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Liquid Crystals

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Liquid crystal-polymer composites

Anomalous electro-optical curve

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Liquid crystal-polymer composites containing a low proportion of polymer are of interest because of their low driving voltage, but they can show anomalous electro-optical curves, such as a minimum in the electro-optical curve. We explain the existence of this minimum, by a partial orientation of liquid crystal domains, together with the presence of mobile polymer fragments. This partial orientation is visible using a polarizing microscope, and the presence of polymer that is not linked to the main network is proved by size exclusion chromatography of the liquid crystal extracted from the composite.

1. Introduction

Liquid crystal-polymer composites are a class of materials with many potential applications, and are under development for projection television [1, 2] and certain types of direct view displays [3]. Their advantages over existing technologies are (i) simple manufacturing process, (ii) no alignment layers, (iii) no polarizers, and (iv) large viewing angle. Most of these composites are obtained through a phase separation technique, yielding a composite usually containing 5 to 50 per cent polymer. One advantage of having a very low concentration of polymer is to reduce the driving voltage [4], but of course too little polymer results in poor scattering.

In fact, when reducing the polymer content in a composite, we have often noticed anomalies in the electro-optical curve. In particular, we have observed for different polymer/liquid crystal mixtures, the existence of a minimum in this curve: the aim of the paper is to propose an explanation of this phenomenon.

2. Experimental

The cells are made from two ITO coated glass plates, separated by mylar spacers and fixed together, so that the cell thickness is about 25 μm.

A mixture of liquid crystal, prepolymer and photoinitiator is introduced into a cell by capillarity and photopolymerized (Hg lamp, 9 mW cm^{-2} at 365 nm, for 17 min, so that a porous polymer network in a continuous liquid crystal phase is obtained (PNLC).

The liquid crystal mixtures used are BL012 and TL202 (Merck Ltd, U.K.). The prepolymer mixtures used are PN393 (Merck Ltd, U.K.) and KHEA (20 per cent

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hydroxyethyl acrylate (Aldrich), 80 per cent acrylate mixture Kayarad HX620 (Nippon Kayaku)). The photoinitiator used is Darocure 1173 (E Merck).

Measurements of transmission versus 'maximum voltage applied to the cell' (see figures 4 and 7) are carried out as follows: we increase the voltage applied to a cell from 0 up to the smallest voltage necessary to measure the transmission in the minimum of the curve (i.e. 10 V_{rms}). We repeat this measurement to ensure that the electro-optical response is stabilized, and we record values of the transmission at zero volts (T_{off}) and of the minimum of the curve (T_{min}). Then, we cut the voltage and increase it again, up to a higher value than before (for example 15 V_{rms}), so as to measure a new value of T_{off} and T_{min}, and so on.

Liquid crystal samples extracted from composite cells were analysed by size exclusion chromatography in tetrahydrofuran. The set up is composed of a pumping unit (Waters 610), a system controller (Waters 600E), two columns (Ultrastyragel 100 Å and 500 Å) in series (chosen to measure molecular weights between 50 and 10 000), and a refractometer (Waters 410). Polystyrene standards were used to estimate molecular weights.

3. Results and discussion

3.1. *Initial orientation of domains*

Figure 1 shows the first measurement of the electro-optical curve of a composite cell after photopolymerizing a mixture of 5 per cent prepolymer KHEA and 95 per cent liquid crystal BL012: at low electric field, the cell is more scattering than in the off-state, whereas at high field, the cell is transparent.

Observation of this cell using a polarizing microscope shows that the orientation of liquid crystal domains (separated by the polymer or by defects induced by the polymer) is not completely random; there is a preferred direction.

This partial orientation, which is probably due to flow-alignment when filling the cell by capillarity, explains the poor off-state scattering of our cell. Indeed, if two adjacent liquid crystal domains are nearly parallel, then the scattering is not efficient. Furthermore, when a low electric field is applied, some parts of the liquid crystal will

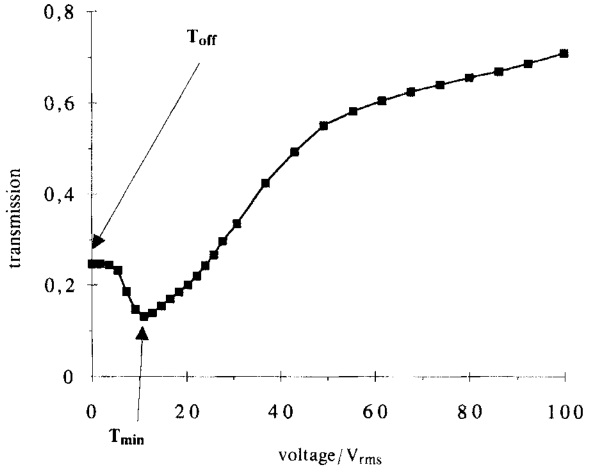

Figure 1. First measurement of the electro-optical curve of a composite cell (5 per cent KHEA, 95 per cent BL012).

Values of the minimum ($T_{off} - T_{min}$) in the first measurement of the electro-optical curve for different liquid crystal/polymer mixtures (per cent) (polymer content: 5 per cent).

	Monomer	
Liquid crystal	KHEA polar mixture	PN393 non-polar mixture
BL012		
$\Delta\varepsilon = 15{\cdot}7$	10·2	10·1
TL202		
$\Delta\varepsilon = 6{\cdot}0$	15·4	0

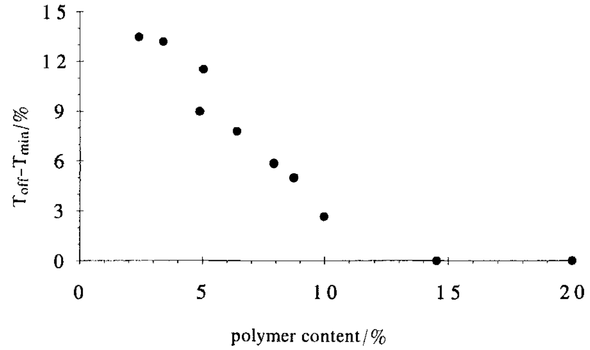

Figure 2. Amplitude of the minimum versus percentage of polymer in the cell (KHEA, Bl012).

begin to orient along the field, thus creating defects in the preoriented domains, so that the cell is more scattering then in the off-state. Of course, a strong field orients all domains, so that the cell is transparent.

This phenomenon is not specific to this formulation: the table shows the amplitude of the minimum measured for other formulations.

The following observations were all made with KHEA/BL012. Figure 2 shows the amplitude of the minimum ($T_{off} - T_{min}$) in the first measurements of the electro-optical curve for cells having different polymer contents. We can see first that the anomaly in the curve is only present for cells containing less than 15 per cent of polymer, and secondly, the less polymer there is in the cell, the bigger is the amplitude of the minimum.

The explanation of the first point is the following: if the polymer content is high enough, the orientation of liquid crystal domains is totally random, as in conventional dispersions of liquid crystal droplets in a polymer matrix, so that no minimum is observed in the electro-optical curve. As for the second point, if the polymer content is reduced, scattering in the off-state becomes less efficient (higher T_{off}) because of partial orientation of liquid crystal domains. Moreover, a low electric field still generates defects and thus refractive index variations of the same magnitude as before, so that T_{min} is less affected by the reduction of polymer content: consequently, ($T_{off} - T_{min}$) increases. We indeed observe that T_{off} increases faster than T_{min} when polymer content is reduced.

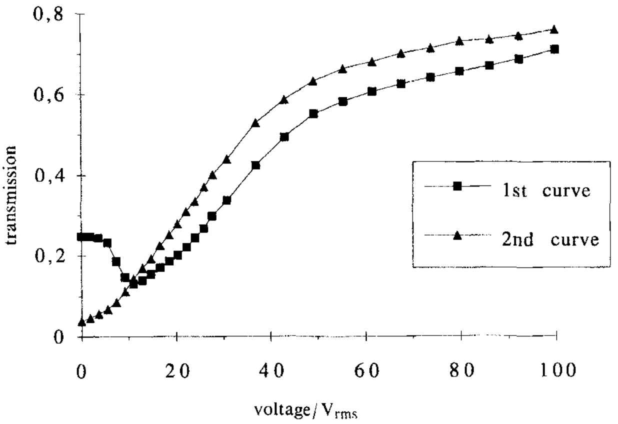

Figure 3. First and second measurements of the electro-optical curve of the same cell (5 per cent KHEA, 95 per cent BL012).

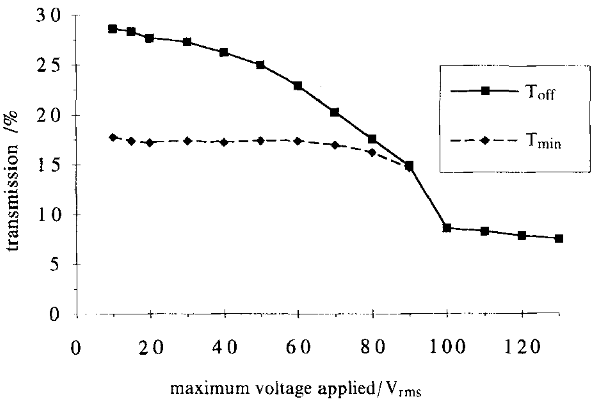

Figure 4. Off-state (T_{off}) and minimum (T_{min}) transmissions versus maximum voltage applied to the cell (5 per cent KHEA, 95 per cent BL012). (Each point on the curve is obtained by recording the electro-optical curve up to the corresponding voltage on the x axis (see Experimental section).)

3.2. *Evolution after applying an electric field*

3.2.1. *Original cell*

The anomaly in the electro-optical curve is a function of the electric field to which the cell has been submitted. In fact, after applying 100 V_{rms}, the next electro-optical curve does not present a minimum (see figure 3).

This effect is seen more precisely in figure 4: T_{min} and T_{off} are represented versus the maximum voltage that has been applied to the cell (see Experimental section). The amplitude of the minimum (i.e. the difference between the two transmissions) decreases gradually with the maximum voltage applied, and the minimum finally disappears at 90 V_{rms}, after which the off-state transmission is no longer a function of the voltage that has been applied to the cell.

The decrease in the off-state transmission must be due to liquid crystal domains which do not recover their initial orientation after an electric field has been applied and then removed: since the domains were partially oriented, this creates greater refractive

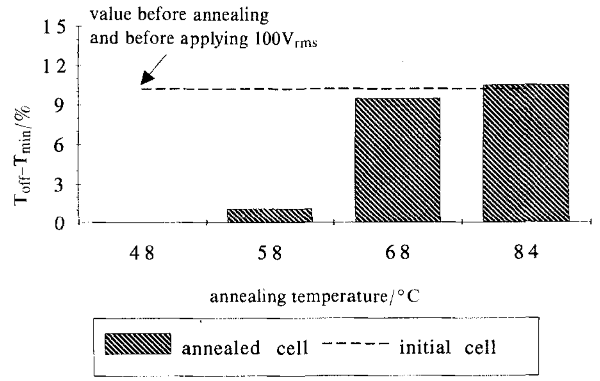

Figure 5. Amplitude of the minimum ($T_{off} - T_{min}$) versus annealing temperature ($T_{N\text{-}I} = 70°C$). ($T_{off} - T_{min}$ is measured by applying up to 100 V$_{rms}$ to the cell (5 per cent KHEA, 95 per cent BL012)).

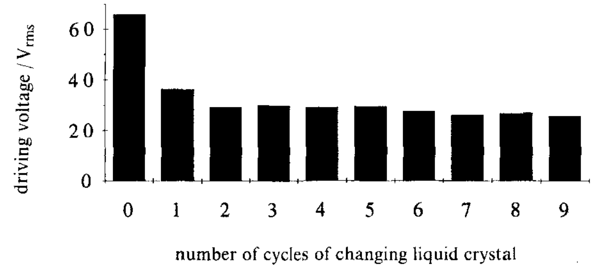

Figure 6. Driving voltage (yielding 90 per cent of transmission) of the same cell versus the number of times the liquid crystal has been exchanged (5 per cent KHEA, 95 per cent BL012).

index variations and thus a lower T_{off}. At low voltages, this is a continuous process, but at about 90 V$_{rms}$, there is an abrupt change in T_{off}, which may be due to irreversible modifications of the orientation of the domains.

Figure 5 shows that annealing the cell at a temperature above $T_{N\text{-}I}$ restores the minimum in the curve which had been suppressed by applying an electric field: the liquid crystal domains seem to recover their initial orientation when cooled from the isotropic phase.

3.2.2. *Cell with fresh liquid crystal*

Since these composites contain a low proportion of polymer, it is possible to extract the liquid crystal (without opening the cell) by immersing the cell in a solvent [5]. A fresh liquid crystal can then be introduced by capillarity into the cell. Figure 6 shows that the cell after such a cycle of changing the liquid crystal is not equivalent to the original cell after polymerization (lower driving voltage), but the cycle does not destroy the polymer network. Indeed, after 9 cycles, the cell still has the same electro-optical properties as after the second cycle. If removing liquid crystal from the cell degraded the polymer network, then we would observe a continuous evolution of the driving voltage.

The cells modified by this operation of exchanging the liquid crystal still show a minimum in the first measurement of the electro-optical curve. Moreover, this minimum remains whatever the applied voltage. We can see in figure 7 that the off-state

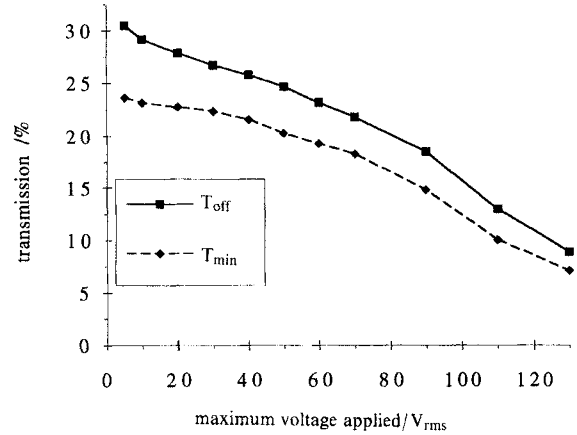

Figure 7. Off-state (T_{off}) and minimum (T_{min}) transmissions versus maximum voltage applied to the cell (5 per cent KHEA, 95 per cent BL012). (Each point on the curve is obtained by recording the electro-optical curve up to the corresponding voltage on the x axis (see Experimental section).)

transmission decreases with increasing maximum voltage applied, but contrary to figure 4, the minimum transmission also decreases, so that the minimum does not disappear, even at voltages four times higher than the driving voltage. The anchoring of the domains has been somewhat modified when exchanging the liquid crystal, because we no longer observe the abrupt modification of orientation.

3.3. *Interpretation*

These data show that applying a strong electric field to a cell modifies the anchoring of liquid crystal domains, but that this modification is no longer possible when the liquid crystal has been replaced by fresh liquid crystal.

Figure 8. very schematically shows our interpretation of the phenomenon: the proportion of polymer in the composite being small, there are some fragments of polymer which are not bonded to the main network. Some of these fragments are sufficiently small to be mobile.

In figure 8 (*a*), we have represented such a mobile polymer fragment in a domain of liquid crystal surrounded by the polymer network. A low electric field (see figure 8 (*c*)) generates defects which result in abrupt refractive index variations, because neighbouring domains are nearly parallel: this explains the minimum in the first electro-optical curve (see figure 1).

At high electric field (see figure 8 (*e*)), the whole domain is aligned and the polymer fragment rotates because of surface forces. When the field is suppressed, the domain cannot recover its initial orientation because of the fragment. As a consequence, subsequent electro-optical curves have a lower T_{off} and do not present a minimum (see figure 3), because this domain is no longer parallel to its neighbours. This rotation of a polymer fragment explains the abrupt variation of T_{off} in figure 4.

The initial orientation of the fragment and thus the minimum in the curve can be recovered by annealing the cell above the nematic to isotropic transition of the liquid crystal (see figure 5).

The operation of exchanging liquid crystal also removes mobile polymer fragments (see figure 8 (*b*)), so that the domain is artificially bigger (see figure 8 (*d*)), explaining

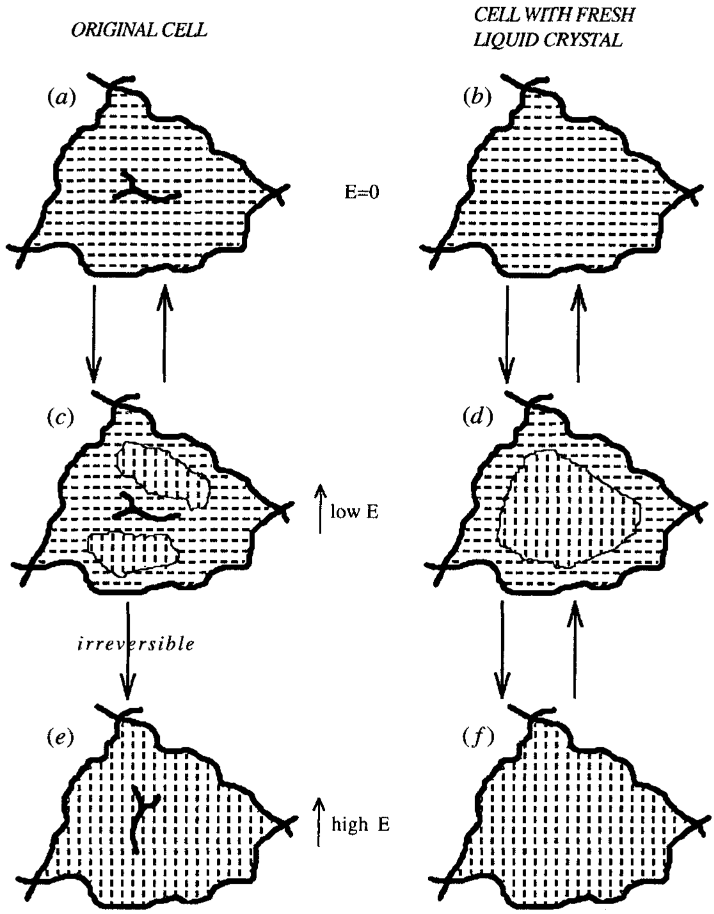

Figure 8. Sketch of the orientation in a liquid crystal domain in a polymer network and the effect of an applied electric field *E*. (*a*, *c*, *e*): a polymer fragment is inside the domain; (*b*, *d*, *f*): the polymer fragment has been removed by exchanging the liquid crystal.

the lower driving voltage [6] (see figure 6). Moreover, after applying and suppressing a high electric field (see figure 8 (*f*)), the domain can recover its initial orientation (surface forces at the interface with the polymer network are no longer opposed by the polymer fragment). Consequently, the minimum does not disappear (see figure 7).

In order to check this interpretation, we have analysed the liquid crystal extracted from a cell by size exclusion chromatography. The chromatogram (see figure 9 (*a*)) definitely shows that some polymer is removed, together with the liquid crystal. Furthermore, the same cell was then filled with fresh liquid crystal which was subsequently extracted and analysed. The chromatogram (see figure 9 (*b*)) shows that no more polymer is removed.

These facts seem to confirm our interpretation, although other explanations may be possible.

4. Conclusions

Liquid crystal-polymer composites with a low content of polymer often show anomalous electro-optical curves. For example, there may be a minimum in the first

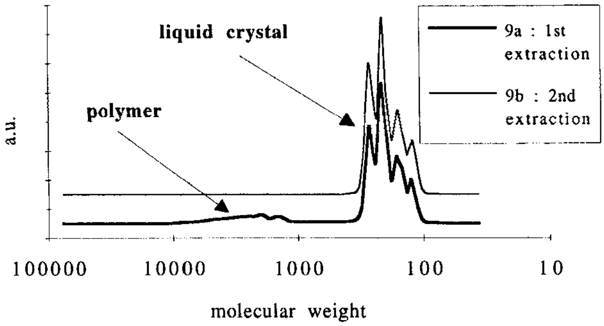

Figure 9. Chromatograms (size exclusion) of the liquid crystal extracted from a composite cell (5 per cent KHEA, 95 per cent BL012). After the 1st extraction, the cell was filled with fresh liquid crystal, which was subsequently extracted: 2nd extraction.

or in all curves. We explain this phenomenon by a partial orientation of liquid crystal domains, together with the presence of mobile polymer fragments; this has been proved by size exclusion chromatography of the liquid crystal extracted from a cell.

Practically, the presence of these fragments may be an advantage, because they both provide a good scattering off-state (once they are oriented in the direction of the field), and a minimal quantity of polymer is required (compared to a continuous polymer network), so that the driving voltage of the cell is comparatively lower.

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[6] It should be noted that the same operation of exchanging liquid crystal from a composite cell containing 20 per cent (instead of 5 per cent) of the same polymer, increases the driving voltage (see [5]). This difference is due to the fact that these two similar composites do not have the same morphology. Indeed, the 20 per cent polymer composite does not contain mobile polymer fragments, as is shown in figure 2.