Wide View Angle Polymer/Liquid Crystal Composite Films

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Abstract: Polymer/liquid crystal (LC) (40/60 by weight) composite films, often called polymer dispersed liquid crystal (PDLC), were prepared by solvent induced phase separation technique. One type of nematic liquid crystals and three types of polymers having different refractive indices (n), leading to the index ratio (n_m/n_a) smaller than, equal to, and greater than unity were used to fabricate films. Viewing angle of the PDLC films was measured with H. V polarized and unpolarized incident lights. When n_m < n_a, maximum transmittance was observed at normal incidence, and the widest viewing angle was obtained when the indices are matched, regardless of the type of polarization. When n_m > n_a, maximum transmittance was observed at an angle away from the normal where the effective refractive index (n_e) matched n_a. Regarding the transient response following an ac pulse, a transmittance overshoot upon turn-off was observed when n_m > n_a, with high applied voltage. This indicates that an index matched state is obtained during relaxation when the applied voltage is high enough for director alignment.

Introduction

Thin composite films composed of micron-sized droplets of low molecular weight liquid crystal (LC) with positive dielectric anisotropy dispersed in an optically isotropic polymer matrix have potential for a variety of electro-optic applications ranging from switchable window to information display. In most conventional forms, they consist of LC droplets dispersed in polymer matrix known as PDLC (polymer dispersed liquid crystal). However, when the LC content is high (usually >80%) liquid crystals form continuous phase and three dimensional polymer networks are dispersed in liquid crystals, resulting in PNLC (polymer network liquid crystals). Basically, practically saves expensive liquid crystals, whereas PNLC reduces driving voltage and response time. In this paper only PDLC films were considered.

PDLC offers a number of advantages over the conventional nematic devices (twisted and super twisted nematic) as well as ferroelectric or emissive ones: i) they require no polarizers, thus increasing brightness of both direct view and projection displays, minimizing heat control problem, and reducing power consumption and weight of device; ii) They require no alignment layers or stringent thickness control, thus greatly simplifying manufacture process, and enabling large area displays; iii) They have wide viewing angle in all directions and high contrast ratio. Especially for a projection system no use of polarizer is highly appreciated because of the considerable decrease of light loss compared to more commonly used twisted nematic and super-twisted nematic materials.

A number of parameters affect the electro-optic performance (light scattering, light transmittance, operating voltage, response time etc) of the composite films. These include film composition and thickness, droplet size, and interaction between polymer and LC. Generally stronger polymer-LC interaction results in smaller droplets due to the better miscibility, leading to the increased driving voltage and the rise time. Factors affecting the droplet size in solvent induced phase separation, encapsulation and polymerization induced phase separation have been well documented in the literatures.
We describe the angular dependency of transmittance of PDLC films using horizontally (H) and vertically (V) polarized and unpolarized incident lights. Three different types of PDLC films, each satisfying \( n_h < n_v \), \( n_h = n_e \), and \( n_h > n_v \) were prepared, and angular discrimination and viewing angles of the films were measured. We shall show that the angular breadth of the transmission peak is also broadest when the indices are matched.

**Effect of Polarization**

The composite film operates on the basis of a fairly simple principle. The nematic LC molecule is optically uniaxial, thus it has an ordinary refractive index \( n_o \) and extraordinary refractive index \( n_e \). When a nematic director \( n \) makes an angle \( \theta \) with the propagation direction \( k \) (Figure 1) of the light linearly polarized parallel to \( n.k \) plane, the refractive index of LC is expressed by Eq. (1):

\[
  n_o = \frac{n_e n_v}{(n_e \cos^2 \theta + n_v^2 \sin^2 \theta)^{1/2}}
\]

For light linearly polarized perpendicular to the \( n.k \) plane, the refractive index of the LC does not vary with \( \theta \), and it is \( n_v \).

For a droplet in PDLC film, directors are configured in various ways depending on the droplet geometry, molecular anchoring at the wall, and direction and strength of the external field. A simple and useful approach is to introduce an effective refractive index of droplet \( n_d \). The effective refractive index of the droplet is obtained from an average ordinary and extraordinary indices of the LC which depend on the director configuration in the droplet. In the absence of external field (unpowered), the direction of nematic director varies randomly from droplet to droplet and the light is scattered by the droplets.

In the presence of electric field (powered), liquid crystals with positive dielectric anisotropy tend to align themselves with the directors parallel to the field direction. In this state, the refractive index for horizontally polarized incident light is equal to \( n_o \) and if \( n_v \) approximately matches \( n_o \), the film will be transparent. Upon removal of the external field, the nematic directors return to their random alignment by the interface energy, and the film becomes opaque.

**Experimental**

**Materials.** In order to get the index ratio \( n_o/n_v \) greater than equal to and smaller than unity one type of liquid crystals (ZLI-1565, Merck) having positive dielectric anisotropy, and three types of polymers i.e. poly(vinyl butyral)(PVB), poly (methyl methacrylate)(PMMA), and poly(vinyl chloride)(PVC) were used to prepare the PDLC films. ZLI-1565 is a nematic liquid crystal mixture composed of phenyl cyclohexane and biphenyl cyclohexane derivatives. The characteristics of these materials are given in Table I.

**Film Casting and Cell Preparations.** Films were prepared by solvent induced phase separation method using tetrahydrofuran (THF) as a co-

<table>
<thead>
<tr>
<th>Materials</th>
<th>Characteristics</th>
<th>Maker</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl butyral) (PVB)</td>
<td>( T_g = 324 K )</td>
<td>Aldrich</td>
</tr>
<tr>
<td>( n_o = 1.485 )</td>
<td>( M_w = 36000 )</td>
<td></td>
</tr>
<tr>
<td>Poly(methyl methacrylate) (PMMA)</td>
<td>( T_g = 378 K )</td>
<td>Lucky</td>
</tr>
<tr>
<td>( n_o = 1.492 )</td>
<td>( M_w = 65000 )</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl chloride) (PVC)</td>
<td>( T_g = 354 K )</td>
<td>Lucky</td>
</tr>
<tr>
<td>( n_o = 1.541 )</td>
<td>( M_w = 84000 )</td>
<td></td>
</tr>
<tr>
<td>ZLI-1565</td>
<td>( n_o = 1.622 )</td>
<td>Merck</td>
</tr>
<tr>
<td>( n_v = 1.492 )</td>
<td>( \eta &gt; 8000 )</td>
<td></td>
</tr>
<tr>
<td>( T_v = 233 K )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( T_v = 358 K )</td>
<td></td>
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</tr>
</tbody>
</table>

solvent. Approximately 20 wt% of the polymer and liquid crystals with a fixed polymer/LC composition (4/6 by weight) were first thoroughly dissolved in THF to form a homogeneous solution. Then the solution was poured on an indium-tin oxide (ITO) coated glass plates and the solvent was evaporated, leading to the dried film thickness (30 μm) controlled by an applicator. As the solvent was evaporated, solidification as well as phase separation occurred. A second substrate was placed on the top of the composite film to fabricate a sandwiched structure of PDLC cell.

**Electro-optic Measurements.** The electro-optic properties of the films were measured using the experimental setup shown in Figure 2. The collimated beam of He-Ne laser (λ = 632.8 nm) was first linearly polarized (when necessary) in V and H directions, and passed through the cell. V and H polarization, depicted in Figure 2, are those perpendicular and parallel to the plane of incidence, respectively. In the aligned droplet, the direction of H is also perpendicular to the directors with normal incidence, but parallel to the axis of rotation. The sample was held on a rotating stand to vary the incident angle of light.

The transmitted light intensity was measured with a photodiode. The output from a function generator was amplified and used to drive the cell. External electric field was applied normal to the film surface to make a homeotropic alignment. The drive signal and the response of photodiode were monitored with a digital storage oscilloscope (Hitachi VC-6023). The transparency of the film depends on the angle and polarization of the incident beam, and is monitored in terms of transmitted beam intensity (I). The distance between the cell and photodiode was about 30 cm. The lined up facilities which were controlled by a laboratory computer were turned on for about one hour before the data were taken.

**Results and Discussion**

**Angular Dependent Transmittance.** The angular dependence of the transmitted light intensity is governed by several factors including i) the angular dependence of effective refractive index for V polarization (Eq. 1), ii) Fresnel transmission coefficients (T1 and T2) from the upper and lower glass-air interfaces of the cell, and iii) the increased path length of the light traveling through PDLC film at an angle θ (Figure 2(b)). Figure 3 shows the angular-dependent refractive indices of ZLI-1565 calculated from Eq. (1) and the refractive indices of three matrix polymers. It is seen that n_PVB is smaller than n_s and n_PVCl matches n_s at normal incidence, whereas n_PVC matches n_s at an incident angle of approximately 40° from the normal.

Figures 4 to 6 show the observed transmitted...
light intensity of the three sample cells with different values of \( n_e \) as a function of incident angle \( \theta \) for both V and H polarized and unpolarized lights. In all cases the value of \( I_0 \) is normalized by the maximum transmittance intensity.

In the case of \( n_e/n_i < 1 \) (PVB. Figure 4), the transmitted light intensity is a maximum at normal incidence and decreases as the incident angle increases regardless of the type of polarization. The decrease is due to the increased back scattering and increased optical path length \( d \) which is given by \( d = d_0 \cos \theta \) (Figure 2). The viewing angle is maximum with unpolarized light and minimum with V polarization. Due to the loss of light when using polarizer, H polarization shows a bit lower transmittance as compared with unpolarized light. With V polarization, the effective refractive index of the droplet increases with incident angle and hence the index mismatch becomes greater, resulting in a small viewing cone.

When \( n_i \) matches \( n_e \) (PMMA. Figure 5) viewing angle of the cell with V polarization is broadened, and no significant difference in transmittance is observed for the three different types of polarization. This type of film is useful in display designs when wide viewing angle is desired.

It is particularly interesting that for \( n_i/n_e > 1 \) (PVC. Figure 6) the angle of maximum transmittance shifts to an angle away from the normal. Maximum transmittance is observed at an incident angle where the effective refractive index of the droplet matches \( n_e \). With \( n_i = n_e \), in Eq. (1), the angle of maximum transmittance is obtained as

\[
\theta = \sin^{-1} \left[ \frac{(n_i/n_e)^2 - 1}{(n_e/n_i)^2 - 1} \right]^{1/2}
\]

The angle of maximum transmittance calculated from Eq. (4) is 40°, which agrees well with the experimental data. The angle of maximum transmittance can be tailored by systematic mismatch of the indices for \( n_e > n_i \) and this suggests that PDLC films can be applied for angular discriminating filters. The angular-dependent transmittance of the PDLC films is important in many applications. For example, in display the angular dependence of transmittance will be useful in designing il-
illumination systems that produces adequate contrast over a specified viewing angles. For windows and other sun light control application the angle of incidence can determine the fraction of incident sun light passing through or backscattered from the film. It is noted that H polarization gives significantly lower transmittance. This is due to the significantly large index mismatch between \( n_v \) of PVC and \( n_e \) (Figure 3). It is seen that angular dependence of H polarized light as well as unpolarized light is nearly independent of index ratio. With H polarization, the direction of polarization is nearly everywhere within the droplet perpendicular to the nematic director and the effect of increased path length is observed.

**Fresnel Correction.** Figure 7 shows the Fresnel reflection corrected (described below) intensity as a function of the incident angle. It is useful to remove the Fresnel reflections at the air-glass interface to examine the intrinsic angular dependence of PDLC film for V polarization. The effect of Fresnel reflection at the air-glass interface is accounted for by

\[
\frac{I_v}{I_i} = \left[ \frac{1}{T_1 T_2} \right] \frac{I_1}{I_0}
\]

where \( I_v/I_i \) and \( I_v/I_0 \) are the ratios of the transmitted light intensity to the incident light intensity of the PDLC film and the cell, respectively (Figure 2). For V polarization, the angular dependence of the product \( T_1 T_2 \) of Fresnel transmission coefficients is given by

\[
(T_1 T_2) = \frac{\sin \theta \sin \theta', \cos \theta}{\sin^2(\theta + \theta') \cos (\theta - \theta')}
\]

where \( \theta' = \sin^{-1}(\sin \theta, 1.52) \), and \( \theta \) is the incident angle. The refractive index of glass was taken as 1.52.

For H polarization, the index variation with incident angle is small since the nematic director is almost perpendicular to the polarization direction (Eq.1). However, optical path length changes with incident angle. For \( n_v \leq n_0 \), maximum transmittance is obtained with normal incidence due to the minimum path length of the light.

**Transient Responses.** Figure 8 shows the angular dependent transient responses of the films with V polarization following an ac pulse of 50 ms. For \( n_v \leq n_0 \) (Figure 8a and 8b) saturation transmittance decreases with the increase of incident angle. When the indices are matched (Figure 8b), responses to turn-on and turn-off are almost instantaneous regardless of the incident angle. However, for \( n_v > n_0 \), normal in-
with normal incidence. The slow turn-off response is probably due to the complete homeotropic director alignment, which takes more time for relaxation.

When \( n_o > n_r \), transmittance increases with incident angle showing a maximum value at about 50° and decreases with further increase in incident angle. It is particularly interesting that normal and near normal incidences show an optical rebound upon turn-off. That is, upon removal of the voltage the transmittance initially increases followed by a slow decay to the off state. This optical rebound is a characteristic of \( n_o > n_r \), and can be explained as follows. In the off state the average refractive index of the droplet, given below is greater than the \( n_r \).

\[
\frac{1}{n} = \frac{2n_o + n_r}{3}
\]

Initial application of the voltage rotates the droplet from random to homeotropic orientation. Meanwhile the refractive index of the droplet decreases from \( n \) to \( n_r \). The droplet passes an index matched state where the transmittance is maximum, beyond which the value of \( n \) falls below \( n_r \). Indices are once again matched during relaxation of the orientation upon removing the power. Only this is seen in the figure. Relaxation of the droplet orientation leads to an increase in \( n_r \) resulting in the index matched state and \( n_r \) eventually becomes equal to \( n \). At incident angles above 20° from the normal, the transmittance is more than doubled and the optical rebound is no longer observed, implying the films are nearly index matched. When the indices are closely matched, response to turn off is almost instantaneous and optical rebound is no longer observed.

Figure 9 shows the voltage dependent transient response of the films with \( V \) polarized light passing in the direction normal to the surface. It is seen that PMMA requires much higher driving power as compared with PVB, probably due to the strong polymer-LC polar interaction.\(^{12,13}\) When \( n_o > n_r \)(PVC. Figure 9c), it is also particularly interesting that transmittance overshoot is clearly observed upon removal of the voltage. It is noted that this optical rebound is observed with only high applied voltage.
Figure 9. Voltage dependent transient responses following an AC pulse of 50 ms: a) PVB/LC, b) PMMA/LC, and c) PVC/LC films(1 kHz).

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References