

Dependence of Cell Gap on Anisotropic Phase Separation of Liquid Crystal and Polymer Composites

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The dependence of cell gap on the anisotropic phase separation of liquid crystal and polymer composites was studied by numerical simulation and experimentation. Numerical results showed that the phase separation morphology depends on cell gap and material parameters. The optimal range of cell gap in the formation of the polymer and liquid crystal layers was suggested with the given material parameters. [DOI: 10.1143/JJAP.46.1585]

KEYWORDS: liquid crystal and polymer composite, anisotropic phase separation, polymer-dispersed liquid crystal

1. Introduction

Recently, devices fabricated by the photopolymerization-induced phase separation (PIPS) of polymer and liquid crystal (LC) mixtures have been widely studied. Among several kind of PIPS, phase-separated composite organic films (PSCOFs)¹ have drawn attention because of their various device applications, such as flexible liquid crystal displays (LCDs),^{2–4} owing to the possibility of constructing a microstructure after cell assembly. Unlike isotropic phase separation (e.g., polymer-dispersed liquid crystal), a PSCOF shows an anisotropic layered structure. Figure 1 shows a schematic diagram of the PSCOF. In the fabrication of a PSCOF, Qian *et al.* demonstrated parameters essential for separating conditions by experimentation and numerical analysis. The relevant parameters were the UV intensity and UV intensity gradient.⁵ More recently, the dependences of the PSCOF morphology on temperature and cell gap have been reported by Wang *et al.*⁶ In their article, it has been indicated that a high process temperature and a small cell gap give an appropriate polymer layer surface morphology, but the full range of the dependence of cell gap on the separation morphology is still poorly understood. To approach this problem, we considered the following two separation morphology aspects: the surface morphology of a solidified polymer layer, which is related to the concentration fluctuation of the LC and polymer boundary, and the macroscopic one-dimensional concentration profile of the solidified polymer layer along the surface normal direction through an LC cell, which is related to the UV intensity gradient. Here, we studied the dependence of the separation morphology on cell gap by experimentation and numerical simulation in more detail, and demonstrated that PSCOF morphology does not depend on cell gap monotonically, but that there is an optimal gap range.

2. Experimental Procedure

LC cells were fabricated using indium tin oxide (ITO)-coated glass substrates by photopolymerization-induced anisotropic phase separation. Alignment layers (Nylon 6) were spin-coated on one substrate followed by rubbing to achieve a homogeneous LC alignment. Note that phase separation is greatly affected by an alignment layer and a

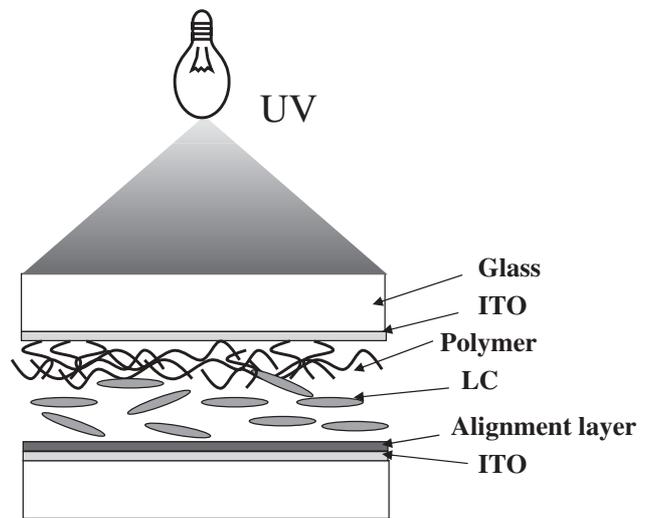


Fig. 1. Schematic diagram of photopolymerization-induced anisotropic phase separation.

prepolymer.⁴ The other substrate used was untreated to enhance phase separation. Cell gap was maintained using glass spacers of 1, 4.5, 9, and 18 μm . A mixture of the nematic LC LC17 and photocurable prepolymer NOA65 (Norland) with a weight ratio of 70 : 30 was introduced into the cells by capillary action at a temperature of 100 $^{\circ}\text{C}$, which is higher than the clearing point of the LC. The cells were exposed to UV light of $\lambda = 350\text{ nm}$ to initiate polymerization at 100 $^{\circ}\text{C}$. The source of the UV light was a xenon lamp operated at 200 W. The UV intensity was controlled to about 0.78 mW/cm^2 . During this process, the LC molecules in the mixture were expelled from the polymerized volume. After exposure, the cells were cut and treated using a hexane solution to remove the LC, so that a picture of the polymer morphology of the top substrate (ITO-only-coated substrate) could be obtained.

3. Theoretical Model for One-Dimensional Anisotropic Phase Separation

The theoretical basis of isotropic photopolymerization-induced phase separation was extensively studied by time dependent Ginzburg–Landau formulation.^{7,8} Since we considered anisotropic phase separation, we assumed that the

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UV intensity gradient is produced in a direction normal to the substrate and phase separation occurs in a one-dimension. On the basis of these assumptions, we used the a one-dimensional kinetic approach.⁵⁾ The basic equation for PSCOFs is the same as that for the diffusion of a binary mixture. The equations for numerical simulation are as follows:

$$\frac{\partial \psi}{\partial t} = -\frac{\partial J_{\psi}}{\partial z}, \quad (1)$$

$$\frac{\partial \phi}{\partial t} = -\frac{\partial J_{\phi}}{\partial z} - \frac{\partial \eta}{\partial t}, \quad (2)$$

$$\frac{\partial \eta}{\partial t} = kI\phi(\phi + \eta), \quad (3)$$

$$J_{\phi} = D\left(-\psi\frac{\partial \phi}{\partial z} + \phi\frac{\partial \psi}{\partial z} - \chi_1\phi\psi\frac{\partial \psi}{\partial z}\right), \quad (4)$$

$$\frac{\partial I}{\partial z} = -Ib\psi. \quad (5)$$

Where ψ , ϕ , and η are the concentrations of the LC, monomer, and polymer, respectively. J_{ψ} and J_{ϕ} are the current densities of the LC and monomer. Polymers were assumed to be immobile owing to their cross-linking structure. D is the mutual translational diffusion constant, I is the UV intensity, and b is the absorption coefficient of the LC molecules. χ_1 is the Flory–Huggins parameter and represents molecule–molecule interactions. It should be noted that χ_1 is not clear for this simple one-dimensional system. Therefore, its value was fixed in the reasonable range of the isotropic mixing state. Here, we assumed that UV is absorbed predominantly by the LC molecules. Let us introduce briefly the physical meaning of the above equations. Equations (1) and (2) indicate the continuity equation of LC and monomer and the second term on the right side of eq. (2) indicates the change in monomer concentration due to polymerization. Equation (3) describes the time dependence of polymer concentration depending on the progress of photopolymerization. Equation (4) describes the current density of the monomer. The current density of the LC is given by $J_{\psi} = -J_{\phi}$. Finally, eq. (5) describes the UV intensity gradient along the substrate normal direction (z direction).

When the above-mentioned equations are transformed in dimensionless coupled equations, there remain two essential bulk parameters, R and L . In this transformation, time is scaled by $\tau = d^2/D$, which represents the time interval for approaching a thermal equilibrium in the cells. $R = kI_0d^2/D$, is related to the polymerization speed, where k is the polymerization rate, I_0 is the UV intensity on the illuminated surface, and d is the cell gap. Another parameter, $L = 1/bd$, is related the UV intensity gradient. As shown in Fig. 1, UV intensity is strongest on the illuminated surface and the intensity decays exponentially owing to absorption by the LC molecules. For numerical simulation, we adopted a finite difference method.

4. Results and Discussion

When the LC/monomer mixture was exposed to the intensity-modulated UV light, the monomers in the high intensity region first underwent polymerization, and the monomers in the low intensity region diffused to the high intensity region to maintain their relative concentration

and joined the polymerization reaction. As a result, the monomers moved toward the solidified polymers and LC molecules were expelled to the low intensity region, resulting in the macroscopic phase separation of the LC and polymer.

Figure 2 shows the scanning electron microscopy images of the PSCOF for various cell gaps. Figures 2(a)–2(d) show the surface morphologies of the solidified polymer layers with the cell gaps of 1, 4.5, 9, and 18 μm , respectively. We observed that the surface roughness is small for small cell gaps and that the surface morphology is rough for large cell gaps, which is consistent with the results obtained by Wang *et al.*⁶⁾ However, for the cell gap of 1 μm [Fig. 2(a)], the planar distribution of the solidified polymers was nonuniform, which may be due to surface defects or nonuniform mixing. For the case of a small cell gap, the surface of the solidified polymer was smooth, but the one-dimensional concentration profile did not exhibit a well-separated layer structure.

To understand the dependence of cell gap on phase separation more clearly, we performed a numerical simulation based on a one-dimensional theory, as described in the previous section. In the numerical simulation, we adopted a finite difference method in space and time, and fixed the mixing ratio of the liquid crystal and polymer at 7 : 3. Figure 3 shows the numerical simulation results for the selected parameters. For a large R or L , the separation morphology became polymer-dispersive, indicating that the concentration of the solidified polymer spreads over the cells. However, for the restricted region, $R < 50$ and $L < 0.1$, the numerical results showed good separation results. We represented the above-mentioned situation by a schematic diagram in Fig. 4. The simulated results are summarized with various R 's and L 's for the schematic diagram in Fig. 4. For a given set of process conditions, such as temperature, UV intensity, polymer, and liquid crystal, the only variable affecting both the parameters R and L is cell gap. Recalling that $R = kI_0d^2/D$ and $L = 1/bd$, we drew the process constant curve with $LR^{1/2} = h$ by eliminating cell gap. $h = (kI_0/D)^{1/2}/b$ is given by the material constant and process conditions. We divided this R – L parameter space into four regions, as shown in Fig. 4. Region 1 represents the appropriate PSCOF structure region, and the cell gap condition satisfies the relation $(1/10)b < d < (50D/kI_0)^{1/2}$, in which we used the well separating conditions $L < 0.1$ and $R < 50$ from the numerical simulation in Fig. 3. Region 3 has a large L (> 0.1) and a small R (< 50), which typically corresponds to a small cell gap. Region 4 has a large R (> 50) and a small L (< 0.1), which corresponds to a large cell gap. Region 2 is similar to Region 1, but it overlaps slightly with the well-separating R 's and L 's (square region in Fig. 4). When the initial process conditions and cell gap lay in Region 2 and if the cell gap is small (large), then the parameters R and L move to Region 4 (Region 3). Hence, a narrow cell gap range for obtaining the PSCOF structure is obtained. Therefore, $h \sim 0.1\sqrt{50} = 0.7$ is a criterion for obtaining the PSCOF structure.

Figure 5 shows the numerical simulation results obtained using different process conditions and initial cell gaps corresponding to the four regions. We set the initial cell gap as $d = 1$, because the cell gap was not involved in the

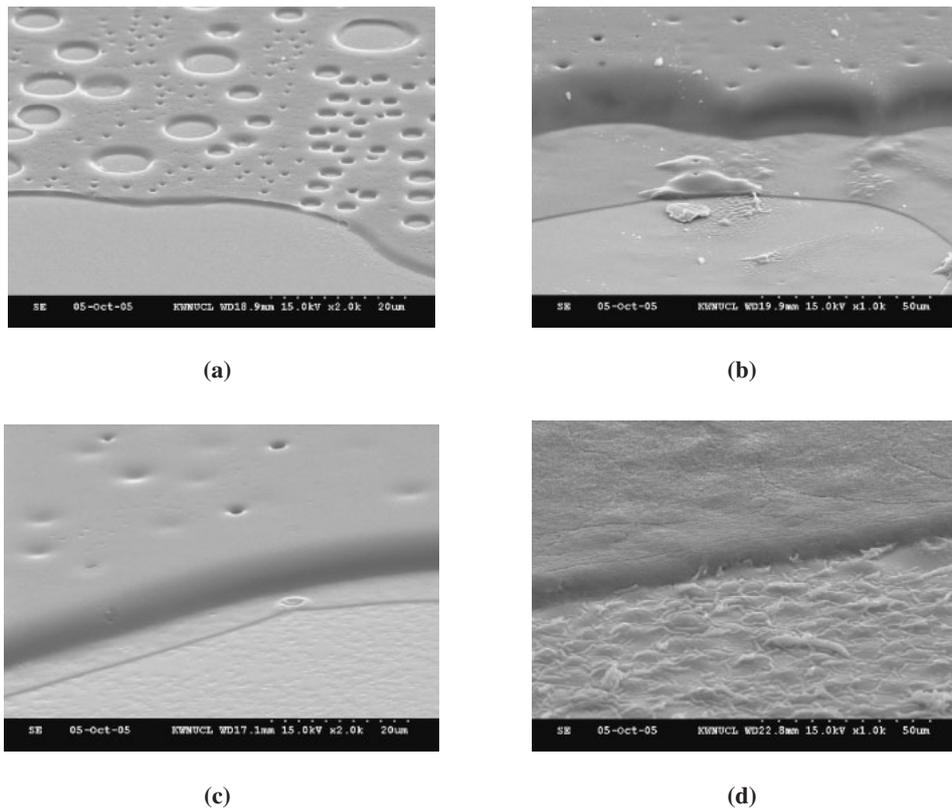


Fig. 2. Scanning electron microscopy images of polymer morphologies on top of substrates for various cell gaps of (a) 1, (b) 4.5, (c) 9, and (d) 18 μm .

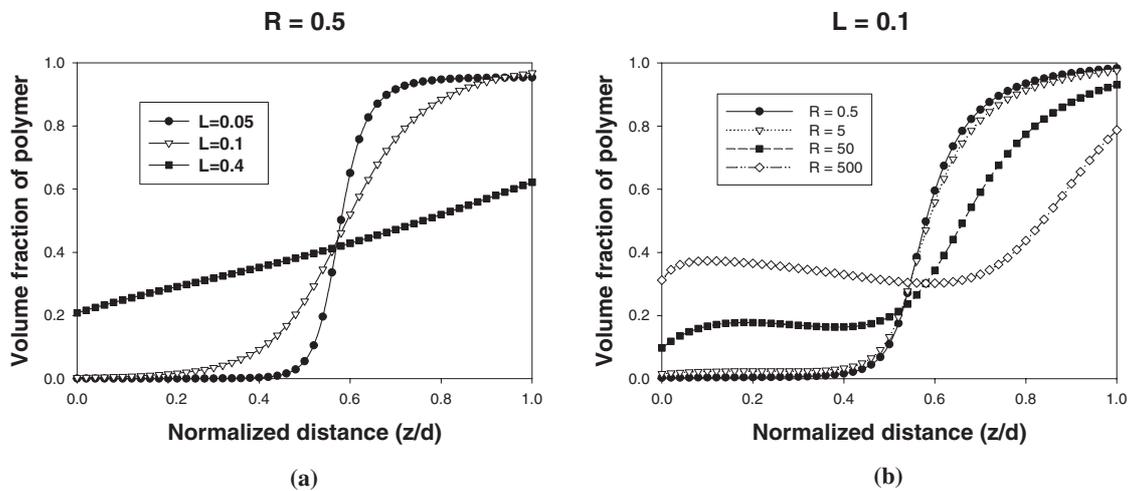


Fig. 3. Numerical simulation results for (a) various L 's and fixed $R = 50$, and (b) various R 's and fixed $L = 0.1$. $z/d = 1$ indicates the UV illumination side.

numerical calculation explicitly, and as the cell gap was varied, the simulation parameters R and L also changed (but h did not). Therefore, the simulation results were changed. For the initial R 's and L 's in the square region (Region 1), there was a wide cell gap range that enabled the formation of the PSCOF structure [Fig. 5(a)] when compared with the case of the initial values in Region 2 [Fig. 5(b)]. For a large L and a small R (Region 3) where $h \gg 0.7$, the polymers were dispersed through the cells [Fig. 5(c)] because of the relatively uniform UV light along the substrate normal direction. The simulation results adequately described the

experimental results for the thin cell as shown in Fig. 2(a), which has a structure similar to that in Fig. 2(a). For a large R but a small L (Region 4), we cannot observe the polymer layer clearly, owing to a rapid polymerization [Fig. 5(d)]. Yet, as shown in Fig. 2 and Wang *et al.*'s results⁶⁾ for a large cell gap (large R , small L), the surface morphology of the solidified polymer was not smooth, which can break the LC alignment. The simulation results did not seem to be consistent with the experimental results. However, it is important to note that the PSCOF structure has two distinct features: the concentration profile of the polymer along the

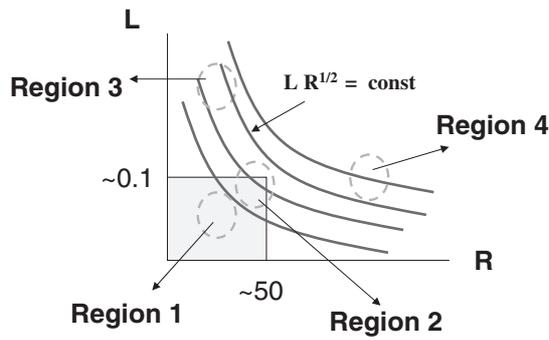


Fig. 4. Schematic diagram of parameter space of R and L . The square region, $R < 50$ and $L < 0.1$, represents the well-separating conditions for R and L .

substrate normal direction and the surface morphology (or smoothness) of the polymer layer (or boundary between the liquid crystal and polymer layer). In our numerical simulation, we did not consider thermal fluctuations in concentration and only considered the concentration profile in the numerical simulation. As an introduction, we briefly discuss the meaning of R . As shown above, it is the ratio of polymerization time to the time required for approaching a thermal equilibrium. Large R 's indicate that the time to equilibrium cannot follow the polymerization rate. Thus, the

concentration fluctuation at the boundary cannot be compensated for owing to a long recovery time or a relatively rapid polymerization. Now let us apply this to the surface morphology.

For a thin cell (or Region 3), which typically has a small R and a large L (low UV intensity gradient), the UV intensity gradient along the substrate normal direction is small and nearly the same as the dispersed polymer case, except for the slow polymerization in this case. However, the surface morphology of the polymer in the thin cell is smooth, owing to a small R . For a thick sample (or Region 4), which has a large R and a small L , the layered structure can be clearly observed, as shown in the numerical simulation, owing to a high UV intensity gradient. As we discussed earlier, owing to the long recovery time necessary for reaching a thermal equilibrium ($\tau = d^2/D$), the boundary between the liquid crystal and polymer cannot form a uniform and smooth surface. Therefore, the surface is rough for a thick cell gap, as shown in Fig. 2. This can result in the loss of liquid crystal molecule alignment, which is the trade-off relation between the thin and thick cells.

In the fabrication of the PSCOF structure, h must be reduced to obtain a wide cell gap range. Process conditions, such as a low UV intensity and a high process temperature, lead to a low h . Using monomers with a low polymerization rate and a large diffusion constant also leads to a low h ,

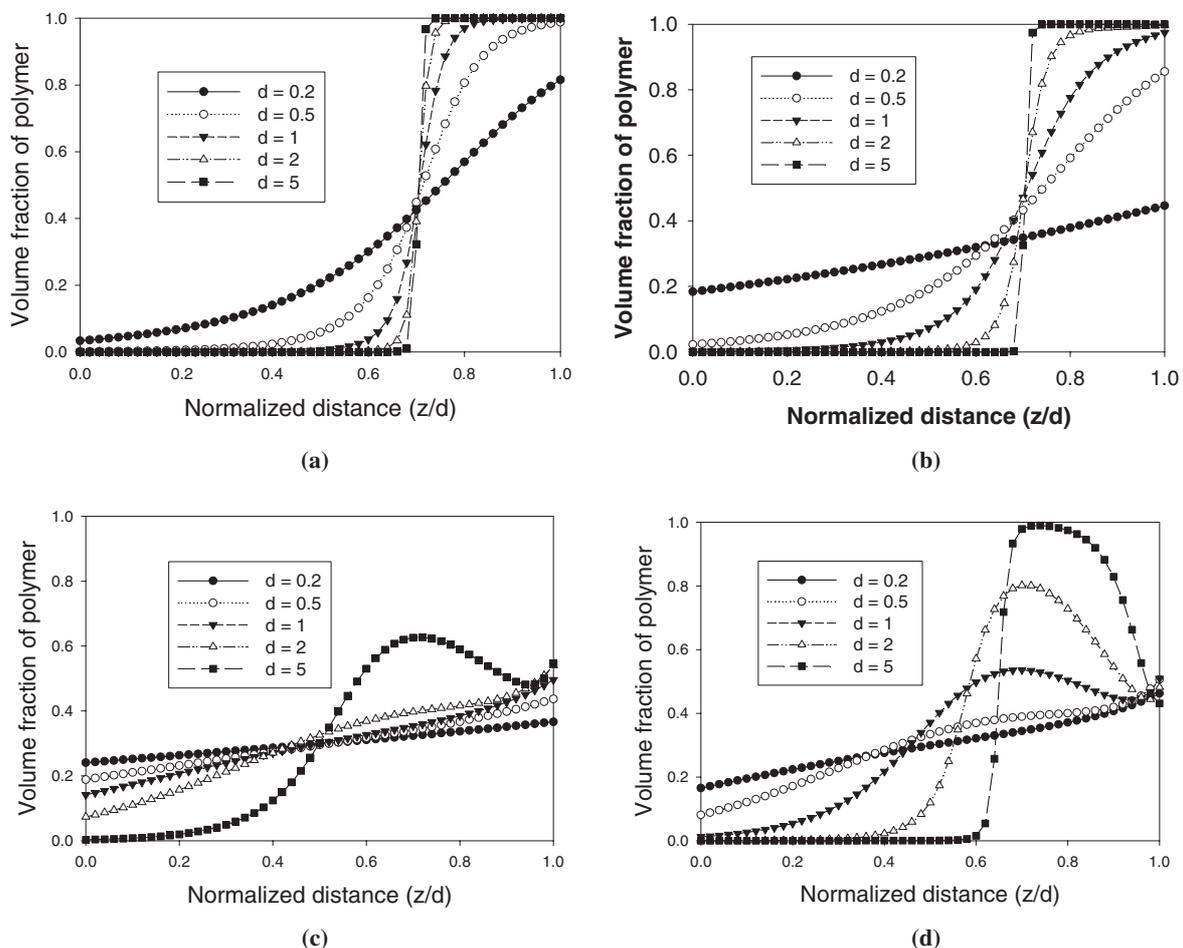


Fig. 5. Numerical simulation results for various initial R 's and L 's for (a) $R = 2.5, L = 0.05$ (Region 1 in Fig. 4), (b) $R = 25, L = 0.1$ (Region 2), (c) $R = 25, L = 0.4$ (Region 3), and (d) $R = 500, L = 0.1$ (Region 4). $z/d = 1$ indicates the UV illumination side.

as well as using liquid crystals with large UV absorption coefficients.

5. Conclusions

We have studied the dependence of cell gap on anisotropic phase separation by numerical simulation and experimentation. By combining experimental and numerical simulation results, we obtained an appropriate PSCOF structure and an optimum cell gap range. For a thin cell, which typically has a small R and a large L , a PDLC-like structure can be obtained, and the boundary between the liquid crystal and polymer is smooth. In contrast, for a thick cell, which typically gives a large R and a small L , the concentration profile can exhibit well-separating conditions. However, the polymer surface morphology is rough and may affect the LC alignment. The optimized cell gap range for obtaining an appropriate PSCOF structure is given by $(1/10)b < d < (50D/kI_0)^{1/2}$ through numerical simulation when $h = LR^{1/2} \ll 0.7$. To obtain a wide optimal cell gap range, the use of polymers with a slow polymerization and/or high mobility, the use of liquid crystal materials with a

high degree of UV absorption, and the used of process conditions, such as a high process temperature and a low UV intensity, are required.

Acknowledgements

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