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Liquid-crystalline composites for point temperature measurements

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Abstract. The application of cholesteric liquid crystals and composites containing them for visualization of thermal field and temperature measurement is very well known. Despite all disadvantages as limited precision and adhesion to the studied surface, this method is still of interest. In this work, we present the results of preliminary studies on polymer-dispersed cholesteric liquid crystal (PDCLC) composites designed for visualization and measurement of point temperature changes which can be used in medical diagnostics.
Basing on the results of former studies, the perspective PDCLC preparation method as well as high--performance liquid-crystalline chiral nematics were obtained and applied.
The microencapsulation in poly(vinyl, alcohol) has been chosen as the method of PDCLC preparation while as liquid-crystalline materials the chiral nematics were adopted.
Keywords: material science, liquid-crystalline composites, medical thermography
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1. Introduction

The possibility of application of a thermooptical effect in cholesteric liquid crystals and composites containing them for visualization of thermal fields and temperature measurement is well known since the sixties of the last century [1, 2]. The very first studies were done by J.L. Fergason [3]. However, there is only limited a number of market products mainly targeted on common use as baby thermometers or an advertisement [4]. Nevertheless, such materials are still of interest in more sophisticated applications [5].

The molecular arrangement in a cholesteric phase creates space helix with the pitch p (Fig. 1). The pitch value for the specific substance depends on its twisting power, i.e. on composition in case of multicomponent mixtures. Light falling on such a structure undergoes selective reflection being an analogue to the Bragg diffraction in solid crystals. The wavelength of the maximum of selective reflection depends on the pitch and mean refractive index of cholesteric $\overline{n}$:

$$\lambda = \overline{n}p. \tag{1}$$

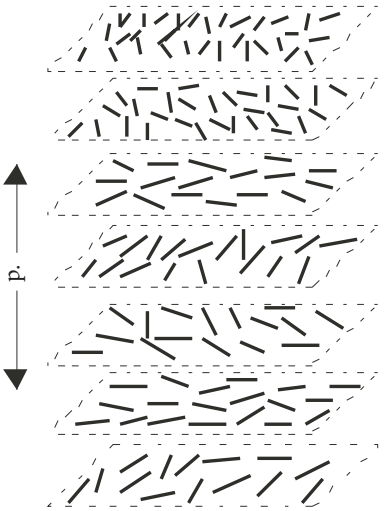


Fig. 1. Supramolecular arrangement in cholesteric liquid crystal.
Dashes show the local orientation of long molecular axes

In a cholesteric phase, the pitch weakly depends on temperature what is connected with thermal expansion only. The situation changes if the substance has got also smectic phase aside from the cholesteric one.

The basis of the thermooptical effect in cholesterics is the fast reorganization from twisted supramolecular helical arrangement in cholesteric phase to the layered one in smectic phase in the temperature range near cholesteric — smectic phase transition (Fig. 2). In this way, wavelength of the maximum of selective reflection rapidly changes, namely decreases due to unwinding of the helical structure with temperature decrease. Those changes can be observed visually as the colour change for visual light if the cholesteric is placed on the black substrate absorbing all wavelengths passing through the cholesteric film except this selectively reflected. This allows for easy visual assessment of the actual temperature field of the object on which cholesteric is deposited.

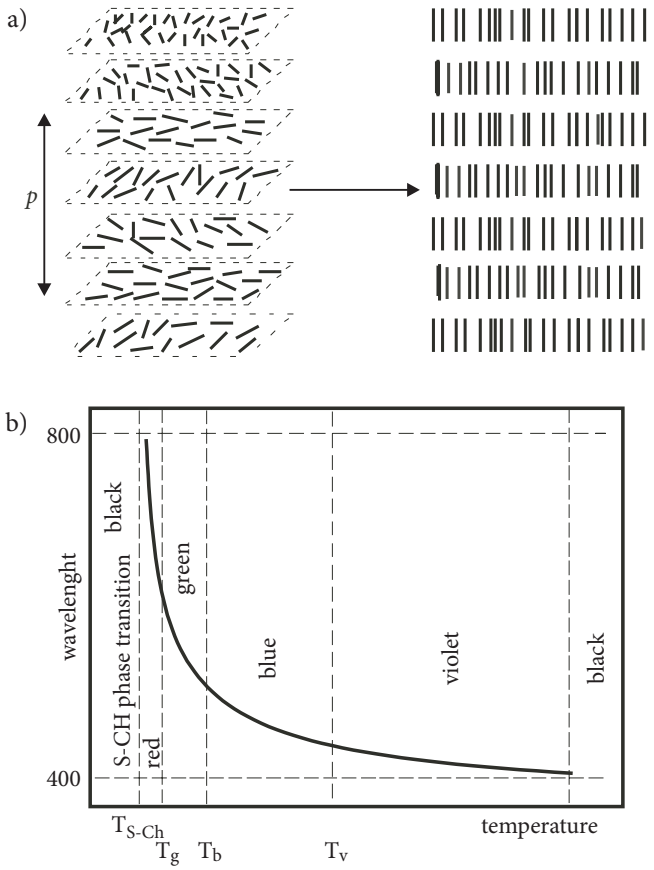


Fig. 2. a) The change of supramolecular structure during cholesteric-smectic phase transition; b) temperature dependence of the wavelength of the maximum of selective reflection near temperature of this phase transition

The above effect can be adopted in practice if the thermooptical parameters enlisted in Table 1 match respective requirements what is always obtained using multicomponent cholesteric mixture.

Table 1

Main CLC thermooptical parameters and their notations used in this work

Parameter	Description
ΔTc — temperature range of the colour response	Temperature range between the starting blue colour and the vanishing of red colour
ΔT_g — temperature range of the individual colours	Temperature range between the starting of the given colour and the vanishing of it

cont. of the table 1

$T_{b\to g}$ — temperature of colour transitions	b — blue, g — green, y — yellow, o — orange, r — red,
a_T — temperature sensitivity	The smallest temperature difference which can be distinguished visually as different colours
Δl — spatial resolution	The shortest distance between two points of thermal image with distinguished colours

There are two main groups of cholesterogens: cholesterol esters presented below in Fig. 3 and chiral nematogens (see Tables 2 and 3). Cholesterol esters are easier for synthesis and cheaper but chiral nematics give much larger possibility to modify thermoptical parameters of the cholesteric mixture due to the larger variety of individual compounds.

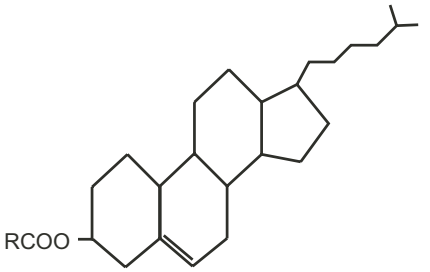


Fig. 3. Chemical formula of the cholesterol esters

The useful form of the application is thermographic foil being a polymer-dispersed cholesteric liquid crystal (PDCLC) composite. The schematic cross-section of PDCLC is presented in Fig. 4.

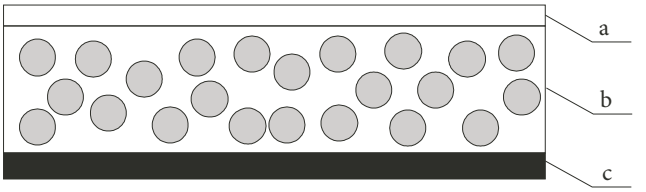


Fig. 4. The schematic cross-section of PDCLC thermographic foil: a) protective polymer film; b) PDCLC composite; c) black polymer substrate

As the material of polymer matrix of PDCLC, many film-forming polymers can be used, e.g. poly(vinyl alcohol), poly(vinyl acetate) or polyurethanes. There are also different techniques used for composite preparation (microencapsulation and several modifications of phase separation) as well as for PDCLC film formation, mainly spin coating and blade coating.

Despite many works were conducted, showing perspective applications of the above effect and materials in medical diagnosis, liquid crystal thermography has been never widely adopted in medicine. This was caused by two reasons, for the first thermography is not considered as the main diagnostic method in case of nearly all diseases, and for the second, nowadays health institutions use thermocameras which recently became reliable and relatively cheap.

In this work, we present the results of preliminary studies on new generation of PDCLC composites designed for visualization and measurement of point temperature changes which can be used in medical diagnostics by family doctors.

2. Experimental

During the first stage of studies, described in this paper, we adopt the simplest and the most environmental friendly procedure of PDCLC, namely dispersing of liquid crystal mixture in water solution of poly(vinyl alcohol) — PVA. In this process, a liquid crystal mixture is mechanically dispersed in the polymer solution to get droplets of wanted mean diameter. The system is heterogeneous during the whole process. Then, the emulsion is deposited onto a substrate and solvent evaporation leads to the solidification of the polymer with liquid-crystalline droplets "frozen" inside the matrix. Similar process was used for preparation of PDCLC containing cholesterol esters.

At first, PVA solutions of different compositions were prepared to find the best one for PDCLC formation. Basing on former experience [6] we chose PA-18GP (Shin Etsu Chemical Co.) as the polymer matrix. The set of samples consisted of water solutions of different PVA concentrations as well as such solutions doped with ethanol with the aim to reduce solution viscosity and to speed up solvent evaporation. The solutions contained from 10 to 20 per cent by weight of PVA.

The components were vigorously mixed at 60°C for 10-20 minutes. The viscosity of the obtained solutions was measured by Ubbelhode viscosimeter.

Poly(vinyl acetate) — PVAC (Aldrich) m.w. 100 000 was used as alternative material of the polymer matrix. In this case, the solvent-induced phase separation (SIPS) was used. It means that the both system components are dissolved in the same solvent the evaporation of which causes droplet nucleation and composite stabilization. In this case, PVAC solutions in butyl acetate were prepared. The concentration of those solutions varied from 10 to 20 percent by weight of PVAC with respect to the solvent.

All obtained solutions were studied from the point of view of thin films formation. As the substrates, the glass plates of 0.5-mm thickness were used for spin-coating deposition while black poly(ethylene terephthalate) foil was used for blade-coating. In the latter case, the wanted PDCLC layer thickness was achieved by polymer string spacers so, the final thickness of the PDCLC was from 9 to 20 μm.

The samples prepared on glass substrates were designed for microscopic studies of the composite morphology while for those on polymer foil, being the target ones, the durability on mechanical stresses was observed as well as the temperature range of the colour response.

The temperatures of phase transitions in synthesized compounds and mixtures were studied by polarization microscope equipped with programmable heating stage (Linkam). The colour transitions were observed visually, also using programmable heating stage.

3. Results and discussion

In Fig. 5, the dependence of viscosity on the composition of the solution measured by Ubbelhode viscosimeter is given.

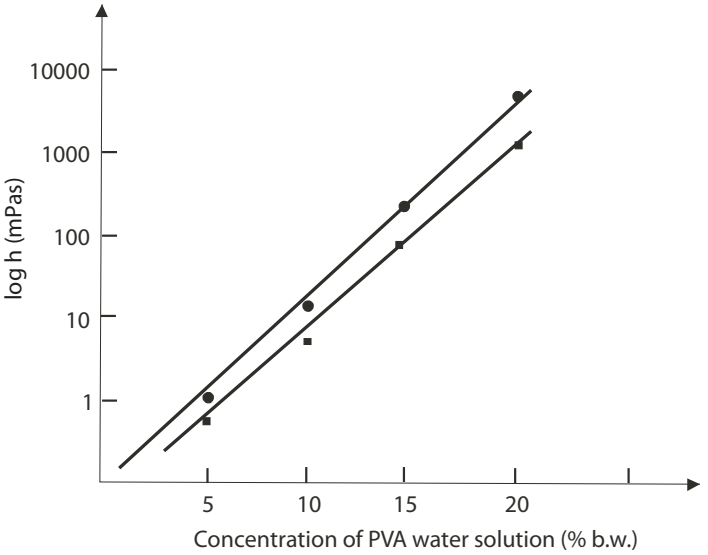
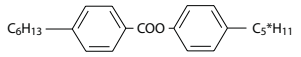
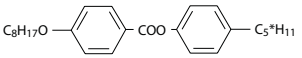
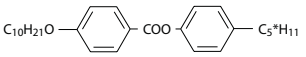


Fig. 5. The concentration dependence of the PVA solutions viscosity: ● — 10% b.w. EtOH; ■ — 20% b.w. EtOH with respect to water

The composition and properties of the basic mixture (BM) are gathered in Table 2.

Table 2

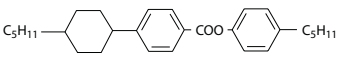
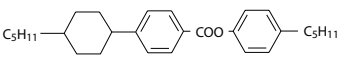
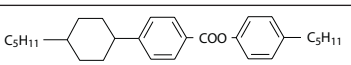
The data of the basic mixture [7]

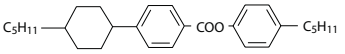
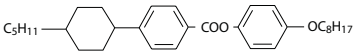
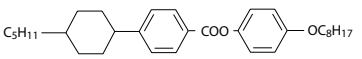
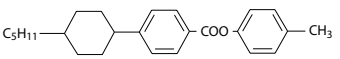
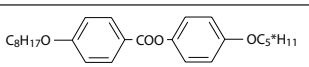
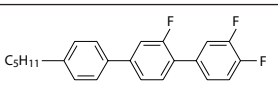
Compound formula	Concentration (per cent b.w.)
	18
	23
	59
Temperatures of phase transitions SmA 25 N 34 Iso Temperatures of colour transitions 25.1 blue 24.4 turquoise 34.1 green 23.9 red	

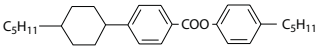
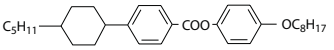
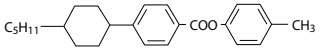
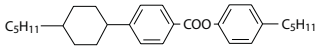
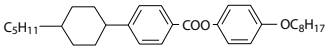
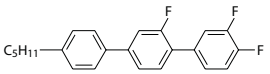
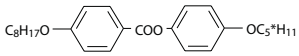
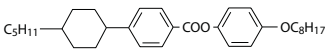
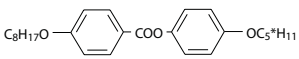
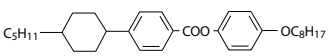
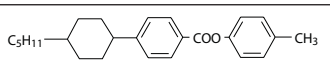
The colour response for basic mixture is observed from 23.9°C to 25.1°C. To achieve medical requirements, the temperature range of the colour response should be shifted from 32.5 to 35.5°C. This aim was achieved by the change of the composition of basic mixture. In Table 3, the composition and thermooptical parameters of the obtained mixtures are given.

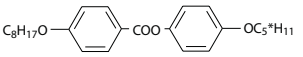
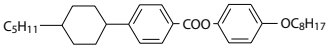
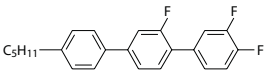
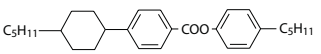
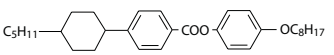
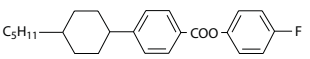
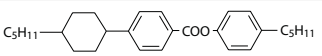
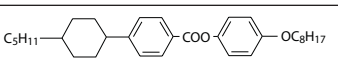
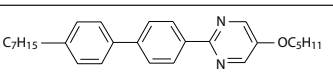
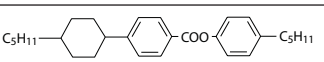
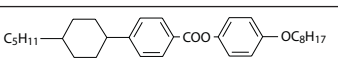
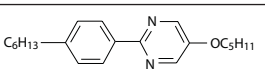
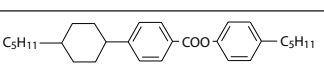
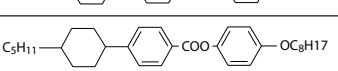
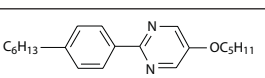
Table 3

The data of the modified mixtures

Mixture code name	Composition and properties	Concentration (per cent b.w.)
Mix 1	BM	88.3
		11.7
	SmA 32.1 N 44.8 Iso 35.7 blue 34.1 green 33.7 orange 33.1 red 32.1	
Mix 1A	BM	86
		14
	SmA 34.1 N 46 Iso 40 blue 36.5 green 35.3 orange 34.5 red 34	
Mix 1B	BM	87.675
		12.325
	41 deep blue 35.2 blue 35 green 34.7 orange 34.3 red 33.5	

Mix 2	MB	84.5
		15.5
	SmA 37.3 N 48 Iso 38.7 blue 37.8 turquoise 37.6 green 37 red 36	
Mix 3	MB	88.45
		11.55
	SmA 31.7 N 41 Iso 34.6 deep blue 32.5 blue 32 turquoise 31.4 green 31.3 yellow 31.1 red 30.8 black *34ºC 464 nm *33ºC 626 nm	
Mix 3A	MB	86
		14
	SmA 33.9 N 51 Iso 37.2 blue 35.7 turquoise 35 green 33.2 yellow 33.1 red 32.7 black	
Mix 4	MB	89.2
		10.8
	SmA 33.1 N 45.3 Iso 33.4 blue 33.5 turquise 33.5 green	
Mix 4A	MB	90
		10
	SmA 30 N 37 Iso 29 blue 28.6 green 28.1 yellow 27.6 orange 27.5 red	
Mix 5	MB	90
		10
	SmA 32.3 N 41.2 Iso 36 blue 33 green 32 red	

Mix 6	MB	92
		3
		3
		2
	SmA 29 N 42.3 Iso 30.8 blue 29.8 green 29.7 red	
Mix 7	MB	92
		3
		3
		2
	SmA 31.1 N 41.2 32.5 blue 30.6 green 30.2 orange 29.9	
Mix 9	MB	88
		7
		5
	SmA 29.1 N 41 Iso 34.9 deep blue 33.5 blue 33 green 30 orange 29.7 red 29 *33ºC 673 nm *32ºC 464 nm	
Mix 10	MB	86
		6
		5
		3
	36.5 blue 32.7 green 32.2 orange 32.0 red 31.8	

Mix 11	MB	86
		6
		5
		3
	35.4 green 34.7 yellow 32.4	
Mix 12	MB	90
		4
		4
		2
	38.5 deep blue 36.3 blue 35.5 turquois 34 green 33.6	
Mix 13	MB	90
		4.5
		4.5
		1
	37.8 deep blue 32.1 green 32 yellow 31.5 red 31.3	
Mix 14	MB	90
		4
		4
		2
	33.0 deep blue 30.2 green 30 yellow 29.8 orange 29.7 red 29.5	
	MB	88.5
Mix 14A		4.5
		4.5
		2.5
	38.2 deep blue 35.7 blue 33.7 azure 33 turquoise 33.2 green 31.9 orange 31.6 red 31.2	

All mixtures presented in Table 3 were dispersed in polymer matrices according to former procedures and the colour response of the obtained composites were studied.

It was found that the parameters of colour response in PDCLC differ from the pure liquid-crystalline material. In case of PVA based PDCLC, the temperature range of the colour response ΔTc was about a few tenths of Celsius degree lower than for pure liquid crystal mixture. The spectral composition was not changed; however, the intensity was lower. On the other hand, in case of PVAc based composites, the ΔTc was remarkably lower, from 10 to even 15 Celsius degrees, moreover red and green colours vanished. This effect was probably connected with residual presence of the solvent affecting the phase situation of liquid-crystalline mixture.

For this reason, the SIPS method including PVAc was rejected and the PVA based dispersions were treated as the target composites.

The results of application of the obtained PDCLC in medical diagnosis will be described separately.

4. Conclusions

1. New polymer-dispersed cholesteric liquid crystal composites designed for medical thermography were obtained.
2. The dispersing of the chiral nematic mixtures in water solution of PVA was found to be the most convenient for composite preparation.

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Kompozyty ciekłokrystaliczne do punktowych pomiarów temperatury

Streszczenie. Zastosowanie cholesterycznych ciekłych kryształów i kompozytów je zawierających do wizualizacji pól cieplnych i pomiaru temperatury jest dobrze znane. Niezależnie od niedogodności, jakimi są ograniczona precyzja i adhezja do badanego podłoża, metoda ta jest ciągle interesująca. Niniejsza praca przedstawia wyniki wstępnych badań nad kompozytami typu PDCLC, zawierającymi cholesteryczne ciekłe kryształy, a przeznaczonymi do wizualizacji i pomiaru punktowych zmian temperatury, co może znaleźć zastosowanie w diagnostyce medycznej.
W oparciu o wyniki poprzednich badań wytypowano i zastosowano perspektywiczną metodę otrzymywania kompozytów oraz nowe materiały ciekłokrystaliczne.
Wykorzystano dyspergowanie w wodnym roztworze poli(alkoholu winylowego) ciekłokrystalicznych nematyków chiralnych.
Słowa kluczowe: inżynieria materiałowa, kompozyty ciekłokrystaliczne, termografia medyczna
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