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Evolution of the switching current during the preparation of polymer network–ferroelectric liquid crystal microcomposites

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The polymer network–ferroelectric liquid crystal (FLC) microcomposites are prepared by UV crosslinking of a chiral prepolymer diluted in a FLC. A fast cross-linking process involving 20 mW cm^{-2} UV intensity produces material with ferroelectric properties which have strongly deteriorated compared with the pure FLC. By a slow process using a UV intensity of 2 mW cm^{-2} the ferroelectric properties are less affected. It is supposed that the very dense polymer network, which arises during the fast process, is responsible for hindering the switching process and decreasing the spontaneous polarization. The photopolymerization kinetics are determined by measuring the switching current during the UV irradiation. The characteristic time of cross-linking is mainly reflected in the evolution of the spontaneous polarization and rotational viscosity with time.

1. Introduction

In recent years, anisotropic gels have been attracting considerable attention from the fundamental point of view as well as for their potential for electro-optic applications [1–6]. They are usually obtained by *in situ* polymerization of small percentages of a monomer in a non-reactive liquid crystal matrix. The resulting microcomposites combine both the mechanical shock resistance of polymers with the electro-optic properties of the non-reactive liquid crystals [4, 7]. Furthermore, these materials raise some challenging fundamental aspects such as polymer growth in anisotropic media or the behaviour of liquid crystals in confined environments.

Many papers have been devoted to the influence of cross-linking conditions on the gel characteristics such as morphology and electro-optic properties [6–11] or the relation between the polymer network and the electro-optic performance [2, 6, 8].

Recently, a direct influence of a liquid crystal phase on polymerization kinetics has been observed [12–14]. It was shown that an ordered medium, such as a smectic C* phase, leads to enhanced polymerization rates when compared with cross-linking made in the isotropic phase.

In previous work [15], we have studied microcomposites based on ferroelectric liquid crystals (FLC) and analysed the role played by different UV curing conditions on the spontaneous polarization ($\mathbf{P}_S$) and tilt angle (θ). Two photopolymerization procedures have been applied: a *fast curing process* (a high UV intensity applied for a short time) and a *slow curing process* (a lower UV intensity for a longer irradiation time). It has been shown that materials doped with a small percentage of a photocross-linkable chiral liquid crystal exhibit spontaneous polarization far smaller than for the FLC alone [12]. This indicates that the photocross-linkable molecules introduce disorder. The lowered $\mathbf{P}_S$ is still observed for composites made by the fast curing process [6, 15]. The decrease in $\mathbf{P}_S$ arising after polymer network formation mainly reflects the fact that the network hinders the switching of liquid crystal molecules especially in the vicinity of the sample surface [6]. On the other hand, the polarization value almost recovered to the value found in the pure FLC by using the slow curing process. These results are summarized in figure 1

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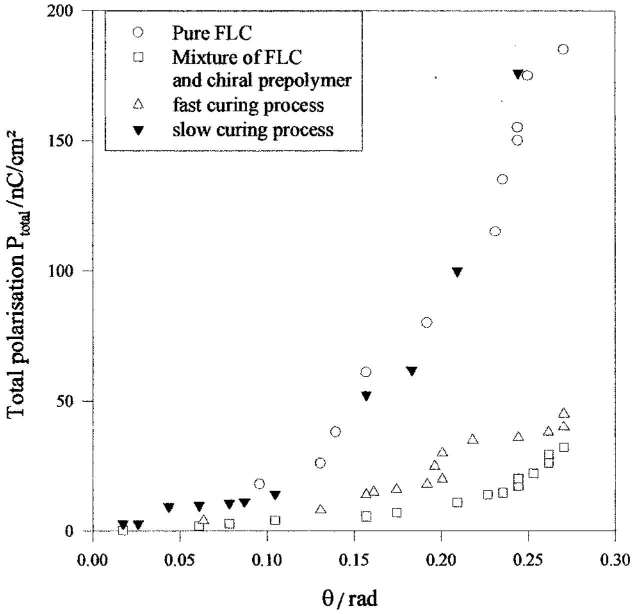

Figure 1. Spontaneous polarization as a function of the tilt angle for various UV curing conditions.

showing variations of the spontaneous polarization as a function of the tilt angle, which remains nearly unaffected by the curing process. The optical micrographs presented in figure 2 illustrate the effect of the polymerization conditions on the quasi-bookshelf structure (figure 2, photo 1). These photographs as well as the results in figure 1, indicate that polymerization conditions may strongly influence the spontaneous polarization and switching properties of the ferroelectric microcomposite as well as the sample alignment. The observed fall in polarization mainly comes from this loss of alignment. Then, the two-fold symmetry axis is not everywhere parallel to the electric field *E*, a necessary condition for measuring the full $\mathbf{P}_S$. Furthermore, as the polymer network mimics the LC arrangement in which the polymerization occurs [16], the $\mathbf{P}_S$ cannot be recovered after UV curing even by treatment with a high voltage.

In the present report we will focus on the study of the spontaneous polarization and the ferroelectric switching during the polymerization process in order to understand the degree to which they are affected by the polymerization procedure. The results could afford

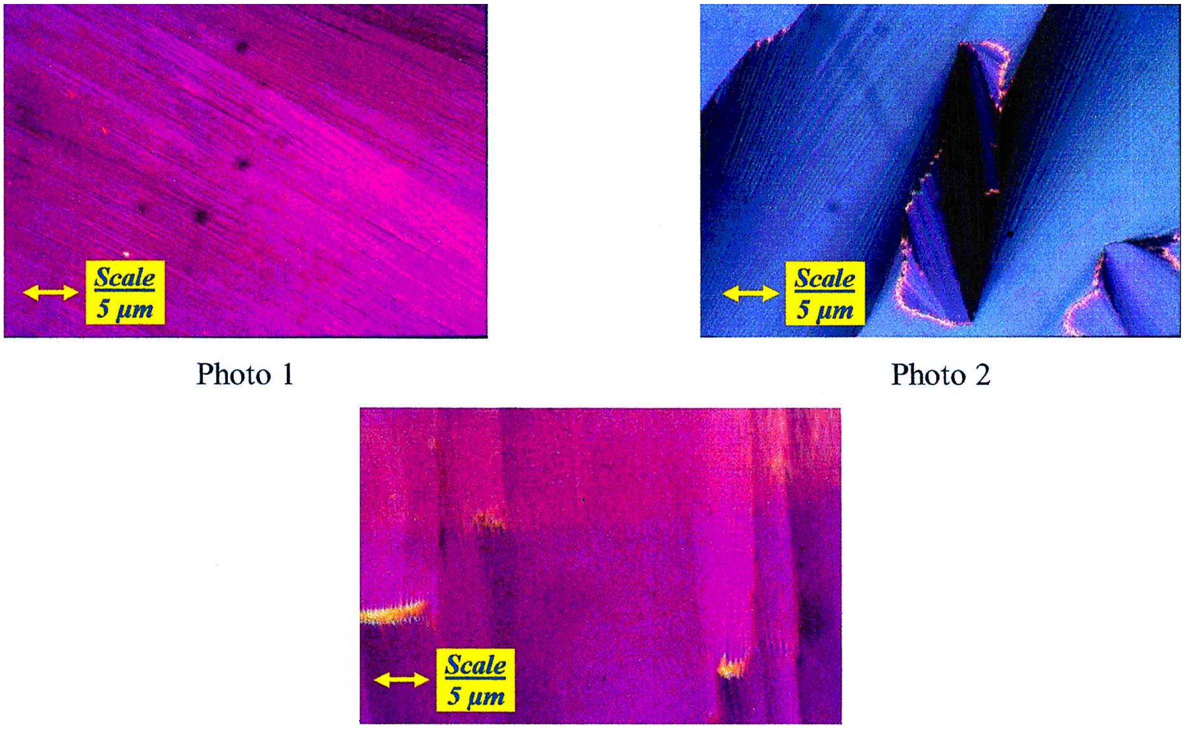

Photo 1

Photo 2

Photo 3

Figure 2. Textures observed on samples between crossed polarizers (thickness 4 µm, polyimide coated glass walls, unidirectionally rubbed). Samples were cooled from the isotropic phase to 40°C in the SmC* phase at a rate of 0.2°C min^{-1}. Photo 1, FLC alone; photo 2, ferroelectric composite obtained by the *fast curing process*; photo 3, ferroelectric composite obtained by the *slow curing process.*

information on the correlation between the polymerization kinetics and the ferroelectric properties of the final composite.

2. Experimental

2.1. *Materials*

The ferroelectric liquid crystal used in the experiments was a mixture (here denoted as G1) synthesized by one of us. G1 consists of molecules which are quite stable to UV radiation. Details regarding G1 composition can be found in [17]. The ferroelectric liquid crystal is then blended with 3 wt % of reactive chiral monomer. Tables 1 and 2 list the phase sequences and transition temperatures of the different materials used. Photopolymerization is initiated using Irgacure 907 (Ciba-Geigy).

2.2. *Sample preparation*

Cells for polarization measurements were made of two ITO coated glass plates spaced by about 4 µm. The conductive surface was 0.25 cm^2. The cells were filled by capillarity. The homogenous alignment of the sample was achieved using rubbed surface coatings of polyimide.

Before UV curing, samples were heated into the isotropic phase, and then slowly cooled at a rate of 0.2°C min^{-1} to 40°C in the SmC* phase. This treatment results in a bookshelf structure. The temperature of the sample was controlled by a Mettler FP52 hot stage.

In order to investigate the evolution of the total polarization during the photocross-linking process, two curing conditions were used, which yield the same UV exposure. These processes denoted as *slow* and *fast* are defined in table 3.

Table 1. Phase sequence of G1 (°C).

Cr	− 14	SmC*	64	SmA	83	N*	108	I

Table 2. Phase sequences of the photocross-linkable polymer (°C).

Before cross-linking					After cross-linking		
Glass	− 10	N*	106	I	Glass	65	N*

The polymerization-induced phase separation was initiated by a mercury lamp and carried out in the SmC* phase at 40°C.

2.3. *Measurements*

In order to study variations of polarization during the photocross-linking process, we measured the current passing through the cell under a triangular electric field. The sample was submitted to 70 Hz triangular waves generated by a HP33120A function generator and amplified by a TREK 50/750. The maximum voltage amplitude was +/− 90 V. The current was measured by detecting the voltage drop across a 5 kΩ resistor (R_S) in series with the measured cell. This resistor is sufficiently small in comparison with the impedance of the cell. The current was stored in the HP54610B oscilloscope. The whole set-up was computer controlled through HP Visual Engineering Environment®.

When a voltage $V_0(t)$ is applied to the cell, the voltage drop $V(t)$ measured across the R_S resistor is:

$$V(t) = R_S I_{\text{total}}. \tag{1}$$

This induced current roughly comes from three contributions [18–21]:

$$I_{\text{total}} = I_C + I_I + I_P \tag{2}$$

where I_C is the current due to induced polarization, I_I is the ion flow, and I_P is the contribution from the switching of the spontaneous polarization. Assuming that the liquid crystal cell can be regarded as a resistor R_{LC} and a capacitor C_{LC} connected in parallel, equation (2) becomes:

$$I_{\text{total}} = C_{LC}\frac{\mathrm{d}V}{\mathrm{d}t} + \frac{V}{R_{LC}} + \frac{\mathrm{d}\mathbf{P}_S}{\mathrm{d}t}. \tag{3}$$

A typical signal recorded in the SmC* phase is shown in figure 3. The peak seen in this figure is a result of $\mathbf{P}_S$ reversal.

3. Results and discussion

3.1. *Fast curing process (a)*

Figure 4 presents the evolution of the switching current during the photocross-linking process. Differences

Table 3. Cross-linking conditions.

Fast process (a)			Slow process (b)		
Temperature/ °C	UV intensity/ mW cm^{-2}	Irradiation time/ min	Temperature/ °C	UV intensity/ mW cm^{-2}	Irradiation time/ min
40	20	10	40	2	100

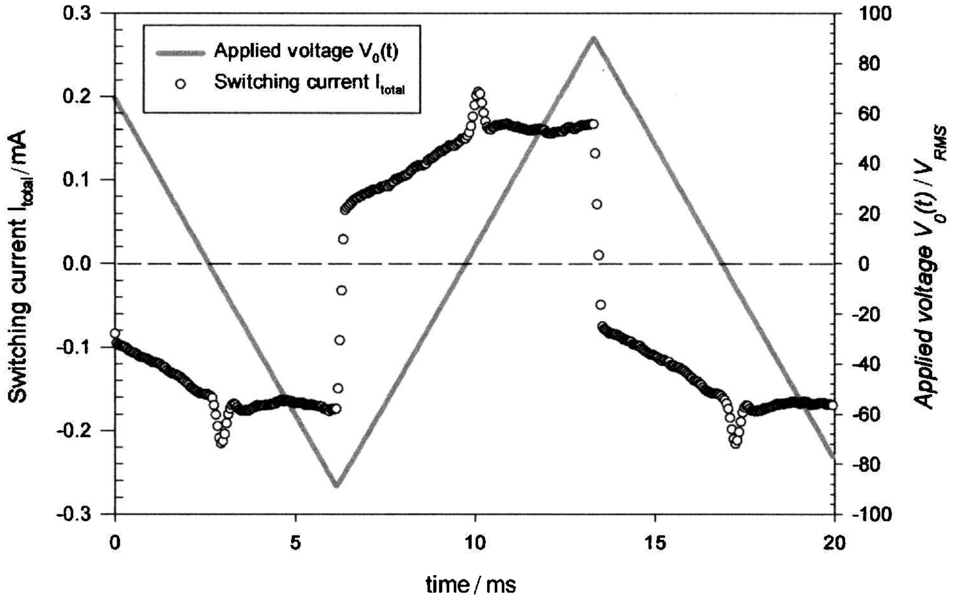

Figure 3. A typical recorded switching current and applied voltage as a function of time.

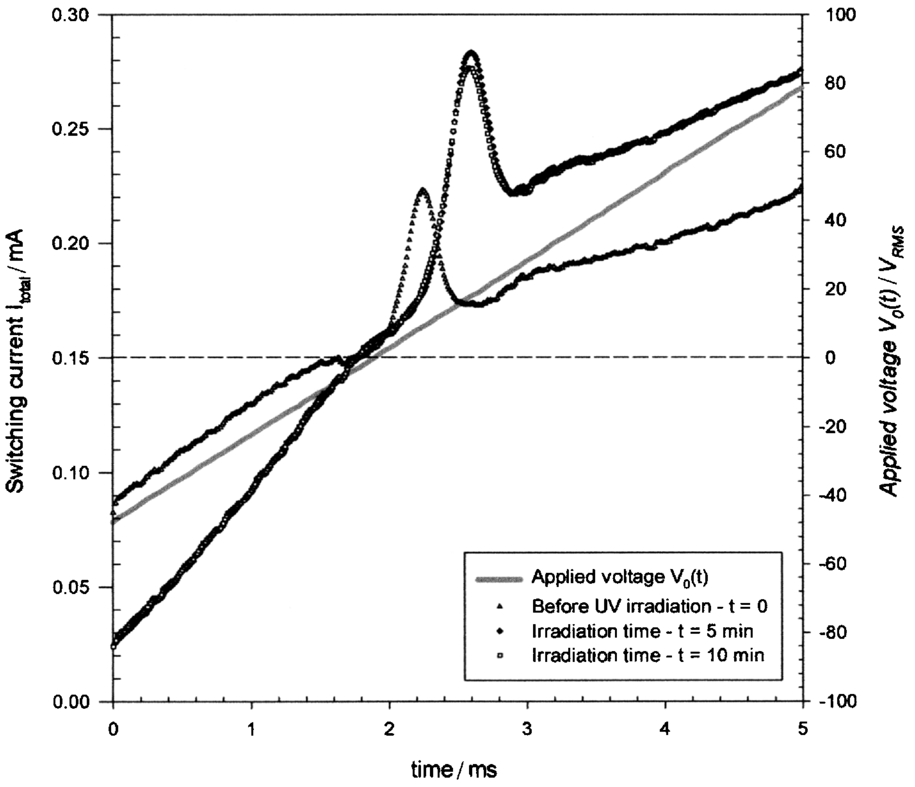

Figure 4. Switching current as a function of time/voltage measured at various stages of the fast curing process.

exist between results obtained before and after UV curing. Results obtained after 5 and 10 min of photopolymerization are almost the same. For this reason, the following discussion will mainly concern the ferroelectric behaviour before and after 5 min of polymerization.

Differences in current detected before and after UV curing (see figure 4) are:

(i) The onset of the peak of the polarization reversal in the UV irradiated material is delayed compared with the non-polymerized state.

(ii) The area of the peak is nearly the same for all detected currents.

(iii) The slopes of the current differ for UV irradiated and non-irradiated materials.

For interpretation of the above results it is necessary to have in mind that the recorded current I_{total} is the sum of three components, see equations (2) and (3). The ionic current I_{I}, which represents the sample conductivity is proportional to the $I_{\mathrm{total}}(V(t))$ slope. The current peak represents I_{P}, the integration of which gives the value of the spontaneous polarization. The current I_{C}, connected with the sample capacity, is given by the jump in current at the maximum field (see figure 3), which equals the sum of the currents at $t=0$ and $t=5$ in figure 4. The polymerization process can affect all these contributions.

To understand the switching current behaviour, several effects have to be considered. One is the screening of the applied field by a layer of ions trapped near electrodes. This effect is known even in pure FLC, where the ions are captured on polymer layers which are applied to electrodes to improve the alignment of FLC [22–25]. Electron microscopy studies have shown that in photo-cross-linking of a cholesteric polymer in a nematic solvent, the polymer preferentially nucleates on the electrodes [16]. As we are using the same photocross-linkable monomer as in [16], a similar behaviour could be expected for the SmC* solvent. The surface polymer layer created by the photopolymerization can allow the trapping of ions at the surfaces and enhance the screening effect. The screening effect effectively increases the threshold field for $\mathbf{P}_{\mathrm{S}}$ switching, which is manifested in the delay of the polarization reversal peak (see (i) above). Besides, the threshold field may also be increased by the increase in rotational viscosity due to the polymerization, as explained in more detail in § 3.3.

The area of the current peak determined by the integration of the data in figure 4 gives the same $\mathbf{P}_{\mathrm{S}}$ values for all the curves in figure 4, equal to 17 nC cm^{-2}. This value is far smaller than the polarization found for G1, the pure FLC ($\mathbf{P}_{\mathrm{S}} \approx 150$ nC cm^{-2}) [15]. In the material before UV irradiation, the observed decrease is, to some extent, due to both a dilution effect and an increase of disorder inside the LC structure brought about by the chiral prepolymer. After UV irradiation, the decrease in $\mathbf{P}_{\mathrm{S}}$ comes from the network-hindering effect on the LC molecules adjacent to the network interface. In microcomposites prepared under a high UV intensity by the fast curing process, a highly cross-linked and dense polymer network arises [8], because the diffusion of components is not fast enough to follow the chemical photoreaction. Such a network can bring about a strong hindering effect [6, 15, 26]. In the present case, we can consider that the number of dipoles involved in the polarization reversal is roughly constant at any stage of the curing process.

The slopes and jumps in the switching current, which reflect the conductivity and capacitance of the material show a non-linear behaviour. Also, an effect of the Maxwell–Wagner interfacial effect [27] is likely to play a role. These phenomena will be studied elsewhere.

3.2. *Slow curing process (b)*

Variations of the switching current during the slow curing process are shown in figures 5 and 6. At the beginning of the curing process, an evolution of the switching current is observed, but after about 20 min the switching curves become almost identical (see figure 6).

For an irradiation time less than 2 min, the reversal peak is still delayed with regard to that before UV irradiation. For longer irradiation, only slight differences in delay are noticeable, but the peak still increases till approximately 20 min. The value of $\mathbf{P}_{\mathrm{S}}$ determined by integration of peaks is shown in figure 7.

From figures 5, 6 and 7 it is not only possible to analyse the effect of the gradual polymer growth on the ferroelectric properties ($\mathbf{P}_{\mathrm{S}}$ values and switching), but also to follow the polymerization kinetics. The evolution of the switching current and its saturation (figure 6) give information on the course of the polymerization reaction and its termination [28, 29], respectively.

Moreover, from the switching current the rotational viscosity can be determined. The coefficient of rotational viscosity γ_{φ} characterizes the ability of the director to rotate on the SmC* helix, which is connected with the dynamics of the polarization reversal [18, 30, 31]. The coefficient γ_{φ} is defined as

$$\gamma_{\varphi} = \frac{S P_{\mathrm{S}}^{2} E_{\mathrm{m}}}{I_{\mathrm{m}}} \tag{4}$$

where S is the area of the electrode and I_{m} is the maximum switching current at $E=E_{\mathrm{m}}$. Equation (4) enables us to calculate the rotational viscosity from the switching current data. The evolution of γ_{φ} during the irradiation process is shown in figure 8.

Figures 7 and 8 exhibit characteristics that can be connected to monomer conversion curves of UV-curable polymers [3, 28, 29]. The kinetics of photo-induced chain polymerization are usually described in terms of initiation, propagation and termination. The conversion rate p as a function of the irradiation time may be approximated as [28, 29]:

$$p = 1 - \frac{M}{M_0} = 1 - \exp\left(-\frac{t}{\tau}\right), \tag{5}$$

where M is the molar concentration of monomers, M_0 is the initial molar concentration of monomers, τ is the characteristic time of the polymerization process and t is the irradiation time. τ is related to the nature of the compounds involved and to the kinetics of the reaction

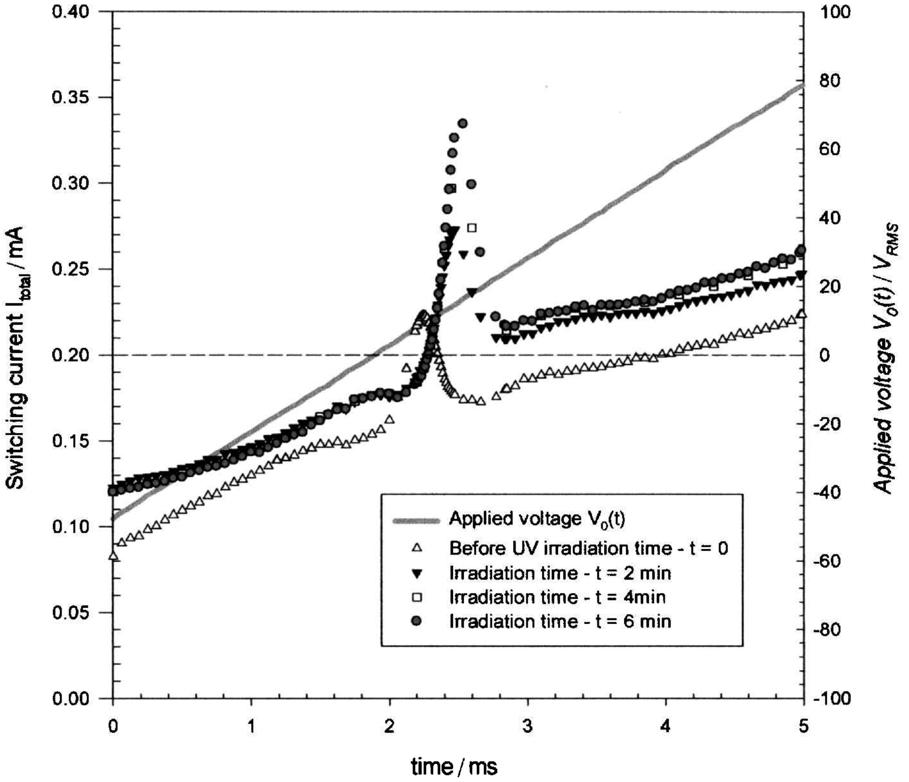

Figure 5. Switching current as a function of time/voltage at various stages of the slow curing process.

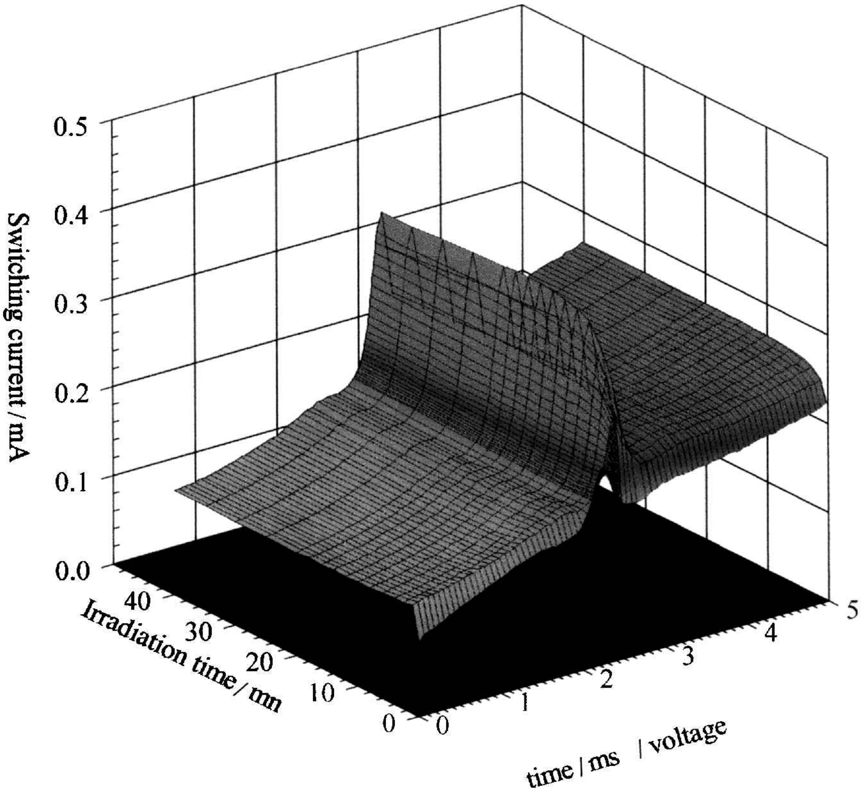

Figure 6. Switching current as a function of time/voltage and the irradiation time for the slow curing process.

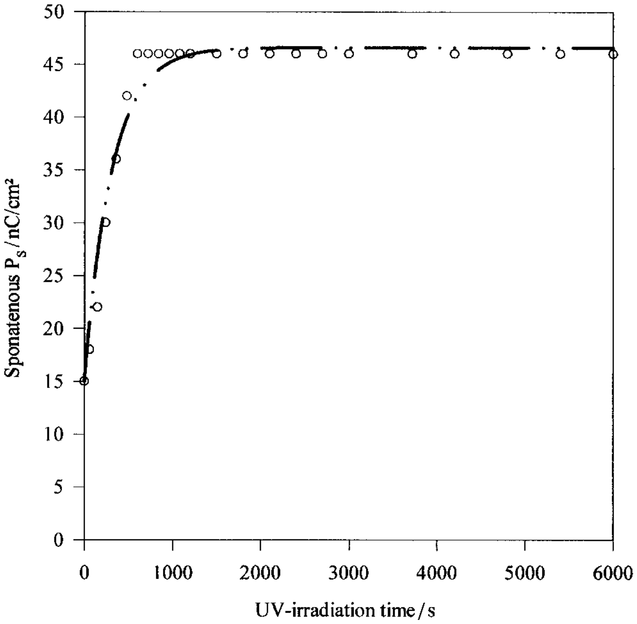

Figure 7. Spontaneous polarization as a function of the irradiation time for the slow curing process. The dashed curve corresponds to an approximate fit to equation (7 *a*).

by the following [28, 29]:

$$\frac{1}{\tau} = k_\mathrm{p}\left[\ln 10 \times \frac{\varepsilon\phi c}{k_\mathrm{t}}\right]\sqrt{I_0} \approx 2.3k_\mathrm{p}\frac{\varepsilon\phi c}{k_\mathrm{t}}\sqrt{I_0} \qquad (6)$$

where I_0 is the incident UV light intensity, k_p and k_t are the rate constants for the propagation and termination reactions, ε, ϕ and c characterize the photoactive agent and are, respectively, its molar absorption, quantum yield and concentration.

The evolution of $\mathbf{P}_\mathrm{S}$ and γ_φ as functions of the irradiation time can be approximated as

$$\mathbf{P}_\mathrm{S}(t) \approx P_0 + P_\mathrm{sat}\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\} \qquad (7a)$$

$$\gamma_\varphi(t) \approx \gamma_\varphi^0 + \gamma_\varphi^\mathrm{sat}\left\{1 - \exp\left(-\frac{t}{\tau}\right)\right\}. \qquad (7b)$$

From figures 7 and 8, it is seen that equations (7 *a*, *b*) satisfactorily fit the experimental results. The fitting constants are in table 4. We mention that the characteristic time τ is the same for both $\mathbf{P}_\mathrm{S}$ and γ_φ data. For this reason, we can suppose that the polymerization proceeds with the time τ as well.

Table 4. Slow process (b): Values of fitting parameters for monomer conversion evolution applied to the total polarization and the rotational viscosity.

P_0/ nC cm^{-2}	P_sat/ nC cm^{-2}	γ_φ^0/ mPa s	$\gamma_\varphi^\mathrm{sat}$/ mPa s	τ/ s or min
14.8	31.2	18.72	152	314 or 5

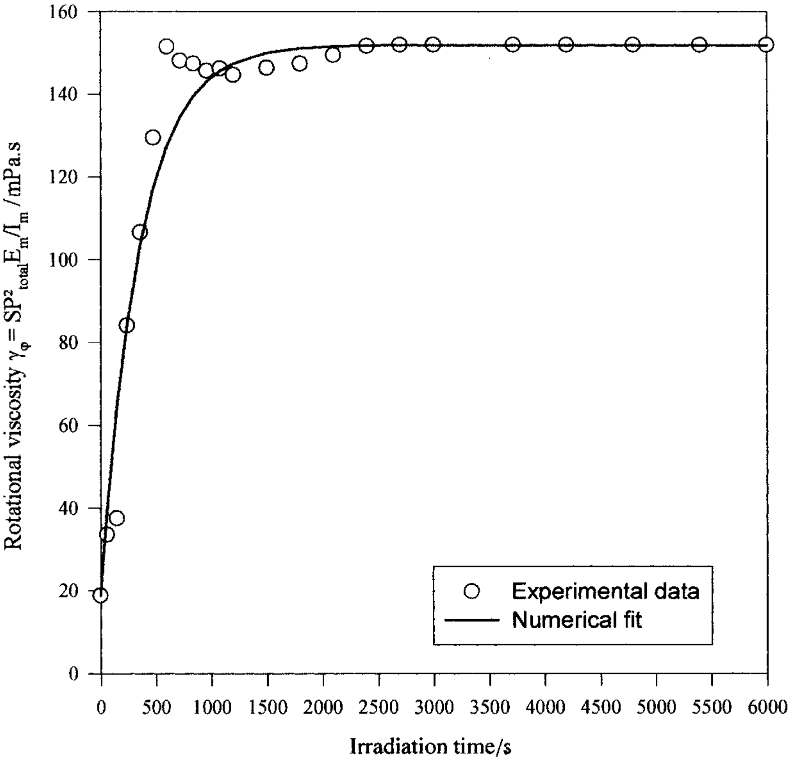

Figure 8. Evolution of the rotational viscosity γ_φ during the cross-linking by the slow curing process: the full curve is a fit to equation (7 *b*).

Assuming that the same kinetic constants are also valid for the fast curing process (a), equation (6) gives a characteristic polymerization time of about $314/10^{1/2} \approx 99$ s.

Knowledge of the characteristic time of a polymerization process is essential in designing a curing procedure for preparation of ferroelectric microcomposites. Moreover, measuring variations of the switching current during the polymerization process could be a way to study the influence of other factors, e.g. the temperature or pooling voltage, involved during the microcomposite elaboration step.

4. Conclusion

It has been shown that the ferroelectric properties of a composite—namely the $\mathbf{P}_S$ value, threshold field and switching speed given by the viscosity—depend on the kinetics of the photopolymerization process. The *fast curing process*, which leads to a very dense polymer network brings about a strong hindering of switching and a strong decrease of the $\mathbf{P}_S$ values compared with the pure FLC. On the contrary, the *slow curing process* produces a polymer network that affects the liquid crystal matrix only slightly, so that the ferroelectric properties of the resulting microcomposite are less diminished.

The photopolymerization kinetics are described by examining the evolution of the switching current as a function of the irradiation time for a low UV intensity ($2\,\mathrm{mW\,cm^{-2}}$). It is found that the time evolution of the spontaneous polarization and the rotational viscosity during the photopolymerization process follow the same law with equal characteristic times. It can be concluded that the same law applies for the photopolymerization kinetics. The same technique, i.e. measurement of the switching current during the irradiation time, could be used for studies of the photopolymerization kinetics in more detail, in terms of its dependence upon temperature, UV intensity, or electric field.

Further investigations on the nucleation and growth of the polymer network must be carried out. Especially, it would be interesting to draw a parallel between the polymerization process and the nucleation patterns obtained by electron microscopy.

Finally, this study could be completed with dielectric studies. Particularly, the role of trapping of ionic charges by the polymer network in relation to the sample capacity (Maxwell–Wagner effect) should be elucidated.

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