COMPARATIVE STUDY OF PDLC COMPOSITES BASED ON NEMATIC AND SMECTIC LIQUID CRYSTALS

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Two different polymer dispersed liquid crystals (PDLC) systems have been prepared by dispersing two mesogenic compounds: a first one with a nematic mesophase 4-cyano-4'-pentylbiphenyl and a second one with a smectic mesophase: Butyl-p-[p'-n-octyloxy benzoyloxy] benzoate in a biocompatible polymeric matrix: polyvinyl alcohol boric acid. Combining the advantages of PVA with the ones of boric acid, the PVAB proved to be able to interact with the liquid crystals molecules constraining them to form droplets with a narrow dimensional polydispersity as was observed by polarized optical microscopy (POM) and scanning electron microscopy (SEM). The systems have been characterized also by differential scanning calorimetry (DSC), revealing once more the interactions established between the polymeric matrix and the liquid crystal molecules. In order to estimate the potential biocompatibility of the developed systems, their wettability was determined by measuring the water to air contact angle and by calculating the surface forces, being observed that the structure of the liquid crystals is an essential parameter influencing the characteristics of the PDLC composites.

INTRODUCTION

Prepared for the first time by Ferguson in 1984,1 polymer dispersed liquid crystals (PDLC) are an important class of materials, consisting in micrometric liquid crystal droplets dispersed in a polymeric matrix, successfully combining the properties of the two components.2,3 Different polymers have been used as matrices for PDLC preparation: chitosan,4 polyethylenoxide,5 polyacrylates,6 polyvinyl alcohol,7 polystyrene,8 polysulfones,9 while as liquid crystals, generally the CN-biphenyl based compounds are used.10 The PDLC composites are appropriate for a large range of applications such as holographic systems, lenses, lasers or smart windows.11-16 More recent studies brought out to light new applications of the PDLC systems in food industry and bioengineering such as: smart food packaging,17 biosensors18 or tunable artificial irises.19,20 Of course, when such bio-applications are envisaged, biocompatible materials are required.

Given this context, we propose the use of polyvinyl alcohol boric acid (PVAB), a biocompatible polymer which combines the advantages of polyvinyl alcohol with the antibacterial properties of boric acid, as a polymeric matrix for PDLC preparation. From the structural point of view, this polymer brings the advantage of the presence of the boron atom. Recent studies demonstrated that borated-polymers

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present the ability to slow down the neutrons by elastic collisions and in combination with neutrons absorbing materials can be successfully used for neutron radiation shielding.\(^{21,22}\) Boron containing materials were effectively used in cancer therapy, for capturing neutrons.\(^{23}\) Moreover, our previous studies revealed that the presence of the boron atom, which is deficient in electrons, facilitates strong interactions with the liquid crystal molecules.\(^{24,25}\)

Two PDLC systems were prepared by the microencapsulation method, using two different liquid crystals: a commercial nematic mesogen: 4-cyano-4’-pentylbiphenyl (5CB) and a smectic liquid crystal, synthesized in our laboratory: Butyl-p-[p’-n-octyloxy benzoyloxy] benzoate (BBOB). Different and complementary techniques such as polarized light microscopy (POM), scanning electron microscopy (SEM), and differential scanning calorimetry (DSC) were involved in the characterization of the resulted systems in terms of morphology and thermotropic behavior. The surface properties have been also evaluated by measuring the water to air contact angle (WCA) and by calculating the surface forces.

## RESULTS

### The preparation of the PDLC composites

Two different polymer dispersed liquid crystals (PDLC) systems have been prepared using two mesogenic compounds: a first one with a nematic mesophase 4-cyano-4’-pentylbiphenyl (5CB) and a second one with a smectic mesophase: Butyl-p-[p’-n-octyloxy benzoyloxy] benzoate (BBOB) in a biocompatible polymeric matrix: polyvinyl alcohol boric acid (PVAB). For each liquid crystal four composites were obtained by changing the mass ratio between the components, starting from 90 to 10 PVAB to liquid crystal and ending with 60 to 40 (Table 1). The composites have been obtained by the microencapsulation method and presented different morphological and electro-optical properties, depending on the liquid crystal structure and on the ratio between the two components.

In order to characterize the PDLC composites in terms of liquid crystal droplets’ shape and size, dimensional polydispersity, their distribution and stability, the resulted systems were characterized by polarized light microscopy (POM), scanning electron microscopy (SEM) and differential scanning calorimetry.

### Polarized light microscopy

Polarized light microscopy is a visual technique which provides the first information concerning the shape, size and distribution of the liquid crystal droplets.\(^{26}\) For all samples, regardless the liquid crystals structure, birefringence was observed under polarized light at room temperature (Fig. 1). For both composites, A and B, the samples looked different depending on the amount of the liquid crystal used. Thus, the samples A1, A2 and B1, B2 presented birefringent individual and intensely colored droplets, while the samples A3, A4 and B3, B4 presented an almost continuous birefringent texture\(^{27}\) because of the high density of the droplets which makes them overlap on the cross-section of the PVAB matrix.\(^{28}\)

The samples heating revealed a different behavior of the composites according to the liquid crystal structure used in their preparation. Therefore, the heating of the A samples led to the isotropization of the liquid crystal droplets, the largest ones reaching the isotropic state much faster than the smallest ones. During this process, the density of the droplets decreased and radial droplets were observed for all samples, from A1 to A4 (Fig. 2). The complete isotropization revealed a white shadow which surrounds the isotropic droplets. These two facts show the ordering propagation from the liquid crystal to the polymer matrix, indicating strong interfacial forces between the liquid crystal and the polymeric matrix, the PVAB polymer being able to anchor the liquid crystal molecules, stabilizing the smallest droplets by interfacial forces.\(^{29}\)

### Table 1

The composition of the obtained PDLC systems

<table>
<thead>
<tr>
<th>Code</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Liquid Crystal</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
<td>10</td>
<td>20</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>% PVAB</td>
<td>90</td>
<td>80</td>
<td>70</td>
<td>60</td>
<td>90</td>
<td>80</td>
<td>70</td>
<td>60</td>
</tr>
</tbody>
</table>

* For A samples the liquid crystal is 5CB and for B samples the liquid crystal is BBOB
Fig. 1 – POM images of the prepared PDLC composites at room temperature.

Fig. 2 – POM images of the PDLC composites during heating.

The heating of the B samples did not reveal any crystalline-smectic transition, only the slow isotropization of the droplets. Also in this case, the isotropic droplets remained surrounded by a white shadow, indicating also for the BBOB liquid crystal the existence of strong interactions between the polymer and the liquid crystal molecules, due to the presence of the electron deficient boron atom and the electron rich cyan and esteric groups respectively of the liquid crystals.
A further investigation of the POM images of the samples gave information regarding the alignment of the liquid crystal molecules. A different alignment was observed in correlation with the chemical structure of the liquid crystal used. Therefore, for the A samples, the appearance of the radial droplets revealed the radial configuration of the director field, meaning that the liquid crystal molecules are disposed with the long axes perpendicular on the droplet wall (Fig. 3). In the case of the second system, the B samples, the thermotropic behavior suggests that the liquid crystal molecules are distributed with the long axes parallel with the droplet wall. These two different arrangements of the liquid crystal molecules can be explained if we think at the involved chemical structures of the liquid crystals and of the polymeric matrix. Therefore, the polymer contains the boron atom which has a deficit in electrons, while the liquid crystal molecules contain one and respectively two groups rich in electrons (1 cyano group in the case of 5CB and 2 esteric groups in the case of the BBOB liquid crystal). This makes the liquid crystals be anchored in one point in the case of 5CB and in two points in the case of BBOB.

**Scanning electron microscopy**

It is well known that the electro-optical properties of the PDLC composites depends in a mandatory manner on the size and dimensional polydispersity of the liquid crystal droplets, an acceptable behavior being obtained for droplets with sizes lower than 10 µm. In order to evaluate these two parameters, the composites films have been examined using SEM. The films were analyzed, after the liquid crystal was removed with methanol, in the case of the A samples and after the heating at 80 °C, the BBOB liquid crystal to reach the isotropic state, in the case of the B samples.

All samples presented micrometric pores, with spherical shape, uniformly distributed in the composites' films (Fig. 4). The density of the pores depends on the amount of the liquid crystal used for PDLC preparation, increasing from A1 to A4 and from B1 to B4 respectively (Fig. 4). Moreover, the spherical shape of the resulted pores indicates the fact that the interfacial forces are surprisingly strong, constraining the BBOB liquid crystal to form round droplets instead of forming batonnets, which are characteristic for the smectic A liquid crystals.31

For all samples, regardless the liquid crystal structure and mesophase, the pores’ size was in the micro domain, with values and dimensional polydispersity depending mainly on the amount of the used liquid crystal (Fig. 5). Firstly, it has to be mention that the BBOB liquid crystal generated bigger droplets than 5CB, for all the tested ratios between the two components. Thus, the mean diameter of the pores increased from 3.41 µm for the sample A1 to 4.22 µm for the sample A4, and from 6.3 µm for B1 to 7.37 for B4. As can be observed the size of the pores varies in a narrow domain (~1 µm), revealing the independence of the strength of the interactions on the amount of the used mesogens. Very interesting was the fact that the standard deviation decreased with the increase of the amount of the liquid crystal, reaching a minimum value for the maximum amount of liquid crystal for both composites.
Fig. 4 – SEM images of the PDLC composites.

Fig. 5 – Standard deviation and mean diameter for the PDLC composites.

Fig. 6 – DSC of the PDLC composites and of the pure liquid crystals.
Differential scanning calorimetry

DSC was used as a complementary method for PDLC composites characterization giving information about the liquid crystals segregation, dimensional polydispersity of the droplets, the miscibility of the liquid crystals and polymeric matrix, the morphological stability of the obtained materials. For comparison, DSC was performed also for the used liquid crystals.

The pure 5CB liquid crystal presents two transitions in the heating scan, at 18.5 °C corresponding to the crystalline nematic transformation, and at 35.8 which corresponds to its isotropization (Fig. 6). The thermal behavior of the PDLC composites prepared using 5CB, especially of the A4 sample presents some differences in comparison with the pure liquid crystal. First, the crystalline-nematic transition occurs at a higher temperature for the PDLCs, more evident in the case of A4, indicating the fact that the formed crystallites are stabilized by the strong interface forces of the PVAB matrix. The second aspect concerns the isotropization which is wider than the one of the pure liquid crystal, indicating the dimensional polydispersity of the droplets. As expected (See the SEM data), the narrowest transition was obtained in the case of the sample A4, which presented almost monodisperse droplets.

In the case of the BBOB liquid crystal, the DSC revealed in the heating scan two transitions at 54 °C and at 70 °C which correspond to the crystalline-smectic transformation and isotropization respectively. Very interesting is the fact that no smectic-nematic transition could be distinguished in the DSC. The PDLCs composites showed no significant changes in comparison with the pure liquid crystal, presenting the same two transitions, but at slightly different temperatures, at 51.9 °C and 69 °C.

It has to be mentioned that in all cases the samples were analyzed in multiple heating/cooling cycles, with precise reproduction, indicating the morphological stability of the obtained PDLC systems.

Wettability and surface free energy measurements

The obtained PDLC composites are designed for bio-applications, that is why their surface properties are important parameters which must be investigated. In order to be used as biomaterials, an appropriate hydrophobic/hydrophilic balance must be achieved, leading to a proper wettability of the resulted material. Intense studies revealed that a moderate wettability of a material, corresponding to a water to air contact angle (WCA) in the range 60-90°, is the first requirement which must be fulfilled by a potential biomaterial. On the other side, in the case of biomaterials designed for ocular applications, a water to air contact angle around the one of the natural cornea of 50° is desired. In this context, the WCA of the obtained PDLC composites and of the polymeric matrix was measured (Fig. 7).

![Fig. 7 – Water to air contact angle of the PDLC composites obtained.](image-url)
Firstly it has to be mentioned that the PVAB presents a water to air contact angle of 58°, being a little bit too hydrophilic for bio-applications. The encapsulation of the two liquid crystals into the polymeric matrix generated an increase of the hydrophilicity of the material, leading to higher values of the WCA. In this manner, 6 of the 8 obtained materials present a moderate hydrophilicity, having the WCA in the range 60-90°, making them suitable for potential biomedical applications. In the case of the other samples B1 and B2, obtained using lower amounts of BBOB, the WCA was equal to 47° and 53° respectively, values which are very close to the one of the natural cornea, and recommending them for ocular applications.

Further, by measuring the contact angle with other two liquids: dimethylformamide and diiodomethane, the surface free energy (SFE) was calculated for all samples. As you can observe (Table 2) the PVAB polymer presented a quite high value of the surface free energy of 48.09 mN/m. The encapsulation of the liquid crystals, regardless their structures, generated a decrease of the SFE, most probably due to physical interactions which are established between the PVAB and the liquid crystal molecules.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\gamma_{tot}$ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>42.09</td>
</tr>
<tr>
<td>A2</td>
<td>41.94</td>
</tr>
<tr>
<td>A3</td>
<td>42.12</td>
</tr>
<tr>
<td>A4</td>
<td>43.61</td>
</tr>
<tr>
<td>PVAB</td>
<td>48.09</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL**

**Materials**

4-Cyano-4'-pentylbiphenyl 98%, polyvinyl alcohol boric acid (Mw=54 000, 4% water content) were purchased from Aldrich. BBOB liquid crystal was synthesized according to a method described in the literature.35

**PDLC obtaining**

The PDLC systems were prepared by the encapsulation method. A solution of 7.5 % PVAB (0.1125 g of polymer in 1.5 mL of water) was prepared at 90 °C. The solution was further cooled at room temperature. To this solution, under vigorous stirring, a 5 % solution of the liquid crystal in chloroform was slowly added. A white suspension was obtained. The resulted mixture was stirred for 3 hours at room temperature. Every 30 minutes, the mixture was stirred for 5 minutes on a vortex. The final PDLC composites were cast under the form of films and dried under vacuum, at 50 °C.

Different weight ratios between 5CB or BBOB liquid crystals and PVAB polymeric matrix were used, in order to prepare PDLCs with different amounts of liquid crystal (Table 1).

**Equipment and measurements**

The thermotropic behavior of the 5CB and BBOB liquid crystals and of the PDLC composites was investigated using an Olympus BH-2 polarized light microscope, under cross polarizers, with a THMS 600 hot stage and LINKAM TP92 temperature control system.

The PDLC composites films were observed with a field emission scanning electron microscope (Scanning Electron Microscope SEM EDAX – Quanta 200) at an accelerated electron energy of 10 or 20 keV. The average pore size was estimated from four randomly chosen images.

Differential scanning calorimetry (DSC) was performed on a METTLER Toledo STAR system, under nitrogen atmosphere (nitrogen flow 120 mL/min). Transition temperatures were read at top of the endothermic or exothermic peaks.

The static contact angle of the PVAB and composite films was determined by the sessile drop method, at room temperature and controlled humidity, within 10 s, after placing 1 µL drop of water on the film surface, using a CAM-200 instrument from KSV- Finland. Contact angle was measured at least 5 times on different sites of surface, the average value being considered. In order to obtain the components of the free surface energy and the total free surface energy of the composite films, the contact angle at equilibrium between the studied surface twice distilled water was measured. The contact angle was measured by fitting the drop profile using Young-Laplace equation.

**CONCLUSIONS**

Two polymer dispersed liquid crystals (PDLC) composites were prepared by the microencapsulation method, using two mesogenic compounds: a nematogen - 4-cyano-4'-pentylbiphenyl and a smectogen - Butyl-p-[p'-n-octyloxy benzoyloxy] benzoate in a bio-friendly polymeric matrix: polyvinyl alcohol boric acid. The presence into the polymers structure of the electron deficient boron atom proved to be able to confer a homeotropic anchoring for the first used liquid crystal, and a planar anchoring for the second liquid crystal, due to their different chemical structure. The ability of the biopolymer to act as a carrying matrix was evaluated by POM, SEM and DSC. The water to air contact angle was measured for all samples and, very important, for both composites, the obtained film presented moderate wettability, which makes them suitable for applications in the biomedical field.

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