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J. Nourry; P. Sixou

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Formation of polymer network liquid crystal microcomposites: evolution of mechanical properties during the curing process

J. NOURRY and P. SIXOU*

Laboratoire de Physique de Matière Condensée, CNRS UMR 6622, Parc Valrose,
F-06108 Nice Cedex 2, France

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Liquid crystal/polymer network composites with small amounts of photocrosslinkable cholesteric prepolymer are described. Rheological experiments are used to study the evolution of the mechanical properties of the composite material during the UV curing process. The behaviour of the complex shear modulus during the formation of the polymer network leads to a gelation-like description. Corresponding critical exponents have been proposed and discussed in the frame of percolation.

1. Introduction

In recent years, much work has been devoted to polymer/liquid crystal microcomposites, mainly because of their promising potential in electronic displays and smart windows applications [1–3]. Depending on the mass content of polymer in the system, after phase separation (temperature, solvent or photochemically induced phase separation), the microcomposite obtained exhibits either a closed porosity (polymer dispersed liquid crystal, PDLC) or an open porosity (polymer stabilized liquid crystal, PSLC) [4]. Advantages of these materials against single liquid crystals have been fully reported [1, 2] and it emerges that the elaboration process is an essential stage to the electro-optic performance of the microcomposite. Not only have the respective proportions of liquid crystal and polymer to be taken into account, but also the path to phase separation is important.

According to the operating method, completely different morphologies are observed [5–13]: polymer fibres of tenths of microns, polymer balls of ten or so microns diameter, and even tablet-like patterns.

The principal points to be taken into account and usually reported in the literature can be roughly and succinctly summarized:

- (1) Different morphologies are observed depending on the liquid crystal phase (smectic, nematic or isotropic). Thus, for the same liquid crystal compound, there has been reported a polymer ball-like morphology for a sample prepared in the isotropic phase, whereas the same preparation in

the nematic phase yields a texture half of polymer balls and half of fibres. Fibres are observed for the case of the smectic phase [6].

- (2) A high UV power leads to a polymer ball pattern whose size is smaller than that obtained for materials irradiated under lower intensities [9]. Furthermore, threshold voltages are smaller and OFF states are less scattering.
- (3) Irradiation time seems to play a lesser role in determining the size and shapes of the polymer balls excepted for very short times. It has been reported that materials prepared with a short irradiation time reveal lower threshold voltages and clearer ON states.
- (4) When the polymer ball morphology is observed, the size of the pattern is connected to the polymer concentration [7, 8].
- (5) Even in the same liquid crystal phase, temperature changes introduce modifications to the morphologies. Polymer balls and fibres, as well as the average porosity size are larger [8]. Consequently, more diffusive materials in the OFF state with smaller threshold voltages are obtained [8].
- (6) Reports [9] have suggested that the photo initiator amount has also to be considered. The lower its value the larger the ball size, but smaller contrasts and higher threshold voltages are found.
- (7) Finally, even with identical operating methods, morphologies obtained can be different for different monomers of the same chemical family [7, 8, 12, 13]

The above list is intended to illustrate that the elaboration of the microcomposite is quite a complex

* Author for correspondence, e-mail: sixou@unice.fr

problem in which the relevant parameters involved may have combined or opposite effects. Furthermore, some of them may be difficult to assess. For instance, as has been shown in [14], in some cases, we have to take into account the behaviour of each compound, regardless of the others, especially when we have sandwiches between two glass walls. For instance, the polymer can preferably adopt a planar alignment, whereas the non-reactive liquid crystal molecules exhibit homeotropy. This is the case for most cyanobiphenyl liquid crystals [13].

However, all of the previous investigations and qualitative models proposed [7, 8] only deal with the final material characteristics. None of them includes indications concerning the elaboration path.

The present work considers polymer networks in which the polymer is in the minority (less than 20 wt %). Moreover, unlike most of the previous papers quoted, the experiments reported concern composites obtained by *in-situ* photopolymerization for a solution of cholesteric monomers dissolved in low molar liquid crystals. We carry out investigations on the elaboration of the microcomposite by following the evolution of the composite's mechanical behaviour, analysing at any stage of the polymerization process the growth of the polymer network and the inner structural modifications. As a conclusion, a qualitative scheme is drafted in order to explain the formation of the microcomposite.

2. Experimental

2.1. Materials

The liquid crystal material, 5CB, used in our study is a single component cyanobiphenyl. The photocrosslinkable polymer is a polysiloxane with both reactive and mesomorphic side groups. It is a cholesteric liquid crystal which reflects light in the visible range. The phase sequences of the different materials are shown below. Photopolymerization is initiated using Irgacure 907 (Ciba-Geigy).

The 5CB phase sequence (data from E. Merck):

$$\text{Cr } 24 \text{ N } 35.5 \text{ I } (^{\circ}\text{C}).$$

The phase sequences of the photocrosslinkable polymer:

before crosslinking, glass – 10 N* 106 I;

after crosslinking, N* glass 65 N* ($^{\circ}\text{C}$).

Concerning the mechanical studies, the polymerization-induced phase separation was initiated by a mercury lamp and carried out in the nematic phase at 25°C . The UV irradiation intensity was about 0.5 mW cm^{-2} .

2.2. Set-up and measurements

Figure 1 summarizes the experimental set-up as far as the mechanical studies are concerned. Measurements

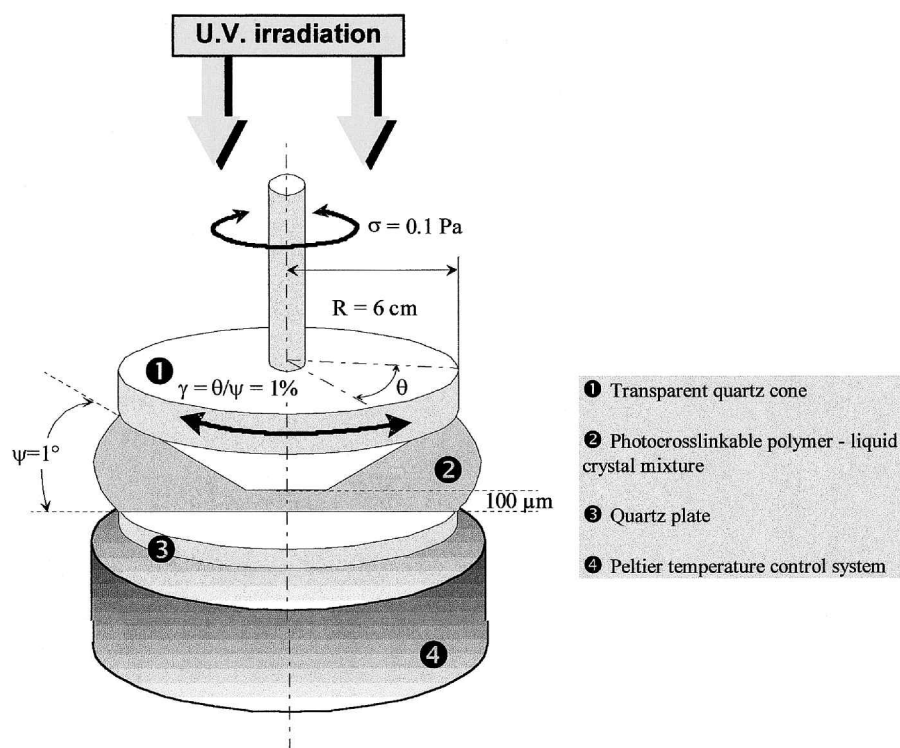


Figure 1. Measurement of the shear complex modulus G^* with a cone and plate device.

were carried out using a Carri-Med CSL 100 rheometer (Carri-Med Ltd, Dorking UK) in its constant strain mode [15, 16].

The photocrosslinkable polymer–liquid crystal mixture (2) is placed between a cone (1) and a flat plate (3) with a gap set to 100 μm; both have transparent polished quartz surfaces. The angle (1°) between the cone and the plate is rather small.

Experiments were made at 25°C; mixtures were thermally controlled by a Peltier system from –10 to 100°C.

Customarily, in rheological experiments, a stress σ is applied to the sample and the corresponding deformation γ is measured. As for our apparatus, a permanent feedback exists between these two measurements. In fact, for a desired strain we try to find out the correct stress [14, 15]. Strain and stress are recorded simultaneously.

For the present studies, an 0.1 Hz oscillatory movement about a vertical axis is imposed on the upper plate. The lower plate is held firm. The whole apparatus is computer driven. Displacement of the cone and the torque applied are assumed to be proportional to the strain γ ($\gamma = \theta/\psi$) and to the stress σ , respectively.

Since the plates are transparent, it is possible to study the mechanical properties of the material during the photocrosslinking process. But, in order to introduce as few disturbances as possible on the final microcomposite material, only small deformations were considered. The strain γ was set to 1% and the stress σ to 0.1 Pa. In these restrictions, σ and γ are proportional [16]:

$$\sigma = G^* \gamma = (G' + iG'') \gamma = |G| \exp(i\delta) \gamma \quad (1)$$

where G^* , G' and G'' are, respectively, the complex, the storage and the loss moduli of the material. Customarily, the loss tangent, defined as $\text{tg } \delta = G''/G'$, is considered. Both the phase lag δ and $|G|$ completely describe the whole mechanical behaviour of the material. One should note that $\text{tg } \delta$ usually varies with both temperature T and angular rate ω . In particular for a polymer, the loss tangent passes through a maximum at the material's glass temperature, T_g [17].

In gelation processes, rheological properties are characterized in the limit of low frequencies [18]. In this framework, G' is related to the Coulomb shear modulus G_s of the material, while G'' is connected to its shear viscosity η_s .

3. Results

Variations of the real, G' , and the imaginary, G'' , components of the complex shear modulus during the photopolymerization process are shown in figure 2. Different concentrations of polymer have been considered.

For small concentrations of polymer (3 wt %), both the storage and the loss moduli undergo only small variations and are only slightly affected by the polymerization process taking place. Both G' and G'' are in the same range of order (10^{-2} Pa).

On the contrary, at higher percentages of polymer (6 or 10 wt %), the moduli vary by approximately three orders of magnitude (from 10^{-4} to 10^3 Pa). Particularly, when their variations are reported as a function of UV irradiation time, a discontinuity is observed. This occurs after different delays depending on the polymer concentration. The higher the concentration, the smaller the delay. For 10 wt %, G' and G'' plateaus are not clearly observed (figure 2). This early data break comes from the rheometer feedback procedure of measurement. Furthermore the variation range of the moduli is seven orders of magnitude and the accuracy is not very good for low values of the moduli; this can explain why the stored moduli for both 6 and 10 wt % are lower than the modulus for 3 wt %.

4. Discussion

The curve discontinuities observed for both G' and G'' in figure 2 are analogous to descriptions of gelation or percolation models [17–28].

At the very beginning, of the UV irradiation, the composite material is a homogenous viscous fluid. As the photopolymerization proceeds, polymer clusters of growing size appear in the bulk sample. As a consequence, the viscosity of the material increases. After a critical irradiation delay t_c , a cluster spreads throughout the sample connecting both the glass cone and plate surfaces. At t_c a gelation-like phenomenon occurs. Beyond t_c the composite material behaves like a solid. Furthermore, both the polymerization rate and the conversion increase with increasing prepolymer concentration [12]. This remark suggests that the gelation time t_c has to decrease with prepolymer concentration. This fact is in agreement with the data reported in figure 2.

Static gelation phenomena can be described by the Flory–Stockmayer tree-like percolation model [24]. According to this theory, on approaching both sides of the gel point p_c , the mechanical behaviour of the material is different [17, 22–27]:

$$\begin{aligned} p \rightarrow p_c^+ \quad \eta_s &= \eta_0 (p_c - p)^{-k} \\ p \rightarrow p_c^- \quad G_s &= G_0 (p - p_c)^\alpha \end{aligned} \quad (2)$$

where η_0 and G_0 are constants depending on the microscopic properties of the medium; k and α are critical exponents; p is the conversion factor linked to the fraction of links formed between monomers. In other words, p corresponds to the number of links at a given time related to the maximum number of available links.

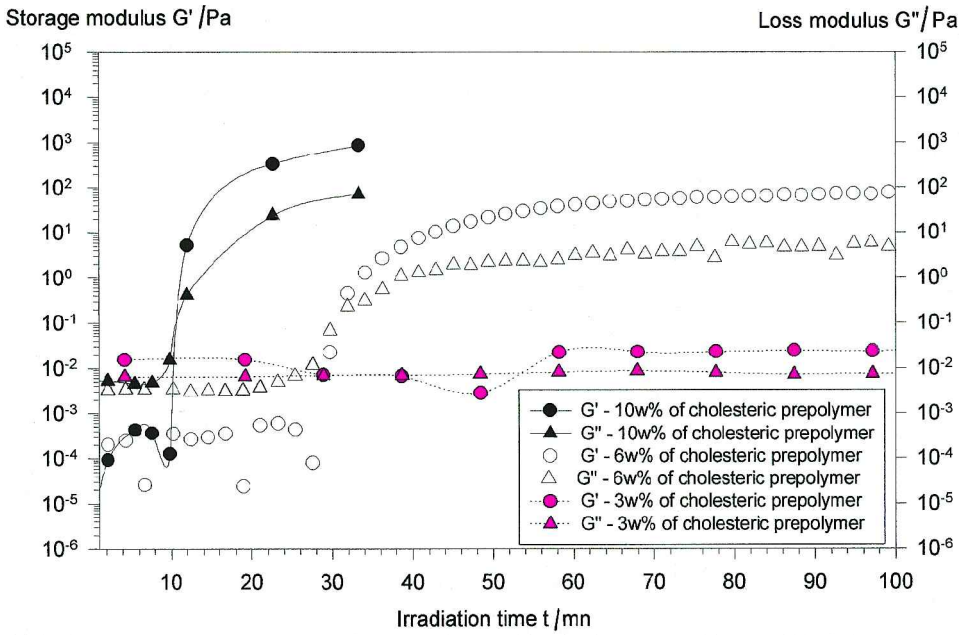


Figure 2. Storage and loss moduli as a function of the irradiation time.

At the initial time, $p = 0$, there is no link. At $p = 1$, all allowed links are set and we have a macroscopic cluster connecting the extreme parts of the sample.

In fact, at the gel transition, it has been observed that $(p - p_c)$ is most often proportional to the time shift $(t - t_c)$ or the temperature shift $(T - T_c)$ [17, 25–28].

Previous considerations mainly concern static experiments. In fact, for polymer gelation obtained in dynamic

conditions, such as those considered in our experiments, a similar description holds in terms of percolation theory and power-law behaviour [27].

At the very first, the viscoelastic material is a viscous liquid and the G' and G'' shear moduli are given by [27]:

$$G' \approx \omega^2 \quad \text{and} \quad G'' \approx (t_c - t)^{-k} \omega. \quad (3)$$

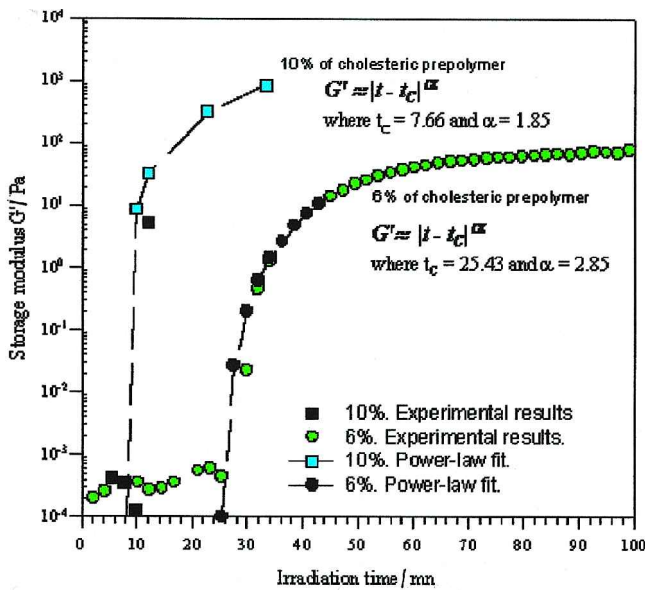


Figure 3. Loss modulus: approximation of the gel point in the framework of the power-law percolation theory.

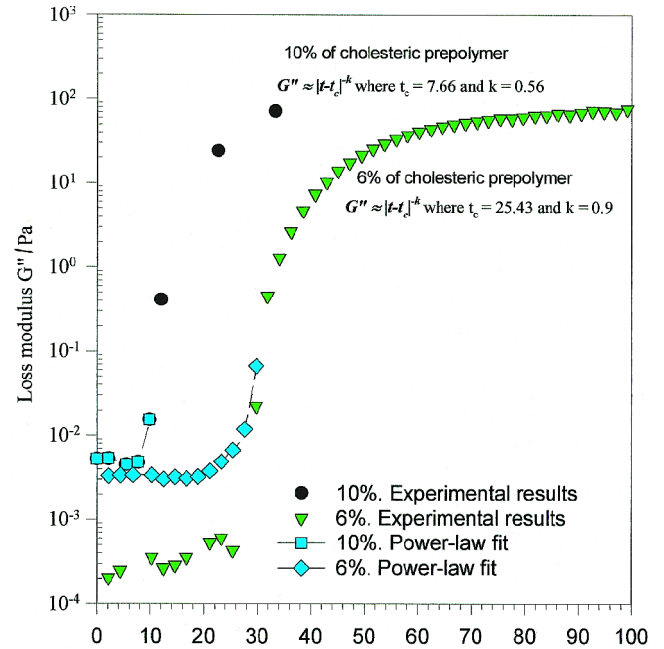


Figure 4. Storage modulus: approximation of the gel point in the framework of the power-law percolation theory.

At the end of the gelation, the material behaves like a solid, and the result is that [27]:

$$G' \approx G_0(t - t_c)^\alpha \quad \text{and} \quad G'' \approx (t - t_c)^{-k} \omega \quad (4)$$

Figures 3 and 4 focusing, respectively, on the loss shear modulus G'' , and the storage modulus G' , reconsider the mechanical data found at any stage of the photopolymerization process in the scheme of a power-law variation.

From figures 3 and 4, the critical exponents can be calculated, and the table gives the different behaviours observed according to the prepolymer concentration. The values reported are of the same order as those found from other chemical gel experiments [17, 25–28].

5. Conclusion

Although a relatively abundant literature is devoted to the polymer gelation phenomenon in isotropic media in the frame of percolation theory, fewer investigations have involved anisotropic media. Our preliminary investigations show the possibility of studying the percolation process in mesomorphic gels. A gel point transition has been observed. Calculations give critical exponents in agreement with those usually obtained for chemical gels.

The experimental system described in this paper offers a large range of possible adaptations. Numerous parameters could be easily modulated. For instance, an electric field could be applied during the UV curing process, modifying the anisotropy of the liquid crystal solvent and consequently growth of the polymer network.

In fact, as we have underlined in the introduction, the parameters involved in mesomorphic gelations are numerous and interdependent. Studies are underway to understand the roles played by parameters such as thickness, nature of the low molar mass liquid crystal solvent or the architecture of the monomer and its concentration on the mechanical properties of the final microcomposite. Comparisons between our observations and those published by Finkelmann and Rehage on liquid crystal polymers [29], will be made. An effort has to be made to connect the morphologies observed by electron or optical microscopy and the mechanical characteristics recorded. Moreover, as a relatively poor literature exists on this topic, it should be interesting to

understand connections between the mechanical properties of the material and the growth process.

Finally, in recent years, polymer network growth has attracted considerable attention from the fundamental point of view. Particularly, it has been reported that a phase separation occurs prior to gelation before the aggregation of phase-separated polymer microgel particles. Optical observations between crossed polarizers of the phase separation process are characterized by a sharp increase in the turbidity of the sample [12]. Investigations could be undertaken to study this transition through both the mechanical and optical changes involved. Schematic mechanisms have been proposed [12, 30, 31] to explain polymer network formation, but, none of them has considered the prime role played by nucleation on surfaces at the very beginning of photopolymerization. As treating the glass walls in our experiment is relatively straightforward, the influence of the nature of anchoring forces on the mechanical properties would constitute an interesting study.

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Table. Critical exponents for different prepolymer concentrations.

Prepolymer concn./wt %	Critical exponents	
	k	α
6	0.9	2.85
10	0.56	1.85

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