

Experimental and Numerical Study on Anisotropic Phase Separation of Liquid Crystal and Polymer Composites as Cell Gap Variation

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Abstract

Cell gap dependence on anisotropic phase separation was studied. The numerical results showed that the morphology of phase separation depended on cell gap and material parameters. With numerical simulation and experiments, the optimal range of cell gap in the formation of polymer layer and liquid crystal layer was suggested for given material parameters.

1. Introduction

Recently devices using photopolymerization induced phase separation (PIPS) of polymer and LC mixtures are widely studied. Among several kind of PIPS, phase separated composite organic film (PSCOF)¹ draw much attention because of its device application such as flexible LCDs²⁻⁴ due to possibility of constructing microstructure. Unlike isotropic phase separation (e.g. polymer dispersed liquid crystal), PSCOF shows anisotropic layer structure. Figure 1 shows schematic diagram of PSCOF. In fabrication of PSCOF, Qian. Et.al demonstrated essential parameters of well separating condition by experiment and numerical analysis. The relevant parameters were UV intensity and UV intensity gradient⁵.

More recently, temperature and cell gap dependence on PSCOF morphology was reported by Q. Wang *et al*⁶. In their article, lower cell gap shows better separation morphology between LC and polymer layer. However, there are two aspects of separation morphology. One is smoothness between LC and polymer layer boundary. The other is sharpness of concentration profile of polymer along the surface

normal direction. We here studied the cell gap dependence of morphology by experiments and numerical simulation, and we will demonstrate that the morphology of PSCOF does not depend on cell gap monotonically but there is optimal gap range. This paper is organized as follows: first we will describe the experimental in detail. Next we will review the theoretical basis of 1-dimensionanl PSCOF model and we will discuss the experimental results and numerical simulation results based on 1-dimensional model. Finally, we will summarize our work.

2. Experimental

We used two ITO coated glass substrates. Alignment layer (Nylon 6) was spin coated on one of

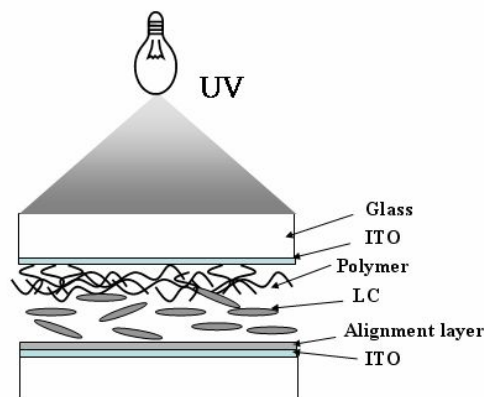


Fig. 1. Schematic diagram of Photopolymerization induced phase separation.

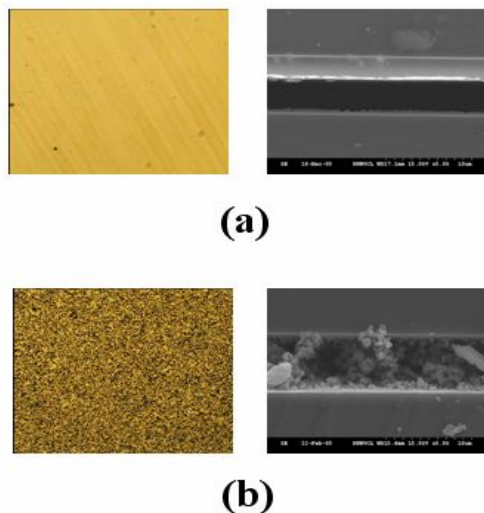


Fig. 2. Microscopic and scanning electron microscopic images of (a) PSCOF and (b) PDLC structure.

the ITO coated glass substrate (bottom substrate) followed by rubbing to achieve uniform alignment. The cell was assembled with glass spacers of $1\mu\text{m}$, $4.5\mu\text{m}$, $9\mu\text{m}$ and $18\mu\text{m}$. The polymer and liquid crystal mixture with mixing ratio of 3:7 was introduced into the cell by capillary action held at isotropic mixing temperature. The polymer used here was NOA 72 (Norland. co.) and liquid crystal was LC17 (supplied by Samsung). After filling the polymer and liquid crystal mixture, UV was exposed onto ITO coated glass substrate (top substrate) of cell. The source of UV light was a Xenon lamp operated at 200W. The UV intensity controlled about $0.78\text{mW}/\text{cm}^2$. After exposure, to take a picture of polymer morphology of top substrate (ITO only coated substrate), the cells were cut and were treated by hexane solution to remove liquid crystal. Figure 2 shows the typical cross-sectional view of two kinds of results of PSCOF and PDLC. It is clear that Figure 2(a) shows well separation of polymer and liquid crystal whereas Figure 2(b) shows the PDLC.

3. Results and discussion

3.1 Theoretical model for one-dimensional anisotropic phase separation

The basic equation for PSCOF is same as that of diffusion of binary mixture. The equations for using numerical simulation are as follow⁵:

$$\begin{aligned}\frac{\partial \psi}{\partial t} &= -\frac{\partial J_{\psi}}{\partial z} \\ \frac{\partial \phi}{\partial t} &= -\frac{\partial J_{\phi}}{\partial z} - \frac{\partial \eta}{\partial t} \\ \frac{\partial \eta}{\partial t} &= kI\phi(\phi + \eta) \\ J_{\phi} &= D\left(-\psi \frac{\partial \phi}{\partial z} + \phi \frac{\partial \psi}{\partial z} - \chi\phi\psi \frac{\partial \psi}{\partial z}\right) \\ J_{\psi} &= -J_{\phi} \\ \frac{\partial I}{\partial z} &= -b\psi I\end{aligned}$$

Where ψ , ϕ and η are concentration of LC, monomer and polymer, respectively. J_{ψ} and J_{ϕ} are current density of LC and monomer. Polymers were assumed to be immobile due to cross-linking structure. D is the mutual translational diffusion constant, I is the UV intensity and b is the absorption coefficient of LC molecules. We here assumed that UV is absorbed predominantly by LC molecules. From the above equations, when transformed to dimensionless coupled equations, there remain two essential bulk parameters R and L . In this transformation, the time is scaled by $\tau = d^2/D$, whose meaning is time to approach to thermal equilibrium of the cell.

$R = kI_0d^2/D$, is related to polymerization speed, where k is polymerization rate, I_0 is UV intensity at illuminated surface and d is cell gap. Another parameter $L = I/bd$, is related to UV intensity gradient. That means as shown in Figure.1, UV intensity is strongest at illuminated surface and due to absorption by LC molecules, intensity shows exponentially decaying profile. From Figure 2, the well separated structure can also gives good liquid crystal alignment, while polymer dispersed case, the microscopic texture shows no preferential optic axis which means loss of liquid crystal alignment. In numerical simulation, we adopted finite difference method.

3.2 Experimental results and discussion

Figure 3 shows the numerical simulation results for selective parameters. We see from the figure that layer formed structure and polymer dispersed structure. For larger R and L , the separation morphology becomes more polymer dispersive. And numerical results show good separation results for $R < 50$ and $L < 0.1$.

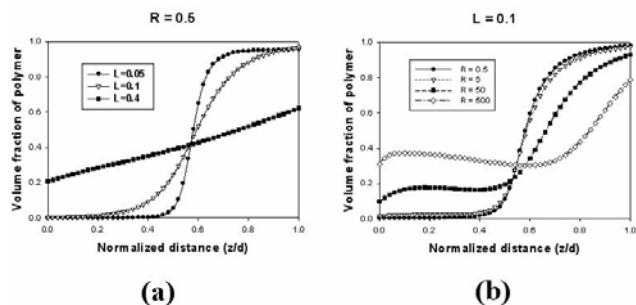


Fig. 3. Numerical simulation results (a) for fixed $R=0.5$ and (b) for fixed $L=0.1$.

We represented the above situation as a schematic diagram as shown in Figure 4. For a given process conditions such as temperature, UV intensity, polymer and liquid crystal, the only variable affecting both the parameter R and L is cell gap. If we remind that $R = kl_0 d^2/D$ and $L = 1/bd$, we can draw the process constant curve, $LR^{1/2} = \text{const}$, by eliminating cell gap. We divided four regions of this R - L parameter space as shown in Figure 4. In figure 4, region 1 represents good PSCOF structure region, and the cell gap condition satisfies the relation $1/10b < d < (50D/kl)^{1/2}$, where we used the well separating conditions $L < 0.1$ and $R < 50$ from numerical simulation. Region 3 is large L and small R value, which corresponds typically to thin cell gap, region 4 is large R and small L value, which corresponds to thick cell gap. And region 2 is almost same as region 1, but it overlap slightly with well separating condition. Hence for the condition corresponding region 4, there is narrow cell gap margin to obtain PSCOF structure. We performed numerical simulation for four kind of initial parameters which are corresponding to each region. Figure 5 shows the numerical simulation results for four regions while cell gap is varying. From Figure 5, we can observe as follows: first, if the curve including

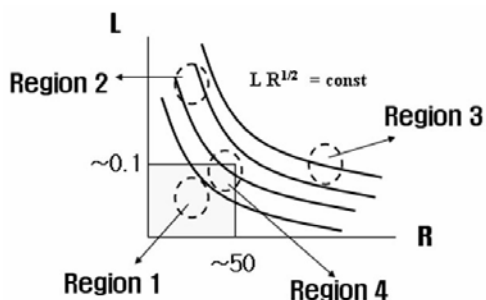


Fig. 4. Parameter space of R and L .

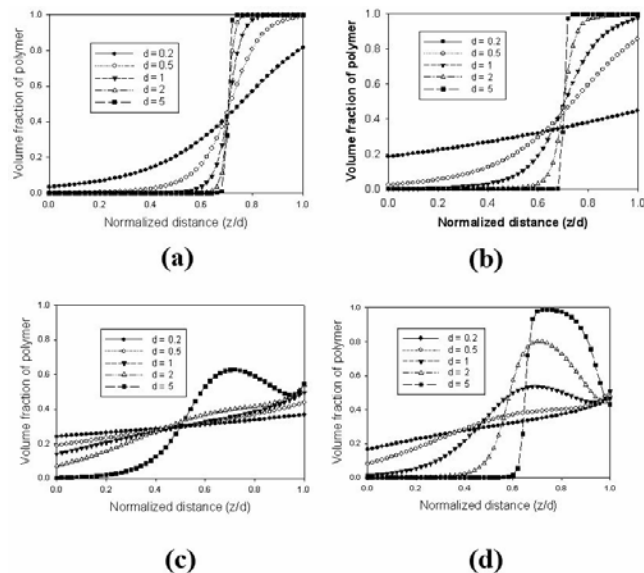


Fig. 5. Numerical simulation results for various initial R and L for (a) $R = 25$, $L = 0.4$, (b) $R = 25$, $L = 0.1$, (c) $R = 2.5$, $L = 0.05$ and (d) $R = 500$, $L = 0.1$.

initial R , L value, does not meet the square region, simulation results also show the polymer dispersed structure as cell gap changed. Second, for initial values deep inside the square, it seems to be wide cell gap range that enables the PSCOF structure. Thirdly, for large L and small R (region 2), because of uniform UV light, the polymers are dispersed through the cell. So in this case, by using high absorption liquid crystal material, it is possible to obtain PSCOF structure. And finally for large R but small L (region 3), it seems to be well separating structure. Only considering the numerical simulation, for the region 3, it shows good separation structure. To make this clear, we fabricated samples of various cell gap and observed the polymer structures.

Figure 6 show polymer morphologies on top substrates of various cell gap. From Figure 6, we can immediately observe that for thin cell, it is hard to obtain uniform texture over all samples. On the contrary, for larger cell gap, the droplet structure on polymer surface does not affect the polymer structure severely. But the boundary surface is not smooth. We think this is the trade-off relation between thin cell and thick cell. The droplet structure of polymer surface and/or polymer liquid crystal boundary is due to by thermally induced concentration noise⁷. In our numerical simulation, we did not consider the thermal concentration fluctuation in numerical simulation. Therefore we did not account for the fluctuation of

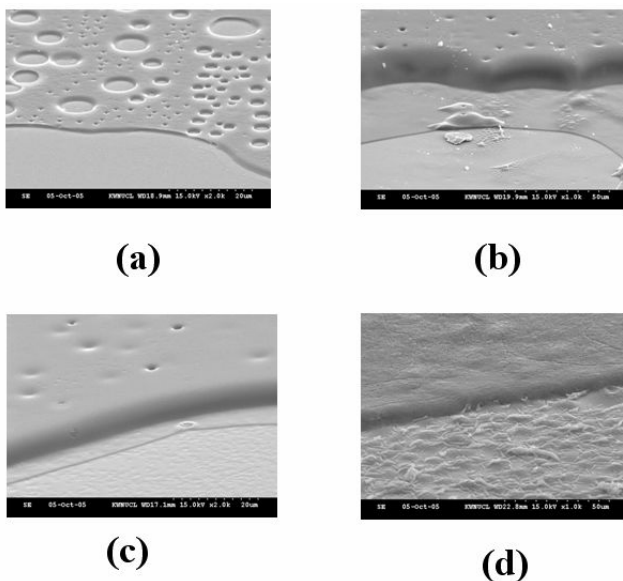


Fig. 6. SEM images of polymer morphologies on top substrates for various cell gap of (a) 1 μ m, (b) 4.5 μ m, (c) 9 μ m and (d) 18 μ m.

boundary between liquid crystal and polymer layer which is related to R . Let's introduce briefly the meaning of R . As shown above, it is the ratio of polymerization time to time to approach to thermal equilibrium. For larger R , that means the time to equilibrium cannot follow the polymerization time. So resultant polymer structure shows locally equilibrium boundary structure between polymer and liquid crystal in vertical direction, i.e droplet structure.

For thin cell, which is small R and large L (low UV intensity gradient), that means uniform UV irradiation along the substrate normal direction, droplet formation due to by concentration fluctuation in lateral direction is critical because the size of polymer droplet is comparable to cell gap. The surface morphology of thin cell, however, was smooth, which could be stem from small R value. Now for thick sample, which is large R and small L , due to high intensity gradient, the layer structure can be clearly observed. But as we discussed just before, due to its slow recovery time of thermal equilibrium (remind $\tau = d^2/D$), the boundary between liquid crystal and polymer cannot formed uniform and smooth surface. So, as shown in Figure 6 for thick cell gap, the surface shows rough morphologies which are consistent with the result of Q. Wang *et al.*⁶. And these can result in loss of uniform alignment of liquid crystal molecules. To reduce the R value with a view point of fabrication condition, there are several ways such as using

polymers with slow polymerization and high diffusion coefficient and using high temperature. Hence the cell gap condition satisfying, $1/10b < d < (50D/kl)^{1/2}$, can gives well separating and smooth polymer and liquid crystal boundary.

4. Summary

We have studied the cell gap dependence of anisotropic phase separation by numerical simulation and experiments. For thin cell gap, which is typically small R and large L value, the uniformity of sample and the absorption of UV light by liquid crystal are important and the boundary between liquid crystal and polymer showed smooth and uniform. On the contrary, for the thick cell gap, which give typically large R and small L , so the polymer surface morphology is rough and affect the LC alignment. To reduce the R value, using polymers with slow polymerization and/or high mobility and high temperature process are required. For the good separation condition, the optimized cell gap range is given by $1/10b < d < (50D/kl)^{1/2}$.

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5. References

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