Biuletyn WAT
Vol. LXVI, Nr 3, 2017

The comparison of electrooptical properties of PDLC liquid-crystalline composites in visual and near-IR ranges

KRZYSZTOF SUŁKOWSKI[1], RAFAŁ WĘGŁOWSKI[2],
STANISŁAW J. KŁOSOWICZ[2]

[1]State Higher Vocational School, Institute of Technology, 33-320 Nowy Sącz, 1a Zamenhofa Str.
[2]Military University of Technology, Institute of Applied Physics,
00-908 Warsaw, 2 Kaliskiego Str., Poland, stanislaw.klosowicz@wat.edu.pl

Abstract. Electrooptical properties of conventional Polymer-Dispersed Liquid Crystals (PDLC) composites were compared in visual and near-IR ranges for the electrically-induced light transmission effect. It was confirmed that the most important for the optical contrast value is the matching of refractive indices of the polymer matrix and dispersed droplets of liquid crystal, as well as matching droplet size and wavelength of incident radiation. The optimization of electrooptical parameters of such materials needs new liquid-crystalline mixtures dedicated for near-IR range. The studied effect can be applied for manufacturing window glasses with electrically adjusted transmission of infrared radiation.

Keywords: material science, liquid-crystalline composites, PDLC, electrooptics, infrared
DOI: 10.5604/01.3001.0010.5387

1. Introduction

PDLC composites contain nano- or micrometric droplets of a liquid crystal embedded in a polymer matrix. The composite film can be used in form of elastic foil or filling of a glass cell of an electrooptical transducer. The main advantages of those materials are: simple preparation methods, elasticity and possibility of deposition onto substrates having a complex shape. Methods of preparation and morphology formation of PDLC composites, mainly concentration, shape, and size of liquid crystal droplets are well known [1-4].

Optical and electrooptical properties of those composites were carefully studied experimentally [1, 3, 5] and theoretically [6-8] for a visual range. It has been shown that most of electrooptical effects observed in thin liquid crystal layers can be reproduced in PDLC. However, the unique effect of electrically induced light transmission in nematic containing PDLC turned to be especially interesting. This effect consists in switching from the initial off-state scattering incident light to the transparent on-state or *vice versa* using electric field with sufficiently high intensity. The proper adjustment of refractive indices of liquid crystal and polymer secures a high optical contrast ratio [3, 9].

The basis of the latter phenomenon is the birefringence of a nematic phase. In each droplet, liquid crystal is aligned in space by chemical and physical interaction between liquid crystal and a surface of a polymer cavity. The essential kinds of such alignment are presented in Fig. 1. The most common is bipolar tangential alignment being the 3-D analogue of homogeneous alignment in thin layers of a nematic liquid crystal.

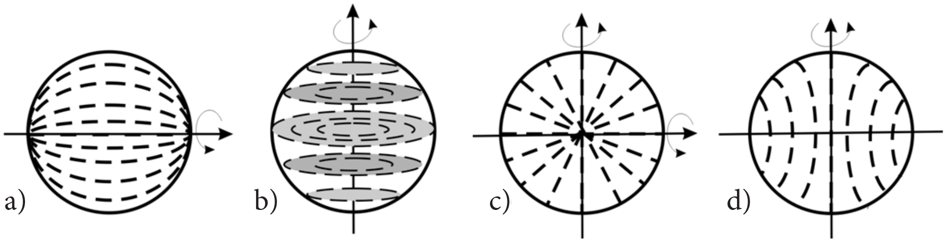

Fig. 1. Space distributions of the local arrangement of long molecular axes (director) in droplets of nematic liquid crystal: a) bipolar tangential; b) toroidal; c) radial and d) axial. Arrows show the direction of the droplet optical axis [10]

Two-point defects of the director field, usually observed due to 3-D alignment pointing out the droplet optical axis. However, optical axes of individual droplets are accidentally oriented in space unless the special technological processes are adopted. From a macroscopic point of view, it means that a liquid-crystalline phase dispersed in polymer shows certain a mean refractive index with respect to incident light. In case of normal light incidence, this mean refractive index is given by the following formula:

$$\overline{n}_{LC} = \frac{2n_o + n_e}{3}, \tag{1}$$

here n_o is the ordinary, while n_e is the extraordinary refractive index of the given nematic material.

Usually a mean refractive index of the liquid crystal droplets $\overline{n}_{LC}$ differs from the polymer refractive index n_p:

$$\overline{n}_{LC} \neq n_p. \tag{2}$$

For this reason, dielectric borders of droplet-matrix exist in the system and the incident light is scattered (off-state).

Application of the ambient electric field, higher than threshold one, to the composite layer causes reorientation of a liquid crystal in droplets and uniform alignment of optical axes of all droplets. Typically, when the nematic is optically positive:

$$\Delta n = n_e - n_o > 0, \tag{3}$$

and its dielectric anisotropy is also positive:

$$\Delta \varepsilon = \varepsilon_{\mathrm{II}} - \varepsilon_{\perp} > 0, \tag{4}$$

electric field aligns the optical axes parallel to field lines. It means that for normally incident light, liquid crystal droplets show an ordinary refractive index.

If in such a case, the ordinary refractive index of a liquid crystal is equal to the refractive index of the polymer matrix:

$$n_o = n_p, \tag{5}$$

dielectric borders vanish and the system becomes transparent (on-state), what is schematically presented in Fig. 2.

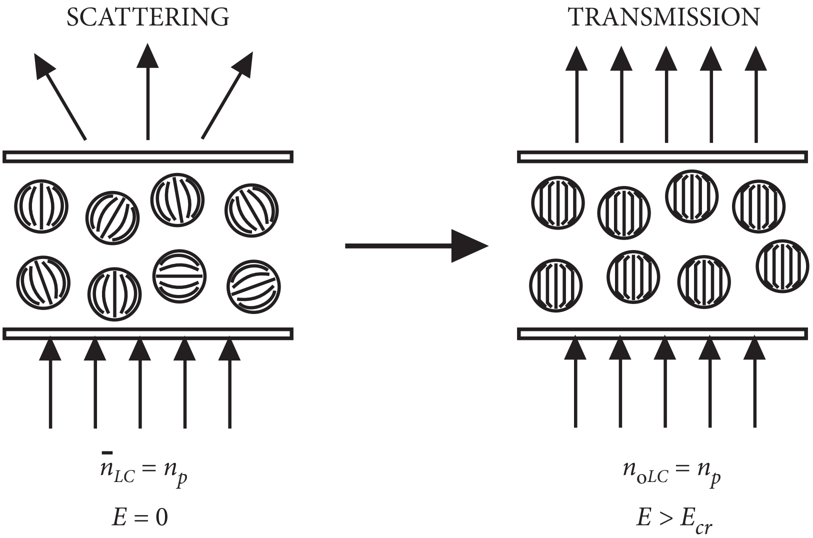

Fig. 2. Illustration of electrically induced light transmission in a PDLC composite. Dashes inside droplets represent a director field

The effect of electrically induced light transmission has been applied for manufacturing window glasses with electrically adjusted transparency (so called intimacy glasses) and specialized electrooptical transducers.

Considerably less works have been devoted to PDLC electrooptics in the infrared range [11-14]. Moreover, any liquid-crystalline materials, dedicated for composites working in this range, have been developed. On the other hand, materials for this range of radiation are of interest due to the possible applications in infrared optics and holography [15]. PDLC composites for infrared range can be also used for construction of window glasses with electrically adjustable transmission of heat radiation, e.g. for residential buildings or greenhouses.

The aim of the presented work was a comparison of electrooptical properties of PDLC composites containing nematic liquid crystals in visual and near infrared ranges. The studied materials have been originally designed for a visual radiation range. It means that adjustment of refractive indices of composite components has been done for the wavelength $\lambda = 589$ nm.

The studies have been performed for the samples with different content of liquid crystal and different morphology. The obtained results are the base for designing PDLC composites with increased optical contrast ratio in the near IR range.

2. Experimental

As the method of PDLC preparation, photopolymerizarion-induced phase separation has been chosen because it is simple, fast, and allows to obtain the samples with desired morphology. NOA-65 (Norland Optical Adhesives) photocurable polymercaptane resin has been used as a precursor of the polymer matrix. This material as the optical glue has got a proper refractive index equal to 1.52 and high transparency for visual light and near-IR. As nematic materials, the mixtures W-765, W-1815, W-1867 and W-1929 (Institute of Chemistry MUT) containing mainly isothiocyanates have been adopted. Those materials have been successfully applied for preparation of PDLC with a high optical contrast ratio in a visual range. Their optical properties are gathered in Table 1.

TABLE 1

Optical parameters of the used NLC mixtures

LC	$\Delta\varepsilon$ [20°C 1 kHz]	Δn [20°C]	n_o [20°C]	n_e [20°C]
1815	10.27	0.1858	1.5212	1.707
1929	21.56	0.317	1.565	1.883
1867	15.99	0.330	1.547	1.877

The preparation process has been conducted according to the former experience described elsewhere [4, 11]. Measuring cells have been constructed with BK7 glass 0.5 mm thick with deposited conducting layer of indium-tin oxide. The thickness of a composite film equal to 10, 15, or 18 mm has been fixed by polymer spacers.

Measurements of electrooptical parameters of the studied samples have been performed in the setup schematically presented in Fig. 3. As a source of visual, light the P8018 6V-15W bulb, fed by stabilized power supply Agilent E 3646A, has been used. Semiconductor CW lasers with power of 5 mW, emitting radiation at wavelengths of 980, 1060, and 1550 nm have been adopted as sources of infrared radiation. The measuring cells have been fed by voltage pulses with different amplitude and time by the Agilent 33220A generator.

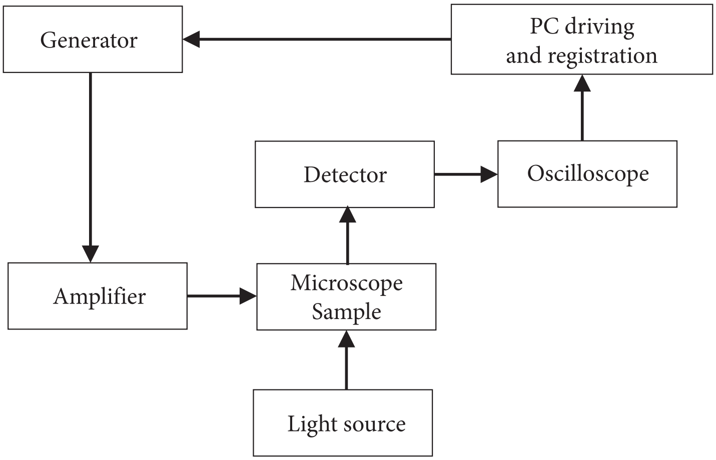

Fig. 3. The scheme of the setup for measurements of electrooptical characteristics

In Fig. 4, the images presenting examples of the morphology of the studied samples obtained by the scanning electron microscope Quanta 3D FEG Dual Beam are presented while in Fig. 5 the images obtained in the polarizing microscope Biolar (PZO) are given. According to predictions, an increase in the liquid crystal content leads to the increase in the mean droplet diameter.

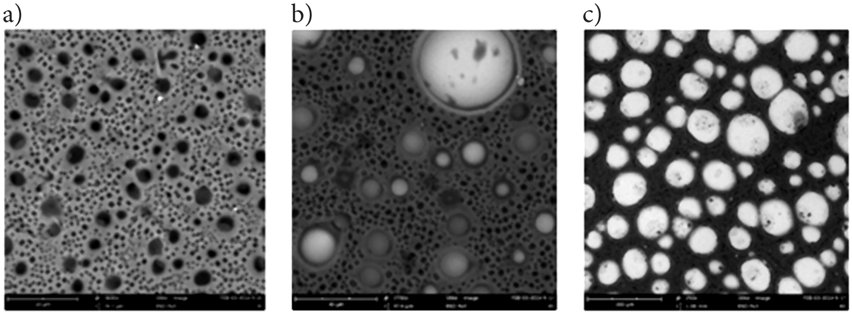

Fig. 4. Examples of SEM images of samples of PDLC composites containing:
a) 30; b) 45 and c) 60 per cent by weight of liquid crystal

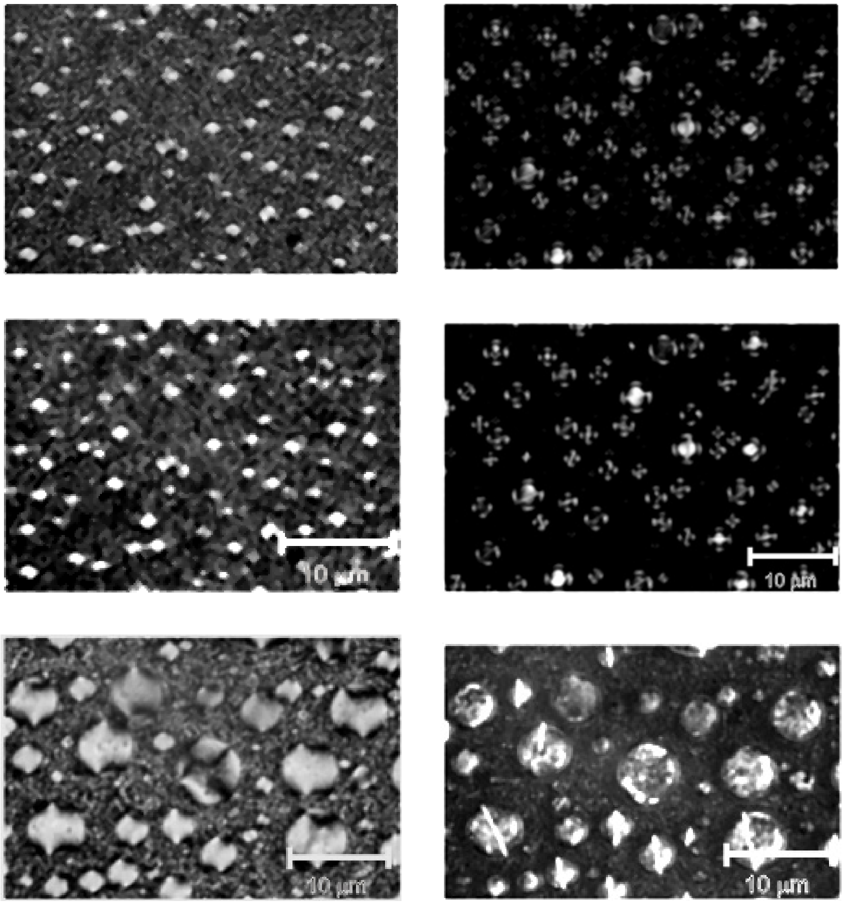

Fig. 5. Examples of morphology of PDLC composites with different size of liquid crystal droplets registered in an optical microscope between crossed polarizers

3. Results and discussion

In Fig. 6, the examples of spectral characteristics of composite samples containing different content of a liquid crystal obtained by means of a spectrometer with the PIN 20 photodetector (FLC Electronics) are presented.

The transmittance of 18-μm thick composite samples in off-state initially slightly increases and then remarkably decreases with a wavelength of an incident beam. The increase in a liquid crystal content, i.e., concentration of its droplets leads to reduction of the film transmittance, especially in off-state. The transmittance in on-state stronger decreases in the infrared range what is caused mainly by absorption in liquid-crystalline material, because the polymer practically does not absorb within a studied radiation range [13]. The transmittance becomes slightly higher in both

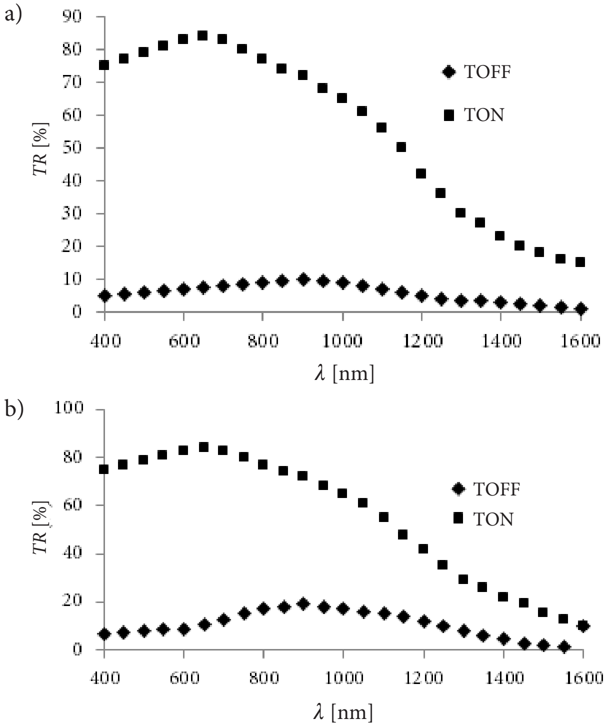

Fig. 6. The examples of transmittance vs. wavelength for studied PDLC samples containing respectively: a) 30 and b) 60 per cent b.w. of liquid-crystalline mixture in off- and on-states, PDLC thickness 18 μm

studied ranges for the samples containing droplets the diameter of which is by the order of magnitude larger than the wavelength of incident light due to lower scattering intensity. For both presented compositions, any dependence of transmittance on a droplet size has been observed as it has been expected.

The results obtained for 10-μm thick samples are similar with slight transmittance increase in off- and on-states due to obvious lower scattering intensity.

The representative static electrooptical characteristics of PDLC are presented in Figs. 7 and 8, while in Fig. 9 the representative dynamic electrooptical characteristic is given. The highest value of transmittance (100%) has been normalized to a value obtained for an empty cell. Tables 2-4 summarize the electrooptical parameters for the studied samples. The following notations are used: TR_{OFF} — the transmittance in off-state, TR_{ON} — the transmittance in on-state, $CR = TR_{ON}/TR_{OFF}$, U_{10} — switching-on voltage for which the transmittance increases by 10% with respect to TR_{OFF}, U_{90} — saturation voltage for which transmittance increases by 90% with respect to TR_{OFF}, t_{ON} — time since application of a voltage pulse after which the sample reaches TR_{90} transmittance t_{OFF} — time since switching off the voltage pulse after which the sample reaches TR_{10} transmittance. All measurements have been performed at room temperature (22°C).

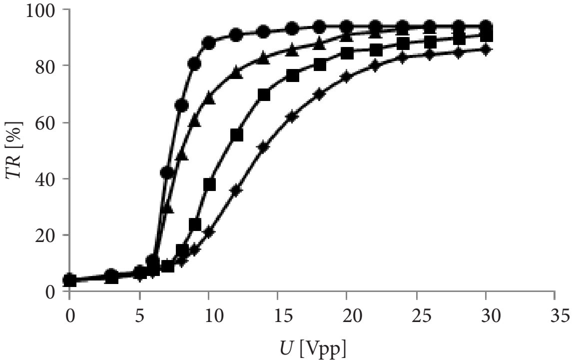

Fig. 7. Static electrooptical characteristics in visual light for PDLC composites containing respectively: 30 — ♦, 45 — ■, 50 — ▲ and 60 — ● per cent by weight of liquid crystalline mixture W-1815, rectangular pulse frequency of $f = 1$ kHz, $\lambda = 589$ nm, PDLC thickness 18 μm, average droplet diameter 3 μm

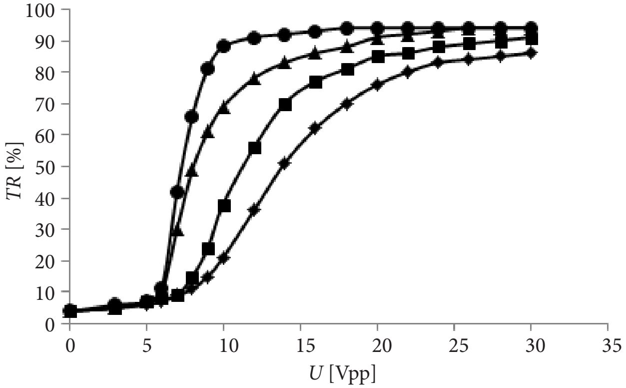

Fig. 8. Static electrooptical characteristics in near IR region for PDLC composites containing respectively: 30 — ♦, 45 — ■, 50 — ▲ and 60 — ● per cent by weight of the liquid crystalline mixture W-1815, the rectangular pulse frequency of $f = 1$ kHz, $f = 1$ kHz, $\lambda = 1550$ nm, PDLC thickness 18 μm, average droplet diameter 3 μm

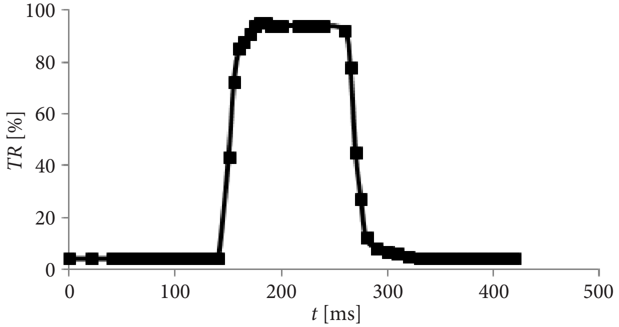

Fig. 9. The example of dynamic electrooptical characteristic of PDLC composite containing 45 per cent by weight of the liquid crystalline mixture W-1815, rectangular pulse with amplitude 30 V_{pp} and the frequency $f = 100$ Hz, PDLC thickness 18 μm, and average droplet diameter 3 μm

Table 2

Static electrooptical parameters for PDLC composites with different composition, the rectangle pulse frequency $f = 1$ kHz, $\lambda = 589$ nm, the liquid crystal mixture W-1815, PDLC thickness 18 μm

Liquid crystal content [% b.w.]	TR_{OFF} [%]	TR_{ON} [%]	CR	U_{10} [V]	U_{90} [V]
30%	5	87	17.4	3	20
45%	5	93	18.6	3	18
50%	6	94	18.8	3	14
60%	7	94	15.7	3	10

Table 3

Static electrooptical parameters for PDLC composites with different composition, the rectangle pulse frequency $f = 1$ kHz, $\lambda = 1550$ nm, the liquid crystal mixture W-1815

Liquid crystal content [% b.w.]	TR_{OFF} [%]	TR_{ON} [%]	CR	U_{10} [V]	U_{90} [V]
30%	5	86	17.2	3	20.5
45%	5	91	18.2	3	15
50%	6	94	18.3	3	12
60%	7	94	15.7	3	9.5

Table 4

Switching times for PDLC composites with different composition, $U = 30$ Vpp, $f = 1$ kHz, the liquid crystal mixture W-1815, PDLC thickness 18 μm

Liquid crystal content [% b.w.]	t_{ON} [ms]	t_{OFF} [ms]
30%	1.5	16.0
45%	1.6	48.0
50%	3.2	56.0
60%	0.8	71.0

As one can see, the T_{ON} transmittance increases with the increase in a liquid crystal content in the composite according to expectation because simultaneously increases a mean droplet diameter and reduction of the remnant scattering for saturation voltage, i.e., for uniform orientation of droplet optical axes. The changes of T_{OFF} transmittance are negligible.

The increase in the mean droplet diameter causes also the decrease in saturation voltage, because for larger droplets the effect of the anchoring energy on the surface of polymer cavity on the liquid crystal orientation in the whole droplet volume is lower. The optical contrast ratio increases with concentration of droplets and then slightly decreases due to decrease in the light scattering intensity. This effect means the increase in T_{ON} and is caused by mismatching of the mean droplet diameter and wavelength of incident radiation.

The decrease in t_{ON} and t_{OFF} for composites with larger content of liquid crystal is caused by the increase in a mean droplet diameter and so, the lower effect of anchoring on the director reorientation. Switching times do not depend on wavelength of incident radiation.

For $\lambda = 1550$ nm, the deviation from full matching of liquid crystal, polymer, and glass substrates refractive indices takes place. For this reason, to increase an optical contrast ratio in IR range, one should elaborate new liquid crystalline materials dedicated for this radiation range.

The effect of liquid-crystalline material is shown in Table 5 presenting a comparison of electrooptical parameters for the studied PDLC composites.

As one can see, in case of the same transducers in the same conditions and the same PDLC morphology these parameters depend on the used liquid-crystalline material.

The next stage of the studies will involve an application of liquid crystal and polymer with refractive indices matched for different wavelengths of IR radiation, liquid-crystalline material with lower absorption in the IR range as well as doping of the liquid-crystalline mixture by dichroic dyes absorbing in the near-IR.

TABLE 5

Electrooptical parameters of PDLC containing different nematic liquid crystals; liquid crystal content 30 per cent by weight, mean droplet diameter 2 μm, temperature 22°C, PDLC thickness 15 μm

Nematic mixture	TR_{OFF} [%]	TR_{ON} [%]	U_{10} [V]	U_{90} [V]	t_{ON} [ms]	t_{OFF} [ms]	CR
$\lambda = 589$ nm							
1815	7	82	6	14	5.0	10	11.8
1867	5	43	5	13	3.0	9.0	8.6
1929	7	38	4	15	4.0	8.5	5.4
$\lambda = 980$ nm							
1815	11	72	6	14	5.0	10	6.5
1867	6	37	5	13	2.5	8.5	6.2
1929	9	32	3	15	3.5	7.5	3,6
$\lambda = 1064$ nm							
1815	14	67	5	14	3.5	8.0	4.8
1867	9	43	4	13	2.0	7.0	4.8
1929	16	40	4	15	2.5	7.0	2.5
$\lambda = 1550$ nm							
1815	55	82	3	14	2.0	7.5	1.5
1867	48	73	2	13	2.0	6.0	1.5
1929	52	70	2	15	2.0	5.0	1.3

4. Conclusions

1. The PDLC composites exhibit different electrooptical properties in visual and IR ranges.
2. To increase an optical contrast ratio in near-IR range, liquid-crystalline materials dedicated for this range should be formulated.
3. PDLC composites with improved properties should be adopted for the construction of window glasses and transducers with electrically adjusted transmission of IR radiation.

This work has been supported by the Polish National Research and Development Center within Key Project POIG.01.03.01-14-016/08 *New photonic materials and their advanced applications* and the Scholarship Fund of the State Higher Vocational School, Nowy Sącz.

Received February 10, 2017. Revised March 31, 2017.

REFERENCES

[1] Kłosowicz S.J., Żmija J., *Optics and electro-optics of polymer-dispersed liquid crystals: physics, technology and application*, Optical Engineering, 34(12), 1995, 3440-3450.

[2] Kłosowicz S.J., Aleksander M., *Effect of polymer-dispersed liquid crystal morphology on its optical performance*, Opto-Electronics Review, 12(3), 2004, 305-312.

[3] Bouteiller L., LeBarny P., *Polymer-dispersed liquid crystals: preparation, operation and application*, Liq. Cryst., 21(2), 157-174 and References therein, 1996 .

[4] Ellahi M., Liu F., Song P., et al., *Characterization and Morphology of Polymer-Dispersed Liquid Crystal Films*, Soft Materials, 12(3), 2014, 339-345.

[5] Doane J.W., [w:] *Liquid Crystals: Applications and Uses*, Ed. B. Bahadur, World Scientific, Singapore, London, New York, vol. 1, Chapt. 14 and References therein, 1990.

[6] Žumer S., Doane J.W., *Light-scattering from a small nematic droplet*, Phys. Rev. A, 34(4), 1986, 3373-3386.

[7] Pajeda S., Pajediene S., Vaisnoras R., Adomeniene O., Gasparrini F., Rogante M., Rustichelli F., Yang B., *Electrooptical response in PDLC film*, Proc. SPIE, 3318, 1998, 422-426.

[8] Loiko V.A., Zyryanov V.Y., Maschke U., Konkolovich A.V., Miskevich A.A., *Small--angle light scattering and transmittance of polymer film, containing liquid crystal droplets with inhomogeneous boundary conditions*, Journal of Quantitative Spectroscopy & Radiative Transfer, 113(18), 2012, 315-322.

[9] Bowley C.C., Crawford G.P., *Improved reflective displays based on polymer-dispersed liquid crystals*, J. Opt. Technol. 67(8), 2000, 717-722.

[10] Węgłowski R., *Electrooptical properties of PDLC doped with inorganic nanocrystals*, Thesis (in Polish), Military University of Technology, Warsaw, Poland, 2013.

[11] McCargar J.W., Doane J.W., West J.L., Anderson T.W., *Polymer-dispersed liquid – crystal shutters for IR imaging*, Proc. SPIE, 1455, 1991, 54-60.

[12] Presnyakov V.V., Galstyan T.V., *Spectral properties of the IR-140 dye in liquid crystal matrices*, Proc. SPIE, 5260, 2003, 418-422.

[13] Manaila-Maximean D., Rosu D., Kłosowicz S.J., Czupryński K.L., Aleksander M., *Polymer-dispersed cholesteric liquid crystals reflecting in the infrared region*, Molecular Crystals and Liquid Crystals, 417, 2004, 683-689.

[14] Li W.B., Zhang H.X., Wang L.P., Ouyang C.B., Ding X.K., Cao H., Yang H., *Effect of a chiral dopant on the electro-optical properties of polymer-dispersed liquid-crystal films*, J. Appl. Polym. Sci., 105(4), 2007, 2185-2189.

[15] Galstyan A.V., Hakobyan R.S., Harbour S., Galstyan T.V., *Thermal modulation of diffraction in near infrared sensitive holographic polymer dispersed liquid crystals*, Opt. Comm., 241(1-3), 2004, 23-28.

K. SUŁKOWSKI, R. WĘGŁOWSKI, S. J. KŁOSOWICZ

Porównanie właściwości elektrooptycznych ciekłokrystalicznych kompozytów typu PDLC w zakresie widzialnym i bliskiej podczerwieni

Streszczenie. Porównano właściwości elektrooptyczne konwencjonalnych kompozytów typu PDLC (*Polymer-Dispersed Liquid Crystals*) w obszarze widzialnym i bliskiej podczerwieni dla przypadku efektu elektrooptycznego elektrycznie indukowanej transmisji światła. Potwierdzono, że na wartość współczynnika kontrastu optycznego najbardziej wpływa dopasowanie współczynników załamania matrycy polimerowej i zawieszonych w niej kropel ciekłego kryształu, jak również dopasowanie przeciętnego rozmiaru kropel i długości fali padającego promieniowania. Optymalizacja parametrów elektrooptycznych takich materiałów wymaga opracowania nowych mieszanin ciekłokrystalicznych przeznaczonych na zakres bliskiej podczerwieni. Badany efekt może być wykorzystany do wytwarzania szyb okiennych o elektrycznie regulowanej transmisji promieniowania podczerwonego.

Słowa kluczowe: inżynieria materiałowa, kompozyty ciekłokrystaliczne, PDLC, elektrooptyka, podczerwień

DOI: 10.5604/01.3001.0010.5387