

Cellular porous patterns in phase separating coatings under humidity-assisted flow

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1. Introduction

Ordered convection patterns emerge in evaporating solution films when fluctuations of local surface tension drive interfacial liquid motions enhanced by the upward flow from the bulk. The linear stability analysis has shown that the convection onsets when the Marangoni number (Ma), defined as the interfacial force relative to dissipative forces, exceeds the critical value. For a given interfacial stress, an increasing viscous stress due to a rise in solution viscosity and film shrinkage resists the fluid motion to dissipate the pattern.

Extensive studies have been attempted to conserve convection-induced microstructures by solidifying the film before the patterns dissipate. However, little attention has been paid for time-variations in Marangoni numbers during drying. Indeed, most of the previous studies have focused on initial thermo-capillary convections and discussed the pattern formation based on a Marangoni number at the beginning of evaporation. In this study, flow- induced pattern formation in polystyrene/cellulose-acetate-butyrate/tetrahydrofuran solution coating was investigated based on a direct visualization and mass loss measurements under different humidity. Water-vapor diffusion into coatings not only quenches the system into thermodynamically unstable region to induce a phase separation, but also promotes a cellular convection driven by concentration-dependent surface tension variations. The coupling between the flow and the phase separation promoted complex surface patterns with ordered pores, verified by estimated

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Marangoni number variations.

2. Experimental

The experimental apparatus is shown schematically in Fig.1. We used tetrahydrofuran (THF, Wako), polystyrene (PS, $M_n=115000$, $M_w/M_n=1.8$, Wako) and cellulose acetate butyrate (CAB, $M_n=30000$, 13.5 wt% acetyl group, and 38.0 wt% butyryl group, Aldrich) as purchased to prepare binary (THF/PS and THF/CAB) and ternary solutions. The solution was deposited on a glass substrate with an initial film thickness of 500 microns. The coated area was specified to be 25 cm^2 by gluing 1.0 mm thick aluminum shim on the substrate. The coating was then mounted on an electronic balance (Sartorius LP1200S) to measure the decrease in film mass, which was stored in a personal computer at a sampling rate of 2.5 Hz. Simultaneously phase structure formation during drying was directly visualized from the bottom using an optical microscopy (VH-5000, Keyence). The coating was continuously heated by a glass conductive heater (Kitazato MP-10DMH) by regulating the current through it. The substrate temperature was monitored using $50\text{ }\mu\text{m}$ thick thermocouple attached at the substrate bottom surface. Environmental humidity was varied between 0.80×10^{-2} and 1.78×10^{-2} g-water/g-dry-air by supplying water vapor from a heating liquid pool. Cloud points of the solution were determined by measuring variations in sample

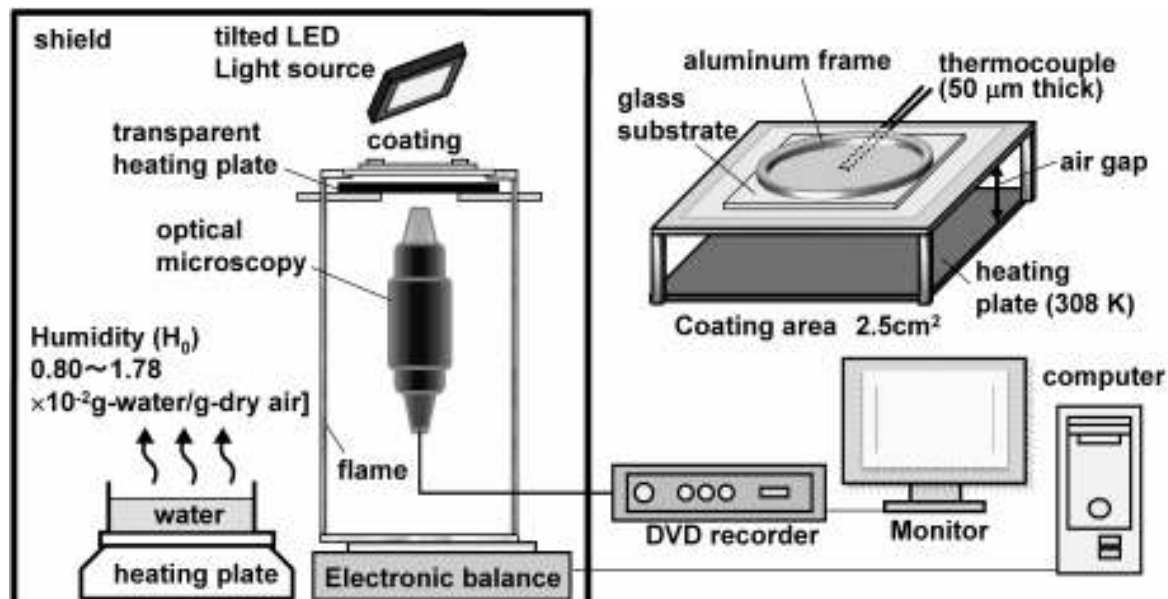


Figure 1 Experimental apparatus

transmittance with solvent or water concentrations at the wavelength of 400nm using UV-VIS spectrometer (MultiSpec-1500, Shimadzu). The solution temperature and water concentration at the free surface were estimated assuming quasi-state, one-dimensional heat and mass balance equations, and used for estimations of two Marangoni numbers Ma_T and Ma_H , defined based on temperature-dependent and water-concentration-dependent surface tension variations, respectively.

3. Results and discussions

Figure 2 shows optical images of dried coatings obtained at different humidity and initial solvent concentrations. Uniform porous surface with pore geometry of 7 μm in diameter and 1 μm in depth was obtained under high solvent concentration/humidity conditions. In contrast, translucent films were fabricated at low solvent concentrations and low humidities. Under intermediate conditions, the dried coatings involved multi-scale structures combined with pores aligned in a cellular manner and those uniformly distributed in the interior of the cells. The characteristic sizes of cells and pores were tunable by controlling humidity and initial solvent concentration (not shown).

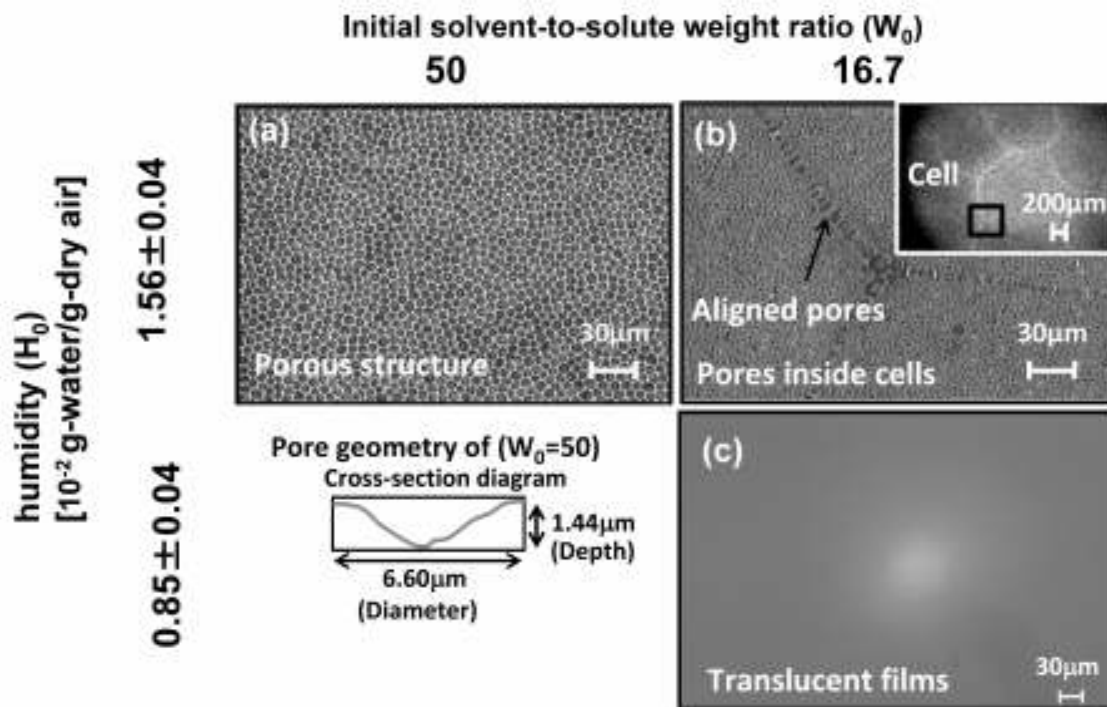


Figure 2 Optical surface images of CAB/MEK binary coatings dried under different conditions.

Initial solvent-to-solute weight ratio $W_0=16.7$

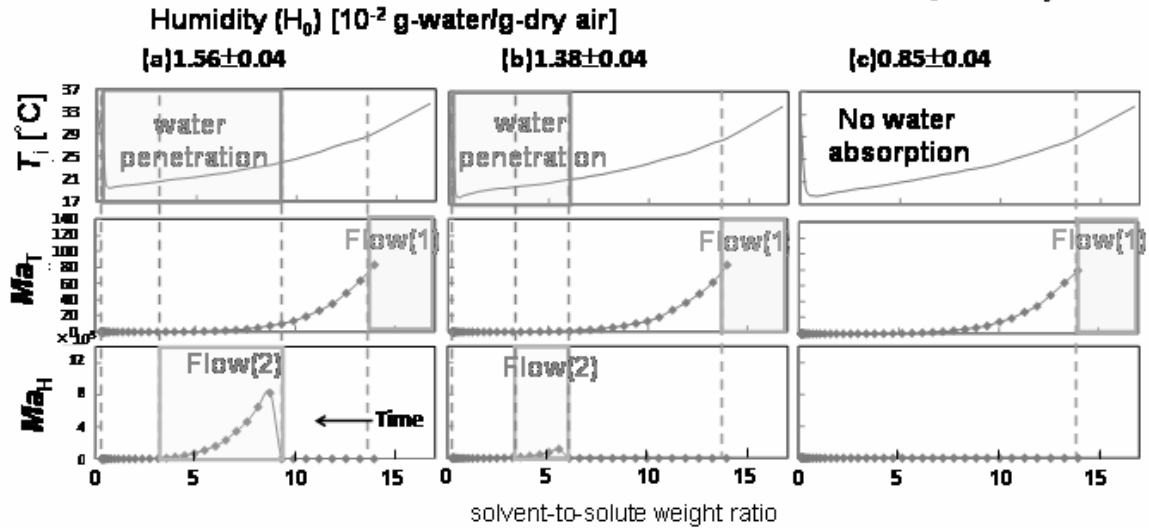


Figure 3 Variations in estimated surface temperature and Marangoni numbers with residual solvent contents under different humidity conditions.

In order to address the pattern formation in detail, we estimated the variations in surface temperature and Marangoni numbers under different drying conditions. The Marangoni numbers were found to exceed the critical value for the onset of convection in certain drying regimes 1 and 2 shown in Figure 3. The convection driven by the temperature-dependent surface tension variation develops in the initial stage of drying but it readily dissipates in the intermediate stage. In contrast, as the surface temperature drops below the dew point due to the evaporative heat loss, a water penetration from the surrounding air onto coating surface begins at high humidities (Fig. 3a and 3b), promoting a secondary convection driven by the concentration-dependent surface tension variations. Furthermore, the estimation of surface water concentration showed that the local composition passes through the binodal curve and the system becomes unstable as the water penetrates, giving rise to promote a phase separation between polymer-rich and water-rich domains. These facts suggest that the humidity-assisted secondary convection couples with the phase separation to promote aligned porous structures on the coating surface.