

# Self-assembly of solvent in phase-separating polymeric films

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Polymer components in an immiscible polymer blend solution spontaneously separate into phases with different compositions when solvent evaporation quenches the solution in a particular location in two-phase regions. Previous experimental studies have shown that the phase separation enhances the drying of solvent in a particular range of polymer compositions [1, 2]. The enhanced solvent diffusion has been attributed to the self-assembly of solvent molecules toward phase interfaces. However, no experimental evidence has been provided to prove the existence of such solvent assembly, owing to intrinsic difficulties in tracking the local compositional changes in immiscible fluids. This study aims at directly visualizing the solvent distribution at phase interfaces using fluorescence microscopy. The solutions contained cellulose acetate butyrate (CAB) and poly(dimethylsiloxane) (PDMS) dissolved in methylethylketone (MEK) as the common solvent. 8-anilino-1-naphthalenesulfonic acid (ANS) was used as a MEK-soluble fluorescence probe in the polymer blend solutions. The in-situ microscopy during drying revealed that the ring-like structures with a certain fluorescence intensity developed at the interfaces between the phase-separating bright and dark polymer domains (Fig. 1). The interfacial ring phase evolved in the intermediate evaporation stage and disappeared before the drying completed. Preliminary spectra measurements showed that the fluorescence intensity of solvent/ANS mixture has an intermediate intensity level compared to those of CAB/ANS and PDMS/ANS solutions. These facts imply that the solvent is localized at the phase-separating interfaces in the course of drying. Furthermore, simultaneous mass loss measurements of the drying samples showed that the solvent drying was enhanced in phase-separating films compared to non-separating binary polymer solutions. As shown in Fig. 2, the normalized drying enhancement ratio, defined as the increase in drying rate compared to that in binary solution, increases almost linearly with increasing the area of ring structures, suggesting that the solvent assembly at the polymer domain interfaces assists the solvent diffusion in phase-separating films.

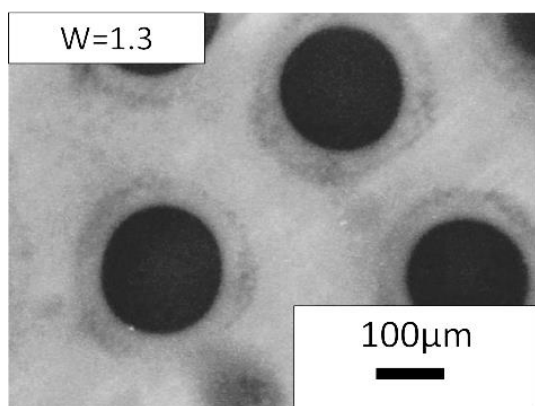


Fig. 1. Fluorescence image of top surface of drying film at the solvent-to-polymer mass ratio of  $W=1.3$ .

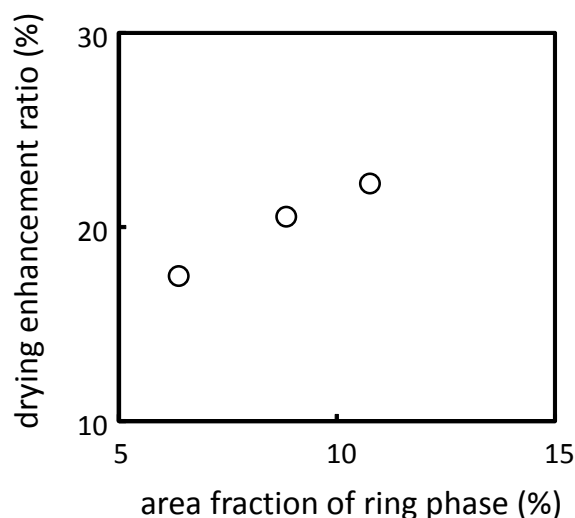


Fig. 2. Variations in drying enhancement ratio with the area fraction of ring phase.

## References

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2. M. Yamamura et al., *Journal of Chemical Engineering of Japan*, **45**(6), 441-443 (2012)