

Light-Directed Solvent Diffusion in UV Curable Coatings

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Light-tunable microstructuring in polymeric coatings have received considerable attentions in fabrications of optical, photovoltaic, and energy-storage devices. A typical example includes photo-induced phase separation in ultra-violet (UV) curable coatings, in which photo-polymerization reactions quench the liquid into thermodynamically unstable state [1]. However, solvent diffusion in photo-curable coating is still far from complete understanding because of inherent reaction-diffusion coupling. We here provide new experimental evidence that UV irradiation can promote guided diffusion of solvent molecules along the direction of light, even toward the opposite direction with respect to evaporation.

We used methyl-ethyl-ketone (MEK) as solvent, phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide as photo-initiator, and polyester-acrylate (Toagosei, Aronix-M9050, $M_w=1000\sim 1500$) as photo-reactive monomer, respectively. Those chemicals were used as purchased. The ternary solution was coated on a glass or ZnSe prism with a certain thickness ranging between 200 and 800 μm . The UV light of 365 nm in wavelength and $20.0 \sim 45.0 \pm 0.3 \text{ mW/cm}^2$ in intensity was irradiated for 1 s to promote photo-polymerization reactions in the solution.

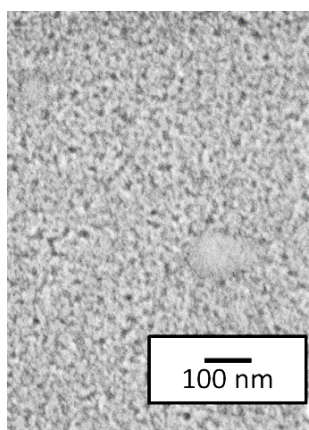


Fig. 1 SEM image of the bottom surface of dried film. The 800 μm -thick-solution was dried on a 28.5 $^\circ\text{C}$ substrate until the average initiator concentration reached 0.305 g-initiator/g-solvent, followed by UV irradiation of 45.0 mW/cm^2 for 1 s from the top. The photo-induced phase separation proceeded to create solvent-rich domains, which became pores of less than 50 nm in diameter after the subsequent solvent evaporation.

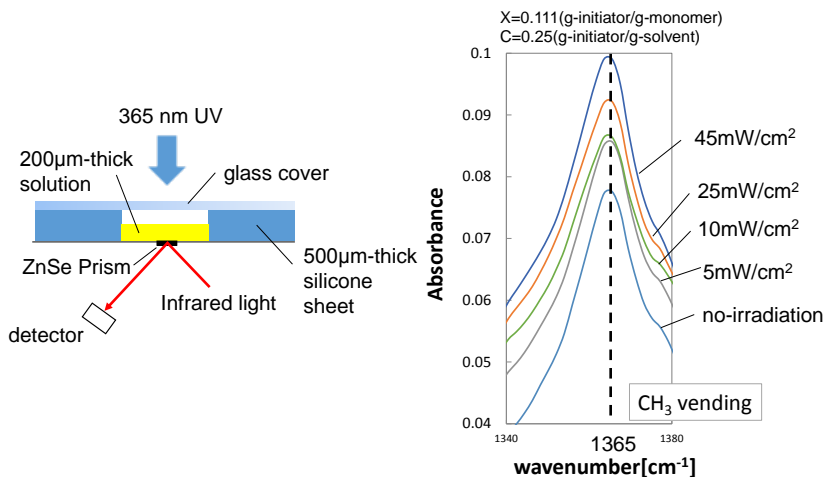


Fig. 2 The setup of ATR-FTIR spectroscopy to measure local concentration in the vicinity of coating bottom (left). The measured IR absorbance peak attributed to methyl-group in solvent molecule increases with increasing light intensities, showing light-directed solvent motion toward the bottom (right). The initiator-to-monomer mass ratio was 0.111 g-initiator/g-monomer, and initiator-to-solvent mass ratio was 0.25 g-initiator/g-solvent at the onset of UV irradiation.

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Figure 1 shows a typical SEM image of dried film surface. We obtained porous polymer films with distributing pores of less than 50 nm in diameter. Upon UV irradiation, generated radicals attack monomer molecules to promote polymerization reactions. As the polymeric component is immiscible with solvent, thermodynamic instability triggers a spontaneous phase separation between polymer-rich and solvent-rich phases. The latter phases become pores after subsequent solvent evaporation. Our experiments revealed that no distinct pore was created at too high (or low) solvent concentrations at the onset time of UV irradiation, implying an optimum drying condition to promote porous structures. Furthermore, UV irradiation from the bottom surface promoted different phase structures compared to that from the top of the coating (not shown here).

To examine the diffusion behavior in curing films, we first conducted FTIR spectroscopy in a closed system (Shimadzu, IRAffinity-1, MIRacle 10). The 200- μm -thick solution was coated on a specified area of 1 cm^2 by gluing a 0.5 mm-thick silicone shim on the substrate. The glass cover was set on the shim surface to minimize solvent evaporation during the measurement. ATR (Attenuated Total Reflection) setup allows us to measure the local concentration in the vicinity of liquid-substrate (ZnSe prism) interface. Fig. 2 shows the variations in IR spectra with different intensities of UV light irradiated from the top. The absorbance peak at 1365 cm^{-1} is attributed to the vending vibration of methyl group in solvent molecules. The absorbance monotonically increases with increasing the light intensity, indicating that UV irradiation from the top directs solvent diffusion toward the bottom surface of the film.

To investigate the effect of polymerization reaction on the light-directed solvent diffusion, we plotted the difference in IR absorbance peak height at the wavelength of 1365 cm^{-1} against monomer conversion, defined as amounts of polymerized monomers relative to the initial amount of the monomer. The amount of reacted monomer was quantified from IR absorbance peak at 1635 cm^{-1} associated with the vibration of C=C double bond in monomer molecules. The absorbance peak was calibrated with that at 1710 cm^{-1} of unreactive C=O bonds in the solvent and the monomer. As shown in Fig. 3, the IR absorbance increases with increasing the conversion, indicating that more solvent molecules move along the direction of UV light. With a further increase in conversion, the absorbance reaches a plateau at a critical conversion of $\phi_c \sim 20\%$, and then increases again at higher conversions. The supplemental laser beam scattering experiments revealed that the phase-separated structures evolved at high conversions above the critical value ($\phi > \phi_c$), suggesting that the photo-induced phase separation accelerates the solvent diffusion directed by the light. Furthermore, the absorbance obeys a single master curve at different initiator-to-monomer mass ratios.

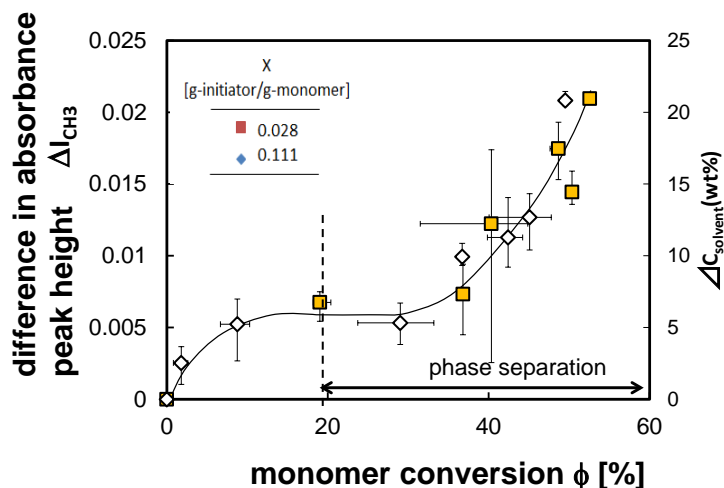


Fig. 3 Variations in IR absorbance of methyl group in solvent with monomer conversion. The absorbance shows a two-step increase with increasing the conversion, and obeys a single master curve at different initiator-to-monomer mass ratios.

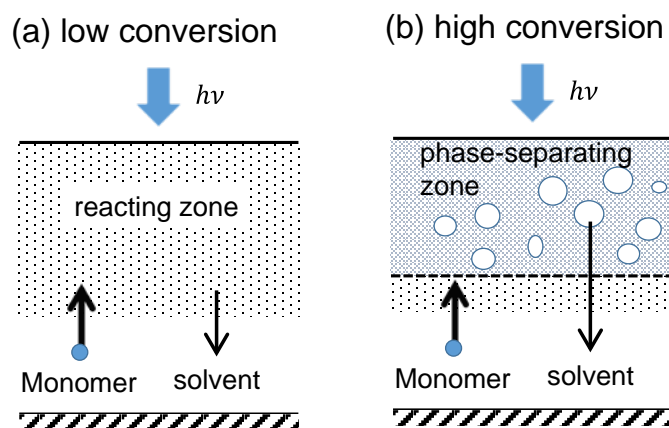


Fig. 4 Physical models of light-directed solvent diffusion. (a) low monomer conversion (b) high monomer conversion with phase-separated structures.

Although it is not immediately clear why solvent molecules move along the direction of UV irradiation, our results imply a unique coupling between the photo-polymerization reaction and the solvent diffusion. Fig. 4 depicts a plausible physical model of the light-directed solvent diffusion at two different monomer conversions. Upon light irradiation from the top, the light intensity decays exponentially across the thickness, leaving a reacting zone in the upper layer of the film. The polymerization reaction in the upper layer induces a concentration gradient of monomer component, which drives a monomer diffusion from the unreacted lower layer toward the upper layer. The resultant mutual diffusion of monomer and solvent gives rise to guide the diffusion of solvent molecules toward the bottom (Fig. 4a). In phase-separating systems, on the other hand, solvent-rich phases distribute in the upper layer. Solvent molecules are possibly squeezed out from that layer as the film shrinks via the polymerization reactions, leading to show an accelerated solvent diffusion toward the bottom of the film.

Next, we investigated how the light-guided solvent diffusion impacts drying kinetics. In the case when UV light is irradiated from the top of an evaporating liquid film, the light-directed diffusion may compete against the evaporation-driven mass flux and push the solvent molecules back from the evaporating surface toward the bottom. Thus we expect that solvent evaporation rate can change upon simultaneous UV irradiation. To check this, we conducted mass loss measurements of drying monomer-initiator-solvent ternary solution films. The 800 μm -thick sample solution was coated on a glass substrate. The substrate was heated to maintain a constant temperature of 28.5 $^{\circ}\text{C}$. The initial initiator-to-solvent and initiator-to-monomer mass ratios of the solution were 0.0609 g-initiator/g-solvent, and 0.0694 g-initiator/g-monomer, respectively. First, the solution was dried for a certain time until the average initiator concentration reached 0.0649 g-initiator/g-solvent. Then the solution was exposed to 365 nm UV light with an intensity of 45 mW/cm^2 within 1 second. Fig. 5 illustrates drying-rate curves under two different irradiation conditions. In the absence of UV irradiation, the drying rates monotonically decrease with increasing the photo-initiator concentrations. On the contrary, the drying rate in the presence of photo irradiation exhibits a spike at the time of light irradiation. The preliminary temperature measurements using infrared thermometer indicated that the film surface temperature increased 12 K just after the UV irradiation, implying that the rapid increase in evaporation rate stems from the heat generated by the photo reaction. At later drying times, the drying rates under UV irradiation show lower values compared to the case of no light irradiation, despite the higher temperatures at the film surface. These facts are consistent with the light-directed solvent diffusion in closed systems. When the short-time UV irradiation promotes local photo reactions and subsequent phase separation, the solvent diffusion emerges along the direction of light, i.e., in the opposite direction to its evaporation. As a result, the solvent concentration at the evaporating surface, and thus the vapor pressure of solvent, decreases to retard the drying. The similar results were obtained when we systematically increased the initiator-to-solvent mass ratio at the onset of UV irradiation.

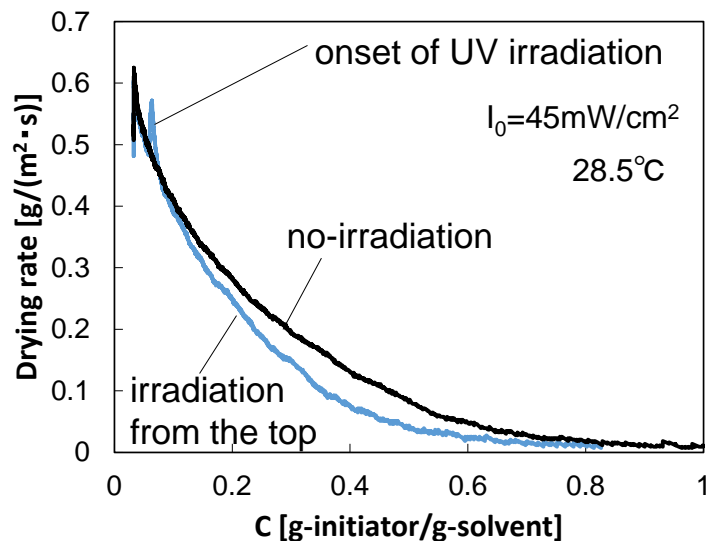


Fig. 5 Variations in drying rates with initiator-to-solvent mass ratios. The drying rate increases just after the onset of UV irradiation (blue curve), but decreases and shows a lower value compared to the case of no light irradiation (black curve).

Recently, Wang et al. demonstrated photo-polymerization of N-isopropyl acrylamide dissolved in carbon disulfide, and synthesized hierarchical polymeric films with a microparticle layer underneath a skin layer [2]. However, the internal solvent diffusion in curing films has not been fully addressed. Extensive studies have been reported when photo-responsive monomers react in solvent-free systems, but, to the best of our knowledge, not previously when the solvent diffusion couples with the photo-induced phase separation. We need further studies to elucidate how phase structures alter the mass flux of solvent diffusion in a quantitative sense, and how the light-directed diffusion, in turn, impacts the phase separation and final microstructures in dried films.

References

- [1] Nakanishi, J. Phys. Chem. Lett. (2013), 4,3978-3982
- [2] Wang L. and Ding Y., European Polymer Journal 66 (2015) 99-107