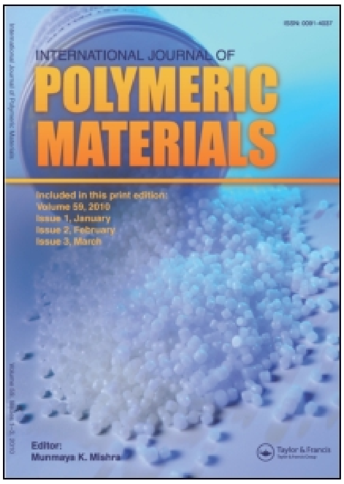

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Dielectric Relaxation and Optical Transmittance of PVC Membranes Modified by Nematic Liquid Crystal

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Dielectric Relaxation and Optical Transmittance of PVC Membranes Modified by Nematic Liquid Crystal

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This study intends to present some further research in polymer-dispersed liquid crystal (PDLC) systems [1]. These PDLC type cells were produced based on a low-cost commercial polymer (PVC) and liquid crystal E48 (Merck), using a modified solvent preparation method (SIPS). These cells were characterized electro-optically and by low frequency dielectric relaxation (20 Hz to 1 MHz) experiments.

Results are encouraging; the prepared composites show regular microstructures and optical transmittance changes induced by the electric field, introducing an alternative way of producing low-cost PDLC electro-optical cells.

Keywords: dielectric relaxation, liquid crystal, optical transmittance, PDLC, PVC

INTRODUCTION

The discovery of electro-optic effects in a polymer-dispersed liquid crystal (PDLC) by Fergason in 1981 [1,2] and the subsequent preparation by Doane et al. of structures containing liquid crystal droplets suspended in a polymer matrix [3], gave rise to intense scientific

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Address correspondence to P. Simeão Carvalho, Departamento de Física, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre 687, 4169-007 Porto, Portugal. E-mail: psimeao@fc.up.pt and technological work in polymer-dispersed liquid crystal (PDLC) materials and display device, that lasts until today.

The physical properties of liquid crystals (LC) can be extremely changed when immersed in a polymer matrix [1,4–6]. In particular, the dielectric strength and relaxation frequency of dielectric relaxation modes of pure LC and polymer are usually changed in PDLC samples. In some cases, new dielectric relaxation modes are observed [5]. The understanding of how these relaxation processes influence the electro-optic properties of polymer/LC structures can be important for applications.

Polyvinyl chloride (PVC) polymer has been described in the literature combined with LC in several contexts, in order to achieve new physical properties for a wide range of applications, such as modified membranes for electrochemical sensors [7], injection-modulated blends with liquid crystal polymers (LCP) for high-performance plastics [8] or as interfaces to induce surface molecular orientation [9].

In this work we present studies of dielectric spectroscopy and electro-optical response of a commercial LC (E48) and chiral additive (CB15) combined in modified membranes of PVC/E48 and PVC/E48/CB15, over the frequency range 20 Hz–1 MHz. The possibility of using such compounds for the fabrication of low-cost electro-optical devices is discussed.

EXPERIMENTAL

Sample preparation was done in typical chemical laboratory conditions, minimizing air and dust exposure during procedures. The overall mass of the sample was calculated, for a 50 μm thick film, in the order of 10 mg/cm^2.

Selected proportions of liquid crystal and PVC were weighed with a microscale; the mixture was dispersed in tetrahydrofurane (THF) in a closed 10 ml volumetric phase, under ultrasonic agitation at 60°C for approximately 30 min.

The resulting solution was transferred to a petri plate, and suitably covered for controlled THF evaporation; slow drying time of 24 to 48 h was necessary to achieve a dense solid PVC network and convenient segregation of the liquid crystal phase.

The resulting film was carefully cut and placed between two glasses coated with ITO, avoiding formation of any air bubbles; the set was pressed and sealed with epoxy transparent resin and tip electrodes were glued with silver paint to each ITO glass. Thickness of the assembly was verified with micro profilometer.

In order to establish proper comparisons, we have studied samples of pure PVC and E48, as well as membranes of PVC/E48. The effect of a

TABLE 1 Samples Composition and Thickness

	PVC	E48	E48/CB15	PVC/E48	PVC/E48/CB15
Composition (weight %)	100	100	98:2	20:80	20:78:2
Thickness (μm)	65	25	50	50 and 25	49

chiral additive CB15 (Merck) in E48 and PVC/E48 modified membrane was also investigated. The average thickness of the studied samples and composition is indicated in Table 1; for the dielectric study of E48 sample, we have used a commercial cell from E.H.C. (Japan) with homogeneous alignment.

The dielectric properties of the samples were studied over the frequency range 20 Hz–1 MHz. The complex dielectric constant (ε', ε'') was measured with a HP4284A LCR meter, as a function of the bias voltage (0 V–40 V), at a measuring ac field E_{ac} of 0.01 V/μm.

The electro-optical response to electric fields of PVC/E48 and PVC/E48/CB15 membranes, was also studied for several frequencies. The light intensity transmitted through the sample, I_t, was measured by means of a BPW21 photodiode from R.S. Components Ltd. (spectral bandwidth between 440 nm and 680 nm) attached to a polarizing microscope; a halogen bulb was used as a light source.

Optical loops were recorded during sample switching, using a modified square wave generated by a HP33120A signal generator and amplified by a Kepko (Bop 1000 M) signal amplifier.

Texture observations were done with polarizing microscopy and photos were taken with a digital MOTIC 2000 camera (2 megapixel resolution).

All measurements were done at room temperature.

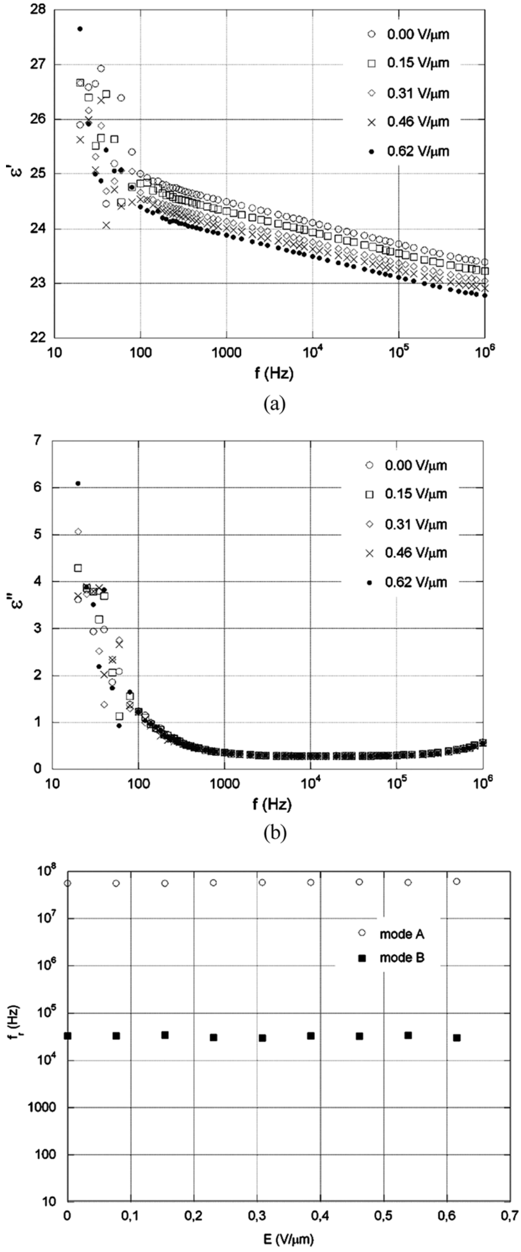
RESULTS AND DISCUSSION

Dielectric Relaxation

Figures 1a and 1b show, respectively, the frequency dependence of the real (ε') and imaginary (ε'') parts of the complex relative dielectric constant, $\varepsilon^* = \varepsilon' - j\varepsilon''$, as a function of the bias electric field in pure PVC samples. Within the frequency range studied, a slight dispersion is imposed by the bias field only below 100 Hz.

Assuming a Cole-Cole type independent relaxation of dielectric charges, data was fitted to the usual expression

$$\varepsilon^*(\omega) = \varepsilon(\infty) + \sum_j \frac{\Delta\varepsilon_j}{1 + \left(i\frac{f}{f_{r_j}}\right)^{\beta_j}} + \frac{1}{(i\omega\tau_c)^{\gamma}} \tag{1}$$



(a)

(b)

(c)

FIGURE 1 Frequency dependence of (a) ε' and (b) ε'', and (c) relaxation frequency of collective modes under electric field, in PVC.

where $\Delta\varepsilon_j$, f_{r_j} and β_j are the dielectric amplitude, relaxation frequency and dispersion parameter of the j-th relaxation mode, respectively; f is the frequency of the applied field. The last term in expression (1) accounts for ionic conductivity, with γ expressing the dispersion of "conducting times" [10].

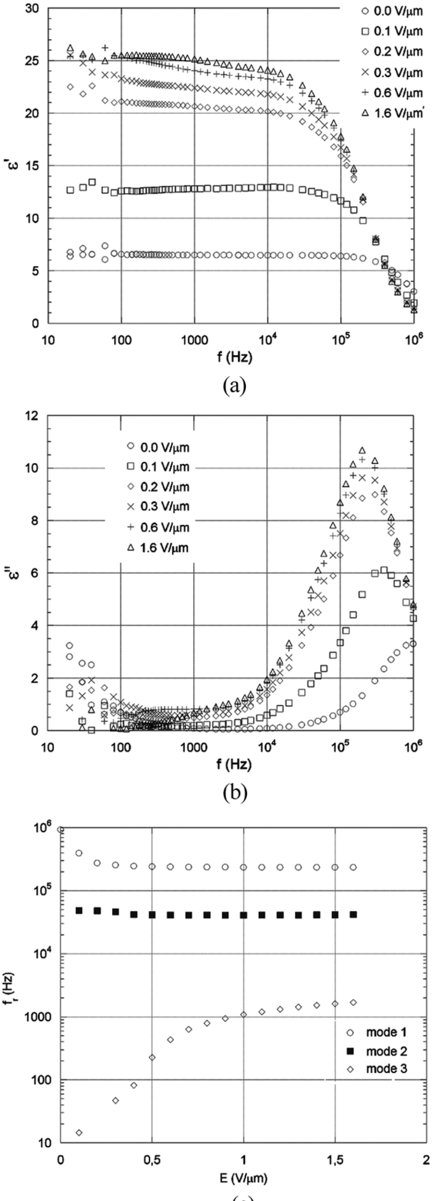
Two relaxation modes poorly influenced by the bias field were achieved for PVC (Figure 1c): a highly poly dispersive one with a relaxation frequency around 20 kHz and with a very small dielectric amplitude (results not shown here), and a clearly visible monodispersive mode at very high frequency (relaxation frequency above 1 MHz) that is usually associated to a cut-off frequency coming from the electrodes resistance [11].

In pure liquid crystal samples, the dielectric spectra are richer. For the E48 and the liquid crystal chiral mixture E48/CB15 (98:2 weight proportion) samples, the dielectric dispersions exhibit a strong influence of the bias electric field (Figures 2a and 2b for E48; Figures 2d and 2e for E48/CB15). In both samples, three relaxation modes were found: two of them with high relaxation frequency (modes 1 and 2) and the third with much lower relaxation frequency.

In the E48 sample, the major effect in the dielectric response is observed for the high frequency relaxation modes, whose dielectric amplitude is increased by the bias field while their relaxation frequency decreases slightly; modes 2 and 3 could only be detected under field and they seem to be triggered by the bias field. The relaxation frequency of the lowest relaxation frequency mode (Figure 2c) increases with the bias field, which may be related to some molecular vibration that is enhanced by the field.

For the E48/CB15 mixture, the values of ε' are much lower when compared to those of E48 sample. However, the values of ε'' are much higher at low frequency, suggesting considerable polar mobility. In this mixture, the major dielectric response to the bias field comes once more from modes 1 (highest relaxation frequency) and 3 (lowest relaxation frequency) (see Figure 2f). In this sample, the bias field reveals more clearly the contribution of mode 3, which in fact has a very similar behavior to the corresponding mode in E48 sample. Relaxation mode 2 does not seem to be influenced by the bias field, as observed for the corresponding mode in E48.

PVC/liquid crystal membranes show significant changes in the dielectric behavior of samples (Figures 3a and 3b for PVC/E48; Figures 3d and 3e for PVC/E48/CB15). For both PVC/E48 (25 μm thick) and PVC/E48/CB15 membranes (in both cases, 80:20 molecular weight proportion), the dielectric dispersion is incredibly reduced and the bias field seems to have only some influence below approximately

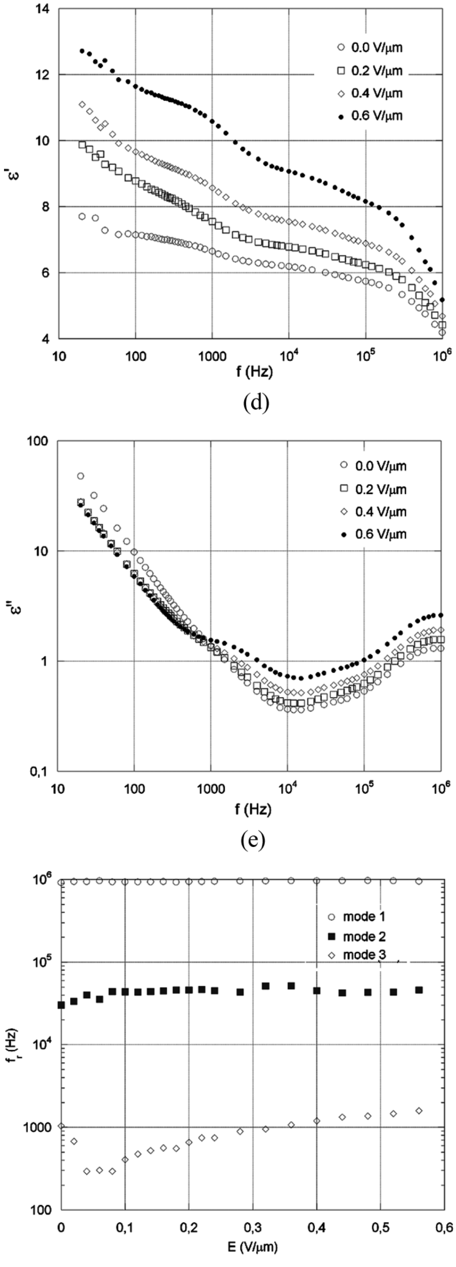


(a)

(b)

(c)

FIGURE 2 Frequency dependence of (a) ε' and (b) ε'', and (c) relaxation frequency of collective modes under electric field, in E48; frequency dependence of (d) ε' and (e) ε'', and (f) relaxation frequency of collective modes under electric field, in E48/CB15.

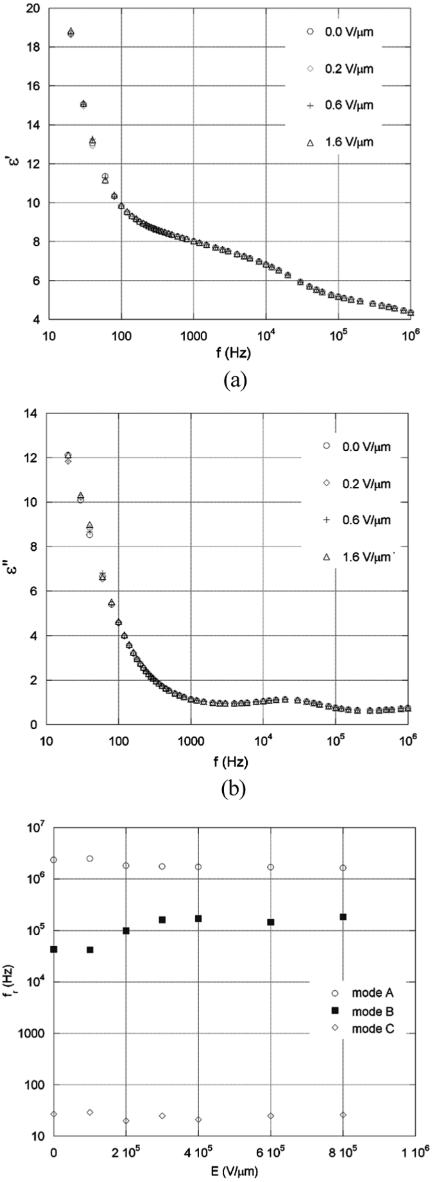


(d)

(e)

(f)

FIGURE 2 Continued.

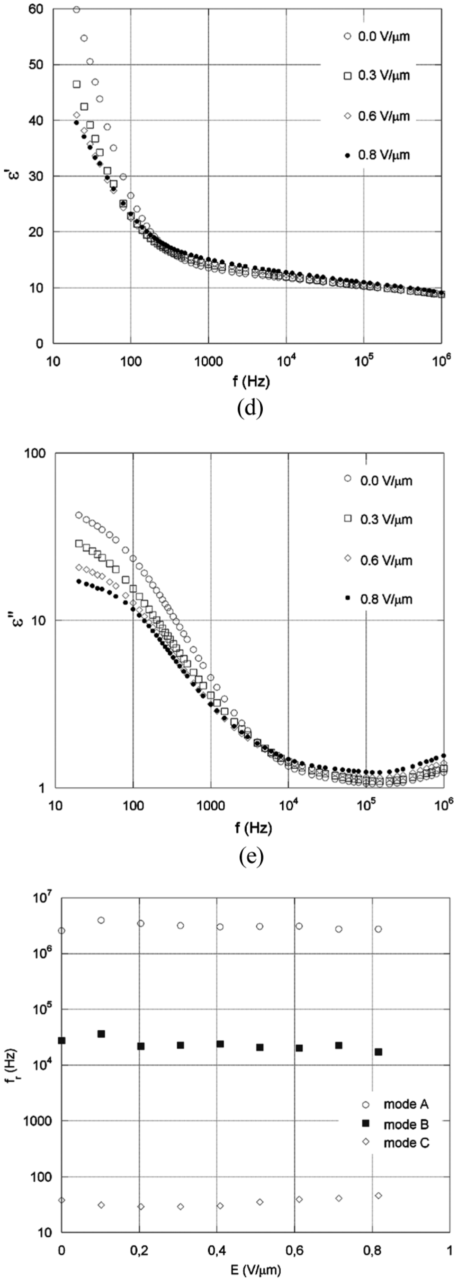


(a)

(b)

(c)

FIGURE 3 Frequency dependence of (a) ε' and (b) ε'', and (c) relaxation frequency of collective modes under electric field, in PVC/E48; frequency dependence of (d) ε' and (e) ε'', and (f) relaxation frequency of collective modes under electric field, in PVC/E48/CB15.



(d)

(e)

(f)

FIGURE 3 Continued.

10 kHz. The dielectric amplitude, as well as the relaxation frequency of collective modes found in these samples (Figures 3c and 3f) resemble mainly some of those found in the neat PVC sample (Figure 1c), but are so different from those in pure liquid crystal samples that a reliable relation between all these modes is difficult to establish. These results suggest that the polymer network constrains the mobility of the liquid crystal molecules in such a way that collective modes are hindered, at least above 10 kHz.

Although the dielectric spectra in modified PVC membranes are poor, the molecular orientation can, however, be imposed in very strong electric field, resulting in very interesting electro-optical results.

Optical Transmission of Light

In the absence of electric field, the neat PVC sample was completely transparent, while all other samples were opaque to visible light and presented a milky look due to light scattering.

Texture observation of PVC-based membranes under polarizing microscope allows us to distinguish a regular polymer network whose cavities contain liquid crystal. This network is clearly visible under $V_{ac} = 80\,\mathrm{V}$ (alternating voltage at a frequency of 50 Hz) in the PVC/E48 (50 μm thick) membrane, although with this voltage the global sample is still opaque (Figure 4a). Increasing the voltage turns the sample more transparent and the network less visible (Figure 4b), but the length of the network cavities remains unchanged (about 540 μm). Similar results were also obtained for the PVC/E48/CB15 sample.

The optical transmission of the samples was studied as a function of the AC voltage and frequency, for both PVC/E48 and PVC/E48/CB15 samples. Once again, results were similar and for simplicity we will only present those concerning the PVC/E48 sample.

Information about the light scattering behavior for each state of the membrane is given by the optical transmittance (T), defined as the ratio between the intensities of the incident (I_o) and transmitted (I_t) light:

$$T = \frac{I_t}{I_o} \tag{2}$$

In this study, we applied a particular square wave function voltage as shown in Figure 5, consisting in two steps at 0 V, one at +V and another at −V; such function allowed us to measure the optical response between the 0 V (OFF) state and the ±V (ON) state. The evolution of the optical transmittance with the field can also be seen in this figure.

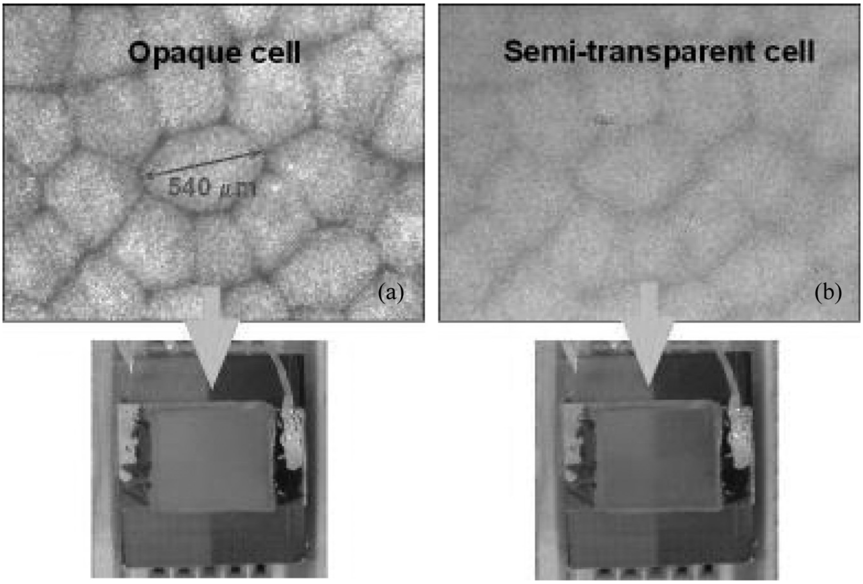


FIGURE 4 Texture observation of 25 μm thick PVC/E48 membrane under polarizing microscope, in (a) OFF (opaque) and (b) ON (semi-transparent) states, and the corresponding photographs of cells with a colored pattern below. The polymer network is visible in both states, although more clearly in OFF.

As for the optical contrast, it is defined as:

$$R = \frac{I_{t_{ON}}}{I_{t_{OFF}}} = \frac{T_{ON}}{T_{OFF}} \tag{3}$$

In Figure 6a, a plot of the optical transmittance of the 50 μm thick sample is shown, of both T_{OFF} (0 V applied, OFF state) and T_{ON} (±V applied, ON state) for different applied fields, at a frequency of 50 Hz. Three observations may be made from this figure.

1. The light transmitted at the initial OFF state (0 V applied) is already about 53% of the incident light;
2. Once we apply the electric field, at the frequency of 50 Hz, we no longer obtain the initial OFF state at zero field, because T_{OFF} increases slightly with the field;
3. Maximum of the optical transmittance is nearly obtained at about 400 V ($E = 8$ V/μm), where it presents a nice flat ON state that corresponds to almost 70% of the incident light.

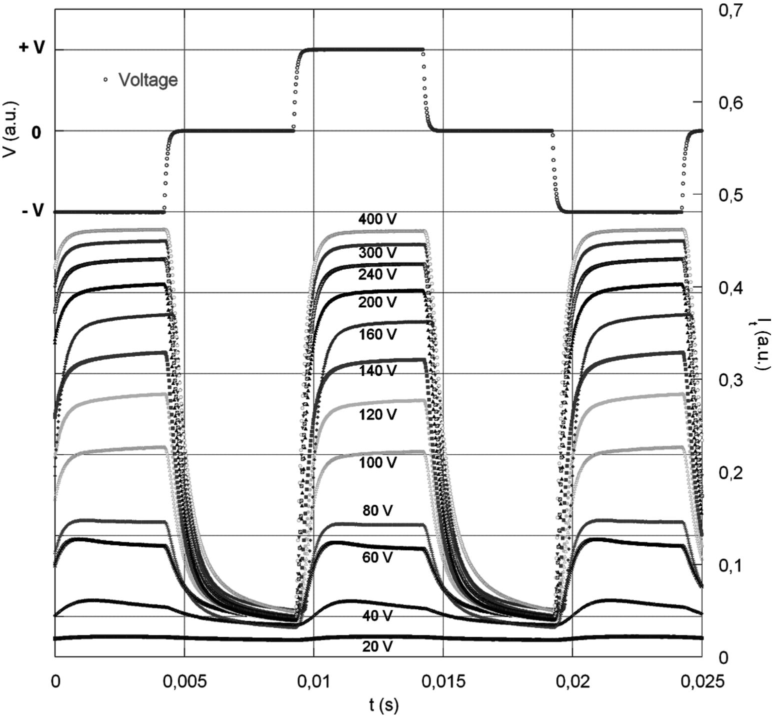


FIGURE 5 Particular square wave function voltage, used for measuring the light transmitted by the sample I_t for different amplitudes of the electric voltage. The wave function presented in this figure has a frequency of 50 Hz.

The optical contrast, R, between the ON and OFF states increases with the amplitude of the field E and its highest value is about 1.27, as seen in Figure 6b. This behavior is expected, as a consequence of the evolution of T_{ON} and T_{OFF} with the field, shown in Figure 6a.

We were also able to compute the response times, τ_{up} and τ_{down}, corresponding to whereas the optical signal was from OFF to ON state and vice versa, respectively. These response times were taken as the interval of time between the instant the field changes and the instant when the change in light intensity is 90% of $(I_{t_{ON}} - I_{t_{OFF}})$. Although Figure 6c shows that both τ_{up} and τ_{down} decrease with increasing field, the response time τ_{up} being always smaller than τ_{down}. They present somehow a different behavior, and we believe they are influenced differently, as we shall discuss later.

Although T_{ON} is strongly dependent on the intensity of the electric field (Figure 6a), it is however T_{OFF} that has a significant variation with the frequency of the field (Figure 7a). For an electric field of

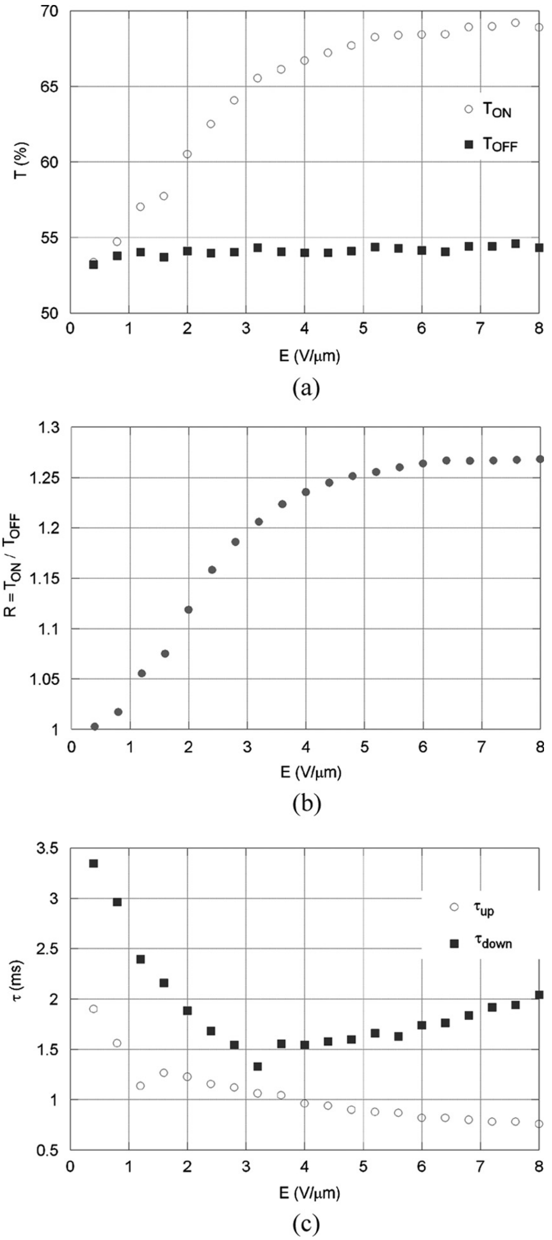


FIGURE 6 (a) Optical transmittance, (b) optical contrast and (c) response times τ_{up} and τ_{down} in 50 μm thick PVC/E48 membrane, as a function of the amplitude of the electric field E. The frequency was 50 Hz.

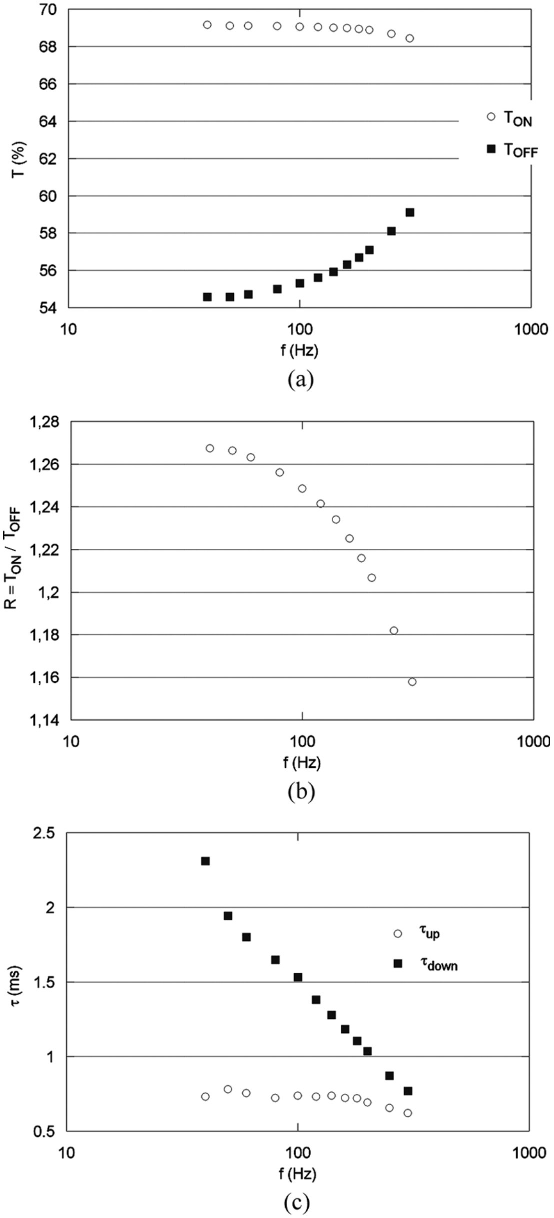


FIGURE 7 (a) Optical transmittance, (b) optical contrast and (c) response times τ_{up} and τ_{down} in 50 μm thick PVC/E48 membrane, as a function of the frequency *f*. The electric field amplitude was 8 V/μm.

8 V/μm, the optical transmittance at the OFF state increases from 54% at 40 Hz to nearly 60% at 300 Hz, but T_{ON} remains nearly constant (∼69%). This means that, to the naked eye, the cell becomes more and more transparent as the frequency of the field is increased. As a consequence of this combined fact, the optical contrast R decreases abruptly with the frequency (Figure 7b).

The response times τ_{up} and τ_{down} present once more a distinct behavior with the frequency: τ_{up} is poorly influenced by f, but τ_{down} decreases substantially as the frequency increases (Figure 7c).

Combining these results with those from Figure 6c, we can conclude that τ_{up} depends mainly on the intensity of the electric field (for fields higher than 2 V/μm, it can be shown that τ_{up} is nearly proportional to $1/E$), while τ_{down} looks like a relaxation time, during which the long liquid crystalline molecules are nearly free to rotate and return to their original position; therefore τ_{down} behaves according to a relaxation process (influenced by elasticity and viscosity of the medium, and by the frequency and intensity of the applied electric field).

CONCLUSIONS

PVC is a simple, highly resistant and low-cost transparent polymer, with the particularity that the high dipolar moments of the chlorine atoms cause an electrostatic effect that enhances the molecular segregation of the hydrophobic liquid crystal molecules.

Relaxation modes in liquid crystals are strongly influenced by the electric field. However this influence is dramatically reduced by the polymer presence, as shown in this work. The polymer matrix seems to freeze out the LC collective modes, masking their presence in the PVC-LC membranes and apparently giving rise to new ones.

Fortunately, these membranes are optically active under strong electric field and the formation of a PVC network (regular microstructure) is undoubtedly associated with the optical transmittance of cells.

The optical response of the PVC-modified membranes is strongly influenced by both the amplitude of the electric field and its frequency. The operational response times between ON (semi-transparent) and OFF (opaque) states may depend on the relaxation frequency of the newly formed collective modes in the membranes, especially those at low frequency.

Low frequency dielectric measure is a suitable method for characterizing the collective molecular orientation, electrical capacitance and dielectric losses in cells. The dielectric relaxation of collective modes tells us how much time molecules take to return to the undisturbed state, so it may be related to the electro-optical response time of liquid crystal based systems. Therefore, we assume that the characterization of modes and respective relaxation frequencies can be a pertinent asset to optimize operational response time, contrast ratio and operating power in liquid crystal devices (LCD).

The PVC-LC compounds show optical transmittance changes induced by the electric field, with potential applications in functional LCD. Further research will pursue higher quality manufactured samples and microstructure tailoring management, with enhanced optical contrast ratio, lower operational voltage and optimized operational response time.

REFERENCES

[1] Drzaic, P. S. (1998). *Liquid Crystal Dispersions*, World Scientific, Singapore, p. 5.

[2] Fergason, J. L. *SID Digest* (1985).

[3] Doane, J. W., Vaz, N. A., Wu, B. G., and Zummer, S. *Appl. Phys. Lett.* **48**, 269 (1986).

[4] Miyamoto, A., Kikuchi, H., Kobayashi, S., Morimura, G., and Kajiyama, T. *Macromolecules* **24**, 3915 (1991).

[5] Williams, G., Shinton, S. E., and Aldridge, G. A. *J. Polym. Sci.* B **39**, 1173 (2001).

[6] Dubois, F., Daoudi, A., Legrand, C., Buisine, J.-M., and Laux, V. XIX International Liquid Crystal Conference, Edinburgh, UK, p. 495 (2002).

[7] Reddy, S. M., Gangadharan, B., and Manini, J. *Anal. Chim. Acta* **508**, 71 (2004).

[8] Meng, Y. Z., and Tjong, S. C. *Polymer* **40**, 2711 (1999).

[9] Suively, C. M., and Koenig, J. L. *J. Mol. Struct.* **521**, 121 (2000).

[10] Fukui, M., Orihara, H., Suzuki, A., Ishibashi, Y., Yamada, Y., Yamamoto, N., Mori, K., Nakamura, K., Suzuki, Y., and Kawamura, I. *Jpn. J. Appl. Phys.* **29**, 329 (1990).

[11] Gouda, F., Sharp, K., and Lagerwall, S. T. *Ferroelectrics* **113**, 165 (1991).