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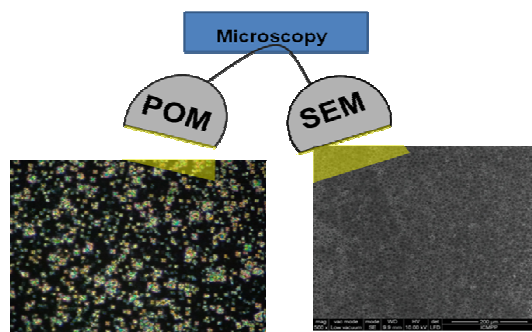
PDLC composites with narow size polydispersity and radial droplet configuration were obtained using polyvinyl alcohol boric acid as carrying matrix.

Monodisperse PDLC composites generated by use of polyvinyl alcohol boric acid as matrix

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Abstract

Polymer dispersed liquid crystal composite (PDLC) based on polyvinyl alcohol boric acid (PVAB) as polymer matrix and 4-cyano-4'-penthylbiphenyl (5CB) as liquid crystal have been prepared by encapsulation method. PVAB was used as polymer matrix for the first time. Polarized light microscopy, scanning electron microscopy, differential scanning calorimetry and contact angle measurements were employed to explore the obtained PDLC systems. Optical properties were studied by photoluminescence spectroscopy. It was concluded that PVAB promotes homeotropic alignment, uniform distribution and narrow size polydispersity of the liquid crystal droplets. Moreover, the PDLC films show features of biocompatible materials, keeping the promise of their bio applications.

Keywords: polymer dispersed liquid crystals; polyvinyl alcohol boric acid; radial droplets; contact angle; surface free energy

1. Introduction

Polymer dispersed liquid crystal (PDLC) composites are a quite new class of materials which combine film forming ability and mechanical strength of the polymers with unique electro-optic properties of liquid crystals (LC), making them suitable for a large range of opto-electronic applications in different domains, from electronics to biomedical devices [1-6]. The PDLC preparation consists in liquid crystal dispersion as micrometric droplets into a carrying matrix, to create a light modulating layer [6]. The optical modes of liquid crystal droplets are different from the ones in isotropic compounds, due to LC birefringence and specific configuration of the director field within the droplet, which is a consequence of physical interaction between liquid crystal and matrix [7]. The carrying matrix enables formation of droplets, their size and distribution, gives them mechanical support, and determines their anchoring and thus their optical properties. This is the reason why, the choice of the two composite components is an important aspect of PDLC preparation, leading to specific composite properties and thus potential applications. Moreover, chemical structure of polymer matrix affects the PDLC optical properties, too [8], and its nature

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determines the application addressed. Many combinations of liquid crystals and matrix polymers have been used in PDLC preparation. As liquid crystals, usually CN-biphenyl based liquid crystals are used [6, 9]. Poly(methylmethacrylate)s, polyethylenoxides [10], poly(styrene)s, poly(dimethylsiloxane)s [11], polyacrylates [12] thiol–ene polymers [13], epoxy resins [14], or various curable monomers [15], polysulfone [16], polyvinylalcohol [17], chitosan [18] already proved their ability to act as carrying matrix for PDLC preparation, providing different liquid crystal alignments, and thus different optical properties. Polyvinyl alcohol (PVA) is first and one of the most used matrix polymers [9] due to its good properties e.g. non-toxicity, water solubility avoiding thus unpleasant organic solvents, completely biodegradability, good chemical stability, film forming ability and low liquid crystal solubility, which recommend it for many human and environmental friendly applications. PVA promotes a strong planar anchoring of the liquid crystal into PDLC composite [19]. Studies dedicated to obtaining homeotropic alignment of liquid crystals into PVA matrix concluded that a third component of the PDLC composite – a surfactant, is required to achieve this goal [20]. The surfactant physically interact with liquid crystal molecules and determine their perpendicular alignment on the polymer surface and therefore the change of the director configuration, the planar anchoring of the PVA being turned into a homeotropic one. Besides, the interactions developed between LC molecules and surfactants provide surface stabilization and thus droplet narrow size. But the use of an additional composite component arise new problems regarding the composite formulation and it is costly due to the complexity of used processes.

To avoid the problems encountered by surfactant use, we propose to replace PVA/surfactant blend with polyvinyl alcohol boric acid (PVAB). The electron deficient boron into PVAB polymer has the potential to promote electrostatic attraction with dipole moment of liquid crystal molecules and thus creates the premises of homeotropic anchoring. Besides, PVAB have the advantage to preserve all the good PVA properties plus antiseptic properties of boric acid, the materials based on it being excellent candidates for biomedical devices as tunable artificial iris [4], or biosensors [21] for instance. This study is dedicated to the obtaining of PDLC composites based on PVAB matrix and 4-cyano-4'-pentylbiphenyl (5CB) liquid crystal. The ability of PVAB to act as a PDLC matrix, the maxim percent of liquid crystal which can be dispersed, the anchoring forces and the alignment type have been studied by polarized light microscopy, scanning electron microscopy, differential scanning calorimetry and by contact angle measurements. Besides, the water-in-air contact angle of the PDLC films gave information about their potential biocompatibility.

2. Results and discussions

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Novel PDLC composites, based on polyvinyl alcohol boric acid as a polymer matrix and 4-cyano-4'-penthylbiphenyl liquid crystal have been prepared by encapsulation method, in various component ratios. The composites formed free standing, flexible films. The structural properties of the new composites (e.g. liquid crystal droplet formation, their size, polydispersity, distribution and configuration, anchoring effect and morphologic stability) were studied by polarized light microscopy (POM), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM).

Polarized light microscopy

To gain information regarding the PVAB ability to act as polymer matrix for PDLC composites, the obtained PDLC films were observed by polarized light microscopy, during multiple heating/cooling cycles. All the samples present birefringence in polarized light, at room temperature: (a) birefringent, intense colored droplets for the samples with small content of liquid crystal (C1, C2) (Figure 1a) and (b) birefringent continuous fine texture in the case of the samples with high content of liquid crystal (C3, C4, C5) (Figure 1b). The fine texture is currently observed for PDLC films with high liquid crystal content due to the great droplet density which overlap across the film thickness [2, 16, 18].

The sample heating revealed a progressive droplet isotropization: starting with the largest ones and finishing with the smallest ones. As isotropization advanced and droplet density decreased, clear radial droplets could be seen for all the samples (Figure 1c, d). The isotropic droplets are surrounded by a milky shadow. The thermotropic behavior during the subsequent cooling scan was similar to the first heating scan, but inverted: the smallest droplets appeared firstly, followed by the larger ones. No changes of thermotropic behavior were noted in further heating/cooling scans, indicating composite film stability, as consequence of polymer – liquid crystal immiscibility. The faster isotropization of the larger droplets compared to the smaller ones indicates the stabilization effect of the PVAB matrix upon LC droplets, by interfacial interactions. Moreover, the milky shadow around the isotropic droplets suggests that the interfacial interaction determine an ordering of the polymer chains next to the liquid crystal molecules, too.

The visual inspection of the composite samples through POM gives information regarding the alignment type into the LC droplets. The observed radial droplets indicate a radial configuration of the director field with a point topological defect in the center named radial hedgehog defect [22]. It can be seen as a black point in the middle of the droplets (Figure 1c, d). That means that LC molecules are anchored with their long axes perpendicular on the droplet wall, rational explained by attraction forces between the electron reach CN end-groups of the 5CB molecules and electron deficient boron of the PVAB. Thus, as expected, PVAB polymer has a homeotropic anchoring

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effect upon cyano containing liquid crystals. This is contrary to the PDLC composites based on pure PVA matrix which promote planar alignment with liquid crystal molecules oriented parallel to the droplet wall [17, 19, 23]. The turn of the planar alignment of 5CB liquid crystal droplets embedded in PVA into homeotropic alignment when encapsulated in PVAB reflects the influence of boric acid, and more specific of the boron atom. It is reasonable to affirm that polyvinyl acid boric acid can successfully replace the PVA in PDLC obtaining when homeotropic alignment of liquid crystal droplets is targeted.
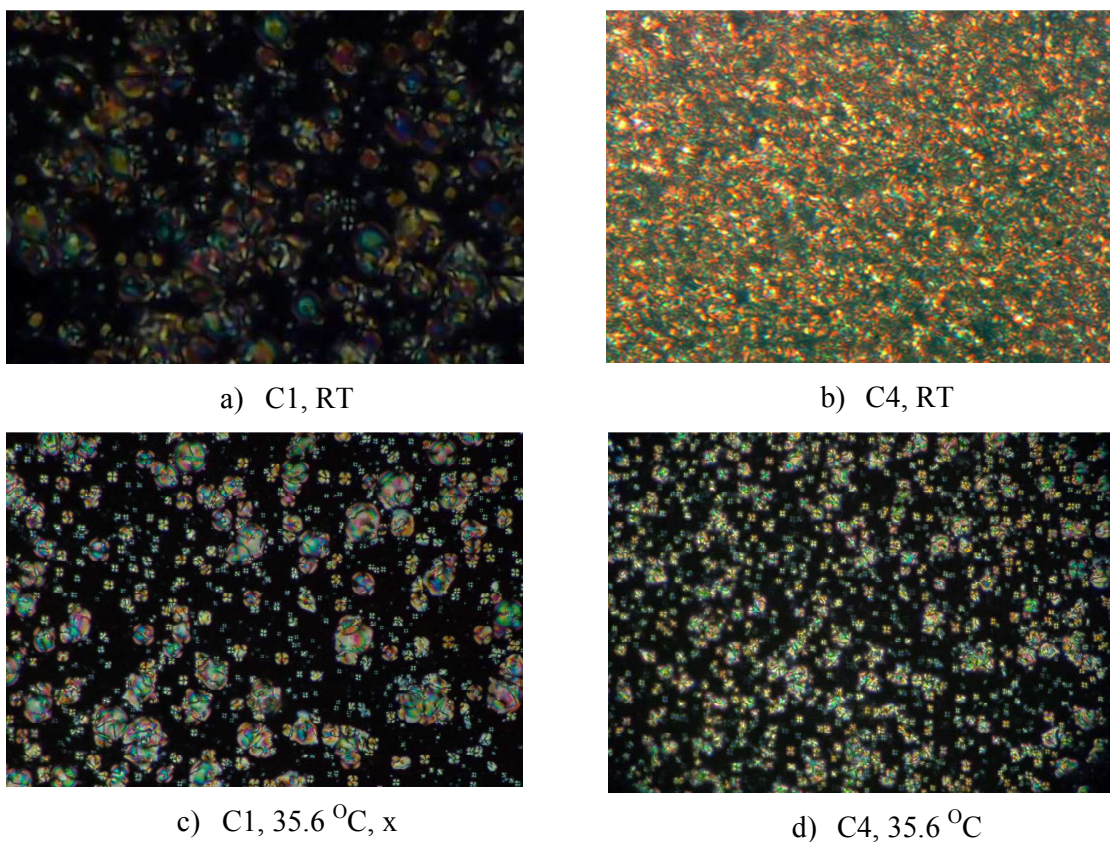

a) C1, RT   b) C4, RT

c) C1, 35.6 ^{O}C, x   d) C4, 35.6 ^{O}C

Figure 1. Polarized optical microscopy images of PVAB composites

Scanning electron microscopy

Systematic studies on PDLC composites demonstrated that satisfactory electro-optical properties are reached for a uniform distribution of the LC droplets with diameter in the $1 - 5$ μm range; neither submicron-sized, nor larger droplets above 10 μm do not scatter light efficiently [24, 25].

To gain insight on the size and distribution of the liquid crystalline droplets into the studied composite materials, scanning electron microscopy (SEM) has been performed on film samples resulted by removal of the liquid crystal with methanol (Figure 2).

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Morphological observation by SEM of the residual PDLC composite after LC removal reveals spherical pores regularly distributed on the polymer surface. The spherical shape suggests enough low interfacial tension between PVAB and 5CB to not transfer deforming stress shear from the matrix to liquid crystal during hardening by solvent evaporation. Thus, the droplet forming tendency of the liquid crystal is not affected, PVAB proving to be a good matrix from this point of view. The droplet density increases as the 5CB content increases, a sponge like structure being observed for the sample with 40% content of 5CB (C4). Despite of the high pore density, no interconnected pores can be seen, the cavities are independent, with thin walls, suggesting that interfacial forces are strong enough to keep the droplet integrity and not allow the droplet collisions [26]. The samples containing lower content of 5CB (C1, C2, C3), show droplets with large size polydispersity, from 200 nm to 5 μm, but a narrow diameter polydispersity, around 4-5 μm, is reached for the C4 sample with higher content of liquid crystal. On the other hand, the sample containing 50% of 5CB shows interconnected pores, indicating that for this liquid crystal content into PVAB, the interfacial tension/interfacial force balance is not enough to hinder the droplets coalesce, because of their high density. (No image capture was possible for the 5C sample with 50 % of 5CB, because of its fast degradation.)
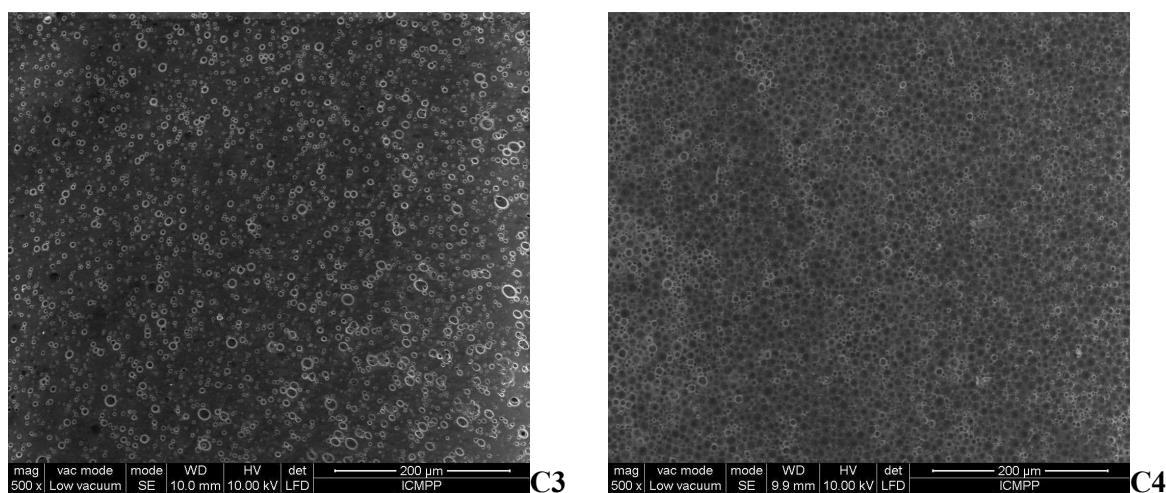
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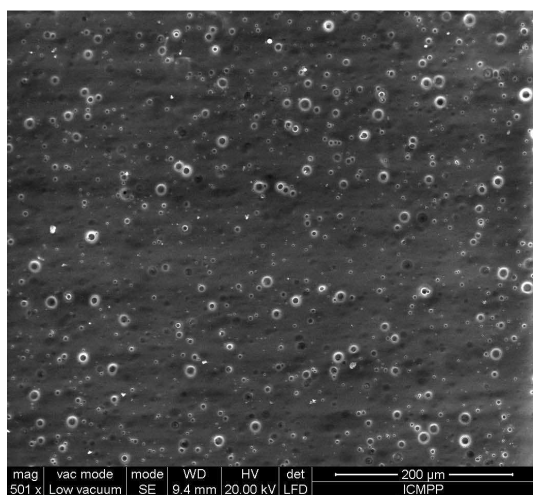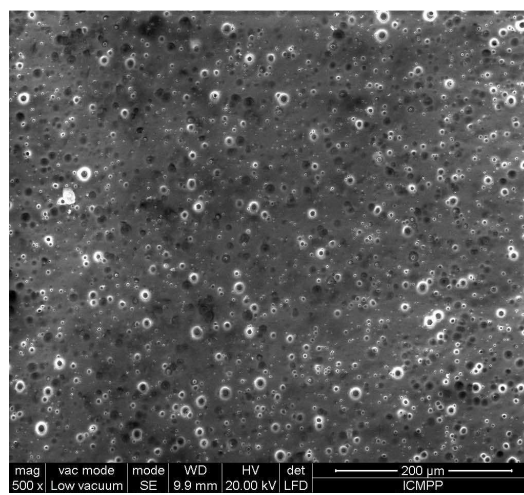
Figure 2. SEM microphotographs of the PDLC-composites

An important disadvantage underlined in reported literature regarding PDLC matrix polymers is their partial miscibility with liquid crystal component, which led to a "polymer rich matrix" [2, 6, 12, 27, 28], with lower T_g and worse optical properties. On the other hand, because a part of the liquid crystal is lost in the polymer matrix and it doesn't segregate as droplets, a higher percent of liquid crystal must be used (usually about 50/50 weight ratio between the two components), increasing the obtaining costs. As can be seen, by the use of PVAB as a polymer matrix, PDLC composites with high droplet density and narrow size polydispersity are obtained for 40 % content of liquid crystal, pointing for good optical properties.

Calorimetric studies

Differential scanning calorimetry has been employed as a complementary method to characterize the PDLC composites. The shape and the transition temperature values in DSC curves give precious information regarding the dynamic of LC droplet segregation, their size distribution, anchoring forces, and very important give the temperature range in which they can be used in practical applications [27, 28].

To correctly attribute the thermal transitions of the PDLC composites, the DSC curves of the two pure composite components have been firstly registered. The temperature program was chose to obtain clear transitions, that is: cooling with 1 ^{O}C/min up to – 50 ^{O}C/min – to favor total 5CB crystallization; and heating with 5 ^{O}C/min up to 50 ^{O}C – to assure complete isotropization.

In these conditions, the 5CB pure liquid crystal exhibit: a large exothermic peak around -11 ^{O}C in first cooling scan – corresponding to crystallization; two sharp endothermic peaks in first heating scan, an intense one at 18.5 ^{O}C – attributed to the crystalline-nematic phase transition and a weak one at 35.8 ^{O}C – corresponding to isotropization; a sharp exothermic peak at 35.1 ^{O}C –

attributed to isotropic-nematic transition and a large exothermic peak ascribed to crystallization, in second cooling scan. The next heating/cooling cycles are similar to first heating/second cooling scan. The exothermic peak attributed to crystallization was broad and had multiple superposed maxima indicating a slow polymorphic crystallization, dependent upon the thermal pre-history treatment, as already has been demonstrated by calorimetric, X-ray diffraction and Raman spectroscopy studies [29, 30].

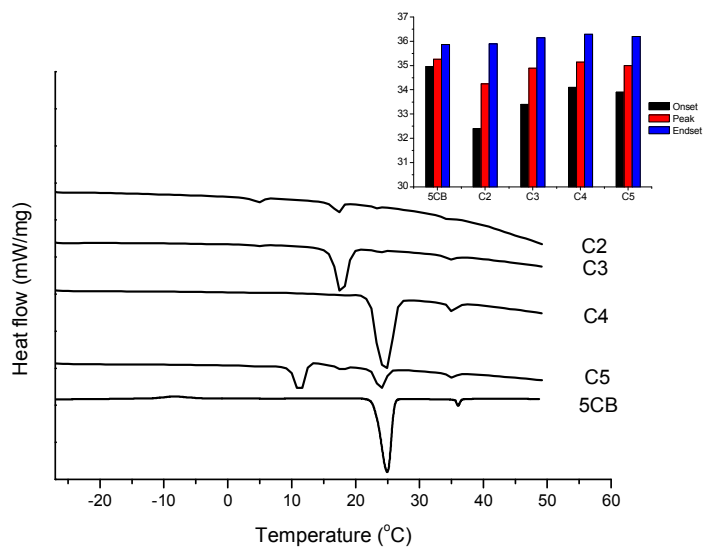The PVAB show an inflection point of the DSC curve at 67 ^{O}C, during heating/cooling scans corresponding to the glass transition. As can be seen, there is no superposition of the thermal transitions of the two components (Figure 3a).

a)

b)

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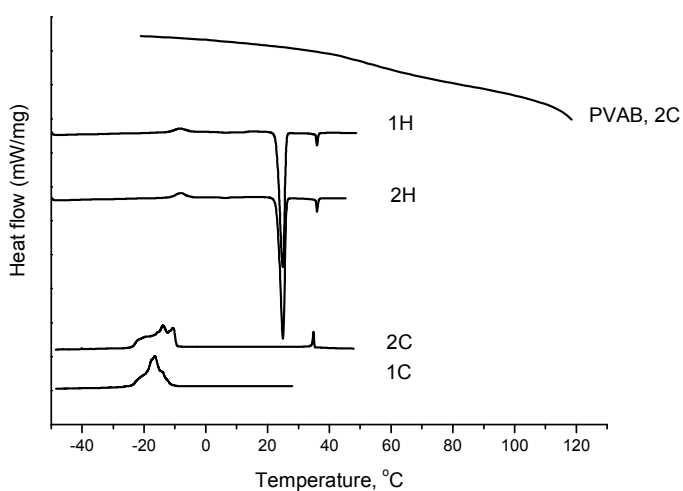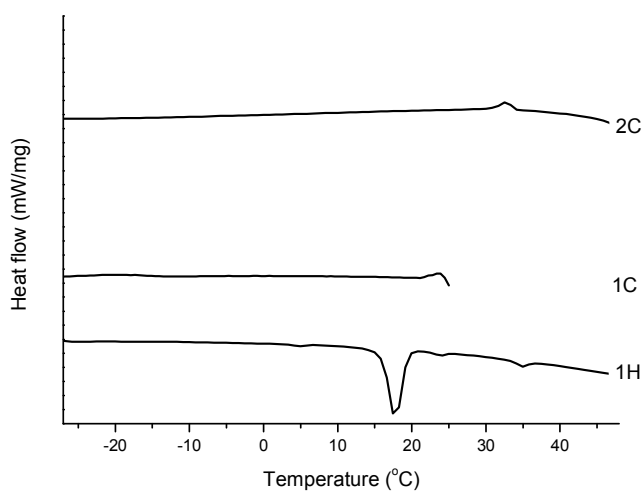
c)

Figure 3. DSC curves of a) 5CB and PVAB; b) C3; c) first heating scan of the PDLC
composites and 5CB, inset: graphical representation of the isotropization endotherm

In comparison with pure 5CB, the DSC curves of PDLCs exhibit clear differences in terms
of peak number and shape. DSC curves of C3 composite is given as an example in figure 3b.

First, the isotropization peak is large, reflecting the droplet size polydispersity and different
intensity of anchoring forces (Figure 3c). It is expected that the anchoring forces to exert a stronger
stabilizing effect in the case of the smallest droplets and weaker for the larger ones. The
temperature range corresponding to the isotropization process is the narrowest for the C4 composite
indicating the narrowest droplet diameter polydispersity, as SEM exhibited too. The peak is left-
tailed with lower temperature maxim for the composites with smaller LC content (C1, C2, C3);
symmetric with the highest temperature maxim for the C4; and right- tailed with smaller
temperature maxim for C5 sample. These data reveal that higher/smaller droplet ratios is shifted to
the higher diameter droplet for samples with low content of liquid crystal; to smaller diameter
droplet for samples with high content of LC; and reach an equilibrium of the droplet diameter, a
narrow polydispersity, respectively, for C4 composite.

The second aspect of the DSC curves, regard the crystalline – nematic transition. While 5CB
exhibits a sharp endotherm, except C4, all the composites show multiple, large endotherms
suggesting different crystallite size and morphology. Remarkable, the C4 composite present a single
endotherm indicating once again the narrow polydispersity of the droplet size which afford similar

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crystallites from the morphological point of view. The higher transition temperature compared to pure 5CB (24.8 ^{o}C *versus* 18.5 ^{o}C) is the result of anchoring effect of the PVAB matrix, which stabilize the crystallites by interface attraction forces.

The exothermic peak at which 5CB droplets appeared from the isotropic liquid is similar to the endothermic peak accounting for isotropization, but little shifted to higher temperature, compared to pure liquid crystal. This smaller hysteresis between the isotropization and nematic mesophase occurrence is most probably the result of interface coupling between PVAB macromolecules organization and liquid crystal ordering which favors the faster nematic ordering. The reproducibility of the DSC peaks on multiple heating/cooling scans indicates the composite component immiscibility arising droplet stability [27, 28]. This is a very important aspect, indicating that pure liquid crystals segregate in pure PVAB polymer matrix, pointing for good optical properties. The DSC measurements show that PDLC composites can be used in any applications into the -50 – 50 ^{O}C temperature range.

Contact angle measurements and surface free energy calculation

Surface features of the PDLC films give information regarding the physical forces inside the material and also offer a first look on their potential application as biomaterials. To study surface characteristics of the PDLC films, the contact angle at equilibrium between their surface and three pure liquids: twice distilled water, formamide and diiodomethane, was measured (Figure 4) and total surface free energy (γ_{s}^{TOT}), dispersive (γ_{s}^{LW}), polar (γ_{s}^{AB}), acidic (γ_{S}^{+}) and basic (γ_{S}^{-}) components of the surface free energy were calculated (Tabel 2). Surface free energy consists of disperse and polar components. The disperse component of free energy is given by London disperse forces, while for polar part contributes: electrostatic forces, hydrogen bonds and dipole-dipole interactions [31].

Usually, as a material to be biocompatible, it must have moderate wettability which was demonstrated to correspond to a water-in-air contact angle value comprised between 60 and 90 degree [32]. This contact angle value ensures a proper hydrophilic/hydrophobic balance to favour the cell adhesion on the film, and thus to prevent the implanted material rejection.
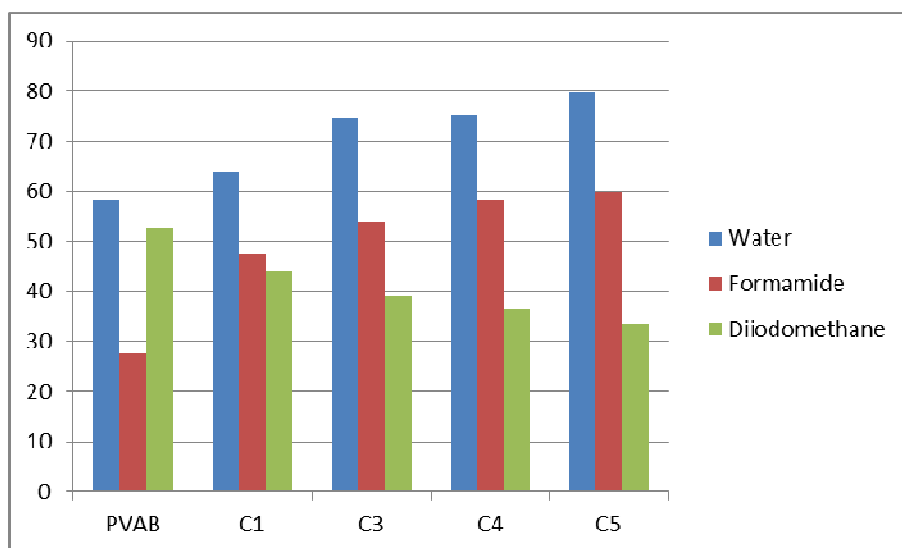
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Figure 4. Mean static contact angles determined by sessile drop method

As can be seen in figure 4, the contact angle value of PVAB film is 58.2 ^{O}, which means an increased wettability, threatening to prevent the cell-cell interactions [32]. By encapsulation of 5CB liquid crystal into PVAB, the water contact angle progressively increases as liquid crystal content increases, reaching the 79.7 value for the C5. This means that by introducing the hydrophobic liquid crystal into the hydrophilic PVAB matrix, a proper hydrophobic/hydrophilic balance is achieved, meaning that PVAB based PDLC films are potential candidates for bio-applications.

In a similar manner, the contact angle made by the PDLC composite surface with formamide polar liquid increases from 38 ^{O} to 60 ^{O}, while that given by diiodomethane apolar liquid decreases, roughly indicating a decreases of the polar group density present at the PDLC film surface compared to pure PVAB matrix.

Surface free energy (SFE) is a material property which reflects its chemical composition and molecule orientation at the material boundary. Thus, the LC molecule configuration into PDLC droplets, drastically influence the SFE value, which can be further electrically switchable and so used to design biosensors as blood sensors and sperm testers [33]. Moreover, the use of a material as biomaterial depends on the appropriate SFE value; high values of surface free energy and polarity proved potential in maintaining multicellular structure [34].

As can be seen in table 2, PVAB has quite high surface energy value of 48.09 mN/m with a major contribution of dispersive Lisfshitz – van der Waals contribution (γ_S^{LW} =32.6), and significant electron donating (γ_S^-=12.6) and electron accepting (γ_S^+=4.75) contributions, attributed to the electron rich oxygen and electron deficient boron, respectively. As expected, these results indicate much larger contribution of basic sites compared to acidic ones, due to the higher number

of rich electron oxygen atoms against electron deficient boron ones into the PVAB chemical structure.

Compared to PVAB polymer matrix, the PDLCs surface free energy exhibits important changes which reflect interactions in volume of liquid crystal – polymer matrix (Table 2). Thus, all the PDLC composites show decreasing polar contribution and especially of the electron acceptor contribution (acidic part) and increasing of dispersive forces, fact rational explained by physical interactions of the electron rich cyano groups of 5CB with electron deficient boron of the PVAB matrix. As 5CB content into PDLC composites increases, the electron deficient sites contribution decreases and dispersive forces contribution increases. The insignificant values of γ_S^+ of C4 and C5 composites indicate extremly low content of electron deficient sites at surface, and agree well with SEM observations which show LC droplets surrounded by very thin PVAB wals, which assure a maxim contact between the liquid crystal and polymer matrix. As a general trend, the γ_s^{ab} component of surface free energy decreases with increasing 5CB content, indicating a less polar surface of the PDLC and thus more stable.

Table 2. Total surface free energy values and components of PVAB-based samples in mN/m.

Samples	γ_S^{LW}	γ_S^+	γ_S^-	γ^{ab}	γ_S^{TOT}	γ_{SL}
PVAB	32.60	4.75	12.63	15.49	48.09	-0.24
C1	37.56	0.43	16.62	5.38	42.94	0.94
C3	39.93	0.12	8.73	2.01	41.94	1.88
C4	41.31	0.02	10.56	0.81	42.12	1.66
C5	42.63	0.03	7.02	0.98	43.61	2.06

An important parameter of the material surface which gives valuable information regarding its biocompatibility is interfacial tension between blood and the film surface (γ_{SL}). It was demonstrated that successful biomaterials have the blood-biomaterial interfacial tension in the range 1 – 3 mN/m [35].

The γ_{SL} values listed in Table 2 indicate that the PVAB matrix is not suitable for blood-contacting applications while the obtained PDLC composites have potential to be hemocompatibile, and so great potential as biomaterial. By 5CB addition a minimization of the thermodynamic driving force for the adsorption of blood components as well as a mechanically stable blood-biomaterial interface is obtained.

Photoluminescence behavior

Studies dedicated to luminescence behavior of the 5CB liquid crystal concluded that its luminescence behavior is the result of the formation and destruction of different monomer and dimer structures [36]. Different environments of the liquid crystal, consisting either in its confining in a matrix [37], or used as matrix for other particles [38], change the monomer/dimer ratio and in consequence the photoluminescence behavior. To see how the PVAB matrix affect the 5CB behavior, photoluminescence spectra of the pure composite components and PDLC composites have been registered, by exciting with 315 nm wavelength [18, 38].

As can be seen in figure 5, the PDLC spectra is a summation of the two pure component spectra, but present special characteristics, too. Thus, PDLC composites exhibit a broad band with maximum at 391 nm, as pure 5CB, and a shoulder at 373 nm as PVAB. The band intensity is higher for the PDLC composites, compared to the pure 5CB, reflecting the increased emission surface by micrometric dispersing. Moreover, the highest intensity is shown by the C1 film with the smallest 5CB content dispersed as nanometric droplets, and so with increased emission surface. The special spectra characteristic consists in the appearance of a sharp, intense emission band at 327 nm, in the UV domain, which can be rational attributed to the interphase interactions. The peak intensity increased as the 5CB content into PVAB matrix decreased in a similar manner as first emission band. This behavior is further interesting for applications in organic solid-state UV lasers.
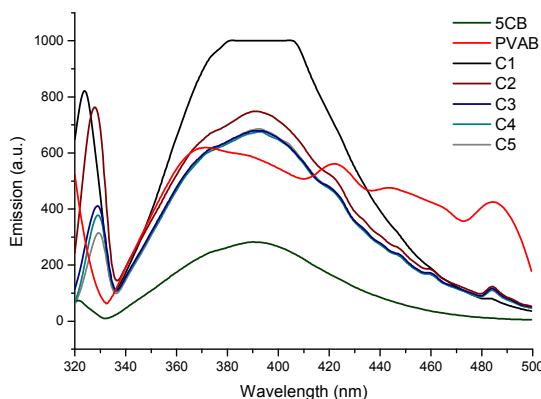

Figure 5. PL spectra of 5CB and PVAB composites

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3. Experimental

Materials

4-Cyano-4'-pentylbiphenyl 98% and polyvinyl alcohol boric acid (Mw=54 000, 4% water content) were purchased from Aldrich.

PDLC obtaining

The targeted PDLC composites were prepared by encapsulation method technique which involved emulsion of liquid crystal in aqueous PVAB media. 7.5 % PVAB solution was prepared by dissolving 0.1125 g of polymer in 1.5 mL of water at 90 ^{O}C, and then slowly cooling at room temperature, to avoid polymer cross-linking. A 5 % solution of 5CB liquid crystal in chloroform was slowly dropped under vigorous magnetic stirring with 750 rot/min when a milky suspension was obtained. The emulsion was magnetically stirred 3 hours at room temperature. To reduce the liquid crystal droplet size, the emulsion was stirred for 5 min, every 30 min, employing a vortex mixer. The finally obtained emulsion was casted on a glass surface and kept for water evaporation. The composites films were further dried under vacuum, at 50 ^{O}C.

Different weight ratios between 5CB liquid crystal and PVAB polymer have been used to obtain PDLC composites with various amounts of liquid crystal (Table 1).

Table 1. The composition of the obtained PDLC composites

Code	C1	C2	C3	C4	C5
% 5CB	10	20	30	40	50
% PVAB	90	80	70	60	50

Equipment and measurements

The thermotropic behavior of the 5CB and PDLC films was studied by observing textures with an Olympus BH-2 polarized light microscope, under cross polarizers, with a THMS 600 hot stage and LINKAM TP92 temperature control system.

Specimen of studied composite films were viewed 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. The morphological observation was carried out for the film samples resulted by removing liquid crystal with methanol.

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 inflection point temperature of the change in the

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DSC curve slope of the first cooling cycle was used to determine the PVAB glass transition temperature.

Photoluminescence spectra were recorded on a Perkin Elmer LS 55 spectrophotometer, in film on glass plates.

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 and three pure liquids: twice distilled water, formamide and diiodomethane, was measured. The contact angle was measured by fitting the drop profile using Young-Laplace equation [31].

The total surface free energy (SFE) (γ_s^{TOT}), dispersive (γ_s^{LW}), polar (γ_s^{AB}), acidic (**γ_s^+**) and basic (**γ_s^-**) components of the surface free energy were calculated using the acid base approach of van Oss and Good [39].

The interfacial tension between blood and the film surface (γ_{SL}) was calculated using the polar-dispersive theory for the free surface energy [40].

$$\gamma_{SL} = \left[\left(\gamma_L^p\right)^{1/2} - \left(\gamma_S^p\right)^{1/2} \right]^2 + \left[\left(\gamma_L^d\right)^{1/2} - \left(\gamma_S^d\right)^{1/2} \right] \tag{2}$$

Where γ^p and γ^d are the polar and, respective, the dispersive components of the free surface energy; L and S stand for the liquid (blood) and the solid, respectively. For calculating γ_{SL} were used the free surface energy components for the tested materials determined by contact angle measurements and those reported in literature for the human blood (γ^d =11.2 mN/m and γ^p =36.3 mN/m) [41].

Conclusions

The obtaining and study of polymer dispersed liquid crystal (PDLC) composites, using polyvinyl alcohol boric acid (PVAB) as polymer matrix revealed a new PDLC carrying matrix which keep the promise of their application in the biological field. PVAB is a biocompatible polymer, soluble only in hot water, transparent, immiscible with liquid crystals, assuring good optical properties. The study demonstrated that PVAB matrix favors homeotropic alignment of the liquid crystalline droplets, due to the interphase attraction forces that arise between electron

deficient boron atom of PVAB and electron rich cyano group of 4-cyano-4'-penthylbiphenyl (5CB) used as liquid crystal (LC). The boron presence into the PVAB structure assure a good balance between superficial tension and attraction interphase forces, to reach uniform distribution and narrow size polydispersity of the LC droplets for PDLC system with high LC content which is 40%. The droplet diameter is around 4 μm, the ideal size for optoelectronic applications. The immiscibility of PVAB polymer matrix and the cyano liquid crystal preclude the loss of liquid crystal as plasticizer in polymer matrix, fact which point for two advantages: (a) use of lower amount of liquid crystal for high content of LC droplets and thus lower costs; (b) the optical properties of polymer matrix are preserved into PDLC composites. Furthermore, the measurements of contact angle and calculation of surface free energy and interfacial tension between blood and the film surface indicated biocompatibility potential of the prepared composites, suggesting their potential for bio- application. The PVAB polymer promises to successfully replace PVA polymer when PDLC composites with homeotropic alignment of liquid crystalline droplets are targeted.

Acknowledgements

References

1. H. Kikuchi, T. Fujii, M. Kawakita, H. Fujikake and K. Takizawa, *Opt. Eng.*, 2000, **39**, 656–669.
2. Y. J. Liu, X. Ding, S-C.S. Lin, J. Shi, I-K. Chiang and T.J. Huang, *Adv. Mat.*, 2011, **23**, 1656–1659.
3. Y-C. Su, C-C. Chu, W-T. Chang and V.K.S. Hsiao, *Opt. Mater.*, 2011, **34**, 251–255.
4. T-C. Hsu, C-H. Lu, Y-T. Huang and W-P. Shih, *Sensor. Actuat. A-Phys.*, 2011, **169**, 341– 346.
5. E. Perju, L. Marin, V. C. Grigoras and M. Bruma, *Liq. Cryst.*, 2011, **38**, 893–905.
6. S. Bronnikov, S. Kostromin and V. Zuev, *J. Macromol. Sci.B.*, 2013, **52**,1718-1735.
7. I. Musevic and M. Humar, *Proc. SPIE 7955*, *Emerging Liquid Crystal Tehnologies VI*, 795509, 2011, doi: 10.1117/12.874688.

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8.   T. Lan, W. Yang, H. Huang and Y. Wang, *RSC Adv.***,** 2014, **4**, 14997-15002.

9.   M. Mucha, *Progr. Polym. Sci.* 2003, **28**, 837 – 873.

10. J. K. Srivastava, R. K. Singh, R. Dhar and S. Singh, *Liq. Cryst.*, 2012, *39*, 1402-1413.

11. A. Tercjak, E. Serrano, M. Larrañaga and I. Mondragon, *J. Appl. Polym. Sci.*, 2008, **108**,1116 -
     1125.

12. P. Song, H. Cao, F. Wang, F. Liu, J. Wang, M. Ellahi, F. Li and H. Yang, *Liq. Cryst*.,2012, **39**,
     1131-1140.

13. T. J. White, L. V. Natarajan, V.P. Tondiglia, T.J. Bunning and C.A. Guymon, *Macromolecules*,
     2007, **40**, 1112–1120.

14. T. Zhang, M. Kashima, M. Zhang, F. Liu, P. Song, X. Zhao, C. Zhang, H. Cao and H. Yang,
     RSC Adv., 2012, **2**, 2144-2148.

15. M. Ellahi, F. Liu, P. Song, Y. Gao, M. Y. Rafique, D. F. Khan, H. Cao and H. Yang, *Soft
     Material.*, 2014, **12**, 339-345.

16. L. Marin and E. Perju, *Phase Transit.* 2009, **82**, 507-518.

17. I. Amimori, N. V. Priezjev, R. A. Pelcovits and G. P. Crawford, *J. Appl. Phys.*, 2003, **96**, 489-
     495.

18. L. Marin, M.-C. Popescu, A. Zabulica, H. Uji-I, and E. Fron, *Carbohyd. Polym.*, 2013, **95**,
     16-24.

19. L. Dolgov, O. Yaroshchuk, S. Tomylko and N. Lebovka, *Condens. Matter. Phys*, 2012, **15**, 1-
     8.

20. A. Teperek, W. Czajkowski and W. Fabianowski, *Proc. SPIE* 2372, Liquid Crystals:
     Materials Science and Applications, 1995, **408**, doi:10.1117/12.215574.

21. S. Sidiq, D. Das, S. K. Pal, *RSC Adv.*, 2014, **4**, 18889-18893

22. B. D. Hamlington, B. Steinhaus, J. J. Feng, D. Link, M. J. Shelley and A. Q. Shen, *Liq. Cryst.,*
     2007, **34**, 861–870.

23. D. Demus, L. Richter, (1978). *Textures of Liquid Crystals*. Leipzig: VerlagChemie, Weinheim.

24. P. S. Drzaic, *Liquid Crystal Dispersion*, World Scientific, Singapore, 1995

25. W. Li, Y. Cao, H. Cao, M. Kashima, L. Kong and H. Yang, *J. Polym Sci. B.,* 2008, **46**, 1369 –
     1375.

26. S. S. Patnaik and R. Patchter, *Polymer*, 1999, **40**, 6507 – 6519.

27. G. M. Russed, B. J. A. Paterson, C. T. Imrie and S. K. Heeks, *Chem.Mater.,* 1995, **7**, 2185–
     2189.

28. G.W. Smith, *Phys. Rev. Lett.*, 1993, **70**, 198–201.

29. T. Mansare, R. Decressain, C. Gors, V. K. Dolganov, *Mol. Cryst. Liq. Cryst.*, 2002, **382**, 97 – 111.

30. D. S. Kang, K. S. Kwon, S. I. Kim, M. S. Gong, S. S. Seo, T. W. Noh, S. W. Joo, *Appl. Spectrosc.*, 2005, **59**, 1136 – 1140.

31. C. Vasile and M. C. Pascu, Surfaces Properties of Polymers, Research Signpost, Trivandrum, India, 2007, 179.

32. Y. Ikada, *Biomaterials*, 1994, **15**, 726–736.

33. Y. H. Lin, T. Y. Chu, Y. S. Tsou, K. H. Chang and Y. P. Chiu, *Appl. Phys. Lett.*, 2012, **101**, 233502.

34. N. Hallab, K. Bundy, K. O'Connor, R. L. Moses and J. J. Jacobs, *Tissue. Eng.* 2001, **7**, 55-71.

35. E Ruckenstein, Sathyamurthy V Gourisankar, A surface energetic criterion of blood compatibility of foreign surfaces, Journal of Colloid and Interface Science, 101(2), 1984, 436-451

36. T. Bezrodna, V. Melnyk, V. Vorobjev and G. Puchkovska, *J. Lumin.,* 2010, **30**, 1134–1141.

37. Y. P. Piryatinski, L. A. Dolgov, O. V. Yaroshchuk, T. A. Gavrilko and S. K. Lazarouk, *Opt. Spectrosc.*, 2010,**108**,70-79.

38. S. Khatua, P. Manna, W-S. Chang, A. Tcherniak, E. Friedlander, E. R. Zubarev, and S. Link, *J. Phys. Chem. C*, 2010, **114**, 7251–7257.

39. C.J. van Oss, Interfacial Forces in Aqueous Media, Dekker, New York, 1994

40. F. Grassy, M. Morra, E. Occhiello, 2000, Polymer Surfaces – From Physics to Technology, John Wiley&Sons, Chichester

41. S. C. H. Kwok, J. Wanga, P. K. Chu, Diamond & Related Materials, 2005, **14**, 78– 85.