

Retarded drying in phase separating polymer coatings

Masato Yamamura, Ryohei Sakomoto, Hiroyuki Kage
Department of Applied Chemistry, Kyushu Institute of Technology
Tobata, Kitakyushu, Fukuoka, 804-8550 JAPAN

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Introduction

In the removal of a volatile component from immiscible polymer blends, Vaessen et al. (2002) and Yamamura et al. (2002) reported the puzzling observations that the polymer phase separation retards the solvent evaporation. Both experimental results suggest that the decrease in evaporation rate is due to a decrease in the molecular diffusion rate rather than the decrease in saturated vapor pressure at the air/liquid interface. However, it is still poorly understood how the immiscible polymer components interact to reduce the diffusion rate in a non-equilibrium solution. Here we present experimental evidence that the interfacial diffusive resistance between separating polymer domains, rather than the resistance in bulk, can be a source of characteristic retardation of solvent evaporation.

Experimental Procedure

The polymer phase separation was induced in the air-free condenser drier (Huelsman and Kolb, 1997, Ramesh and Duda, 2001, Zeng et al., 2002) in order to eliminate the undesirable thermo-capillary flow along the free surface. The bench-top condenser drier consisted of a flat glass plate and a grooved aluminum plate separated by a small gap (Figure 1). The surface temperature of the hot glass plate, T_H , was controlled by the temperature regulator with an accuracy of 0.3 K. The aluminum plate was mechanically grooved to form periodic rectangular patterns with the width of 1 mm. The dimensions of the groove were 0.1 mm in depth, and 1 mm in pitch between grooves. The porous paper films were attached at both edges of the grooves to remove the excess liquid from the

condensing surface. The cold aluminum plate was kept at a constant temperature of $T_C=27.3$ °C above the dew point. The gap clearance between the evaporating and condensing surfaces was varied with an accuracy of $50\ \mu\text{m}$. The polymer solutions were deposited on a square glass substrate mounted on the hot glass plate.

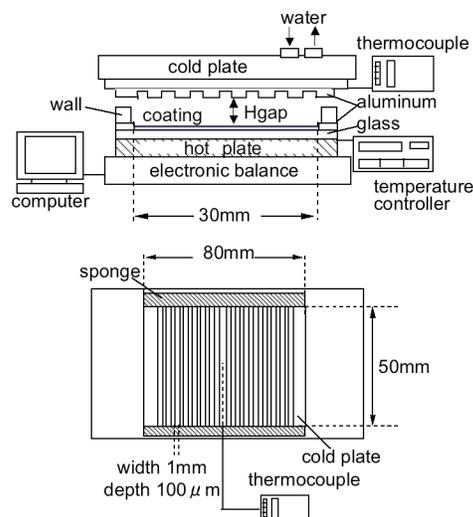


Figure 1 Experimental apparatus

The decrease in mass of the film was measured by an electronic balance and stored in a personal computer to calculate the solvent drying rate. The polymer blends used in this study contained polystyrene (PS, Wako Chemical, $M_n=115,000$) and polycarbonate (PC, Mitsubishi Chemical, $M_n=32,400$). Both polymers are dissolved in tetrahydrofuran (THF, Wako Chemical, as purchased) as a common solvent.

Results and Discussion

Figure 2 shows a typical example of the drying rate curves presented in terms of the solvent content, i.e., the weight ratio of the solvent to the polymers. At high solvent contents (Regime I), the evaporation rates in the ternary solution agree well with those in the binary solutions. With decreasing solvent content (Regime II), the ternary solutions exhibited lower evaporation rates than the homogenous binary solutions. A further decrease in solvent content leads to a regime in which the evaporation rates rapidly fall and converge into a curve (Regime III). The solvent weight fraction at the transition from Regime I to II agreed with the critical concentration below which the phase separation could occur, suggesting that the solvent evaporation is retarded due to the microstructure development via phase separation.

The variation in polymer weight fraction was accompanied by a transition in the

microstructure evolution and a resulting variation in evaporation rate. Top views of final phase morphology are shown in Figures 3a-d for four different weight fractions. Toluene etching showed that the dark phases were polycarbonate-rich domains, which remained after the immersion of the sample in toluene. The isolated polystyrene-rich droplets are randomly distributed in polycarbonate-rich domains at low polymer weight fraction of 0.2 (Figure 3a). With increasing PS/PC weight fraction, the polystyrene-rich phase grows in size and promotes a phase transition from the polystyrene droplet in PC-rich domains to polycarbonate droplet in PS-rich domains (Figure 3b). A further increase in weight fraction leads to an increase in the number density of the polycarbonate-rich droplets (Figure 3c-d).

Figure 4 shows the maximum difference in evaporation rate between the ternary

and binary solutions, Δr , in terms of the weight fraction of polystyrene to polycarbonate. The inset shows the phase diagram obtained from the cloud point measurement. The difference in evaporation rate Δr exhibited a local minimum at the critical weight fraction of unity. The rate difference increases as the polymer weight fractions deviate from the critical weight fraction.

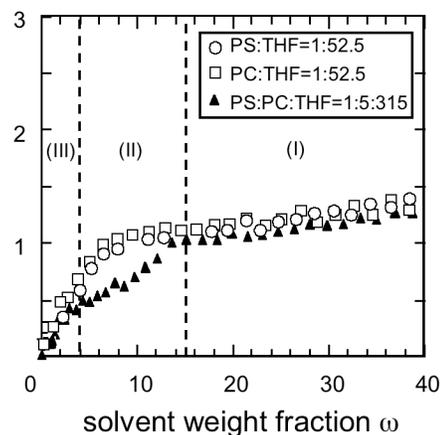


Figure 2 Variation in solvent evaporation rate in binary (open symbols) and ternary (closed symbols) solutions.

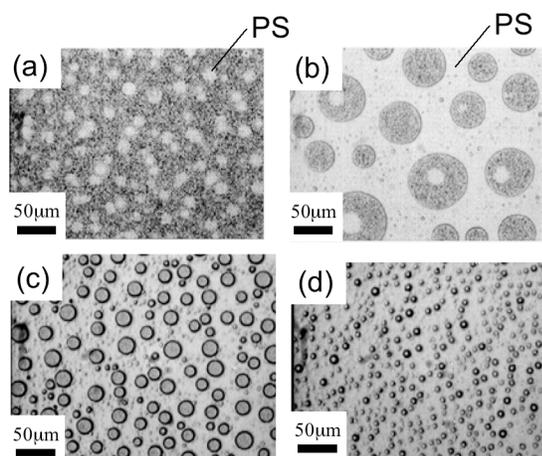


Figure 3 Effect of polymer weight fraction on final domain structures. (a) PS/PC=0.2, (b)PS/PC=1, (c)PS/PC=2, (d)PS/PC=5.

This characteristic drying behavior can be qualitatively explained as follows: The solvent can be enriched at the interfaces between separating polymer domains and form a thin solvent “shell” (Nauman and He, 1994).

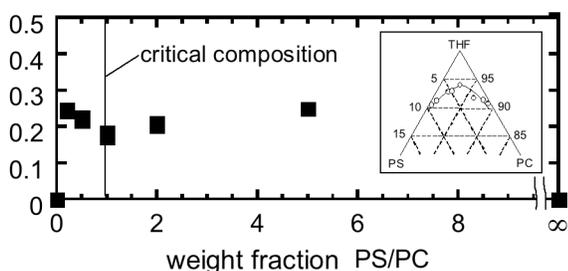


Figure 4 Effect of polymer weight fraction on the maximum difference in evaporation rate between the ternary and binary solutions.

The shell thickness is determined by a subtle balance of two mass transfer rates: the solvent diffusion rate in the thickness direction, J , and that toward the shell, J_s . For the case of $J \gg J_s$, the shell is too thin to play a role on the evaporative mass flux, and hence, would not alter the solvent drying rate. For the alternative case of $J \ll J_s$, on the other hand, most of the solvent molecules transfer to the domain interfaces to form thicker shells. The resulting low effective solvent flux in the thickness direction possibly leads to the retarded evaporation in the phase-separating coating. This is consistent with the larger difference in drying rate in finer microstructures, i.e., at the longer interfacial length between the separating polymer domains (Figures 3 and 4).

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