Biuletyn WAT
Vol. LXVIII, Nr 2, 2019

Recent trends in studies on polymer – dispersed liquid crystal composites

STANISŁAW J. KŁOSOWICZ

Military University of Technology, Institute of Applied Physics,
2 S. Kaliskiego Str., 00-908 Warsaw, Poland, stanislaw.klosowicz@wat.edu.pl

Abstract. The paper presents a review of results of studies in the field of PDLC material science and physics obtained during last few years and shows the main fields of interest in that subject. It covers an application of new polymers and liquid crystalline materials used to prepare those composites, modification of their properties by different inorganic and organic dopants as well as new optical properties. The evolution of scientific interest regarding PDLC composites in recent years is shown.
Keywords: material science, composites, polymer-dispersed liquid crystals, optics, electrooptics
DOI: 10.5604/01.3001.0013.3000

1. Introduction

Polymer-Dispersed Liquid Crystal (PDLC) composites were obtained and carefully studied in the end of the last century. The 3D geometry of liquid crystal microvolumes is very interesting from as basic as application point of view. The results of those studies were gathered in several books and monographic papers [1-4]. In that first period of studies, different methods of PDLC preparation were invented including microencapsulation and several kinds of phase separation. The methods of preparation of PDLC with wanted morphology which affects their properties were developed. Most of electrooptical and thermooptical effects observed in thin layers of different liquid crystal phases were reproduced, moreover unique ones were found, mainly the effect of electrically driven transmission in nematic liquid crystals. PDLC composites have been successfully applied for preparation of thermosensitive foils, intimacy glasses, and electrically driven optical elements.

Nevertheless, studies on those materials are still conducted showing new properties and physical behavior as well as new possibilities of their application. For this reason also nowadays PDLC are of interest as prospective optical materials. Over 200 papers regarding this subject were published in the last four years. In this paper, selected results of those studies are presented and discussed. Because of this selection the paper cannot be treated as a monographic one.

The essential part of the paper was divided into two main paragraphs, however it is easy to notice that the material properties of matrix polymers, liquid crystals and dopants as well as physical properties and effects are highly interconnected. For the reason mentioned above, this classification is more or less arbitrary, nevertheless it reflects the general trends in the subject. The comparison of the number of papers dealing with the main subjects of PDLC research during the last ten years is given in Fig. 1.

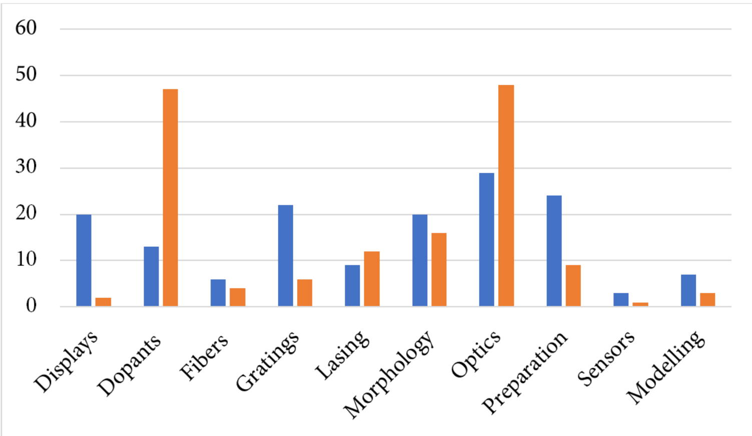

Fig. 1. The comparison of the main subjects of PDLC studies according works published in 2004-2007 (left bar) and 2014-2017 (right bar)

2. Materials

In the recent years, new materials for PDLC preparation were still searched and despite new mesogenic materials also several new polymers were adopted for this purpose. Such studies led not only to extension of a group of suitable materials used as PDLC polymer matrices but also to improvement in composite performance as it is shown by the examples given below.

Marin, Ailincanai, and Paslaru have obtained monodisperse PDLC composites using poly(vinyl boric acid) as the matrix [5]. They confirmed that the distribution of the size of liquid crystal droplets critically affects light scattering in the effect of electrically driven transmission and also have large influence on the optical contrast ratio in other effects. Moreover, the description of monodisperse system is easier what is important for theoretical studies and modelling. For this reason, the preparation of monodispersed liquid crystal droplets is important both from basic and application point of view.

Sotomayor and coworkers [6, 7] introduced copolymer of pentaerythritoltetra-methacrylate and monomethacrylate oligomer poly(propyleneglycol) methacrylate as the matrix material and they observed an enhance of permanent memory effect in PDLC up to 98%. Memory effects in liquid crystals are of interest due to information regarding liquid crystal alignment in different geometries and also possible applications, e.g. in erasable memory devices.

Resetic and coworkers [8] studied liquid-crystalline elastomers dispersed in other elastomeric matrix PDLC preparation. This approach broadened the possible applications of liquid-crystalline elastomers and maybe also preparation of PDLC on elastic substrates, i.e. elastic transducers which are of great interest in processing of light beam [9].

Chinese group [10] applied thiol-ene click reaction to get PDLC with driving voltage lower than usually observed. Typical PDLC composites exhibit quite high driving voltage in comparison with LCD planar geometry, namely from 10 to even 100 Volts. The specific value depends on the composite components, especially on anchoring forces of liquid crystal on the surface of surrounding polymer cave and on PDLC morphology. For this reason, attempts to reduce driving voltage are still important to get systems compatible with LCD transducers.

The application of polyimides for liquid crystal aligning is well known. For this reason, the application of such a polymer as the PDLC matrix seems very interesting. Wang and coworkers [11] showed the application of polyimide to PDLC preparation and they discussed the effect of morphology on electrooptic behaviour of PDLC obtained by thermally-induced phase separation.

3. Doping and its effects

Classic two-component PDLC numerous studies were conducted in which liquid crystalline materials or polymers were modified by dopants of different kind. For instance, liquid crystals are doped by organic dyes to enhance optical contrast ratio in the well-known effect of electrically induced light transmission or to improve holographic features or to obtain lasing effects. Inorganic dopants, including nano-tubes, graphene oxide and nanocrystallites, are used to reduce switching voltages, to modify anchoring conditions and PDLC morphology, or even to trigger off new optic and electrooptic effects. Several examples of such studies are given below.

Sharma and Kumar [12, 13] studied the effect of dichroic dye and carbon nanotubes on the light absorption coefficient as well as on electro-optic performance of PDLC. Dichroic dyes are used as dopants, the spatial orientation of which can be switched via liquid crystal re-alignment caused by the ambient electric field in so called guest-host effect. This effect was earlier adopted for colour LCDs but in PDLC case it can improve the optical contrast ratio of the composite layer, especially in the absorption band of dichroic dye. In this way, the optical contrast ratio in electrically induced transmission effect could be enhanced.

The similar problem was studied by the Korean group [14]. On the other hand carbon multiwall nanotubes as well as dichroic dye can be used for the control of the space orientation of mesogen molecules, dynamics of liquid crystal in droplets, its birefringence and also the droplet size. It was shown that the presence of both dopants decreased response time and increased optical contrast ratio.

Doping with dyes is also well known method used to enhance different optical properties of liquid crystals. Dopants of that kind were used to record holographic gratings in PDLC [15]. Several new PDLC systems including dyes were studied to improve holographic performance. This subject is still present due to looking for prospective materials.

Another effect which can be observed in dye-doped PDLCs is laser generation. Such effects are intensively studied in all systems containing liquid crystals. For instance, Wood, Elston, and Morris observed wavelength-tuneable laser emission in quite complex system including dye-doped achiral nematic crystal embedded into a chiral polymer matrix. [16].

The Chinese group [17] showed the effect of alignment layer deposited on the cell substrate on the behaviour of a PDLC random laser.

Light-by-light processing is one of the important tasks of modern photonics. The example of this effect in PDLC system was shown by Marinova and coworkers [18] who adopted graphene oxide for the reduction of PDLC driving voltage. But after preparation of the hybrid structure, namely PDLC-photorefractive Bi_12SiO_{20}, it worked as optically controlled amplitude modulator. Similar effect was obtained by T.J. Bunning and coworkers using polymerizable liquid-crystalline monomer as matrix precursor and photosensitive low-molecular liquid crystal as dispersed phase [19].

It is worth to underline that dopants insoluble in polymer and liquid crystal are applied in form of nanoobjects. Despite the examples given above such the approach was described by Chinese researchers [20] who doped polymer matrix with graphite nanoparticles dispersed in undec-10-enic acid. Such treatment significantly increased conductivity of PDLC composite reducing driving voltages.

Materials with nonlinear optical properties are very important for modern photonics. Contrary to well-known solid ones, liquid crystalline materials have significant advantage, because their nonlinearities can be driven by ambient electric field. Several years ago this subject was studied by the Polish group showing the enhancement of Kerr coefficient due to the presence of incorganic optically nonlinear nanocrystallites [21] as well as SHG generation by such materials [22]. In this way, switchable nonlinear features were joined with PDLC advantages as elasticity and possibility to deposited on substrates with complex shape at the expense of lower intensity. The studies on that problem are still of interest [23], but due to complexity of the system they should be conducted further to get full explanation of the processes.

Most of works on PDLC optical properties were devoted to visual range, however their behaviour in IR and other ranges is also of interest because our knowledge in this field is still insufficient. Recently, the Polish group has published the paper discussing the effect of PDLC morphology on its optical contrast in the near IR range [24]. It was confirmed that the liquid crystal droplet size should be larger in this case to get high intensity of IR scattering by the composite layer.

In the end, it is worth to mention that several works dealt with theoretical description and modelling of PDLC composites, especially regarding correlation between composite morphology and its optical properties. Chinese scientists modelled the behaviour of silver nanoparticles on the polymer-liquid crystal interface in holographic PDLC [25]. Loiko and coworkers [26] performed calculations for PDLCs with homogeneous and inhomogeneous interphase surface anchoring on the droplet surface. As the result, they got a tool for multicriterial optimization of the optical response of PDLC taking into account its thickness, optical properties of the polymer matrix, as well as size, polydispersity, concentration, and anisometry of liquid crystal droplets. In the next work [27], they introduced opto-mechanical model describing the coherent transmittance and the degree of polarization of forward-transmitted light by PDLC containing elongated droplets of liquid crystal.

4. Final remarks

PDLC composites are still interesting materials from scientific point of view due to unique properties of 3D alignment of liquid crystal in microvolumes and quite complex interaction between matrix polymer, liquid crystal and dopants of different kind. There are also the possibilities to increase the field of their application.

During last ten years the main directions of PDLCs studies were changed [28]. The number of works devoted to application of those composites for information displays, optic fibers and sensors significantly decreased. Also less number of works was devoted to the PDLCs morphology and switchable gratings. On the other hand, optical effects, especially connected with the presence of dopants, became the most important subject of the studies.

It seems now that doping of PDLC composites is the best way to enhance their optical properties and consequently the application possibilities.

New possible applications of those materials are connected with optical elements and processing of light beam.

The presented work has been supported by the Ministry of Science and Higher Education within Statutory Activity of the Military University of Technology.

Received February 20, 2019. Revised March 12, 2019.

Stanisław Józef Kłosowicz https://orcid.org/0000-0002-2256-8428

REFERENCES

[1] Doane J.W., [in:] *Liquid Crystals: Applications an Uses*, ed. Bahadur B., World Scientific, Singapore, London, New York, 1990, vol. 1, chapter 14.

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

[3] Bouteiller L., LeBarny P., *Polymer-Dispersed Liquid crystals: preparation, operation and application*, Liq. Cryst., 21, 2, 1996, 157-174.

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

[5] Marin L., Ailincai D., Paslaru E., *Monodisperse PDLC composites generated by use of polyvinyl boric acid as matrix*, RSC Adv., 4, 72, 2014, 38297-38404, DOI:10.1039/C4RA06426G.

[6] Mouquinho A., Luis N., Sotomayor J., *New polymer to enhance the permanent memory effect of polymer-dispersed liquid crystals films*, J. Appl. Polym., 23, 133, 2016, DOI: 10.1002/app. 43482.

[7] Santos R.,Silva M.C., Mouquinho A., Sotomayor J., *Full permanent memory effects in PDLC films*, Mol. Cryst. Liq. Cryst., 611, 1, 2015, 123-131, DOI: 10.1080/15421406.2015.1030199.

[8] Resetic A., Milavec J., Zupancic B., Domenici V., Zalar B., *Polymer-liquid crystal elastomers*, Nature Comm., 2016, 7 art. no 13140, DOI: 10.1038/ncomms13140.

[9] Papers published in Material Matters, 12, 3, 2017.

[10] Shi Z.Q., Shao L.S., Zhang Y.L., Guan Y., Wang F., Deng F.F., Liy Y., Wang Y.H., *Fabrication of polymer-dispersed liquid crystals with low driving voltage based on the thiol-ene click reaction*, Polym. Int., 66, 7, 2017, 1094-1098, DOI:10.1002/pi.5365.

[11] Wang Dong, Zhang Li, Xing Yan, Gao Hong, Wang Kewen, Yang Zhou, Hai, Mingtan, Cao, Hui, He Wanli, Yang Huai, *Study on the electro-optical properties of polyimide-based polymer-dispersed liquid crystal films*, Liq. Cryst., 42, 12, 2015, pp. 1689-1697.

[12] Sharma V., Kumar P., *Studies of absorption coefficient cum electro-optic performance of polymer dispersed liquid crystal doped with carbon nanotubes and dichroic dye*, Physica B, 524, 2017, 118-122, DOI: 10.1016/j.physb.2017.08.056.

[13] Nam-Seok Oh, Yun-Ho Shin, Ho-Yong Kang, Soon-Bum Kwon, *High performance dye-doped emulsion type PDLC for transmittance variable devices*, Mol. Cryst. Liq. Cryst., 644, 1, 2017, 137-144, DOI: 10.1080/15421406.2016.1277471.

[14] Kumar P., Sharma V., Jaggi C., Malik P., Kumar Raina K., *Orientational control of liquid crystal molecules via carbon nanotubes and dichroic dye in polymer dispersed liquid crystal*, Liq. Cryst., 44, 5, 2017, 843-853, DOI: 10.1080/02678292.2016.1247476.

[15] Villa-Manriquez F.J., Ortiz-Gutierrez M., Perez-Cortes M., Ibarra-Torres J.C., Olivares-Perez A., *Holographic gratings recorded in PDLC mixed with crystal violet dye*, Optik, 144, 219-223, DOI: 10.1016/ijleo.2017.06.089.

[16] Wood S., Elston S.J., Morris S.M., *Laser emission from a dye-doped achiral nematic liquid crystal dispersed into a chiral polymer scaffold*, Mol. Cryst. Liq. Cryst., 632, 1, 2016, 89-96, DOI: 10.1080/15421406.2016.1185587.

[17] Lihua Ye, Congsheng Lv, Fangije Li, Yan Wang, Bo liu, Yiping Cui, *Effect of alignment layer on polymer-dispersed liquid crystal random laser*, J. Mod. Opt., 64, 14, 2017, 1429-1434, DOI: 10.1080/09500340.2017.1291864.

[18] Marinova V., Tong Zhon Fang, Petrov S., Karashanova D., Yi Hsin Lin, Shiuan Huei Lin, Ken Yuh Tsu, *Graphene oxide doped PDLC films for all optically controlled light valve structures*, Proc. SPIE, 9970, 2016, DOI: 10.1117/12.2238508.

[19] De Sio L., Ouskova E., Lloyd P., Vergara L., Tabiriyan N., Bunning T.J., *Light-addressable liquid crystal polymer dispersed liquid crystal*, Opt. Mat. Expr., 7, 5, 2017, pp. 1581-1588.

[20] Jianhua Wang, Shuhui Shi, Xian Han, Shiqi Zhou, Baoyan Zhang, *The effect of nanographites dispersed in Undec-10-enic acid on optical property and morphology of PDLC films*, Colloid. Polym Sci., 290, 16, 2012, 1659-1664, DOI: 10.1007/s00396-012-2698-7.

[21] Węgłowski R., Kłosowicz S.J., Majchrowski A., Tkaczyk S., Reshak A.H., Pisarek J., Kityk I.V., *Enhancement of the Kerr response in polymer-dispersed liquid crystal complexes due to incorporation of BiB_3O_6 nanocrystallites*, Materials Letters, 64, 2010, pp. 1176-1178.

[22] Zegadlo K.B., El Ouazzani H., Cieślik I., Węgłowski R., Żmija J., Klosowicz S., Majchrowski A., Myśliwiec J., Sahraoui B., Karpierz M.A., *Nonlinear optical properties of polymer dispersed liquid crystals doped with $La_2CaB_{10}0_{19}$*, Optical Materials, 34, 10, 2012, pp. 1704-1707.

[23] Chia-Ming Chang, Yi-Hsin Lin, Reshetnyak V., Chui Ho Park, Manda R., Seung Hee Lee, *Origins of Kerr phase and orientational phase in polymer-dispersed liquid crystals*, Opt. Express, 25, 17, 2017, 19807-19821, DOI: 10.1364/OE.25.019807.

[24] Sułkowski K., Węgłowski R., Kłosowicz S.J., *The comparison of electrooptical properties of PDLC liquid-crystalline composites in visual and near-IR ranges*, Biuletyn WAT, 66, 3, 2017, pp. 15-26, DOI: 10.5604/01.3001.0010.5387.

[25] Kun Gui, Jihong Zheng, Kangi Wang, Daoping Li, Songlin Zhuang, *FDTD modelling of silver nanoparticles embedded in phase separation interface of H-PDLC*, Article ID 298913, Journal of Nanomaterials, vol. 2015, DOI: 10.1155/2015/298913.

[26] Loiko V.A., Zyryanov V.Ya, Konkolovich A.V., Miskevich A.A., *Light transmission of polymer-dispersed liquid crystal layer composed of droplets with inhomogeneous surface anchoring*, Optics and Spectroscopy, 120, 1, 2016, pp. 143-152.

[27] Loiko V.A., Konkolovich A.V., Zyryanov V.Ya., Miskevich A.A., *Polarization of light by a polymer film containing elongated drops of liquid crystal with inhomogeneous interfacial anchoring*, Optics and Spectroscopy, 120, 1, 2016, pp. 143-152.

[28] Węgłowski R., Aleksander M., Kłosowicz S.J., *Development trends of polymer-dispersed liquid crystals*, Biuletyn WAT, 58, 1, 2009, pp. 87-97.

S. J. KŁOSOWICZ

Bieżące kierunki badań nad kompozytami polimer – ciekły kryształ

Streszczenie. W artykule przedstawiono przegląd wyników badań w zakresie inżynierii materiałowej i fizyki kompozytów ciekłokrystalicznych typu PDLC, otrzymanych w ciągu ostatnich czterech lat, oraz główne obszary zainteresowania w tym temacie. Obejmuje to zastosowanie nowych polimerów i materiałów ciekłokrystalicznych wykorzystanych do otrzymywania kompozytów, modyfikację właściwości kompozytów za pomocą różnych domieszek nieorganicznych i organicznych, jak również nowe właściwości optyczne PDLC. Wskazano na zmiany kierunków zainteresowań badawczych w ostatnich latach.

Słowa kluczowe: inżynieria materiałowa, kompozyty, ciekłe kryształy rozproszone w polimerach, optyka, elektrooptyka.

DOI: 10.5604/01.3001.0013.3000