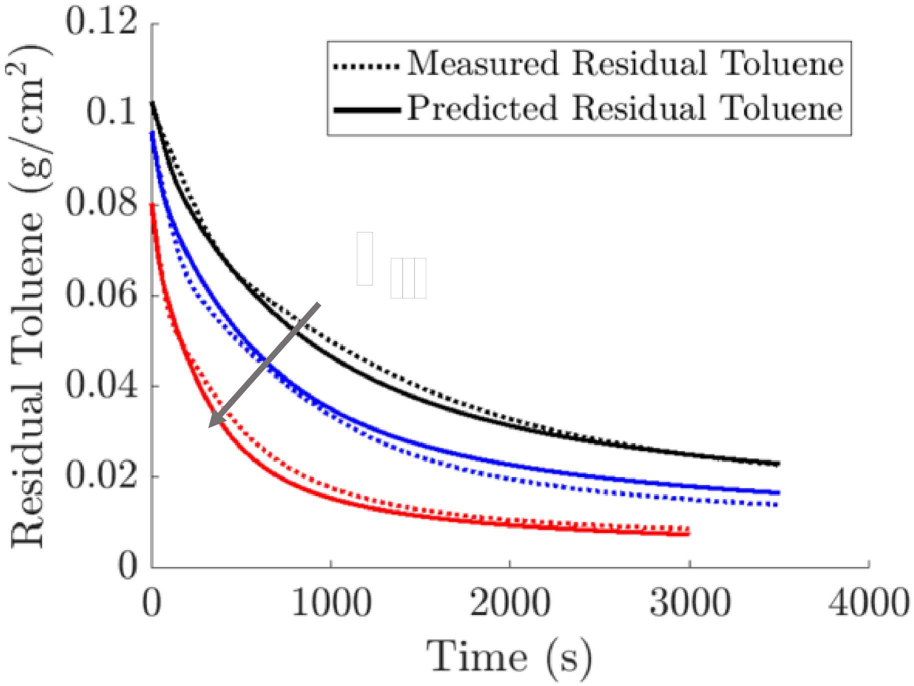
Total Regression Error

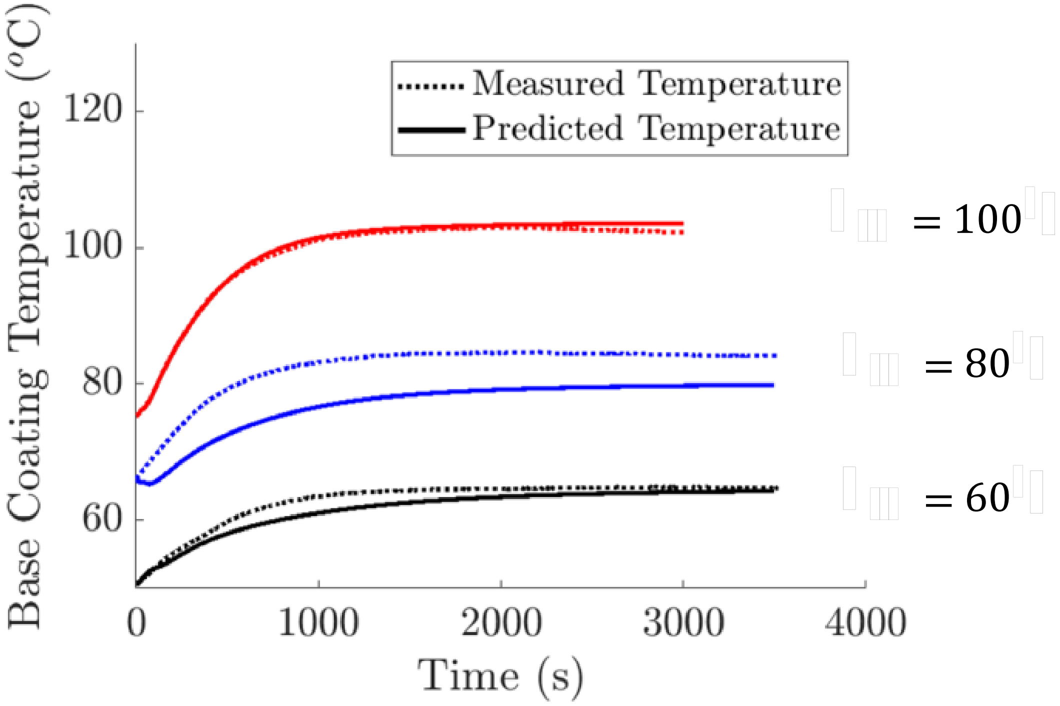
$$e_{total} = \sqrt{\sum_{k=1}^{N_{exp}} \frac{0.5\left(e_1^k\right)^2 + 0.5\left(e_2^k\right)^2}{N_{exp} - 1}}$$



Model Predictions: Residual Solvent and Coating Temperature

30 wt% poly(vinyl acetate) in toluene

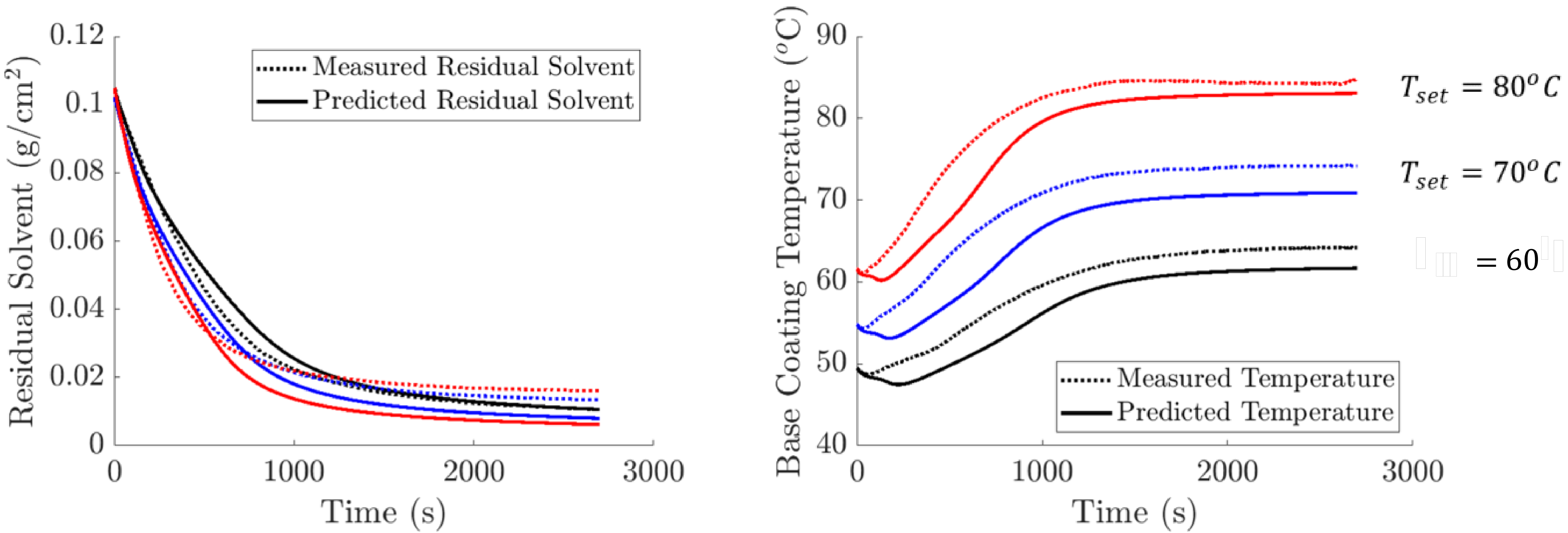




Model predictions for residual solvent and coating temperature agree well (within 10%) for typical polymer-solvent systems

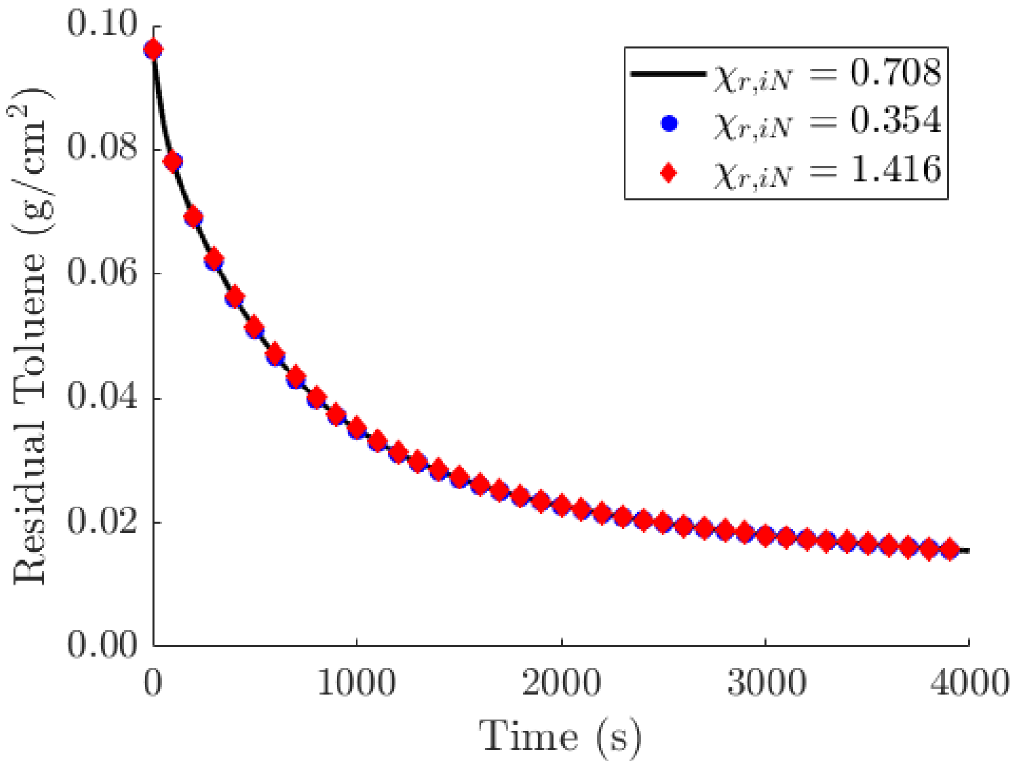
Model Predictions: Two Solvent System

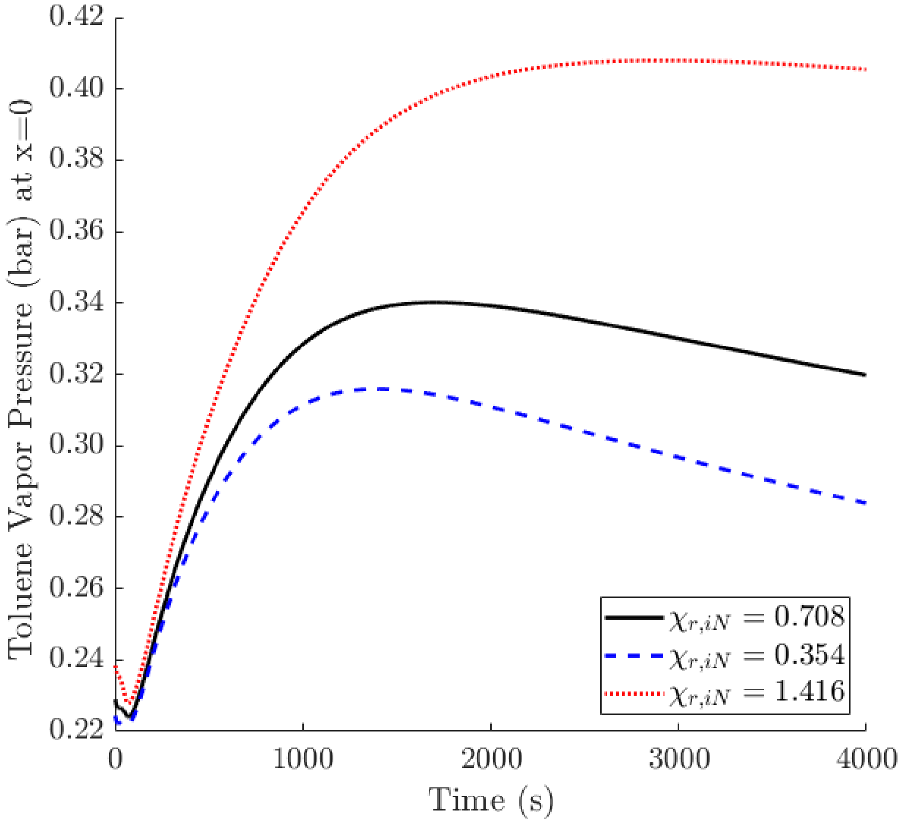
20 wt% poly(vinyl acetate) in toluene/ethanol (5:7 by weight)



Final residual solvent tends to be overpredicted using regressed parameters:
Skin formation and viscoelastic drying effects likely culprit

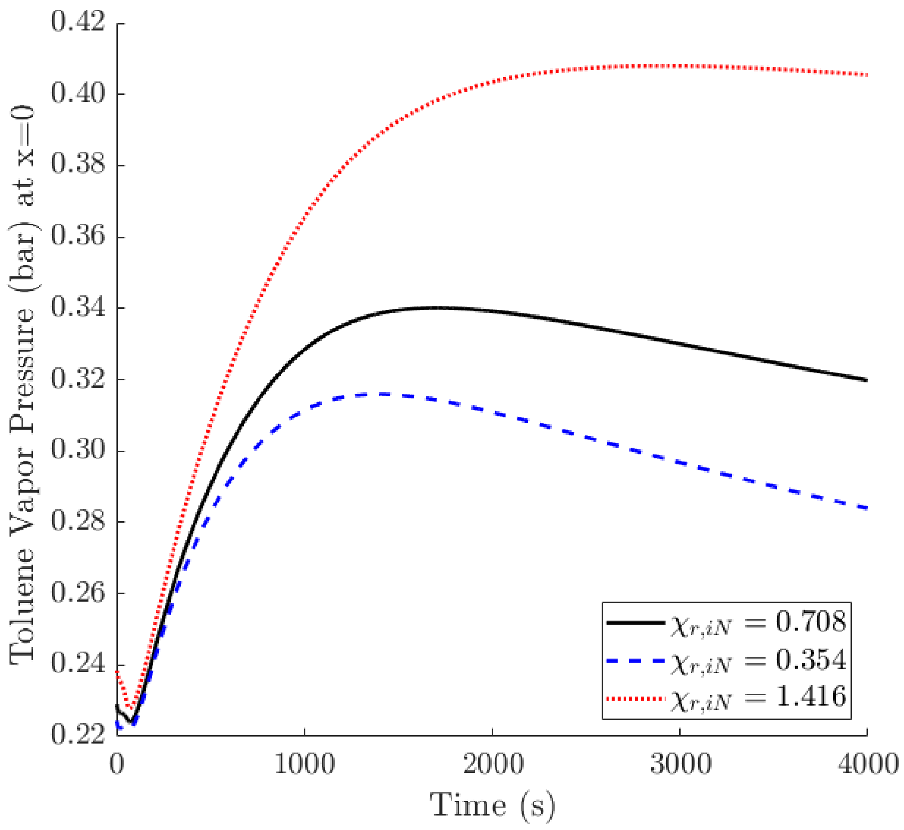
Challenges: Regression of Flory-Huggins Parameter

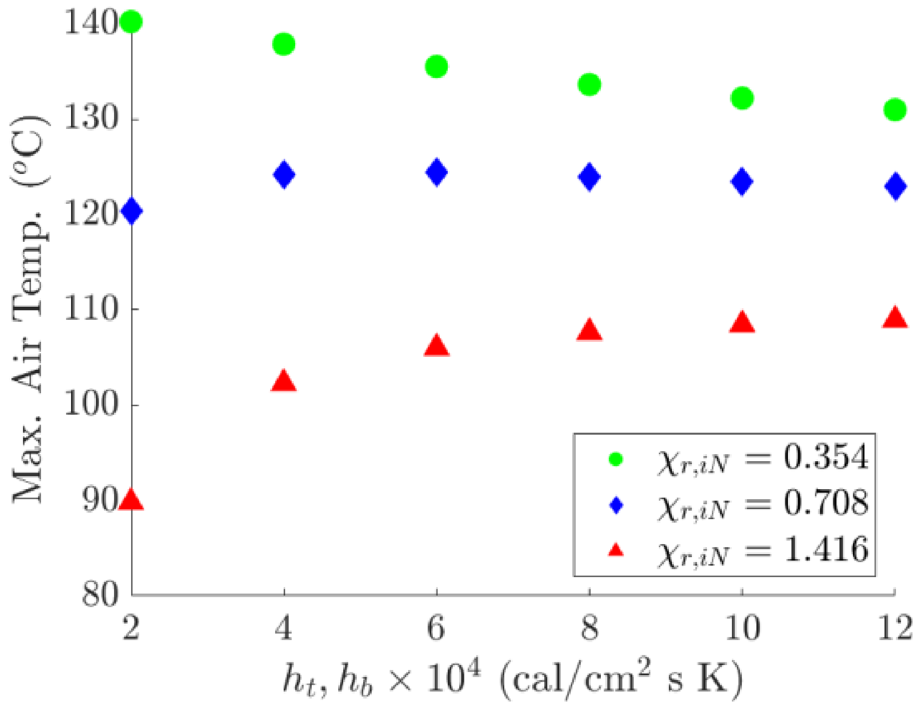




Predicted residual solvent is insensitive to the Flory-Huggins parameter, while important measures used to predict defect formation (e.g., vapor pressure) remain sensitive!

Variability in Process Limits with Flory-Huggins Parameter



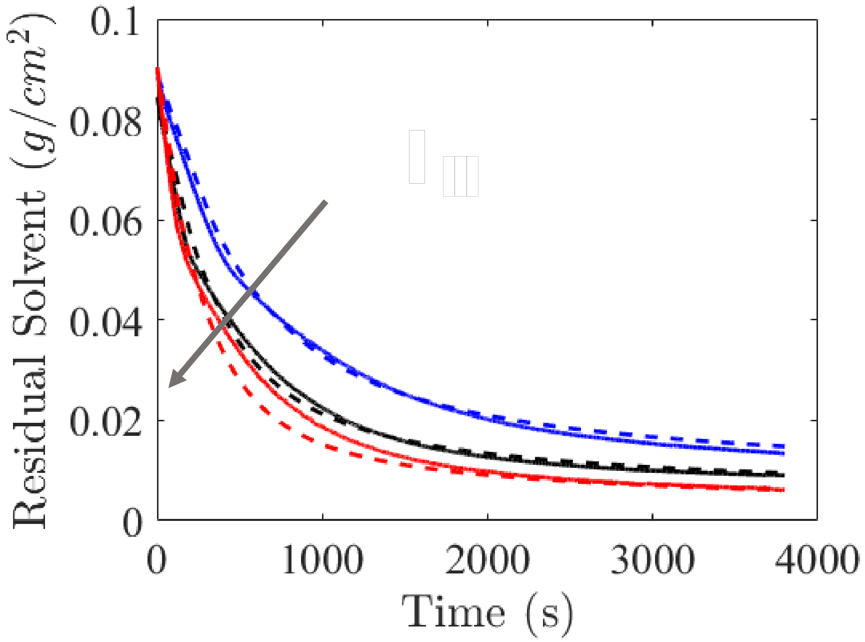


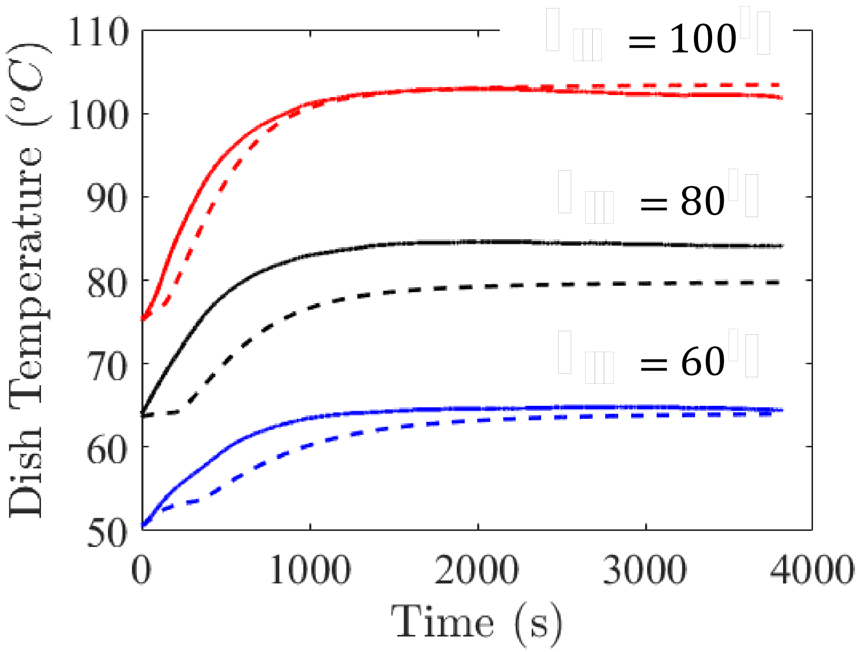
Process limits for drying defects (e.g., boiling and blistering) vary strongly with Flory-Huggins parameter

This approach is not always useful for predicting process limits!

Summary and Conclusions

- Developed complementary experimental and computational tools to regress key drying parameters
- Regressed parameters yield quantitative predictions of coating composition and temperature, useful in dryer sizing/design
- **Updated diffusivity and mass transfer models are needed to address viscoelastic skin formation in fast-drying coatings**
- **Additional experiments are needed for the regression of thermodynamic parameters (e.g, Flory-Huggins parameter)**





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