Biuletyn WAT
Vol. LVIII, Nr 1, 2009

Development trends of polymer-dispersed liquid crystals

RAFAŁ WĘGŁOWSKI, MAREK ALEKSANDER[1], STANISŁAW J. KŁOSOWICZ

Military University of Technology, Institute of Applied Physics, 00-908 Warsaw, 2 Kaliskiego str.
[1]Technical Institute, State Higher Vocational School, Nowy Sącz

Abstract. The main up-to-date problems regarding studies of polymer-dispersed liquid crystal (PDLC) composites are presented. This regards main composite components and dopants, preparation methods and the composite morphology, optimization of known electro- and thermooptical properties and looking for new effects and especially new applications. The paper presents a review of recent problems regarding PDLC composites. Results obtained by the authors are used as the illustration.
Keywords: PDLC, nonlinear optics, fiber optics
Universal Decimal Classification: 548-14

1. Introduction

Polymer-dispersed liquid crystals (PDLCs) are well known since over twenty years. Usually they are described as two-phase composites containing liquid crystal (LC) droplets of different shape — spherical, ellipsoidal or flat embedded in a solid polymer matrix [1]. The first ten years of their studies were mainly devoted to preparation, relations between properties of components and PDLCs morphology and their electrooptic properties. Because nematics were used at first as LC materials, the main electrooptic effect studied was electrically-induced light transmission of the PDLC film [2]. Then, composites containing chiral nematics were introduced enabling to observe colour effects due to selective light reflection driven by electric field [3]. In the end of the last century, PDLCs with ferro- or antiferroelectric smectics exhibiting bistable or tristable electrooptic switching, respectively [4, 5] have been obtained and studied. In this way, all LC phases interesting from application point of view can be used as the components of PDLC.

Depending on components and a procedure of a preparation process, PDLCs exhibit different morphology, i.e., concentration, size, and shape of LC droplets, moreover the director field distribution inside those droplets. The morphology crucially affects electro- and thermooptical properties of the composites and therefore is essential for their applications [6].

Those composites are also very interesting research material due to curvilinear geometry of LC phase and unique role of anchoring conditions, droplet size effects, and differentiated director distribution.

However, PDLC systems are interesting mainly from an application point of view due to simple construction and technology of electrooptic transducers in comparison with classic LCD technology, but they have also several drawbacks as relatively high driving voltage [7].

Recent studies on PDLC are focused on new PDLC systems with improved performance which can significantly widen the possible applications. This problem includes preparation of new composite systems of dedicated LCs and new polymer binders, precise adjustment of morphology but also studies on the properties of LC in polymer cavities to better understand electrooptic and thermooptic behaviour of the composites. The second, main group of interest is the study on different optical effects in PDLC as well as application of these effects for information display, light processing, and sensing.

In Fig. 1, the number of papers devoted to PDLC, divided by the subject, published in the last three years (they are divided in more or less arbitrary way due to possible interconnection) is given to illustrate the present situation.

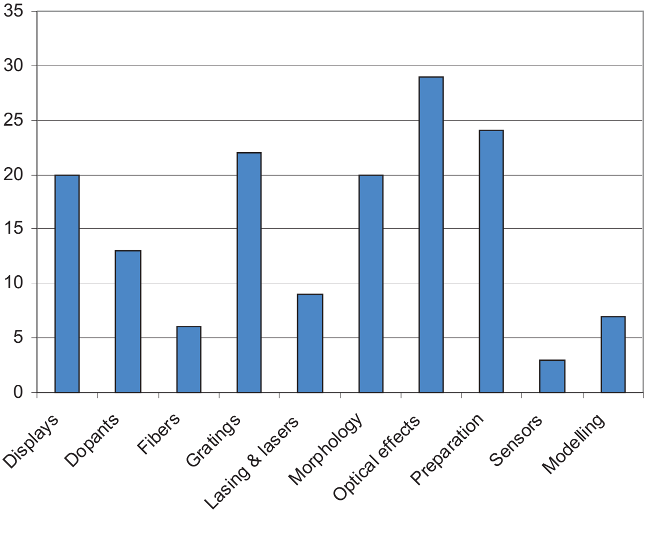

Fig. 1. The main directions of PDLC studies according works published in 2004-2007

In this paper, the authors present a brief overview of recent PDLC studies illustrated mostly by their experimental results.

2. Materials

2.1. General remarks

The choice of PDLC components depends mainly on the research or application aim, moreover chosen electrooptical or thermooptical effect and preparation method. Different kinds of phase separation [7] are usually used for PDLC preparation, however, sometimes also microencapsulation is used [8]. The classic situation requires fulfilment of at least the following requirements: the proper matching of refractive indices, extremely low solubility of components in final composite, the absence of light scattering by polymer, sufficiently high concentration of LC droplets, and wanted director field inside droplets [6, 9].

Most of these general requirements can be fulfilled by the adjustment of LC material to a given polymer. This means that changing a chemical structure of components of LC mixture one can maintain wanted properties affecting electrooptical bevaviour, e.g., number and temperature ranges of liquid-crystalline phases, elastic constants, viscosity, helical pitch and/or spontaneous polarization. On the other hand, those changes in a structure can significantly change anchoring conditions on the surface of polymer cavity, solubility in prepolymer and cured polymer, and surface tension in uncured polymer. In this way one can obtain wanted effect with better performance, e.g., shorter switching times, lower driving voltages, and higher optical contrast.

2.2. Polymers

Taking into account wanted properties of the PDLC and the measuring/application system, the following polymer groups are most often used: optical photocurable glues and film-forming materials, especially low-melting thermoplastics and water or organic soluble polymers. However, for some possible applications one should use other polymers.

Thiol-enes are the interesting group of polymers for PDLC binders. They are photocurable, transparent in visual spectrum, have the excellent adhesion to glass and the proper refractive index being used as optical glues. Recently, thiol-enes different from classic NOA-65 and NOA68 (Norland Optical Adhesives) are studied as potential PDLC binders.

PDLC designed for GHz applications should exhibit very small losses what is not fulfilled by the most of typical polymer binders. Polyethylene or polypropylene seems to be a good choice in this case but those polymers have not been used for PDLC preparation till recently due to high melting point and poor solubility in organic solvents. So, what we should do?

To obtain polyethylene and polypropylene based PDLC, the commercial polyethylene and/or polypropylene has been dissolved in a hot (70°C) cyclohexane. Then, 20 per cent by weight of nematic LC (W-765 Institute of Chemistry MUT) has been added and the system was carefully mixed. The solvent has been evaporated at 40°C for three days and then the obtained mixture has been placed at the ITO coated glass substrate with 8-μm spacers, covered with upper glass plate, weighed, and heated. Because LC has acted as plasticizer, the uniform melt has been obtained at about 130°C for polyethylene and at about 120°C for polypropylene. The melt has been cooled with cooling rate from 1 to 10 Celsius degree per minute. As a result, LC droplets have emerged in polymer binder (see Fig. 2). The droplet size depended on cooling rate and varied from ca. 1 μm for the slowest cooling to ca. 3-4 μm for the fastest cooling.

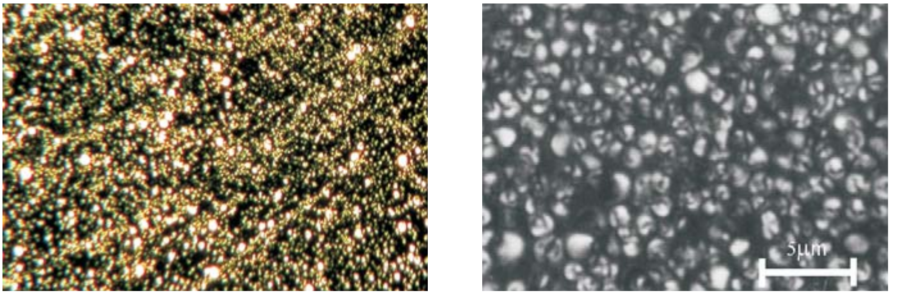

Fig. 2. The images of droplets of W-765 nematic mixture in polyethylene obtained in polarizing microscope; fast cooling — left and slow cooling — right

2.3. Liquid crystals

Using multicomponent mixtures one can easy prepare the LC material devoted to a given polymer binder. This task includes in particular:

— proper choice of LC material from used electrooptical effect point of view (e.g. anisotropy of dielectric permittivity, spontaneous polarization, refractive indices),
— matching LC and polymer refractive indices, what increases optical contrast between off- and on-state in case of electrically induced transmission and reduces scattering noise for other electrooptical effects,
— low viscosity decreasing switching times,
— low anchoring energy reducing driving voltage,

— long-term stability, especially when exposed to temperature changes and UV radiation.

In case of PDLC, the relationships between polymer and liquid crystal, especially mutual solubility are playing a crucial role.

For this reason, many different groups of mesogenic materials, moreover modyfying isotropic dopants, are currently used in PDLC composites.

2.4. Dopants

The dopants used in PDLC systems can be divided into three main groups:

1. Morphology agents, e.g., binder plasticizers or aligning dopants. For instance, fluoroalkyl terminated polyurethane oligomer added to polyurethane acrylate resin acted as surface modifying agent on electro-optical properties of PDLC lowering driving voltage [10]; an introduction of additional polymeric material forming microcapsules containing LC and giving remarkable reduction of the hysteresis effect [11].
2. Optical agents, e.g., dichroic dyes [12, 13], inorganic materials, e.g. fullerenes [14], nanotubes [15] and nanocrystals [16], metalomesogens [17]. Those dopants are used for improving optical contrast ratio, decreasing switching times and driving voltage, and modifying PDLC electrooptic characteristics, e.g., the slope of static characteristic.
3. Other dopants, especially sensing ones, e.g., reacting with physical, chemical or biological agents.

3. Morphology

Electrooptical properties of PDLC depend on the LC phase embedded into polymer matrix and the composite morphology, i.e., concentration, size and shape of LC droplets, moreover the director (the vector describing local orientation of long mesogen molecular axes) field inside droplets. The three former mentioned morphology features can be determined during preparation of PDLC composite [6, 18].

The spatial distribution of the director inside droplets depends on the interactions between LC and the surface of polymer cavity and can be modified by the mentioned aligning dopants.

The mean droplet size decreases with an increase in the solidification ratio. The higher curing ratio, the larger is concentration of droplets, however, it depends also on the LC content in the PDLC composite. In case of Photopolymerization Induced Phase Separation (PPIPS), the curing ratio is inversely proportional to the UV flux what enables precise adjusting of a droplet size from about 100 nm up to hundred μm [19].

LC droplets are usually more or less spherical due to surface tension. However, it is possible to obtain ellipsoidal droplets by several techniques [20]. This action is necessary in many cases described below.

The first method consists in a preparation of the PDLC film in which thermoplastic is used as a polymer binder. Then, the film is locally heated above the plastic deformation limit and stretched. As a result, the composite is elongated therefore LC droplets are elongated. The mean aspect ratio of elongated liquid crystal droplets obtained in this way is usually from 2 to 4. LC droplets deformed by this method are usually flat.

The second method consists in an application of electric field during phase separation. The electric contribution to the LC elastic deformation energy enforces elongation of droplets, either parallel or perpendicular to the field depending on the sign of dielectric permittivity of LC — $\Delta\varepsilon$. LC materials with $\Delta\varepsilon < 0$ are of the special interest because electric field elongates their droplets parallel to the substrata. For LC showing the dispersion of $\Delta\varepsilon$, a dual-frequency driving can be used, e.g., low-frequency field aligns LC and elongates droplets with their optical axes parallel to glass substrates (perpendicular to the field), while high-frequency field reorients parallel to the field so perpendicular to the substrates. The droplet elongation obtained by this way is rather small (aspect ratio up to 1.5) due to limited intensity of electric field which can be applied to the PDLC film without breakdown.

The third way adopts low-frequency shearing of the system during PPIPS process therefore solidification of the polymer leads to the stabilization of droplets elongated by mechanical stress.

If droplet size is smaller than the film thickness, deformed droplets are usually the ellipsoids of revolution; in the opposite case they are flat.

Elongation of LC droplets usually enhances electrooptical and thermooptical performance of PDLC. The mechanism of this enhancement depends on the nature of a chosen optical effect. One of the advantages of such droplets' shape is better optical filling of the PDLC film cross-section and so the higher optical contrast ratio of the electrooptical switching. Additionally, elongated droplets have uniform orientation of optical axes what also increases the optical contrast ratio. The same reasons regard electro- and thermooptical effects using selective reflection from chiral nematics.

In some cases, new effects are observed for flat droplets, e.g., high optical quenching in PDLC containing monodroplet later of LC or polarization of incident light [21]. It is also necessary to observe electrooptical switching in ferro- and antiferroelectric liquid crystals [22, 23].

4. Effects and properties

The essential electrooptic effects observed in PDLC composites containing different liquid crystal phases are gathered in Table 1. Despite the nature of the effect, the relationships between PDLC morphology and electrooptic properties of PDLC described below are observed.

TABLE 1

Electrooptic effects in PDLC composites

Phase	Electrooptic effect	Possible applications
N	Electrically-induced light transmission Initially optical axes of LC droplets are distributed statistically — composite layer scatters incident light. Electric field continuously aligns LC director inside all droplets parallel to the field. For proper refractive indices matching composite layer it gives switching between scattering off-state and transparent on-state. In reversed mode initially optical axes of LC droplets are aligned — PDLC transmits incident light. Electric field continuously aligns LC director inside all droplets perpendicular to the field leading to scattering on-state	Light shutters and simple amplitude modulators, space light modulators, linear polarizers, switchable gratings, holography, outdoor displays, flexible displays, fiber optic elements
N*	Bistable switching For LC mixtures with $K_{33} > K_{22}$ the threshold voltage unwinds the helix. The cell has been switched from selective reflecting state to the transparent state, i.e. from colour to the transparent state	Displays, optical switches
N*	Pitch expansion For $K_{33} < K_{22}$ above the threshold field the helixis unwound continuously with the field increase — λ_{max} is shifted to red (black background is needed for visual observation)	Optical filters and deflectors
SmC*	Bistable switching The effects analogous to surface-stabilized ferroelectric liquid crystal and deformed helix ferroelectric are observed depending on the relation between droplet size and helical pitch	Displays, fast optical modulators, fiber optic elements
SmC_A*	Tristable switching The effect is similar to that one observed in thin layers of SmC_A*. The static electrooptic characteristic depends on LC material and varies for W-switching to V-switching	Displays, fast optical modulators, fiber optic elements

The thickness of PDLC transducer, necessary to achieve maximum of the optical contrast in those effects, varies from several micrometers up to 20 micrometers. The contrast ratio depends also on the nature of electrooptic effect and the morphology of PDLC. In general, it increases with the optical filling of the PDLC cross-section with liquid crystal droplets what depends on concentration and shape of liquid crystal droplets. In case of scattering effects it achieves maximum for droplet size fitted to wavelength of incident light. In all effects, the proper refractive index matching is a crucial factor. For electrically-induced light transmission effect, the mismatching of polymer and liquid crystal refractive indices in scattering state should be high while in a transmitting state the refractive indices should be equal. In other effects, refractive indices of PDLC components should be fitted to avoid light scattering.

Driving voltages are usually higher than for LCD type devices due to a large area of the liquid crystal-polymer surface and so an anchoring effect. It depends on the used components (the anchoring conditions of a liquid crystal on the surface of a polymer cavity which can be modified by dopants) and typically varies from several Volts up to several dozen Volts. This feature can be treated as disadvantageous one. The driving voltage increases with the decrease of a droplet size.

On the other hand, anchoring decreases switching times which are usually less by one order of magnitude than for LCD transducers. Switching times usually decrease with the size of a liquid crystal droplet.

There is also the possibility of doping PDLC components not only to adjust anchoring conditions but also to enhance light absorption/scattering and transmission in wanted areas or to increase optical contrast ratio of the system.

Using wave mixing one can produce switchable gratings in PDLC structures what is important for holographic applications. Especially nanodroplets and elliptical droplets are interesting from holography point of view [24].

5. Discussion

As one can see from Table 1, electrooptic effects observed in PDLC films can be adopted for numerous electrically switchable optical devices. Many of them have been constructed and produced, some other are at the laboratory stage. This includes light modulators also the spatial ones, optical filters and deflectors, and fiber optic switches of different kind.

The main problems regarding PDLC electrooptic transducers to solve are reduction of driving voltage, increase in optical contrast ratio, and design of dedicated liquid crystal mixtures. Especially, the latter problem seems to be very important because liquid crystal mixtures dedicated for LCD applications do not fulfil all requirements for PDLC electrooptic transducers. This regards especially interaction with polymer binder and values of refractive indices.

PDLC composite can be prepared on the objects of complicated shape, e.g., optical fibers [25]. This is important advantage of those composites in comparison with other optical materials. PDLC can be adopted as fiber coating but also as active medium in discrete optical elements. Such elements can contain glass substrates but also can be flexible if polymeric conductive foils are used as substrates. Moreover they can be stable assembled with fibers. In this case polymer binder after solidification stabilizes the position of optical fibers. Composites containing very large liquid crystal droplets are of interest due to low driving voltages and easy assembling the PDLC element with optical fibers.

PDLC seems to be very interesting for these applications starting from couplers, through modulators and beam dividers to polarization controllers.

Another new application of nanodroplet PDLC composites is holography in real time. The series of works prepared in US Air Force Research Laboratory [26] and in other groups has shown the great potential of PDLC systems in writing gratings with electrically switchable diffraction efficiency which can be adopted, e.g., in displays and telecommunication.

6. Conclusions

1. Polymer-dispersed liquid crystals are promising and still underestimated media for a construction of different optical devices. They offer many electrooptic effects even unique ones.
2. Despite technological problems, PDLC transducers are of great interest due to their application advantages including simple technology, relative low cost, electrooptic features and possibility of their adoption in systems of a complex shape.
3. The very promising fields of PDLC application are fiber optic systems and real-time holography.
4. PDLC composites are interesting also as materials for information displays and devices for light beam processing.

This work was partially presented at SPIE Europe Conference on Optics and Optoelectronics 2006 in Prague and in Kiev at American-Ukrainian-Korean Joint Workshop 2007.
Authors are deeply grateful to the Ministry of Science and Higher Education for financial support.

Received May 7 2008, revised July 2008.

REFERENCES

[1] G. P. Crawford and S. Žumer, in: *Liquid Crystals in Complex Geometries*, Chapter 1, ed. G. P. Crawford and S. Žumer, London, Taylor & Francis, 1996.

[2] J. W. Doane, *Polymer dispersed liquid crystals*, in: Liquid Crystals Applications and Uses, Chapter 14, ed. B. Bahadur, Singapore, New Jersey, London, World Scientific, 1990.

[3] P. S. Drzaic, *Liquid Crystal Dispersions*, New York, London, Singapore, World Scientific, 1995.

[4] H. Molsen and H. S. Kitzerow, *Bistability in polymer-dispersed ferroelectric liquid crystals*, J. Appl. Phys., 75, 2, 1994, 710-716.

[5] V. Vorflusev and S. Kumar, *Multistable antiferroelectric liquid-crystal optical modulator*, Appl. Phys. Lett., 73, 22, 1998, 3211-3213.

[6] S. J. Kłosowicz, M. Aleksander, *Effect of polymer-dispersed liquid crystal morphology on its optical performance*, Opto-Electron. Rev., 12, 3, 2004, 305-312.

[7] S. J. Kłosowicz, J. Żmija, *Optics and electro-optics of polymer-dispersed liquid crystals: physics, technology and application*, Opt. Eng., 34, 12, 1995, 3440-3450.

[8] S. J. Kłosowicz, M. Aleksander, P. Obrzut, *PDLC composites with elongated LC droplets*, Proc. SPIE, 5947, OM1-OM7, 2006.

[9] S. Kłosowicz, *Optimization of electrooptical parameters of polymer dispersed liquid crystals*, Opto-Electron. Rev., 2, 58-60, 1993.

[10] Ai Jung, Byung Kyu Kim and Jae Chang Kim, Eur. Polym. J., 42, 10, 2006, 2667-2671.

[11] Jee-Hyun Ryu, Young-Hun Choi, Kyung-Do Suh, *Electro-optical properties of polymer-dispersed liquid crystal prepared by monodisperse poly(methyl methacrylate)/fluorinated liquid crystal microcapsules*, Colloid. Surface A, 275, 1-3, 2006, 126-132.

[12] J.-H. Liu, H-Y. Wang, *Optical switching behaviour of polymer-dispersed liquid crystal composite films with various novel azobenzene derivatives*, J. Appl. Polym. Sci., 91, 2, 2004, 789-799.

[13] A. Masutani, T. Roberts, B. Schuller, A. Yasuda, A. Sakaigawa, G. Cross, D. Bloor, *A novel polarizer-free dye-doped polymer-dispersed liquid crystal for reflective TFT displays*, J. Soc. Inf. Display, 12, 3, 2004, 301-307.

[14] N. Kamanina, *Photoinduced phenomena in fullerene-doped PDLC: Potentials for optoelectronic applications*, Opto-Electron. Rev., 12, 3, 2004, 285-289.

[15] A. V. Sadovoy, V. F. Nazvanov, *Study of the electro-optical response of polymer dispersed liquid crystal doped with multi-wall carbon nanotubes. The anomalous behaviour is attributed to a preliminary partial orientation of molecules in the presence of carbon nanotubes in the dispersed liquid crystal droplets*, Proc. SPIE, 6164, Article number 616407, 2006.

[16] L. Dolgov, O. Yaroshchuk, *Electro-optic properties of nematic liquid crystal filled with mono-dispersed non-organic nanoparticles*, Proc. SPIE, 5257, 2003, 48-57.

[17] J. Zhou, L. Petti, P. Mormile, A. Roviello, *Comparison of the thermo- and electro-optical properties of doped and un-doped MOM based PDLCs*, Optics Comm., 231, 1-6, 2004, 263-271.

[18] M. Aleksander, S. J. Kłosowicz, *Effect of preparation method on morphology of polymer-dispersed liquid crystals*, Biul. WAT, 53, 2-3, 2004, 5-18.

[19] R. Węgłowski, S. J. Kłosowicz, *Submitted to Molecular Crystals and Liquid Crystals* (to be published).

[20] S. J. Kłosowicz, *Electrooptical properties of PDLC containing deformed LC droplets*, Opto-Electron. Rev., 4, 1/2, 1996, 62-68.

[21] A. V. Konkolovich, V. V. Presnyakov, V. Ya. Zyryanov, V. A. Loiko, V. F. Shabanov, *Interference quenching of the light passed through thre monolayer film of the polymer dispersed nematic liquid crystal*, J. Exp. Theor. Phys., 71, 12, 2000, 486.

[22] S. J. Kłosowicz, K. L. Czupryński, W. Piecek, *Polymer dispersed ferroelectric and antiferroelectric liquid crystals*, Mol. Cryst. Liq. Cryst., 351, 2000, 343-349.

[23] S. J. Kłosowicz, W. Piecek, R. Dabrowski, P. Perkowski, *Switching of orthoconic antiferroelectric mixtures in PDLC system*, Mol. Cryst. Liq. Cryst., 422, 2004, 291-296.

[24] M. Jazbinsek, I. Drevensek-Olenik, M. Zgonik, A. K. Fontecchio, G. P. Crawford, *Characterization of holographic polymer dispersed liquid crystal transmission gratings*, J. Appl. Phys., 90, 8, 2001, 3831.

[25] A. W. Domanski, D. Budaszewski, S. Ertman, P. Lesiak, K. Nowecka, T. R. Wolinski, Proc. SPIE, 6608, 2007, 660807.

[26] R. L. Sutherland, R. L. V. P. Tondiglia, L. V. Natarajan, T. J. Bunning et al., Proc. SPIE, 6487, 2007, 6487V.

S. J. KŁOSOWICZ, R. WĘGŁOWSKI, M. ALEKSANDER

Kierunki rozwojowe kompozytów ciekłokrystalicznych typu PDLC

Streszczenie. Przedstawiono najważniejsze współczesne zagadnienia dotyczące badań ciekłych kryształów zawieszonych w polimerach (PDLC). Dotyczy to składników kompozytu, domieszek, metod otrzymywania oraz optymalizacji właściwości elektro- termooptycznych PDLC, zwłaszcza pod kątem nowych zastosowań. Artykuł zawiera przegląd najnowszych problemów dotyczących PDLC ze szczególnym uwzględnieniem wyników uzyskanych w WAT.

Słowa kluczowe: PDLC, optyka nieliniowa, optyka światłowodowa, kompozyty ciekłokrystaliczne
Symbole UKD: 548-14