Electro-optical properties of polymer dispersed liquid crystals containing non-spherical liquid crystal droplets.

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Electro-optical properties of polymer dispersed nematic liquid crystals containing ellipsoidal droplets have been studied. Several methods of droplet deformation have been used. It has been found that optical contrast ratio of PDLC films is larger when PDLC contains deformed liquid crystal droplets.

1. Introduction

Polymer dispersed liquid crystals (PDLC) are two-phase composite structures containing liquid crystal (LC) droplets of micrometer size embedded in a solid polymer matrix [1]. Such a structure scatters incident light, if the mean LC droplet diameter is comparable to the wavelength of incident light, moreover, the mean refractive index of the liquid crystal is different from the polymer refractive index \( n_p \). The mean value of LC refractive index is taken into consideration here, due to statistical distribution of the director (a unit vector describing the local molecular alignment of LC) inside individual LC droplet, in spite of the same molecular anchoring conditions for all droplets. In other words, an optical axis of individual LC droplet is randomly oriented in space what has the consequence that optical properties of the entire composite are determined by the average of those particular orientations. By an appropriate choice of PDLC components, such a scattering structure may be transformed into a transparent one, if sufficiently high bias electric field is applied to PDLC film. This effect is caused by field induced re-arrangement of LC molecules, which become aligned along the intensity lines of the external field. In the case of nematic liquid crystals with positive dielectric anisotropy this statement is completely true. For other liquid crystal phases, electro-optical effects are more complicated [2]. The phenomenon mentioned above, so called electrically induced (or controlled) transmittance, is the base for most of PDLC applications. Electro-optical parameters describing this effect, e.g., driving voltage, switching time and optical contrast ratio depend mainly on the structure of PDLC, especially on film thickness as well as number and size of LC droplets [3]. Because of surface properties of typical PDLC components and features of the preparation method, LC droplets usually exhibit nearly spherical shape. In certain cases, PDLC containing non-spherical LC droplets, especially ellipsoidal ones, may be interesting from the point of view of application [4]. The aim of the present work is to study the electro-optical properties of such PDLC composites.

2. General considerations

Let us consider a PDLC system containing spherical nematic LC droplets with a concentration of \( c \). The intensity of light scattered from this system is proportional to the difference bet-
ween LC refractive index $n_{LC}$ and polymer refractive index $n_p$. In the absence of aligning factors, e.g., electric or magnetic fields, the former parameter may be described as:

$$n_{LC} = \frac{n_o + n_e}{2},$$  \hspace{1cm} (1)

where $n_o$ and $n_e$ stand for ordinary and extraordinary refractive index of LC material, respectively. This averaging is caused by different reasons for different kinds of director field in LC droplets. It is enforced by molecular anchoring conditions in a polymer cavity. In case of radial anchoring, presented schematically in Fig. 1b, Eq. (1) is true for each LC droplet. In case of the most widespread bipolar tangential anchoring, shown in Fig. 1a, Eq. (1) may be applied to the entire composite only, due to the random orientation of the optical axis in particular LC droplet. In fact, Eq. (1) is only an approximation, because in real systems a skin-like layer exists, close to the surface of the polymer cavity. The properties of this layer are intermediate between those of the LC and the polymer. The approximation introduced in such a way, however, does not diminish the generality of our considerations.

A molecular re-orientation of LC occurs when a bias electric field, strong enough to overcome anchoring forces, is applied to the PDLC structure. The molecules of LC with positive dielectric anisotropy, $\Delta \varepsilon > 0$, are aligned near parallel to the field, while for LC with negative dielectric anisotropy, $\Delta \varepsilon < 0$, they are aligned near perpendicular to the field. In the former case, PDLC structure may become transparent, if the optical properties of the LC and the polymer fulfil the following condition:

$$n_o = n_p$$ \hspace{1cm} (2)

The transmittance of PDLC is limited by so-called haze when field is applied. This phenomenon is caused most probably by the existence of the mentioned skin-like layer on the droplet surface. Molecules belonging to this layer are anchored so strong to the surface of the polymer cavity that even high external field could not align them. This phenomenon decreases the optical contrast ratio of the PDLC, described by the following expression:

$$CR = \frac{T_{on}}{T_{off}}$$ \hspace{1cm} (3)

where $T_{on}$ and $T_{off}$ stand for the transmission of PDLC film in on-state – with applied field and off-state – without field, respectively. There are several possibilities of decreasing $T_{on}$ and increasing $T_{off}$. The reduction of the $T_{on}$ may be caused by application of higher field, better matching of PDLC components or the reduction of molecular anchoring strength [5]. The $T_{off}$ may be enhanced by perfect adjustment of LC droplet radius to the incident wavelength [3], increasing of PDLC thickness [3,6] and application of LC with high $\Delta \varepsilon$ insoluble in polymer matrix [5].

If LC is optically negative, i.e., $\Delta \varepsilon < 0$, the reversed electro-optical effect of induced transmission may be obtained. In this case PDLC...
transmits incident light in off-state and scatters it in on state. The suitable refractive index matching condition is described by the following expressions:

$$\bar{n}_{LC} = n_p, n_o \neq n_p$$

(4)

In devices using this effect, LC molecules with radial anchoring conditions (transmitting off-state) are aligned perpendicular to the bias field (scattering on-state). Due to the large haze, caused by the existence of thick transition layer on the surface of polymer cavity, the contrast ratio is low in this case.

One may now ask the question about, what will change if LC droplets will not be spherical?

Let us assume that spherical LC droplets have been deformed and became rotary ellipsoids. Such ellipsoid may be described by two main axes: long $a$ and short $b$ or by the ellipticity (elongation) $\varepsilon = a/b$. The effective, i.e., the largest cross-section of LC droplets of the same volume but different shape may be compared as follows, assuming that LC is an incompressible liquid:

$$\frac{S_{el}}{S_{sp}} = \varepsilon^{-1/3},$$

(5)

for the long axis of the ellipsoid parallel to the surface of PDLC film and

$$\frac{S_{el}}{S_{sp}} = \varepsilon^{-2/3},$$

(6)

for the long axis of the ellipsoid perpendicular to the surface of PDLC film. Here $S_{el}$ stands for the largest cross-section of the ellipsoidal droplet perpendicular to the incident light while $S_{sp}$ is the cross-section of the spherical droplet. In this way, the effective cross-section for incident light in off-state becomes higher for ellipsoidal droplets, independent of the kind of anchoring conditions, i.e., for normal as well as for reversed transmittance control.

The next problem, illustrated in Fig. 2, is even more important. In case of long ellipsoid axis parallel to the surface of PDLC film, the majority of LC molecules is perpendicular (or near perpendicular) to the incident light. In this way, Eq. (1) is not longer valid and the average refractive index of LC should be expressed by the following equation:

$$n_{ef} = \frac{\varepsilon n_o + n_e}{\varepsilon + 1}.$$

(7)

For this reason, also the difference between refractive indices of the polymer and the LC changes in comparison to PDLC containing spherical droplets. Namely, it increases for droplets elongated in the direction parallel to the PDLC surface and decreases for droplets perpendicular to this surface.

Such situation causes a higher intensity of scattered light for “parallel” droplets and lower one for “perpendicular” droplets. This effect should increase the optical contrast ratio measured in case of the electrically induced transmittance.
3. Experimental

Three methods have been used for preparation of PDLC containing non-spherical LC droplets. The first one consists in an elongation of cured PDLC film with simultaneous local thermal stress. This technique may be adopted for those PDLC systems, in which film-forming thermoplastic is used as a material of polymer matrix. The viscous flow of the polymer matrix causes a deformation of the LC droplets embedded in this matrix. In this work such method has been used for obtaining PDLC films on the base of poly(vinyl alcohol) - PVA (PA-18®, Shin-Etsu) by encapsulation. PDLC films have been prepared in a conventional way [7] on the polymer foil. Then they have been separated from this foil, placed over the transversal thin heating element and stretched. Afterwards, the part of PDLC film containing deformed LC droplets has been laminated between two polymer sheets coated by the conducting layer (indium tin oxide – ITO).

The second method uses hydrodynamic deformation of LC droplets introduced by a shearing of LC-prepolymer system during curing a prepolymer. It may be used for those methods of PDLC preparation only, which do not involve a solvent. The photocurable resin NOA-65® (Norland Optical Adhesives) has been chosen as a prepolymer material for this technique. A homogeneous mixture of the prepolymer and LC material, containing glass spacers, has been deposited onto the glass plate with ITO conducting coating and covered by the same plate. Then an arm joined with the shearing device has been glued to the upper glass plate. Afterwards, the upper plate has been forced to make a periodic sliding movement and simultaneously UV illumination has been switched on. The amplitude of this movement has been usually 1 to 2 mm, while the frequency has been changed from 5 to 50 Hz. In this way, LC droplets nucleating due to the polymer curing have been deformed to the ellipsoidal shape. This shape has been stabilized by cured polymer matrix.

The third method consists in an application of bias electric field during nucleation of LC droplets, i.e., prepolymer curing. This method may be also applied for PDLC preparation methods, which do not involve a solvent. If the field is sufficiently high and $\Delta \varepsilon$ of LC is positive, two effects take place. The first one is the homogeneous arrangement of optical axes of LC droplets, while the second one is an elongation of droplets along the field. The latter effect is caused by a contribution introduced by electric field to the total deformation free energy of liquid crystal - $\Delta F$ [8]:

$$
\Delta F = \int f_y dV + \int f_z dS - \int f_x dV - \int f_y dV + \int f_A dS,
$$

(8)

The first term of the above equation describes the volume deformation, the second one – the surface deformation, the third and the fourth terms express the deformations introduced by external electric or magnetic fields, respectively, and the fifth one describes the effect of molecular anchoring. In case of LC with $\Delta \varepsilon < 0$, the molecular orientation and droplet elongation are perpendicular to the field.

The deformation induced by the electric field may be also realized for so-called dual-frequency regime using a dispersion of LC dielectric anisotropy [9]. For instance, LC with tangential anchoring conditions may be aligned by high-frequency field perpendicular to this field, due to negative dielectric anisotropy of LC. In this way, LC droplets are elongated parallel to the film surface. Then, using the same electrodes, low frequency field is applied. In this case, LC exhibits positive dielectric anisotropy and droplets are elongated perpendicular to the film surface. For this reason, optical contrast of the layer may be significantly increased. This method requires however, LC material with special dielectric properties.

Additionally, PDLC layers obtained by encapsulation and containing in PVA matrix relatively large and highly non-spherical LC droplets, due to their coalescence, have been studied. All studied PDLC systems are gathered in Table 1. The detailed properties of nematic LC materials are described elsewhere [5], but it is worth mentioning, that W-790 mixture has negative dielectric anisotropy, while W-22 exhibits ferroelectric smectic phase $S^*_C$. The concentration of LC in PDLC has been chosen about 20% by weight, so the droplet concentration $c$ has been comparable for all studied systems.

Obtained PDLC systems have been studied under polarizing microscope to determine the shape and size of LC droplets. Transmission of
Table 1. PDLC components and methods of preparation

<table>
<thead>
<tr>
<th>Code</th>
<th>Polymer</th>
<th>LC</th>
<th>PDLC preparation method</th>
<th>Preparation method of ellipsoidal droplets</th>
<th>ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>PVA</td>
<td>W-486, W-801</td>
<td>encapsulation</td>
<td>elongation + thermal stress</td>
<td>2-3</td>
</tr>
<tr>
<td>1B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2A</td>
<td>NOA-65</td>
<td>W-486, W-790</td>
<td>photopolymerization induced phase separation</td>
<td>shearing during curing a prepolymer</td>
<td>2-5</td>
</tr>
<tr>
<td>2B</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3A</td>
<td>NOA-65</td>
<td>W-486, W-790</td>
<td>photopolymerization induced phase separation</td>
<td>electric field applied during curing a prepolymer</td>
<td>1-2</td>
</tr>
<tr>
<td>3B</td>
<td></td>
<td>W-22</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4A</td>
<td>PVA</td>
<td>W-486, W-801</td>
<td>encapsulation</td>
<td>droplets with different shapes due to a coalescence</td>
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</tr>
<tr>
<td>4B</td>
<td></td>
<td></td>
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</table>

PDLC films in off- and on-states has been measured in low-angle regime [6]. For all systems $T_{on}$ has been measured under bias voltage higher by 10% than the saturation voltage of the given system.

4. Results and discussion

The results of transmission measurements and optical contrast ratio calculations are presented in Table 2. Transmission is given in arbitrary units. As one can see, the optical contrast ratio is usually higher for ellipsoidal LC droplets in comparison with spherical ones. This effect has been observed for nematic LC with dielectric anisotropy either positive or negative. Pre-orientation of the director by electric field causes lack of possibility to drive PDLC sample after curing by the voltage with the same frequency as used for pre-orientation. There is, however, a possibility to apply dual-frequency addressing which allows to switch the transmis-

<table>
<thead>
<tr>
<th>Code</th>
<th>ε</th>
<th>$T_{off}$</th>
<th>$T_{on}$</th>
<th>CR</th>
<th>$T_{off}$</th>
<th>$T_{on}$</th>
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<td>7</td>
<td>10</td>
<td>75</td>
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<td>4</td>
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<td>1</td>
<td>85</td>
<td>85</td>
<td>1</td>
<td>no effect</td>
</tr>
<tr>
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<td>2</td>
<td>60</td>
<td>15</td>
<td>4</td>
<td>60</td>
<td>15</td>
<td>4</td>
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</tr>
<tr>
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<td>80</td>
<td>10</td>
<td>6</td>
<td>80</td>
<td>13</td>
<td>dual-frequency addressing</td>
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<tr>
<td>4A</td>
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<td>7</td>
<td></td>
<td></td>
<td></td>
<td>high haze</td>
</tr>
<tr>
<td>4B</td>
<td></td>
<td>9</td>
<td>80</td>
<td>11</td>
<td></td>
<td></td>
<td></td>
<td>mean haze</td>
</tr>
</tbody>
</table>
sion of PDLC film. This method may be adopted for both normal-mode and reverse-mode electrically induced transmittance effects but requires LC with suitable dielectric properties.

Systems 4A and 4B contained larger LC droplets than 1A and 1B. For this reason, the alignment of LC molecules introduced by electric field has been better and $T_{on}$ values are higher for those systems. From the point of view of the optical contrast, the crucial effect is introduced by $T_{off}$ value. For this reason, all methods introducing higher level of scattering in off-state should be preferably used.

The application of methods above discussed requires a careful choice of polymer matrix, because the larger polymer elasticity is the larger deformation of LC droplets may be introduced. It is well known, however, that polymer properties may be modified by of low-molecular dopants [10].

The next problem is connected with substrata used for a construction of PDLC cell. For instance, it is very difficult to apply shearing, if conducting polymer sheets are applied as PDLC substrates. For this reason, the application possibility of droplet deformation techniques in case of elastic PDLC devices is limited. For glass substrates, the cost of the instrumentation necessary to carry out the above methods may be very high for large area PDLC cells.

It is worth mentioning, that the switching times for PDLC cells containing non-spherical LC droplets usually have been lower in comparison with PDLC containing spherical LC droplets.

The microscopic picture of ellipsoidal LC droplets is presented in Fig. 3.

5. Conclusions

It has been proven experimentally that PDLC systems containing ellipsoidal droplets of liquid crystal exhibit larger optical contrast ratio for the electro-optical effect of electrically induced transmittance than PDLC containing spherical ones. From the application point of view the most interesting methods of the change of LC droplet shape are:

- the deformation of spherical LC droplets in cured polymer by external electric field, especially for reverse-mode effect and dual-frequency addressing,
- the preparation of elongated LC droplets during polymer curing by means of shearing of the system.

Both possibilities have however, limited application, and may be used for relatively small PDLC devices using glass plates as substrates. It means that deformation of LC droplets may be especially interesting in case of PDLC devices for optical systems.
References


