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SEM Investigations of the Polymer Morphology in the Liquid Crystal-Polymer Composites with Different Polymer Contents

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Scanning electron microscopy was employed to study the evolution of the morphology of liquid crystal-polymer composites with increasing contents of a polymer. The composites were formed by a nematic mixture E7 from Merck and a photocurable adhesive NOA65 from Norland by means of photoseparation. The polymer phase reveals a smooth transition from a polymer network to a sponge-like structure and then to the 'Swiss cheese' morphology with the increasing fraction of a polymer. It is established that the best electro-optic performance is demonstrated by samples with the well-developed sponge-like structure of the polymer phase.

Keywords: liquid crystal; PDLC; polymer network; polymer network liquid crystal

1. INTRODUCTION

The composites of liquid crystals (LC) with polymers (P) represent the separate class of heterogeneous LC systems. In such systems, the phase boundary properties of LC and a polymer are interesting from a scientific point of view [1]. At the same time, LC-polymer composites form a technological basis for optical devices [2,3]. Depending on the polymer concentration in a composite and preparation conditions, one can obtain different structures of the polymer phase. Under the same conditions of preparation, the concentration of components become a decisive factor for the polymer matrix morphology. In the case of a

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low polymer content (≤ 5 vol.%), the polymer network liquid crystal (PNLC) structure is formed [4,5]. In this case, the polymer network is immersed in the LC medium. When the polymer concentration is higher (≥ 20 vol.%), liquid crystal domains dispersed in the continuous polymer matrix are formed [1,6,7]. The corresponding composites are designated as polymer dispersed liquid crystals (PDLC). In the general case of chaotically oriented LC domains, a composite scatters light. Scattering centers appear between the neighboring LC domains, inside the individual domains, and on the LC-polymer interface. In an electric field, the LC is aligned, the amount of optical defects drastically decreases, and the system becomes transparent. The electrically controlled light scattering of LC-P composites has application in switchable windows [8], electro-optic shutters [1–3,9], conceptual models of displays [1–3,10], and switchable gratings [10,11].

The quantity, shape, and orientation of LC domains in the polymer matrix have an influence on the optical properties of the composite. These factors in many respects are determined by the internal structure of the polymer phase. Typically, the polymer structure in LC-polymer composites is obtained as a result of the phase separation of the LC-pre-polymer mixture during the photo- and thermopolymerization or solvent induced polymerization [6,7]. The formation of a polymer morphology is stipulated by several processes, namely: polymerization, phase separation, and phase ordering. These processes are interconnected, and their complex exploration is difficult. They are determined, in turn, by component concentrations and solubilities [5,12], ordering of the LC and polymer phase [4,5], temperature [13], pressure [9], intensity of UV irradiation in case of photopolymerization [14], etc. Different scientific groups concentrate on different aspects of the composite's formation.

In this article, a more attention is paid to the composite morphology in view of the polymer concentration. To pick out the concentration dependence, preparation conditions were kept the same. The majority of the articles mentioned above dealt with either PNLC or PDLC morphologies. We take a wide region of polymer concentrations (6.5–60 vol.%) in order to observe morphologies and transition between them. The SEM is used to give us the possibility to study the structure of the polymer phase and characterize it by such parameters as the density and the shape and size of voids accommodated by LC. This article supplements our previous work concerning the electro-optical properties of LC-P composites [15,16]. The comparison of electro-optical and morphological data shows their correlation. In addition, it allows one to find a morphology of samples most suitable for electro-optical applications.

2. MATERIALS AND METHODS

The commercially available polymer material we used is photo-sensitive adhesive NOA65 from Norland Inc. Chemically, it contains trimethylolpropane diallyl ether, trimethylolpropane trithiol, isophorone diisocyanate ester, and benzophenone photoinitiator. It is a clear, colorless, liquid mixture hardening when exposed to ultraviolet light. The NOA65 composition is widely used in preparation of LC-Polymer composites [12,15–17]. As a liquid crystal, we used the nematic liquid crystal mixture E7 from Merck.

The components were thoroughly mixed under red light to avoid the early polymerization of NOA65. We prepared the mixtures with several polymer concentrations: 6.5, 25, 35, 50, and 60% in volume. The mixture was sandwiched between two glass substrates. The cell gap was maintained by a 20- μm spacer film. The substrates were pressed and glued with epoxy glue. To initiate the polymerization-induced phase separation, the mixtures were irradiated with UV light from a high-pressure mercury lamp ($I = 100 \text{ mW}/\text{cm}^{-2}$, 20 min) at room temperature.

SEM measurements were carried out by using Hitachi S-2600N. It is important to note, that electron microscopy doesn't allow one to investigate the intact sandwiched composite films. For these studies, the samples were disassembled. The top glass substrate was removed, and the remaining part of the sample was immersed into ethanol of purity 98% for 24 h in order to dissolve and extract the LC fraction from the composite. Then the remaining polymer matrix was taken out from ethanol, dried, and coated with gold. So the dark areas in the SEM microphotographs, revealing the absence of the material, corresponded to the original LC domains. Below, we will discuss voids in the polymer matrix or (that is the same) LC domains which occupy these voids.

3. RESULTS AND DISCUSSION

Some numerical data related to the polymer structure are presented in Table 1. Experimental data are organized to make out the correlation between the polymer concentration and structural changes in the composite.

Numerical estimations were made on the basis of our SEM images. On the photos, we chose the field of vision which has an area of $100 \times 100 \mu\text{m}^2$. The average domain size was obtained as the arithmetic mean, when calculated the amount of domains on this area and their rough size. Also we plotted the size distribution for the LC

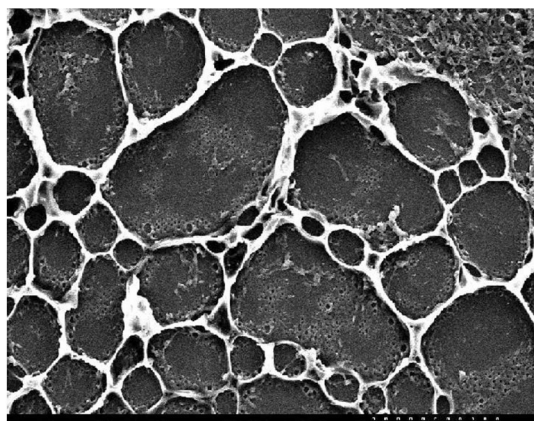
TABLE 1 Statistical Data About the Polymer Morphology in the LC-polymer Composites with Different Polymer Concentrations

Polymer concentration, vol. %	6.5	25	35	50	60
Average size of the network domain, μm	50	9	5	2.1	<1
Half-width of domain size distribution, μm	20–70	7–12	3.5–7.5	1.4–2.2	–
Number of domains per $100 \times 100 \mu\text{m}^2$	2	85	133	271	–

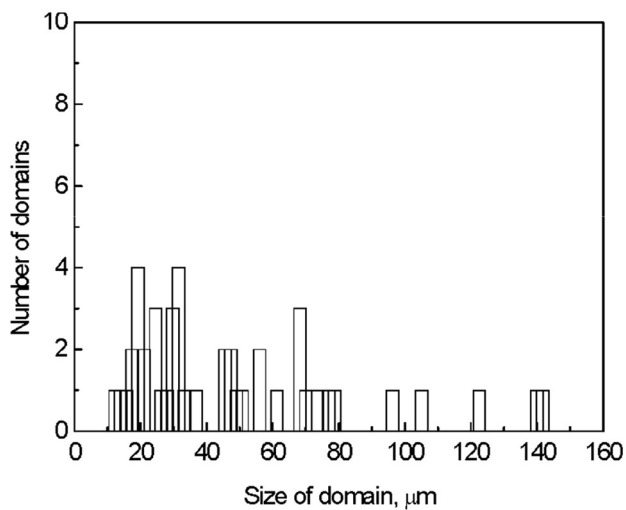
domains in the field of vision and estimated the half-width of this distribution. In Figure 1a, the polymer matrix of the composite with 6.5 vol. % of polymer is represented. This lower polymer content yields the formation of a flimsy polymer network with a small amount of large voids corresponding to LC domains. In this case, the network may contain fibers which are not attached to the glass substrate or each to other. So the composite may be represented as a polymer network floating inside the LC medium. Voids (network loops) corresponding to LC domains have a comparatively large size of 20–70 μm and a non-spherical elongated form. The void size distribution is wide, and there are no voids of prevalent size (Fig. 1b). During the phase separation, the liquid crystal is forced out to the big domains of irregular form because of a low polymer content. Optically, this composite scatters light weakly due to a low system dispersity. Thus, the switching contrast of the composite is poor (between 2:1 and 6:1) [15,16]. Increasing the polymer content up to 25 vol. %, we obtained a structure of the polymer matrix close to that of the PDLC morphology (Fig. 2a). The structure becomes denser, and LC domains are more closely packed. The amount of LC domains is much higher, and they have a smaller size from 7 to 12 μm . The size distribution of the LC domains becomes narrower. The shape of the domains becomes nearly spherical. The polymer network in this case is stronger connected to the substrates of the sample.

The polymer matrix has structure of a sponge. The voids are interconnected so that LC domains are not isolated. This explains why LC flows out of voids if a disassembled sample is placed in ethanol. The optical contrast for this composite becomes higher (from 15:1 up to 45:1), when compared with the previous one [15].

The polymer structure for the LC-P composite with 35 vol. % of the polymer is shown in Figure 3a. It is evident that the packing of LC domains is closer. Figure 3b shows that LC domains become more uniform by size. The average size of domains is 5 μm . So it is getting smaller with the polymer concentration and approaches values most



(a)



(b)

FIGURE 1 Polymer morphology in the LC-polymer composite with 6.5 vol% of a polymer. (a) SEM image of the polymer phase; (b) diagram of the size distribution of voids in the polymer phase.

suitable for a strong scattering of light [6]. A small domain size superposes with the close packing of domains giving the maximal scattering in the field off state. This determines, in turn, the maximization of the switching contrast at a level of 170:1 earlier observed for the composites with 35–40 vol.% of a polymer [15,16].

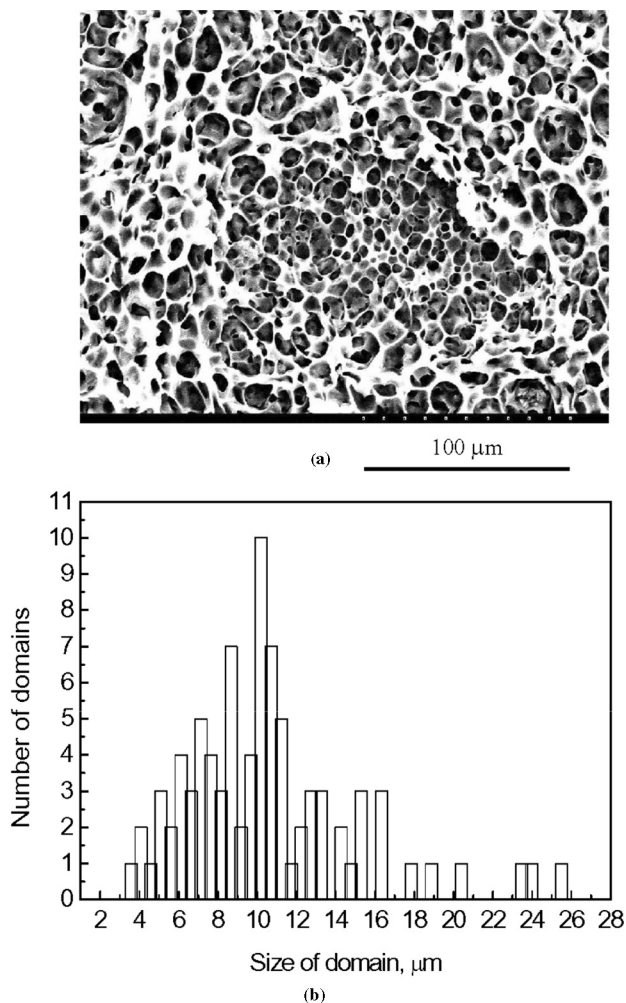
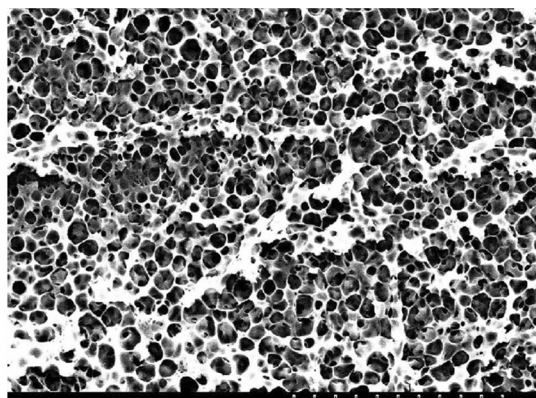
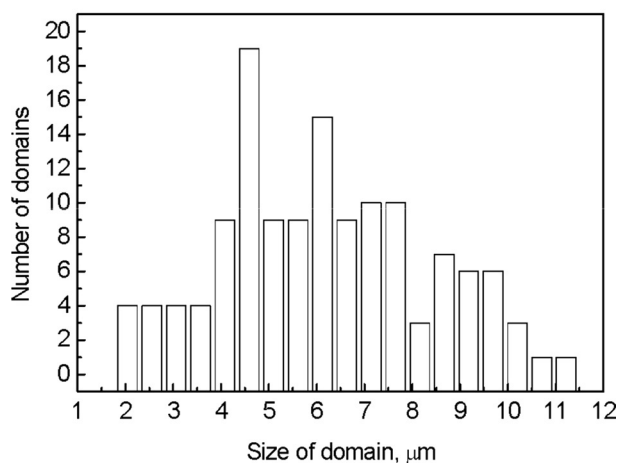


FIGURE 2 Polymer morphology in the LC-polymer composite with 25 vol.% of a polymer. (a) SEM image of the polymer phase; (b) diagram of size distribution of voids in the polymer phase.

The raising of the polymer content up to 50 vol.% leads to a further decrease of the size of LC domains (1.4–2.2 μm) and a narrowing of the size distribution (Figs. 4a and 4b). At the same time, because of the growing polymer part in the composite, the interdomain distance increases and so lengthens the mean free path of light. This weakens the scattering and lowers the switching contrast, which corresponds to



(a)



(b)

FIGURE 3 Polymer morphology in the LC-polymer composite with 35 vol.% of a polymer phase. (a) SEM image of the polymer phase; (b) diagram of size distribution of voids in the polymer phase.

the experimental observation [15,16]. Compared to the samples of a lower polymer concentration, the interconnection of voids considerably decreases, so that the morphology of sample is more similar to the 'Swiss cheese' PDLC morphology.

We also tried to study the morphology of samples with 60 vol.% of the polymer. In the beginning of the scanning, one can observe solitary voids with the diameter less than 1 μm. But the morphology gradually

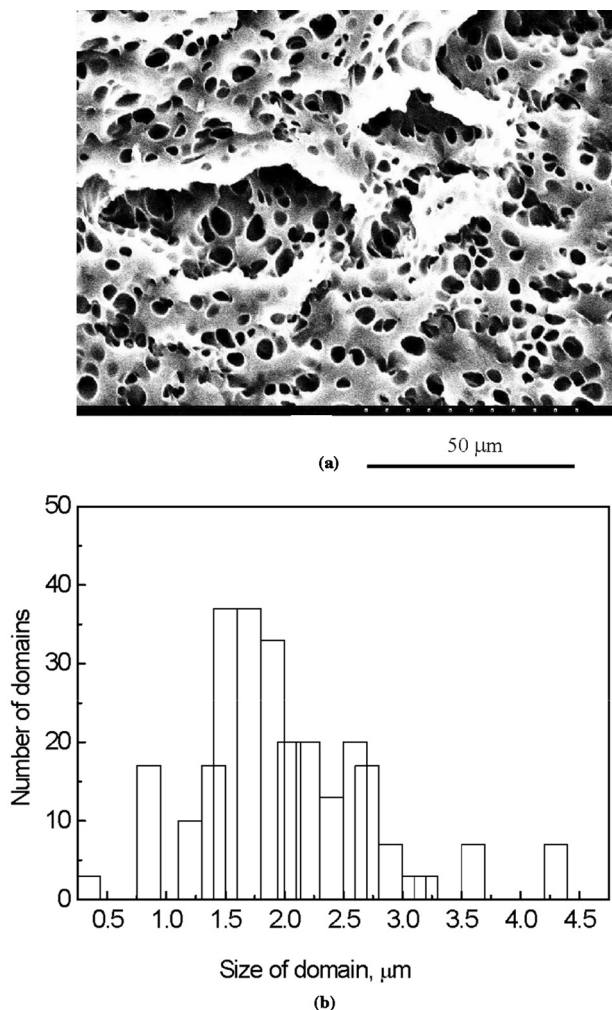


FIGURE 4 Polymer morphology in the LC-polymer composite with 50 vol.% of a polymer. (a) SEM image of the polymer phase; (b) size distribution of voids in the polymer phase.

changed in the process of SEM: the appearance and the growth of new holes were observed (Fig. 5). This can be caused by the sample degradation under the electric field and heat introduced by a measuring system. This sample seems to be too soft for SEM studies because of a high content of the liquid crystal comprised to isolated voids and dissolved in the polymer matrix. The SEM images obtained for

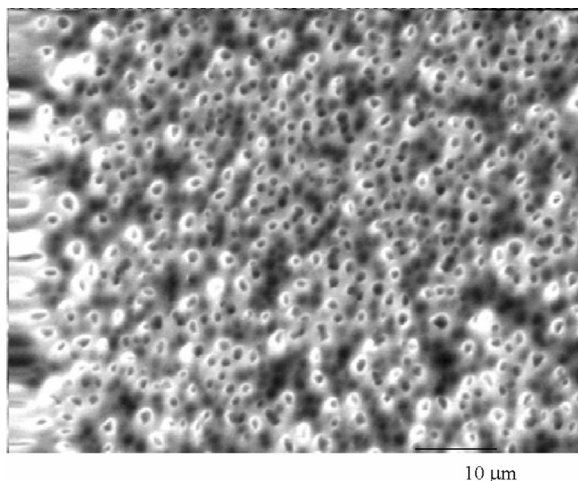


FIGURE 5 SEM image of the polymer phase in the LC-polymer composite with 60 vol. % of a polymer.

this concentration were not analyzed because of the poor reliability of data.

4. CONCLUSIONS

The SEM method is applied to study the evolution of the morphology of liquid crystal – polymer composites with increase in the polymer fraction. These studies reveal the permanent transition from the polymer network of LC to the sponge-like PDLC morphology and then to the ‘Swiss cheese’ PDLC morphology. The increase of the polymer concentration results in narrowing the size distribution of LC domains and the monotonic decrease of their average size. The comparison with electro-optic studies [15,16] shows that the best electro-optic characteristics are demonstrated by samples with the well-developed sponge-like structure having the average size of voids of about 5 μm.

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