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Haze and opacity control in polymer dispersed liquid crystal (PDLC) films with phase separation method

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Polymer dispersed liquid crystals (PDLCs) are materials composed of liquid crystal microdroplets dispersed in a polymer matrix. Their electro-optic properties make them useful for applications as large-area electrically switchable architectural windows (smart windows). For these applications, the key parameters of performance are the haze (both normal and off-axis) and the opacity. In the present work we show how it is possible to prepare a high performance smart window by controlling the haze and opacity of PDLC films using the polymer induced phase separation (PIPS) method.

1. Introduction

PDLC films, which are composed of liquid crystal microdroplets dispersed in a polymer matrix, have been the subject of much academic and industrial research in the past decade [1]. These electro-optical systems can be switched by applying an electric field from a scattering field-off state to a transparent field-on state. This property can be used to construct devices with electrically modulated light and visual transmission for applications in large-area architectural glazing [2]. A good product for these applications should have high opacity in the field-off state and high transparency over a wide viewing angle (low haze) in the field-on state.

There are essentially two technologies used to prepare PDLC films with liquid crystal microdroplet dispersions, namely micro-emulsion and phase separation methods. In the former method (NCAP) [3], an emulsion of polymer, solvent and liquid crystal is formed by mechanical stirring. The emulsion is then coated on a transparent conductive film substrate—usually, indium tin oxide (ITO)-coated PET—and, after drying, it is laminated with another conductive film substrate to give the final PDLC film product. In the phase separation method (PS) [4], a homogeneous solution of prepolymer or polymer, and liquid crystal is coated *in situ* and laminated between two ITO-PET film substrates. The separation of the liquid crystal microdroplets occurs during the gelification and curing of the prepolymer. The rate of polymer hardening, as well as other physical parameters, e.g. viscosity and solubility of the liquid crystal in the polymer, influence the morphology and electro-optics of the PDLC material.

The advantage of the PS method with respect to that of NCAP is that with the PS method it is possible to control the microdroplet morphology [2, 5–7] and consequently the electro-optical performance of the films during the fabrication process of the PDLC, by appropriate optimization of material and processing parameters before and during curing and phase separation. These criteria make the PS method very versatile [8]. Another advantage, which applies to the PS-PIPS method studied here, is the rapid processing without any solvent. On the industrial scale, the UV-PIPS method is faster and easier than the NCAP method for roll-to-roll processing of PDLC films, whereas, the lengthy water evaporation and complete drying process of the unlaminated PDLC layer requires much more time. Furthermore, residual entrapped solvent could decrease the resistivity of the final product [8].

The disadvantage of the PS versus NCAP method is that, due to the nature of the *in situ* microdroplet formation, a significant amount of liquid crystal always remains dissolved (plasticized) in the matrix and does not contribute to the electro-optical behaviour of the liquid crystal microdroplets. This plasticizing effect of the liquid crystal results in a number of unwanted phenomena, e.g. index mismatching and reduction in the off-state scattering, as well as reduction in the mechanical properties of the PDLC film. In the NCAP approach it is possible to select the polymer in order to avoid the absorption of LC in the matrix (e.g. polyvinyl alcohol) [8].

In the literature, there are many reports which address the theory of light scattering in PDLC films, both in the field-off and field-on states. These studies have established the qualitative dependence of the haze and opacity on the index mismatching, LC birefringence and morphology of the PDLC films [2, 4–9].

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In the present work, by taking these correlations into account, we demonstrate how it is possible to find a quantitative rule regarding the material and process parameters in order to produce a high quality PDLC film, i.e. high opacity and low haze, utilizing the phase separation technology.

In the published literature, there is already an approach to producing a haze-free PDLC film by the phase separation method, where an aligned side group liquid crystal polymer is utilized as matrix [10, 11]. In this case, when the liquid crystal droplets were aligned in the presence of an electric field, the PDLC film appeared transparent at all viewing angles in on-state. Nevertheless, due to incomplete phase separation and the impracticality of aligning the polymer matrix during the curing and phase separation processes, the technological development of haze-free PDLC windows by this PS approach has remained far from an industrial application. In the literature, there is also reported the preparation of PDLC films by the NCAP method; the films have low-haze in the field-on state and a large scattering (opacity) in the field-off state [12]. The present study has demonstrated that, in order to obtain a high quality PDLC film for architectural applications, there are specific rules concerning the liquid crystal birefringence and the refractive indices of the starting materials, which could lead to improved performance of the PDLC film. In particular, the index matching condition between the matrix and the ordinary refractive index of the LC should occur at an angle between 15° and 30°, the index mismatching value must not exceed 0·01 and the LC birefringence must lie between 0·08 and 0·12.

In this work, we present a method for preparation of a low-haze and high-opacity PDLC film using the UV-curing phase separation technique (PIPS) [13]. In particular, we report on the quantitative relation between the haze and opacity of PDLC films and on the parameters which influence them, i.e. the index mismatching and Δn. In addition, we also present a correlation between the off-axis haze and opacity in the PDLC films studied, both of which are influenced by Δn of the liquid crystal microdroplets. We will see that it is not easy to prepare a PDLC film which satisfies the requirements of both low off-axis haze and high opacity, because preparation of a PDLC with low off-axis haze is achieved by using a low Δn liquid crystal, while the lower the Δn of the liquid crystal, the lower is the opacity of the PDLC film. We will give the values of the material and process parameters which represent a good compromise for the preparation of high performance smart windows.

Finally, we will present a brief comparison of the rules for preparation of a high quality PDLC film using the NCAP and phase separation methods. We will see that, while in both methods the dependence of haze and opacity on index mismatching ($n_o - n_m$) and Δn of the liquid crystal are qualitatively the same, they are quantitatively different due to the effect of plasticization in the PS method and to differences in the morphologies of the PDLC films obtained with the two technologies.

1.1. *Field-on state light scattering (haze)*

The phenomenon of haze in the field-on state of a PDLC arises from the residual refractive index difference between the polymer matrix and the aligned liquid crystal in the droplets. It is necessary to distinguish between a ‘normal haze’, when the sample is looked at in a direction perpendicular to the film plane, and an ‘off-axis haze’ at other viewing angles. These values depend on various PDLC material and processing parameters.

According to the anomalous diffraction approach (ADA) [9], the residual light scattering for normal light incidence (normal haze) is related to the difference between the ordinary refractive index of the LC, n_o, and the matrix refractive index n_m. For light incidence different from the normal, the scattering depends on both the ordinary (n_o) and extraordinary (n_e) refractive indices of the LC, and consequently a strong influence on the residual light scattering (off-axis haze) of the LC birefringence, Δn, is expected.

The equations of light scattering in the ADA approach indicate that the light scattering of PDLC films is also related to the geometry of the liquid crystal droplets. As will be seen later, we fixed the morphology of all PDLC films studied by proper selection of the process parameters, so that the dependence of haze on the morphology becomes negligible. Consequently, the normal haze in the PDLC films made by the phase separation method and studied here is essentially related to the difference between the ordinary refractive index of the LC (n_o) and the polymer matrix refractive index (n_m). In PDLC film samples, where $n_o \approx n_m$, the off-axis haze largely depends on the optical birefringence (Δn) of the LC utilized in the formulation.

1.2. *Field-off state light scattering (opacity)*

The PDLC films studied in this work, for both the PS and NCAP methods, have microdroplets with a bipolar configuration [14]. In this case, the field-off light scattering strongly depends on the morphology, i.e. the size, number density and shape of the liquid crystal microdroplets. Although the maximum field-off light scattering in the ADA equations depends not only on the sizes of the LC microdoplets, but also on the LC birefringence, we have found that in our system droplet diameters in the 2–3 μm range assure a good field-off light scattering over the range of Δn studied here. For this reason, we processed the PDLC films under conditions (i.e. UV intensity and curing temperature) that provide liquid crystal microdroplet diameters within the above mentioned range [7]. Consequently, for different PDLC samples with the same microdroplet morphology, the opacity can be directly correlated with the optical birefringence (Δn) of the liquid crystal, whereby a higher Δn will result in a larger value of opacity of the PDLC film.

In the application of PDLC for architectural windows, the opacity is evaluated by measuring the percentage of the off-state transmittance using a white light source and a photopic detector (which simulates the behaviour of human eyes). According to the known effect of 'red-bleedthrough' [12], it is presumably the case that systems with lower LC birefringence can be affected by this phenomenon when small microdroplet sizes are considered. In this phenomenon, the reduction of light scattering at long wavelength depends on the product of the LC birefringence and the droplet size, i.e. $<R>\Delta n$. For large values of $<R>\Delta n$, the scattering is independent of the wavelength. While the present study does not address the dependence of opacity on the wavelength, investigations are in progress in our laboratories and will be the subject of a future report.

2. Experimental

2.1. *Sample preparation*

The PDLC samples reported in this work, were prepared with UV-curable (UV-PIPS) processing from homogeneous mixtures of urethane-based prepolymers and nematic liquid crystal mixtures. The liquid crystal mixtures were commercial nematic mixtures, i.e. BL036 and E43 from Merck; TN0403, TN0623, TN10396 and TN8009 from Rolic. The prepolymers used were commercial UV-curable mixtures: NOA65 (Norland) and CN934D60 (Sartomer). All materials were used without further purification. The refractive indices of the cured polymers are 1·524 (NOA65) and 1·505 (CN934D60). During the processing of PDLC films, we introduced small percentages (<5 % w/w) of acrylic acid ($n=1{\cdot}455$) to improve the index-matching of the polymer matrix and the liquid crystal. By changing the relative quantities of prepolymers and acrylic acid it was possible to modify the refractive index of the matrix within the 1·500–1·524 range. The optical properties of the liquid crystals selected cover a range of $\Delta n=0{\cdot}135-0{\cdot}267$ and are reported in the table.

The PDLC film samples with dimensions of about 20 cm^2 were prepared between the ITO-coated PET films with an *in situ* coating and laminating technique, using a specially designed laboratory film coater. Uniformity of the PDLC layer was achieved by using mylar microsphere spacers of 15 μm. All PDLC samples were prepared by curing under a high pressure mercury UV lamp at a curing temperature of 30°C; UV intensity of 20 mW cm^{-2} and UV energy of 2000 mJ cm^{-2}.

2.2. *Haze and opacity measurements*

The haze of the PDLC films was measured with a Macam LSO-4514 haze-meter (figure 1). This instrument is composed of a white light source S (20 W, tungsten halogen lamp; M35 type), a collimator C, a PDLC sample holder H, an integrating sphere and a photopic detector SI (Macam SD101L). The PDLC samples were addressed by a wavefunction generator through an amplifier. The haze for all samples was measured using a square wave electric signal ($\nu=50$ Hz, $V=100$ V). The instrument allows measurement of both normal haze [figure 1 (*a*)] and off-axis haze [figure 1 (*b*)]. In both cases, the haze was calculated measuring the transmitted light scattered more than 2·5° from the direction of incidence with respect to the total transmitted light (ASTM $D=1003$). We chose 30° as the standard angle for measurement of the off-axis. The values of haze were calculated according to the relation:

$$\%\ \mathrm{Haze}=100\times\frac{I_s}{I_s+I_r} \qquad (1)$$

where I_s is the intensity of the light transmitted at more than 2·5° and I_r is the intensity of light transmitted at less than 2·5° from the direction of incidence.

The opacity of PDLC samples was measured with the same photometer as in figure 1, by measuring the field-off transmittance at collection angles less than 1° from the axis of incident light, according to the relation:

$$\%\ \mathrm{Transmittance}=100\times\frac{I_s}{I_i} \qquad (2)$$

where I_i is the intensity of the incident light. The lower the transmittance, the higher the opacity of the PDLC samples.

Table. Ordinary refractive indices and birefringence values of the liquid crystals used.

Parameter	TN8009 (RLC)	TN10396 (RLC)	TN0623 (RLC)	E43 (Merck)	TN0403 (RLC)	BL036 (Merck)
n_o	1·497	1·507	1·507	1·520	1·524	1·527
Δn	0·135	0·163	0·198	0·250	0·258	0·267

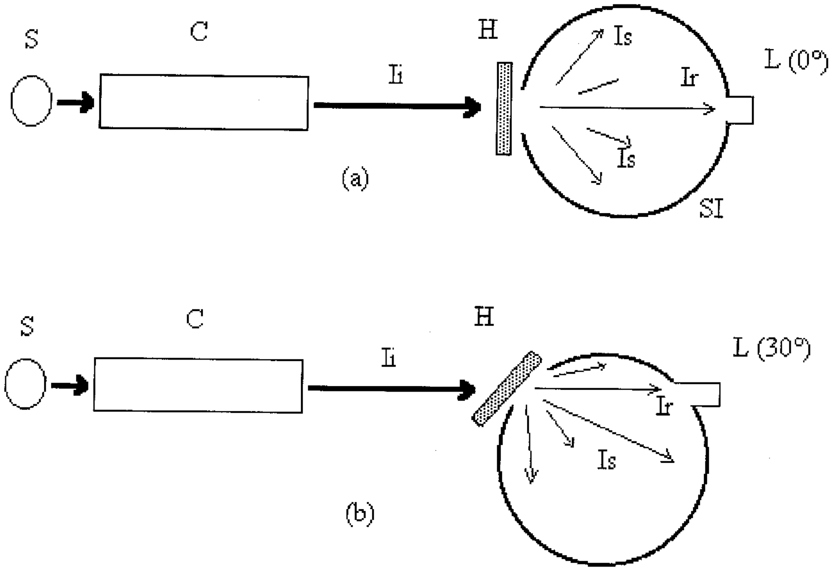

Figure 1. Schematic diagram of the set-up for haze and transmittance measurement: (*a*) normal incidence (haze and transmittance at 0°); (*b*) off-axis incidence (haze at 30°).

3. Results and discussion

3.1. *Normal haze*

We studied the dependence of normal haze on the index mismatching and established a useful rule for selection of the starting materials for PDLC formulation. Consequently, we measured the normal haze of PDLC film samples with different materials and with the same morphology, in order to establish the effect of index mismatching on haze. As explained in the introduction, in the phase separation method it is possible to control the morphology of the liquid crystal droplets by changing some process parameters; in our system, these parameters are UV intensity and curing temperature [7]. We have selected for each sample those process parameters that assure that the effect of morphology does not contribute to the experimental results.

In the evaluation of index mismatching, it must be taken into account that, in the phase separation method a significant amount of LC is always dissolved in the PDLC polymer matrix [8, 15]. The amount of dissolved or plasticized LC depends on the material and process used. In the system reported here, this amount is around 25% based on the combined weight of polymer and dissolved liquid crystal. In this respect, the matrix refractive index n_m, which cannot be measured directly, is not the same as that of the starting pure polymer n_p.

Considering the refractive indices of polymer and liquid crystal, and the solubility of the liquid crystal in the polymer, we can use an 'index mismatching function', $f(n_p, <n>, x)$, which can be written as follows:

$$f(n_p, <n>, x) = n_m - n_o. \qquad (3)$$

The matrix refractive index n_m of the PDLC can be calculated from the relation:

$$n_m = x<n> + (1-x)n_p \qquad (4)$$

where x is the fraction of the liquid crystal dissolved in the polymer matrix, $<n>$ is the average refractive index of the liquid crystal and n_p is the pure polymer refractive index.

Equation (3) can be used to estimate the refractive index mismatching of different polymers by assuming that a fraction of liquid crystal is always dissolved in the polymer matrix. For PDLC films prepared by the UV-curing process, usually the fraction of liquid crystal dissolved in the matrix lies between 20% and 30% by weight. In figure 2 we present an example of the mismatching function for the liquid crystal mixture TN0623 as a function of the polymer refractive index, where 20% and 30% by weight of liquid crystal is dissolved in the polymer matrix. The plot of figure 2 shows that, in order to have a complete index matching ($n_m - n_o = 0$) when 30% of liquid crystal is dissolved in the PDLC matrix, the selected polymer should have a refractive index n_p of 1·478.

According to the equations of the ADA approach, the mismatching function $f(n_p, <n>, x)$ is related to the normal haze of the PDLC films. In figure 3, we report experimental results for the normal haze versus the calculated refractive index mismatching ($n_m - n_o$) of the PDLC films with the same polymer and with four different liquid crystals (TN0403, E43, TN0623 and TN8009). In the calculation of index mismatching, the percentage of liquid crystal dissolved in the polymer matrix is assumed to be 25% in these PDLC films. As can be seen from figure 3, the experimentally measured

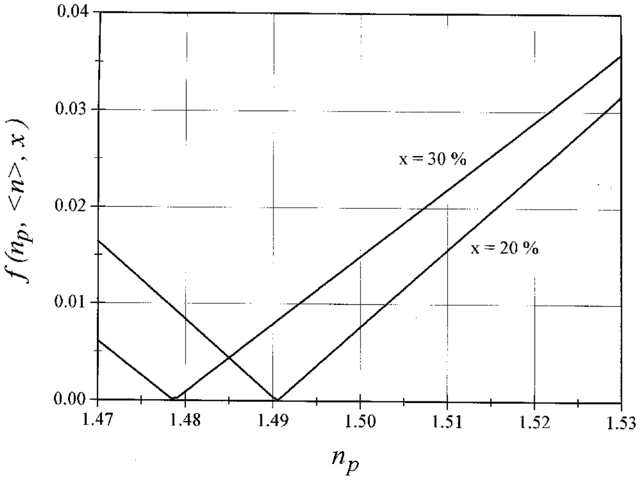

Figure 2. Variation of mismatching function of the liquid crystal TN0623 ($n_o = 1{\cdot}507 - \Delta n = 0{\cdot}198$) with the refractive index of the polymer (n_p) at 20 wt % and 30 wt % of dissolved liquid crystals.

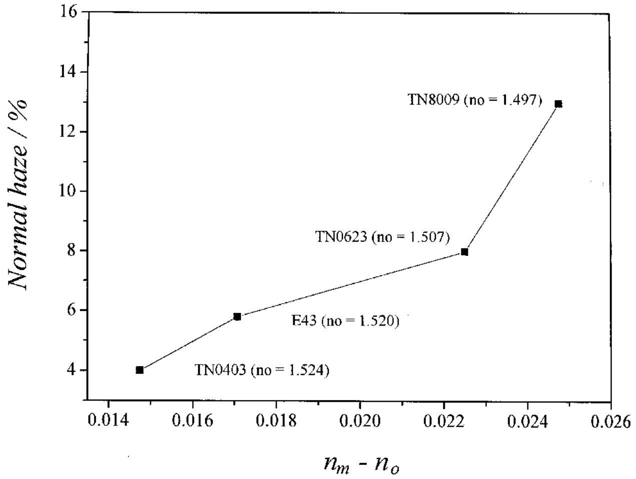

Figure 3. Normal haze of PDLC versus refractive index mismatching ($n_m - n_o$).

values of normal haze are correlated with their calculated index mismatching values. As expected from theory, the smaller the refractive index mismatching, the smaller the normal haze of PDLC samples. In particular, an index mismatching value smaller than 0·017 gives a normal haze smaller than 6 %. This value of normal haze is usually considered as the maximum tolerable target value for PDLC in architectural window applications. It must be noted that the lowest value of normal haze which can be theoretically achieved in this system could not be smaller than 2–3 %, because the background haze of the ITO-PET substrates and the plasticized matrix is usually within this range.

The results for normal haze obtained here are qualitatively in agreement with those found with the NCAP technology [12]. In the NCAP method it has been demonstrated that higher index mismatching value leads to a higher normal haze. In particular, the authors indicate that the normal haze reaches an unacceptable value when the difference between n_m and n_o is greater than about 0·01. The difference between the acceptable mismatching limits with the PS (0·017) and the NCAP (0·01) methods arises, presumably, from the differences in their morphologies and plasticization level, as well as from differences in the background haze of the PET-ITO and polymer matrix substrates. The morphologies of PDLC films obtained by the PS and NCAP methods will be shown in the section on opacity.

3.2. *Off-axis haze*

To study the behaviour of off-axis haze, we prepared PDLC film samples with an index mismatching value of about 0·014, through an appropriate selection of the starting materials, in order to achieve the same normal haze value of approximately 4 %. Also in this case, the morphology of the liquid crystal droplets was fixed in all samples in order to eliminate this contribution to haze.

In figure 4, we present the experimental values of off-axis haze (at 30°) versus Δn for a series of PDLC samples involving different liquid crystal mixtures. As predicted by ADA theory, the plot of figure 4 indicates that Δn of the liquid crystal is directly correlated with the off-axis haze. In particular, if Δn is lower than 0·18 the off-axis haze is below 10 %, a range acceptable for architectural application of PDLC films. In the NCAP method [12], the acceptable off-axis haze value can be obtained by keeping $\Delta n < 0{\cdot}12$ and by selecting materials to provide the index matching condition at non-zero angle,

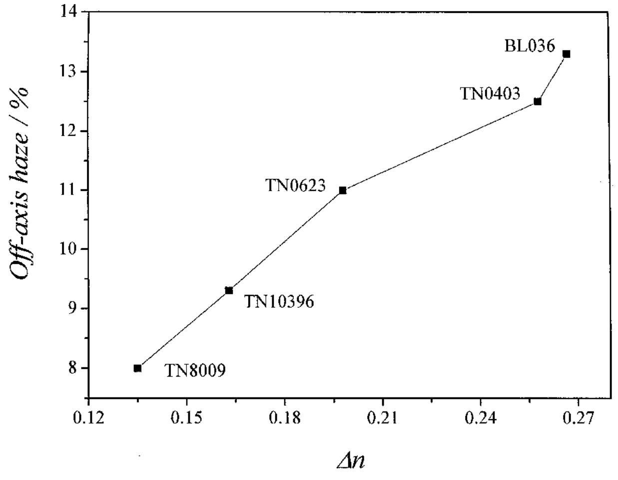

Figure 4. Off-axis haze of PDLC samples versus birefringence (Δn) of the liquid crystals.

preferably between 15° and 30°. Our strategy to obtain low haze PDLC films is different from that utilized for NCAP, because we preferred to match the refractive indices at about 0° to obtain a very low normal haze, reducing the Δn of LC to decrease the off-axis haze. Consequently, the quantitative difference in the Δn limit between the PS (0·18) and NCAP (0·12) methods can be attributed to different index matching conditions, as well as to different LC droplet morphologies. We will see in the next section that in PDLC films made by the PS method the droplet shape gives a lower off-state light scattering than that in NCAP; thus a PDLC film made by the PS method is more transparent if the LC Δn is equal to 0·12.

3.3. *Opacity*

In order to achieve high performance PDLC films, it must be taken into account that the birefringence Δn of the liquid crystal not only influences the off-axis haze, but also contributes to the opacity of the PDLC films. To present the behaviour of the opacity with respect to the liquid crystal birefringence, we report in figure 5 the field-off state light transmission (T-off) versus the Δn of the liquid crystals for the same samples presented in figure 4. The plot of figure 5 indicates that, if Δn is lower than 0·16 the off-state transmittance is higher than 2 % and the film is not sufficiently opaque for window applications.

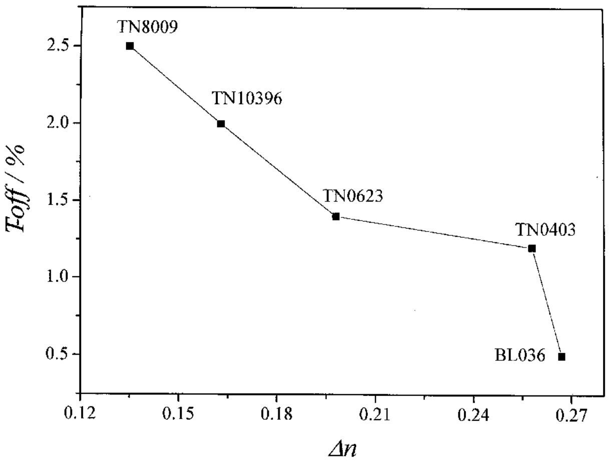

Figure 5. Off-state transmittance (opacity) of PDLC versus birefringence (Δn) of the liquid crystals.

A comparison of these results with those related to off-axis haze (figure 4), indicates that, in the phase separation technique studied here, the optimum birefringence range of the liquid crystal should be within $\Delta n = 0{\cdot}16 - 0{\cdot}18$, in order to obtain a film with a high field-on state transparency at a wide angle of view, and an acceptable field-off state opacity. This optimum birefringence range is different from that in PDLC films produced by the NCAP method, which requires a $\Delta n = 0{\cdot}08 - 0{\cdot}12$, in order to obtain an acceptable low off-axis haze and a high off-state light scattering. Consequently, in the phase separation method, the liquid crystal birefringence has to be higher than that in the NCAP method, in order to have comparable haze and opacity values. The reason for this difference arises mainly from the differences in the microdroplet morphologies of the PDLC films prepared with the two techniques.

In figure 6, we present examples of the microdroplet morphologies of PDLC films obtained with the phase separation and NCAP methods as obtained by scanning electron microscopy (SEM) analysis. In the phase separation technique [figure 6 (*a*)], the size of the droplets is usually uniform and their shapes are spherical, with a three-dimensional random orientation of the symmetry axis; in the NCAP method [figure 6 (*b*)], the

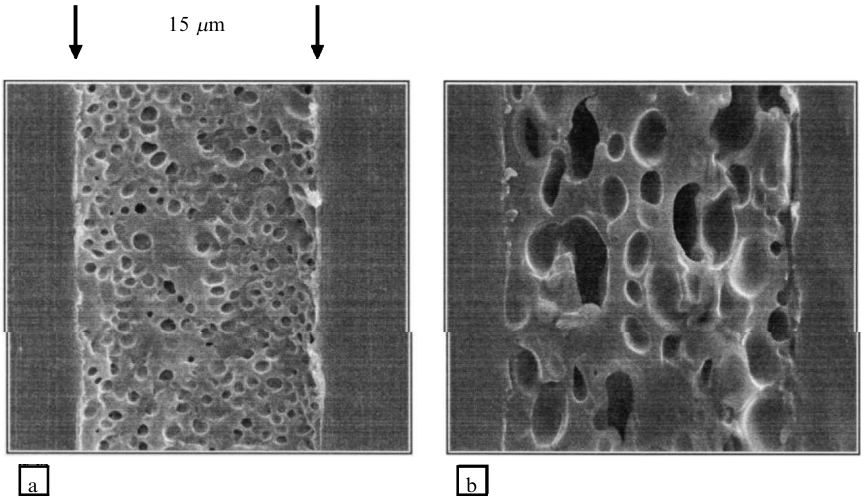

Figure 6. SEM micrographs of PDLC obtained by (*a*) phase separation method (PIPS) and (*b*) micro-emulsion method (NCAP).

liquid crystal droplets are non-uniform in size, having elongated shapes with the symmetry axis aligned in the direction of the film plane. The nature of the morphology in the phase separation PDLC leads to a reduction in the field-off state scattering and, hence, a reduction in opacity of the PDLC films. In fact, samples of PDLC prepared by the PS method having about the same droplet size and film thickness as that in NCAP samples and, using the same LC birefringence, are quite transparent. This behaviour has been previously observed by Vaz and Montgomery [16]. They found that the field-off scattering is larger when the nematic director lies parallel to the film plane rather than when it has a three-dimensional random orientation. Consequently, in order to achieve the same degree of opacity with the phase separation and NCAP methods, in the former method the liquid crystal should have a higher birefringence and the dimensions of the droplets should be smaller than in the latter method, to increase the light scattering.

4. Conclusions

The preparation of high performance PDLC films for architectural applications using a phase separation method can be accomplished by controlling some material and process parameters. These are:

(1) In order to obtain films with an acceptable normal haze, the index mismatching between the refractive index of the matrix and the ordinary refractive index of the liquid crystal should not be higher than 0·017. It must be taken into account that the matrix refractive index is different from the polymer refractive index, because in the phase separation method at least 20% by weight of liquid crystal remains dissolved in the polymer, changing the refractive index of the cured matrix.

(2) In order to have low off-axis haze in the field-on condition while maintaining an acceptable opacity in the field-off state, the liquid crystal birefringence should be between 0·16 and 0·18.

The rules found here for obtaining high quality PDLC films involve the same material parameters (index mismatching and Δn) and are qualitatively the same as those indicated in the preparation of films by the NCAP method. The quantitative differences found in the suggested parameter values between the PS and NCAP methods arise mainly from the differences in the morphology of the PDLC samples and from the amount of LC dissolved in the polymer matrix.

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References

[1] Bouteiller, L., and Le Barny, P., 1996, *Liq. Cryst.*, **21,** 157.

[2] Doane, J. W., 1990, *Liquid Crystal Applications and Uses*, Vol. 1, edited by B. Bahadur (Singapore: World Scientific), Chap. 14.

[3] Fergason, J. L., 1985, SID 85 Digest, 68.

[4] Doane, J. W., Golemme, A., West, J. L., Whitehead, J. B. Jr, and Wu, B. G., 1988, *Mol. Cryst. liq. Cryst.*, **165,** 511.

[5] Smith, G. W., and Vaz, N. A., 1988, *Liq. Cryst.*, **3,** 543.

[6] West, J. L., 1988, *Mol. Cryst. liq. Cryst.*, **157,** 427.

[7] Smith, G. W., 1991, *Mol. Cryst. Liq. Cryst.*, **196,** 89.

[8] Drzaic, P. S., 1995, *Liquid Crystal Dispersion*, (Singapore: World Scientific).

[9] Zumer, S., 1988, *Phys. Rev.*, **37,** 4006.

[10] Doane, J. W., 1991, US Patent 4, 992, 204.

[11] Doane, J. W., West, J. L., Whitehead, J. Jr, and Fredley, D. S., 1990, *SID 90 Digest*, 224.

[12] Drzaic, P. S., Gonzales, A. M., and Konynenburg, P., 1994, *SPIE-Int. SOE*, **2175,** 148.

[13] Smith, G. W., 1990, *Mol. Cryst. Liq. Cryst.*, **180B,** 201.

[14] Crawford, R. O., Boyko, E. P., Wagner, B. G., Erdmann, J. H., Zumer, S., and Doane, J. W., 1991, *J. Appl. Phys.*, **69,** 6380.

[15] Nolan, P., Tillin, M., and Coates, D., *Liq. Cryst.*, 1993, **14,** 339.

[16] Vaz, N., and Montgomery, G. P., 1989, *J. Appl. Phys.*, **65,** 5043.