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Elaboration and electro-optic study of a new type of open porosity PDLC

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A new polymer dispersed liquid crystal (PDLC) system characterized by easy processing and an open porosity has been elaborated. This PDLC is based on a pre-formed, porous, thin polymer film of a commercially available PVDF–HFP copolymer wetted by the eutectic mixture of cyano bi- and ter-phenyls known as E7 (Merck Ltd, UK). This new process is of interest because of its simplicity, and the fact that there is no risk of intermixing between the liquid crystal and the polymer matrix as occurs in a conventional PDLC. An electric field applied across the thin film results in a change in its transmission, due to the reorientation of the liquid crystal director, as already known for closed porosity PDLCs. The electro-optic properties of this PDLC have been studied and semi-quantitatively interpreted on the basis of the response theory of conventional closed porosity PDLCs.

1. Introduction

Polymer dispersed liquid crystals (PDLCs) are a relatively new class of materials that hold promise for many applications ranging from switchable windows to projection displays. PDLCs consist of liquid crystal droplets dispersed in a solid polymer matrix. The micron size droplets are responsible for the unique behaviour of these materials: changing the orientation of the liquid crystal molecules inside the droplets with an electric field results in a variation of the transmitted light [1].

PDLCs are typically prepared by means of either encapsulation [2] (an earlier process) or phase separation [3]. However, there are many problems arising from these methods. Particularly, intermixing between the liquid crystal and the surrounding polymer is often encountered in the latter process, as full phase separation does not come to completion [4]. This intermixing process is detrimental to the electro-optic properties of the device. One way to overcome this difficulty consists in preparing the binding polymer matrix separately from the liquid crystal. This is achieved by a two-step process: first the manufacture of a porous polymer film which is then impregnated with liquid crystal. The various steps of the processing to obtain the polymer network, and the experimental details, are given in the next section. Results of the electro-optic study are discussed and semi-quantitatively interpreted in § 3.

2. Experimental

The method used to prepare the porous polymer film is based on that used in lithium ion plastic batteries technology (Bell Communications Research, Inc.) to manufacture battery separator [5]. A commercially available PVDF–HFP copolymer (polyvinylidene difluoride–hexafluoropropylene) was mixed together with silica and dibutyl phthalate (DBP) as a plasticizer (responsible for the eventual porous structure) in acetone. The mixture was then placed in an oven for 30 min at 55°C in order to dissolve the polymer and then left under stirring for 48 h to ensure a homogeneous mixture. A drop was taken from this solution, spread over a conductive, transparent electrode using a 'bar-coater' and allowed to dry, giving a DBP plasticized PVDF–HFP film. A porous polymer matrix was obtained after extraction of the DBP by three washings with diethyl ether. Differential scanning calorimetry analysis showed that there is no significant amount of DBP remaining in the polymer binder after ether extraction. This process results in an open porosity polymer film. Having made the porous polymer film, a cell was constructed by simply assembling another conductive transparent electrode onto the first one. The thickness of the film was about 10 μm.

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The liquid crystal mixture E7 (Merck Ltd, UK), which is nematic between − 60°C and +61°C, was introduced into the cell as follows. The cell was placed in a small beaker together with a few drops of E7. The beaker was placed in a vacuum vessel which was pre-heated to 120°C (to lower the viscosity of the liquid crystal), and then sealed and evacuated. Once the vacuum had been formed, the liquid crystal was forced into the cell by capillarity: while maintaining the vacuum, the liquid crystal front was observed to rise to the uppermost side of the cell. Thus, the filling of the entire porous matrix was achieved (taking usually a few minutes), and air was then slowly bled into the vessel.

By varying the DBP content of the initial mixture, it was possible to obtain films with different E7 contents. Since DBP and E7 have very similar densities, it was found by weight measurements that a film would absorb as much E7 as DBP initially present in the film. Here, the silica filler acts as a reinforcing agent of the porous polymer film, thereafter avoiding its collapse while being washed with ether.

Electro-optic properties of these PDLC films were measured by the experimental device displayed in figure 1. A light source is placed in front of a lens so that an emergent light beam propagates normal to the plane of the PDLC film. The transmitted light is then focused by a lens onto a photodetector. The photodetector signal is amplified and recorded by a digital oscilloscope. A 1 kHz square voltage was applied to the PDLC film. The experiments were performed with electric field amplitudes ranging from 4 to 30 V µm^{-1}. The transmitted light intensity and the response times (both rise and decay times) were measured. The light intensity was normalized to the light transmission through a cell made simply of two conductive electrodes. Rise and decay times are defined as the time interval between obtaining 10% to 90% or 90% to 10%, respectively, of the total transmission change between the ‘on’ and ‘off’ states.

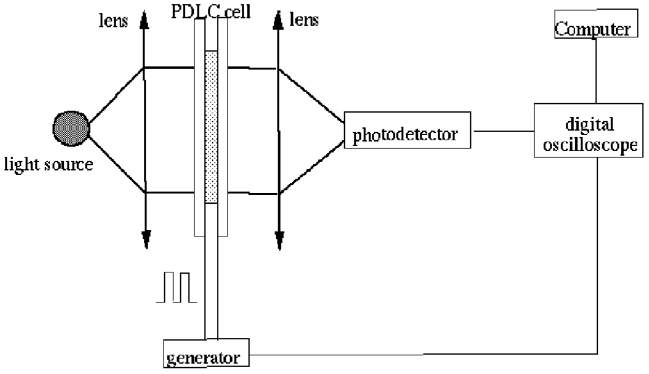

Figure 1. Experimental set-up used to study the electro-optic properties of PDLC films.

3. Results and discussion

The graph in figure 2 shows the light transmission versus the amplitude of the applied field for PDLC films of various compositions. The transmitted light intensity increases with increasing voltage. At zero field, as normal for PDLC films, the light entering the cell encounters media of various refractive index and, as the liquid crystal droplets have a micron size, scattering occurs. As the voltage across the cell increases, the liquid crystal director reorients parallel to the field (E7 has a positive dielectric anisotropy), and then, if the ordinary refractive index of the nematic liquid crystal n_o matches that of the matrix, no scattering occurs [6].

However, unlike conventional PDLCs, i.e. with closed porosity, a continuous rise in the transmission with increasing voltage is noticed. A threshold is usually observed in PDLCs; this defines the required voltage to switch the PDLC film from the off state to the on state. In the case of a bipolar configuration of an elongated droplet, the threshold voltage E_{th} has been found to vary according to the following equation [7]:

$$E_{th} = \frac{1}{a}\left[\frac{K(l^2 - 1)}{\varepsilon_o \Delta\varepsilon}\right]^{1/2} \tag{1}$$

where $l = a/b$ is the aspect ratio of an elliptically elongated droplet of major semi-axis a and minor semi-axis b, $\Delta\varepsilon = \varepsilon_{\|} - \varepsilon_{\perp}$ is the dielectric anisotropy of the liquid crystal and K its effective (mostly bend) elastic constant. As l and a can be related respectively to the shape and overall size of the droplet, equation (1) illustrates their dominant effect on E_{th}.

With the process detailed above, the open porosity is achieved, as illustrated by the scanning electron micrograph of figure 3. This structure with interconnected

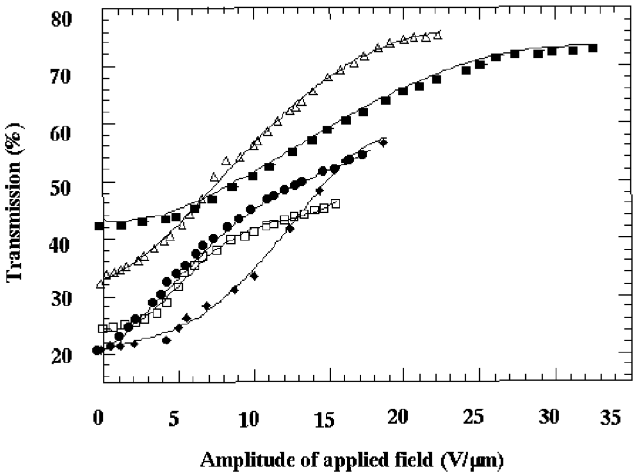

Figure 2. Light transmission versus the amplitude of applied electric field for PDLC films of various compositions. Copolymer : silica : DBP (wt %): 17 : 17 : 66 (■); 17 : 11 : 72 (□); 18 : 7 : 75 (●); 19 : 4 : 77 (◆); 20 : 0 : 80 (△).

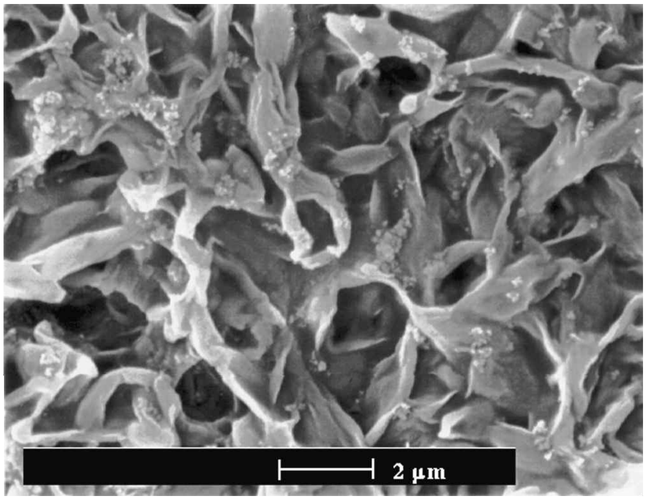

Figure 3. Scanning electron micrograph of an ether-extracted PDLC film with the initial composition copolymer : Silica : DBP (wt %) as 19 : 5 : 76.

pores results in cavities of non uniform shape, having a size in the micrometer range. The shape of a cavity is then defined by a distribution of the radii of curvature, resulting in a distribution of the threshold voltages and consequently to a continuous increase in the transmitted light with increasing voltage.

Figure 4 presents the rise times versus the amplitude of the applied field for PDLC films of various compositions. These rise times are shorter than those usually encountered in conventional PDLC films, but it should be kept in mind that the applied field amplitudes used to measure them are stronger (up to 30 V µm^{-1}). As expected, the rise times decrease with increasing drive voltage. More specifically, if we consider a single elongated droplet whose main axis is at an angle λ with respect to the applied electric field, the rise time is given by [7]:

$$\tau_{\mathrm{on}}^{-1} = \frac{1}{\gamma}\left[\varepsilon_0 \Delta\varepsilon E^2 + \cos(2\lambda)\frac{K(l^2-1)}{a^2}\right] \tag{2}$$

where γ is the rotational viscosity coefficient and E is the effective field applied to the droplet.

For an isolated spherical droplet of dielectric constant ε_2 embedded in a continuous medium of dielectric constant, ε_1, in a uniform electric field, E_1, the field E_2 inside the droplet is given by [8]:

$$E_2 = E_1 \frac{3\varepsilon_1}{2\varepsilon_1 + \varepsilon_2}. \tag{3}$$

For our PDLC films, $\varepsilon_1 = 3.7$ and $\varepsilon_{2\parallel} = 19$ (in the on state) at 1 kHz. Consequently, the effective field in the droplet would be about 2.4 times less than the field applied to the film. Taking into account the values of $\gamma = 3.9 \times 10^{-2}$ kg m^{-1} s^{-1} and $\Delta\varepsilon = 13.8$ for E7 (data from Merck), relation (2) would fit our experimental data for an effective field about six times less than the applied electric field, which means that the dielectric mismatch between the droplet and the polymer matrix cannot fully explain our data. Very probably, the non-negligible electrical conductivity of the liquid crystal also contributes to the drop in the applied electric field.

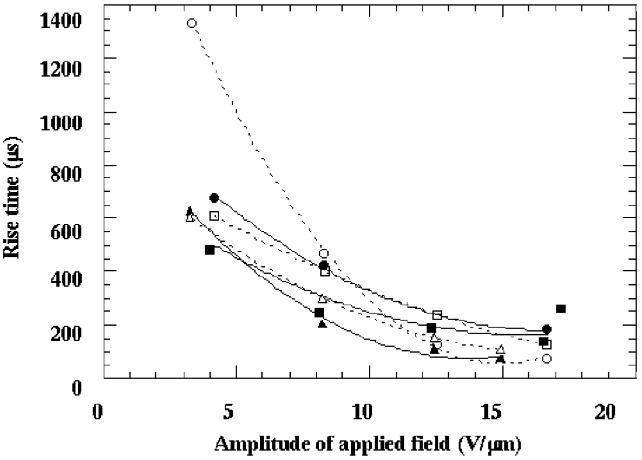

Figure 4. Rise time versus the amplitude of applied electric field for films of various compositions. Copolymer : silica : DBP (wt %): 17 : 17 : 66 (■); 17 : 14 : 69 (□); 17 : 11 : 72 (●); 18 : 9 : 73 (○); 18 : 7 : 75 (▲); 19 : 4 : 77 (△). Lines are guides to the eye.

When the shapes and orientations of the cavities are at random in the PDLC, the calculation of the effective average rise time should include their radius of curvature and orientation distribution functions within the whole sample. However, equation (2) indicates that for λ values close to $\pi/2$, a switching of the droplet occurs when τ_{on}^{-1} cancels, i.e. for a threshold field which is given by equation (1). On the contrary, for small λ values, no real switching takes place, and a continuous variation of the transmission is expected. In addition, the plot of τ_{on}^{-1} versus E^2 should give a straight line with a positive inverse rise time at zero field. This is actually observed in our samples (figure 5). This result confirms that the orientational distribution function of our cavities is not isotropic, but displays some maxima at small λ values, i.e. a significant number of the cavities are oriented in such a way that the nematic liquid crystal director is already almost perpendicular to the film plane, prior to the application of the electric field. This could also explain the rather high values of the transmission at zero field.

Figure 6 presents the decay times versus the amplitude of the applied field for the same PDLC films. These decay times would be expected to remain approximately constant, but the graph shows a noticeable variation with increasing voltage. Unlike the rise times which mainly depend on the amplitude of the drive voltage, the decay times are mostly influenced by the droplet

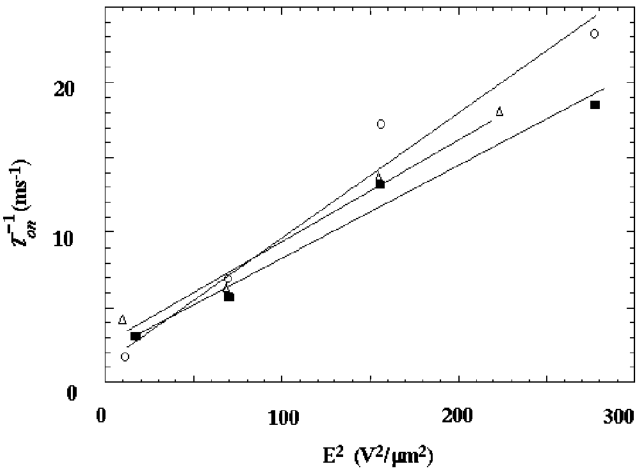

Figure 5. Variation of inverse rise time versus the amplitude squared of applied electric field for PDLC films of various compositions. Copolymer : silica : DBP (wt %): 17 : 14 : 69 (■); 18 : 9 : 73 (○); 19 : 4 : 77 (△).

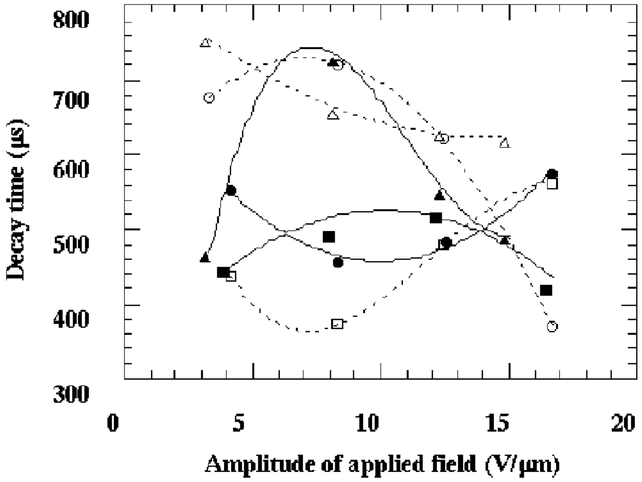

Figure 6. Decay time versus the amplitude of applied electric field for films of various compositions. Copolymer : silica : DBP (wt %): 17 : 17 : 66 (■); 17 : 14 : 69 (□); 17 : 11 : 72 (●); 18 : 9 : 73 (○); 18 : 7 : 75 (▲); 19 : 4 : 77 (△). Lines are guides to the eye.

shape and size. For $\lambda = \pi/2$, it has been shown [7] that:

$$\tau_{\rm off} = \frac{\gamma a^2}{K(l^2 - 1)}. \qquad (4)$$

The scattering of the data in figure 6 is probably due to a variation in the distribution of radii of curvature from sample to sample that results in a distribution of the decay times. In addition, it should be stressed that, in conventional analyses, the anchoring energy of the liquid crystal at the polymer surface is not taken into account for the calculation of the threshold electric field and the response times. Such anchoring effects could also contribute to the scattering of the decay times.

According to the above analysis, film morphology is mostly responsible for the electro-optic properties of our PDLC films, as already known for conventional closed porosity PDLCs. This morphology can be modified either during film processing, or at a later stage by stretching the free standing film. Previous work [7] on the shearing of PDLC cells upon heating have shown that a shear stress may result in a change in the orientation distribution of the cavities, in such a way that their mean axis would reorient along the shearing direction, i.e. for our films, from a direction almost perpendicular to the film plane to a direction almost parallel to it. Electro-optic properties would then be expected to comply better with the desired performances. This possibility is presently being investigated.

4. Conclusion

Switchable liquid crystal/polymer network devices have been made using a novel process. These devices have significant advantages over conventional PDLCs such as easy processing and no risk of intermixing between the liquid crystal and the polymer. The response times are already promising for applications such as light shutters.

The electro-optic properties of our open porosity PDLC films are satisfactorily explained on the basis of the proposed models already established for closed porosity PDLCs: accordingly, from the present data, it is obvious that the geometrical anisotropy of the liquid crystal cavities plays a major role in controlling the electro-optic properties of the PDLC films. Current experiments are in progress to study further the impact of stretching on the electro-optic properties.

In addition, the film morphology can be controlled by the process of forming the polymer matrix. Such improvements are under way.

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