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P. Nolan[a]; M. Tillin[a]; D. Coates[a]
[a] Merck Ltd., Poole, Dorset, England

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High on-state clarity polymer dispersed liquid crystal films

by P. NOLAN*, M. TILLIN and D. COATES
Merck Ltd., West Quay Road, Poole, Dorset BH15 1HX, England

Results are presented which show that the on-state clarity of a UV cured polymer dispersed liquid crystal (PDLC) film depends on the refractive index of the final polymer in the PDLC film, the ordinary refractive index of the liquid crystal, the solubility of the liquid crystal in the prepolymer and the rate at which the film is cured. Liquid crystal mixtures for use in PDLC films are chosen such that the ordinary refractive index of the liquid crystal is equal to the refractive index of the polymer matrix. It has been shown previously that a large quantity of liquid crystal remains dissolved in the polymer matrix, thus increasing the mismatch between the refractive index of the polymer and the ordinary refractive index of the liquid crystal and therefore reducing the on-state clarity. For liquid crystal mixtures which have high solubility in the prepolymer (>60 per cent) the mismatch in the refractive indices can be very large and the on-state clarity of the resulting film can be very poor ($T_{on}<70$ per cent). Results are presented which show that it is possible to increase the on-state clarity of such films by increasing the rate at which these films cure. If the liquid crystal is less soluble in the prepolymer (<45 per cent), a PDLC film formed from such a liquid crystal/ prepolymer system often has very good on-state clarity ($T_{on}>75$ per cent) be it cured slowly or quickly. Results are also presented which show that in order to achieve a true measure of on-state clarity it is necessary to use a small collection angle ($<3°$) in the detecting optics. If larger collection angles are used, the photodetector collects light which is scattered out of the specular beam, thus leading to a false measure of on-state clarity.

1. Introduction

Polymer dispersed liquid crystal (PDLC) displays are promising new materials for projection displays and large area vision products [1]. They consist of micron sized droplets of nematic liquid crystal dispersed in a polymer matrix. They can be formed when a homogeneous isotropic solution of prepolymer and liquid crystal is exposed to UV light or heat, whereupon phase separation of the liquid crystal and the polymer occurs, resulting in an opaque scattering film.

In the 'off' state, the film appears cloudy due to the refractive index mismatch encountered by incident light at the liquid crystal /polymer interface. Light is refracted at the interface and repetitive refractions give rise to a highly scattering film.

On applying a voltage across the film, the liquid crystal molecules within the droplets align homeotropically. If the ordinary refractive index of the liquid crystal is matched to the refractive index of the polymer, the incoming light is no longer scattered and the film appears clear.

It has been shown previously that a significant amount of liquid crystal remains dissolved in the polymer matrix [2, 3]. It was found that the ordinary refractive index of the liquid crystal in the droplets is almost the same as that of the original liquid crystal mixture, but the refractive index of the polymer matrix can dramatically increase. This results in a reduction of the on-state clarity in the resulting PDLC film. This factor was considered during this work and it was found possible to produce very high on-state clarity PDLC films with low operating voltages when liquid crystal mixture, prepolymer and curing conditions were chosen carefully.

* Author for correspondence.

2. Materials and sample preparation

The liquid crystal mixtures used during this work were E7, BL012, BL036 and BL038 [4]. All four are high birefringence liquid crystal mixtures, but because E7 and BL012 have lower nematic to isotopic (N–I) transition temperatures they generally have a greater prepolymer solubility than BL036 and BL038. The physical properties of these liquid crystal mixtures are shown in table 1. The prepolymer used was Norland 65, the refractive index of which is 1·524 in the cured state. A homogeneous solution of E7 or BL012 and Norland 65 was prepared by mixing them together in a 3:2 mass ratio. A sample of this was then cured in a prefabricated indium tin oxide coated cell using a low pressure Xenon lamp (Heraeus Suntest 3 mW/cm^2) [5] for 20 min. A second sample was cured using a medium pressure Mercury lamp (Minicure 500 W/cm^2 [6, 7]. A homogeneous solution of BL036 or BL038 and Norland 65 mixed together in a 2:3 mass ratio was also used.

3. Electro-optic measurements

The equipment used for recording electro-optic data is depicted in figure 1. PDLC films were held in a temperature controlled cell holder on an electro-optic bench. The light source used was a tungsten halogen lamp. Light was focused on to a silicon photodiode using a short focal length lens. The collection angle was varied by using a variable aperture positioned between the sample and the lens. All measurements were automated and recorded using a digital computer.

Table 1. Physical properties of high Δn liquid crystal mixtures.

	E7	BL036	BL012	BL038
N–I	61°C	95°C	70°C	100°C
Δn	0·2246	0·2670	0·2616	0·2720
n_0	1·5216	1·5270	1·5367	1·5270
$\Delta\epsilon$	13·8	17·0	15·7	16·9
Visc.(+20°C)	39 cSt	67 cSt	51 cSt	72 cSt

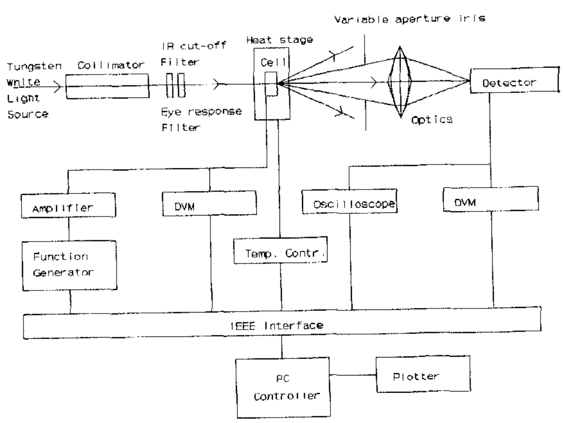

Figure 1. Electro-optic measurement system used during this work.

4. Parameters affecting on-state clarity

4.1. *Cure intensity*

It was found possible to produce high clarity ($T_{on} > 80$ per cent) PDLC films when films were cured quickly, independent of which liquid crystal mixture was used. The on-state clarity of such films was reduced when cured slowly. Table 2 shows the electro-optic data recorded for samples of BL036 and E7 in Norland 65 cured in the Suntest ($3\,mW/cm^2$) and in the Minicure ($500\,mW/cm^2$). The on-state transmission decreased for both samples when cured in the Suntest compared to when cured in the Minicure. This suggests that more liquid crystal remains dissolved in the polymer matrix when a PDLC film is cured slowly. This has the effect of increasing the mismatch between the ordinary refractive index of the liquid crystal in the droplets and the refractive index of the polymer matrix and thus reducing the on-state transmission.

DSC studies carried out on pure Norland 65 showed that it had a $T_g = 17°C$ when cured. Similar studies carried out on a PDLC film containing Norland 65/BL036 cured in the Suntest showed it had a $T_g = -51°C$ whereas a PDLC film containing Norland 65/BL036 cured in the Minicure had a $T_g = -20°C$. These results can be attributed to more liquid crystal remaining dissolved in the film cured in the Suntest than in the film cured in the Minicure. The dissolved liquid crystal acts as a plasticiser in the polymer matrix, thus reducing the T_g of the polymer matrix [2].

The PDLC films which were initially cured under the Suntest were subsequently further irradiated using the Minicure in order to determine if further curing would force the liquid crystal dissolved in the polymer matrix into the droplets, but electro-optic measurements carried out on these films showed no evidence of this occurring.

4.2. *Liquid crystal solubility*

It can be seen from table 2 that there is a significantly greater decrease in on-state transmission for the E7 film than for the BL036 film when cured in the Suntest, compared to when cured in the Minicure. The solubility of E7 in Norland 65 prepolymer at room temperature is typically 65 per cent whereas the solubility of BL036 in Norland 65 prepolymer at room temperature is only 45 per cent. The on-state transmission data presented in table 2 suggests that a greater amount of E7 remains dissolved in the polymer matrix than BL036 when the film is cured slowly. This seems

Table 2. Electro-optic data for films cured under different lamps.

Cell No.	Composition	Cured	T_{MAX}	V_{SAT}
(1)	Norland/BL036	Minicure	81·7%	119·5 V
(2)	Norland/BL036	Suntest	78·7%	32·4 V
(3)	Norland/E7	Minicure	81·6%	66·3 V
(4)	Norland/E7	Suntest	67·2%	16·2 V

Table 3. Electro-optic data for films cured under different lamps.

Cell No.	Composition	Cured	T_{MAX}	V_{SAT}
(5)	Norland/BL038	Minicure	81·7%	137·9 V
(5)	Norland/BL038	Suntest	75·8%	39·2 V
(7)	Norland/BL012	Minicure	81·3%	81·2 V
(8)	Norland/BL012	Suntest	61·5%	21·0 V

to indicate that liquid crystal mixtures which are very soluble (for example > 60 per cent) in the prepolymer have a greater tendency to remain dissolved in the polymer matrix than liquid crystal mixtures which are less soluble (for example < 45 per cent). This is further supported by the results presented in table 3. The solubility of BL038 in Norland 65 at room temperature is 40 per cent whereas the solubility of BL012 at room temperature is typically 75 per cent.

4.3. *Liquid crystal concentration*

The liquid crystal concentration also affects the on-state clarity of a PDLC film. Table 4 shows the electro-optic data (measured at 2° collection angle) for PDLC films containing different Norland 65/E7 ratios cured in the Suntest. The clearest film is the film containing the lowest concentration of E7. This is also the film with the highest V_{sat}, which is partially due to small droplets, which in turn is partially due to the fast cure of the film. As the concentration of liquid crystal increases, both T_{max} and V_{sat} decrease. These observations were also made with films containing different Norland 65/BL036 ratios, as shown in table 5.

These results suggest that the liquid crystal present in a PDLC film prevents the prepolymer from curing as quickly as it normally would if the liquid crystal was not present. They indicate that the rate at which the prepolymer cures is partially dependent on the concentration of liquid crystal dissolved in the prepolymer; the greater the concentration of liquid crystal, the slower the rate of cure and therefore the poorer the on-state clarity.

4.4. *Measure of clarity*

In order to get a true measure of on-state clarity, it is thought that a white light source must be used. As most photodiodes are biased towards the IR end of the spectrum, an eye response filter and an IR rejection filter must also be used to ensure that the photodetector being used in the measuring system does not detect IR light passing through or being scattered by the PDLC film.

Table 6 shows the electro-optic data for PDLC films cured in the Suntest measured at 2° and 12°. To the eye, the on-state clarity of cell (4) was very poor. When a 12° collection angle was used, the recorded on-state transmission of this cell indicated that it was very clear, although it was not. The reason for this was that the incident light was

Table 4. Variation of T_{maz} and V_{sat} as a function of E7 concentration.

Cell. No.	E7 Con.	T_{max}	V_{sat}
(9)	40%	81·4%	70·6 V
(10)	50%	79·9%	31·9 V
(11)	60%	67·9%	23·2 V

Table 5. Variation of T_{max} and V_{sat} as a function of BL036 concentration.

Cell. No.	BL036 Conc.	T_{max}	V_{sat}
(12)	25%	82·2%	70·6 V
(13)	35%	77·9%	31·9 V
(14)	45%	74·0%	23·2 V

being scattered out of the specular beam, although it was being scattered through an angle less than 12°. When the collection was reduced to 2°, the on-state transmission dropped dramatically, giving a more realistic measure of how poor the on-state clarity really was.

When viewed in the on-state, the clarity of cell (2) was very good. There was very little difference in the on-state transmission of this cell measured at 2° and 12°. The reason for this was that very little light was being scattered out of the specular beam in the on-state of this film.

5. Conclusion

High on-state clarity is an important requirement for PDLC films for use in large area vision products. In order to get a true measure of this property a collection angle < 3° must be used.

It has been suggested in this paper that the on-state clarity of a PDLC film can be affected by a number of different factors. These factors are all related to the rate at which the film cures and to the rate at which the liquid crystal phase separates during the PDLC film formation. These factors have been individually identified and investigated separately.

Table 6. Electro-optic data for films measured at different collection angles.

Cell No.	Composition	Coll. angle	T_{MAX}	V_{SAT}
(2)	Norland/BL-036	2°	78·7%	32·4 V
(2)	Norland/BL-036	12°	81·7%	34·3 V
(4)	Norland/E7	2°	67·2%	16·2 V
(4)	Norland/E7	12°	84·6%	17·0 V

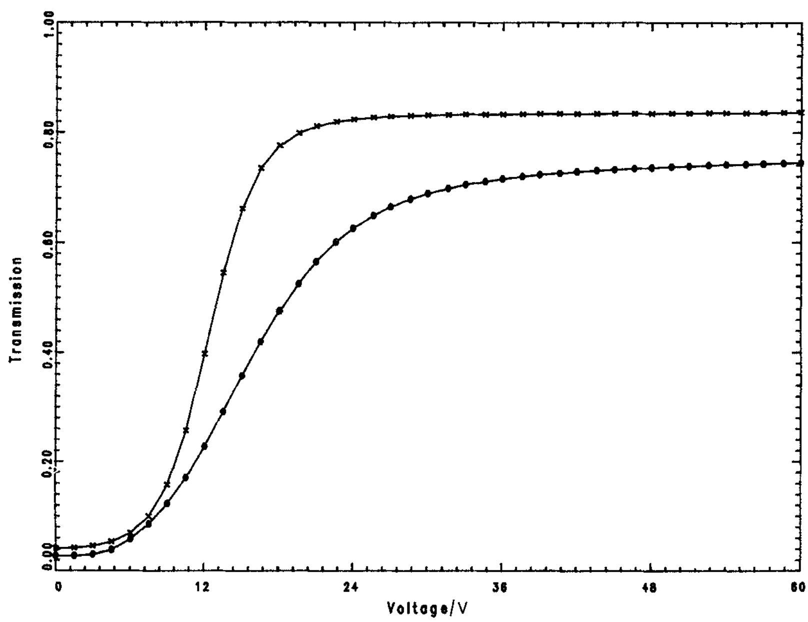

Figure 2. Electro-optic curves for a normal, Norland 65/E7(●), and an optimized-PN295/E7(X), PDLC film.

The results presented in this paper suggest that it is possible to achieve high on-state clarity, high off-state opacity and low voltage operation by choosing the liquid crystal, the polymer and the liquid crystal concentration carefully and by optimizing the curing conditions. Figure 2. shows the electro-optic response curve of an ordinary Norland 65/E7 PDLC film compared to that of a PDLC film for which the above conditions have been optimized.

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[4] Licrilite liquid crystal mixtures from Merck Ltd., Poole, Dorset, England.
[5] Heraeus Equipment Ltd., Brentwood, Essex, England.
[6] Primarc UV Technology, Slough, Berkshire, England.
[7] UV intensities were measured using an IL390B Light Bug, Able Instruments and Controls Ltd., Reading, Berkshire, England.