Formation of polymer structure by thermally-induced phase separation in a dye-doped liquid crystal cell

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ABSTRACT

A dye-doped LC/polymer light shutter with a polymer structure that is formed using the thermally-induced phase separation (TIPS) method is demonstrated. The TIPS method relies on the difference in solubility between thermoplastic polymer and solvent, and thus there is no degradation of the dye during the fabrication process. The light shutter can be fabricated quickly because the optical properties are not affected by the cooling time. The fabricated TIPS cell shows a superior black color with excellent optical properties, such as a low haze value of 0.5% in the transparent state, and a high haze value of 99.1% in the opaque state. This result can be applied for the high image quality of see-through displays using organic light-emitting diodes.

Keywords: liquid crystals, liquid crystal device

1. INTRODUCTION

Recently, various types of light shutters have been studied for application to see-through organic light-emitting diode (OLED) displays [1-6]. Each pixel of a see-through OLED display includes a transparent area through which the objects behind the display panels can be seen along with the displayed images. Therefore, they cannot display the black color because of this area. In addition, the displayed images overlap with background objects can cause poor image quality. For obtaining the high-quality mode, a light shutter must be used at the behind of the see-through OLED display panel, which can exhibit black color and hide the objects behind it.

Light shutters are classified into two types; light scattering and light absorption. For controlling the transmittance to exhibit black color, light shutters based on light absorption has been studied, such as electrochromic devices [7-9], suspended particle devices [10-12], and guest-host liquid crystal (LC) devices [1-6]. However, it is difficult to hide the objects completely with light shutters based on light absorption. To hide the objects completely and exhibit the black color simultaneously, LC light shutters based on simultaneous control of light scattering and absorption have been widely studied. In particular, a dye-doped LC/polymer composite cell have been actively researched for this purpose [3,4].

Polymerized-induced phase separation (PIPS) is widely used to form the polymer structure by UV curing inside the LC cell to fabricate LC/polymer composite cell. However, degradation of dyes by oxidation, which occurred by the photo-initiator during the UV curing, has been reported [3,4]. To solve this problem, fabrication of a dye-doped LC/polymer composite light shutter by thermal curing has been proposed [3]. However, since curing temperature is limited on the range of the nematic phase of the LC for the high optical properties of the fabricated light shutter, fabrication was made at a low temperature. Therefore, the formation of the polymer structure is time-consuming. Moreover, although no degradation of the dye in thermal curing to form polymer structure has been reported, this process also includes a chemical reaction that might cause degradation of the materials.

In this study, we report a dye-doped LC/polymer composite light shutter in which the polymer structure is formed by the thermally-induced phase separation (TIPS) method. TIPS method relies on the difference in solubility between thermoplastic polymer and solvent, instead of any chemical reaction. Therefore, the fabrication process is simple and there is no degradation of the dye. We confirmed that the fabricated dye-doped LC cell exhibits a superior black color as well as high haze value in the opaque state. We expect that the proposed light shutter can be widely used for high visibility of see-through OLED displays.
2. CELL FABRICATION AND OPERATION PRINCIPLE

PIPS is one of the most widely used methods for the formation of the polymer structure inside an LC cell [13]. Fig. 1 (a) shows the schematics of the PIPS method. Initially, the pre-polymer or monomer and initiators are dissolved in the LC. After the bond of the initiator is homolytically cleaved into free radicals by external energy, such as heat or UV, free radicals initiate the process of polymerization. When the pre-polymer or monomer forms a polymer chain, it is no longer miscible with LC and the polymer structure is formed in an LC cell. In this process, free radicals not only polymerize the monomers, but also affects other materials. Free radicals oxidized and degraded dye molecules in a dye-doped LC/polymer light shutter. Low external energy or low reactivity initiator may not result in dye degradation. However, the cell fabrication time may increase [3,4,14].

In contrast, TIPS is a method for the formation of a polymer structure without any chemical reaction. Fig. 1 (b) shows the schematics of the TIPS method. The polymer can be dissolved in an LC at a high temperature [15]. When the temperature of LC/polymer mixture decreased, solidification occurs and a polymer structure is formed in the cell. As mentioned above, the process in the TIPS method does not include any chemical reaction. Therefore, the dichroic dye may not be degraded. The TIPS process is simple because it only requires cooling of the cell from a high temperature to room temperature.

To fabricate a dye-doped LC/polymer light shutter using the TIPS method, we mixed a negative nematic LC mixture (SP0-001, Silchem, China) with poly(butyl methacrylate) (PBMA, Sigma-Aldrich, USA) and 1 wt% of dichroic dye (X12, BASF, Germany). Since the initially-transparent light shutters must be transparent in the initial state, the haze value should be low. The haze of the cell in the initial state can be decreased by index matching [27,28]. For a low haze in the initial transparent state, we chose PBMA because its refractive index (n =1.483) is similar to the ordinary refractive index of the LC mixture used. The physical parameters of the negative LC mixture, SP0-001, are as follows: optical anisotropy, Δn, of 0.282 (n_e = 1.783 and n_o = 1.501 at 589.3 nm and 20 °C) and dielectric anisotropy, Δε, of −4.8 (ε∥ = 3.5 and ε⊥ = 9.3 at 1 kHz and 25 °C). We mixed the LC/polymer mixture in a glass vial by stirring continuously for 24 h at 130 °C. We coated indium-tin-oxide glass with a homeotropic alignment material using a spin coater, and then baked at 230 °C for 1 h for curing. To maintain the cell gap, an empty cell was assembled using silica spacers with a diameter of 10 μm. Then, the LC/polymer mixture was filled into an empty cell through capillary action at 130 °C. The cell was cooled from 130 °C to room temperature over 5 min.

To compare the electro-optic properties of a TIPS cell, a reference cell with a polymer structure formed by the PIPS method using UV light was fabricated. The concentration of the polymer and dye in the two cells was same with TIPS cell in order to compare the performance at the same total transmittance. We mixed 93.8 wt% of negative nematic LC
mixture with 5 wt% of reactive mesogen (RM 257, Merck, Germany), 0.2 wt% of photo-initiator (Irgacure 651, BASF, Germany), and 1 wt% of dichroic dye. The LC/polymer mixture was filled into an empty cell through capillary action at room temperature. The LC cell was exposed to UV light of 5 mW/cm² for 60 min.

The schematic of the structure and operating principle of the fabricated cell is shown in Fig. 2. In the transparent state, the LC and dye molecules are aligned perpendicular to the glass substrate. Therefore, the light scattering and absorption by the LC and dye molecules are minimized so that the LC cell is transparent. When a vertical electric field is applied, the LC and dye molecules are randomly oriented to maximize light absorption and scattering. The fabricated cell blocks the background completely. When the applied voltage is eliminated, the cell returns to its initial transparent state [29].

3. EXPERIMENTAL RESULTS AND DISCUSSION

To confirm the optical properties of the fabricated cell, the electro-optic properties of all the fabricated samples were measured with a haze meter (HM-65W, Murakami Color Research Laboratory) capable of measuring the total transmittance, specular transmittance, and haze. The total transmittance (T_t) is the sum of specular transmittance (T_s), and diffuse transmittance (T_d). The haze (H) can be calculated as H = T_d/T_t. The schematic of the haze meter is shown in Fig. 3.

In LC/polymer composite light shutter, the polymer concentration is an important factor in determining the optical properties of the light shutter [15,18]. To optimize the polymer concentration, we fabricated sample TIPS cells with different polymer concentrations without dichroic dye, and measured the haze value of the sample cells. The voltage-haze curves of the TIPS cells are shown in Fig. 4. When the polymer concentration is 3 or 5 wt%, the haze value of transparent state was less than 1%, which is low as expected. However, for a polymer concentration higher than 7 wt%, the haze value of the cell increased. The light shutter must have a high haze in the opaque state to block the background
completely. The haze values of the cells with polymer concentrations of 5, 7, and 10 wt% approached 99%. We chose the polymer concentration as 5 wt% because the sample cell with the polymer concentration of 5 wt% exhibited a low haze of 0.5% in the transparent state and a high haze of approximately 99% in the translucent state.

Fig. 4. The measured voltage-haze curve of sample TIPS cells with 3, 5, 7, and 10 wt% of polymer concentration.

Fig. 5. Measured total transmittance, specular transmittance, and haze of (a) TIPS and (b) PIPS cells.

Table 1. Measured total transmittance, specular transmittance, and haze of TIPS and PIPS cells.

<table>
<thead>
<tr>
<th>State</th>
<th>TIPS cell</th>
<th>TIPS cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transparent state</td>
<td>Total transmittance</td>
<td>65.4%</td>
</tr>
<tr>
<td></td>
<td>Specular transmittance</td>
<td>65.1%</td>
</tr>
<tr>
<td></td>
<td>Haze</td>
<td>0.5%</td>
</tr>
<tr>
<td></td>
<td>Total transmittance</td>
<td>34.1%</td>
</tr>
<tr>
<td>Opaque state</td>
<td>Specular transmittance</td>
<td>0.3%</td>
</tr>
<tr>
<td></td>
<td>Haze</td>
<td>99.1%</td>
</tr>
</tbody>
</table>

Figure 5 shows the measured optical properties of the TIPS and PIPS cells; total transmittance, specular transmittance, and haze values. The detailed measured values for the transparent and opaque states are summarized in Table 1. The TIPS cell exhibits excellent optical properties with a low haze value of 0.5% in the transparent state and a very high haze value of 99.1% in the opaque state. In the transparent state, the haze value of the PIPS cell is higher than that of the TIPS cell. The haze of the transparent state can be lowered by reducing the amount of polymer or by lowering the curing temperature [19]. The haze value in the opaque state is almost the same on both cells because the polymer concentrations of both cells were same. For the opaque state, we have to apply a somewhat high voltage of 80 V to a TIPS cell.
However, the operation of a light shutter is independent of the operation of an OLED display panel. Each pixel of an OLED panel is driven with thin-film transistors, but a light shutter can be driven simply by a voltage source. However, in the case of energy consumption, further studies are needed for lowering the operation voltage.

There is no significant difference in the total transmittance in the transparent state between TIPS and PIPS cells because we used the same dichroic dye at same concentrations. In the opaque state, however, the TIPS cell shows a lower total transmittance than the PIPS cell. Fig. 7 clearly shows the difference in transmittance. In the transparent state, we can see the printed images through the cell. Although the colors of the cells in the transparent state are different, total transmittance difference is little. In the opaque state, we cannot see the printed images behind LC cells. The TIPS cell exhibits a black color as intended, but the PIPS cell exhibits a dark brown color because the dye is degraded by oxidation reaction during the fabrication process. Therefore, in the opaque state, the total transmittance difference between TIPS and PIPS cells is large.

Figure 7 shows the transmission spectra of the TIPS and PIPS cells. In the transparent state, the specular transmittance of the PIPS cell is slightly lower than that of the TIPS cell for wavelengths shorter than 565 nm. On the other hand, the transmittance of the PIPS cell is higher for wavelengths ranging from 565 to 685 nm. Because of this, the PIPS cell exhibits light brown color. In the opaque state, the transmittance of the PIPS cell is higher than that of the TIPS cell. Even though there is little transmittance difference of the blue wavelength between the TIPS and PIPS cells, there is a significant difference in the transmittance of the red and green wavelengths. Therefore, the PIPS cell exhibits dark brown color. On the other hand, the TIPS cell exhibits a superior black color and blocks the background completely.

![Fig. 6. Images of TIPS and PIPS cells placed on a printed paper.](image)

![Fig. 7. Measured transmission spectra in the transparent and opaque states of TIPS and PIPS cells.](image)

4. CONCLUSIONS

We fabricated a dye-doped LC/polymer light shutter with a polymer structure formed using the TIPS method. Compared with the PIPS method, the TIPS method did not bring about any degradation of the dye with a simple fabrication process.
and reduced the fabrication time. The fabricated cell shows a superior black color with an excellent optical performance with very low haze in the initial transparent state, and high haze in the opaque state. We expect that the proposed light shutter can be used for the high-visibility mode in see-through displays using OLEDs.

ACKNOWLEDGMENTS

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIP) (No. 2017R1A2A1A05001067).

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