**Drying Paths of Phase-Separating Monomer Solution Coatings**

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1. Introduction

Drying process paths, i.e., trajectories of solution compositions on a phase diagram, play a key role in designing microstructures in liquid thin film coatings [1-4]. Previous studies have shown that drying paths in non-ideal solvent mixtures can show bifurcations with unstable/stable nodes [5]. A small change in the initial composition leads to different branches of drying paths, on which one solvent can selectively evaporates while other solvents concentrate. A non-selective drying process, sometimes referred to as pseudo-azeotrope [6], may occur at particular compositions on the border between the branches. It is of practical importance to choose a desirable drying path to manipulate phase-separated structures [7] and suppress drying-induced crack formation [8]. Despite recent progresses in monitoring local compositions of drying solution films using Raman [9-11] and infrared [12] spectroscopies, a direct measurement of drying path is still challenging particularly for opaque films, in which the optical measurement techniques are no longer applicable. In this study, we focused on drying paths of monomer-ethanol-water ternary solution systems that involve vapor-induced phase separation. When a low-molecular-weight acrylic monomer is partially miscible with water, evaporating solutions absorb water vapor from humid air (Fig. 1a) and become thermodynamically unstable, resulting in a spontaneous phase separation into water-rich and monomer-rich phases (Fig. 1b). A further evaporation removes solvents from the former phase and eventually promotes formation of uneven surface topographies, which is sometimes desirable to fabricate antiglare coatings. To understand structure evolution mechanism, we first conducted numerical modeling to predict drying paths as a function of initial compositions, drying temperatures, and solvent concentrations in the gas phase. Next we constructed an in-situ monitoring system of the drying paths by combining simultaneous mass-loss and heat-flux [13] measurements. The measured drying paths agreed with the numerical prediction under particular drying conditions.

Figure 1 Vapor-induced phase separation.

1. Modeling

We predicted drying paths of dipentaerythritolhexaacrylate(DPHA)-ethanol-water ternary systems by assuming uniform concentration/temperature profiles across the coating thickness, a constant mass transfer coefficient, and isothermal drying controlled by gas-phase diffusion. We also assumed that the activity coefficients of the solvents were given by the Universal Functional Group Activity Coefficient (UNIFAC) model and phase separation gave little influence on the drying kinetics as has been done in [1].

Typical examples of the predicted drying paths for 400-m-thick solution coatings are shown in Fig. 2 in cases of (a) zero humidity and high ethanol vapor pressure, and (b) high humidity and zero ethanol vapor pressure in drying air, respectively. The two-phase region, in which phase separation takes place, is illustrated as yellow regime in the ternary phase diagram. The initial compositions are shown as open circles in Fig. 2 where the DPHA (monomer) content was fixed at 1.0 wt%. The predicted drying paths varied with the initial compositions. The ethanol concentration first increases and then decreases with time at high initial ethanol contents (drying path I). No drying paths cross the bimodal curve to enter the two-phase region, indicating that drying proceeds without phase separation. In case of a lower initial ethanol content, the ethanol content monotonically decreases along the drying path III, which eventually enters the two-phase region to promote the onset of phase separation at a certain drying time. In the intermediate case (path II), drying becomes non-selective and near pseudo-azeotrope, i.e., ethanol and water co-evaporate keeping a constant ethanol/water mass ratio. Thus the path II splits the non-separating and phase-separating drying regimes. With a further decrease in the initial ethanol content, the drying path IV shows that the ethanol content first increases due to adsorption of ethanol vapor into the drying solution, followed by a decrease in ethanol concentration in later drying stages. This accompanies a spontaneous phase separation in the two-phase region, showing a drying behavior differs from that on drying path I. Under high humidity conditions (Fig. 2b), more water vapor can be absorbed to trigger phase separation, resulting in a shrink in the phase-separation-free drying regime.



Figure 2 Predicted drying paths at different initial composition. (a) zero humidity and high ethanol vapor pressure in drying air, (b) high humidity and zero ethanol vapor pressure in drying air.

1. Experimental

To determine drying paths of the phase-separating opaque ternary solutions containing ethanol (solvent A), water (solvent B), and DPHA, we combined mass-loss/heat-flux measurements. The sample solution was deposited on a glass substrate with an initial film thickness of 400 m. The coated area was specified to be 25 cm2 by gluing a 1.0 mm-thick aluminum shim on the substrate. The base temperature of the substrate was maintained by regulating the current through the heater located beneath the coating. The variations in the film mass with drying time was measured using an electronic balance to calculate the total drying rate (*r*total), which is a sum of drying rate of each solvent as,



where *r*A and *r*B denote the drying rate of ethanol and water, respectively.

Simultaneously, the heat flux across the coating, *q*(t), was measured using the heat-flux sensor (Captec Co. Ltd.) of 40 mm in diameter. The sensor was attached beneath the glass substrate using a 500-m-thick conductive film with an adhesive layer. To achieve unidirectional heat conduction in the thickness direction, the sensor was surrounded by a dummy plate with the same thickness and the thermal conductivity (Fig. 3). Assuming a steady heat transfer, the heat flux is expressed as the sum of latent heat and the convection heat transfer in the gas phase as

Figure 3 heat flux sensor setup (a) cross-sectional view (b) top view



where *T*i is the film surface temperature, *T*b is temperature of bulk air, *h*Gair is heat transfer coefficient, and Hi are the latent heat of solvent I (i=A, B). Combining Eqs. (1)(2) gives the expression for the drying rate of solvent A as:



The film surface temperature was determined from the measured heat flux, the temperature of the sensor, and the steady-state solution of unidirectional heat conduction across the thickness. Thus simultaneous measurements of *q*(t) and *r*total(t) allowed us to determine the drying rate of each solvent from Eqs. (1) and (3). The residual solvent amounts at different drying times were calculated by integrating the drying rates with time and plotted on the phase diagram to show a drying path.

4. Results

A comparison between the predicted (closed symbol) and measured (open red symbol) drying paths is shown in Fig.4 in case of high air humidity. Each symbol represents the composition at every 40 s drying. The drying process path starts from the thermodynamically stable region but it enters the two-phase region as the ethanol evaporation and the absorption of water vapor proceed, showing a similar drying behavior shown in the drying path III in Fig. 2. The numerical prediction well matched the measurement in early evaporation stages, showing the validity of present modeling in dilute regimes. The predicted drying path deviated from the measurement in later drying times at which ethanol evaporation was almost completed. This is possibly because the internal diffusion in concentrated solution becomes dominant.

Figure 4 Comparison between the predicted (closed symbol) and measured (open red symbol) drying paths.

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