# The method to suppress off-axis haze of PDLC

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#### Abstract

Conventional polymer dispersed liquid crystals (PDLCs) suffer from discrimination of on-state transmittance for oblique incidence light (off-axis haze effect). The point is that refractive index of polymer component is usually adjusted to ordinary refractive index of liquid crystal (LC). So in the applied electric field there is transparent state with matching of LC and polymer refractive indices for the normal light incidence. At the same time, balance of refractive indices is broken and on-state transmittance is smaller for oblique light incidence. To diminish of-axis haze (to broaden viewing angle characteristic of PDLC), refractive index of polymer should be slightly higher than ordinary refractive index of LC. We propose to satisfy this condition by doping PDLC with high refractive index inorganic nanoparticles. In such a way one can continuously vary refractive index of polymer and so optimize system for minimal off-axis haze.

Keywords: PDLC, nanoparticles, transmittance, off-axis haze.

#### Introduction

Polymer dispersed liquid crystals (PDLC) [1,2] belong to scattering LC composites, which present an alternative for oriented LC layers in production of LCD, optical switches and shutters. In contrast to traditional devices based on oriented LC layers, PDLC don't need polarizers, alignment layers and high uniformity of cell gap. These features coupled with high brightness of composite layers make PDLC rather attractive for applications.

Typical PDLC consists of large amount of spherical LC droplets chaotically distributed in polymer (P) matrix. The refractive index of polymer,  $n_p$ , is usually adjusted closely to ordinary refractive index of LC  $n_{LC}^o$ . In the absence of driving electrical field the composite strongly scatters light. The main scattering reason is mismatching of refractive indexes of the polymer and chaotically oriented LC droplets [3]. The droplets orient in the external electric field so that their refractive index approaches  $n_p$ . For normal light incidence this matching of indices yields to the high on-state transmittance of PDLC layers. At the same time, for oblique light, the balance of refractive indices is broken so that scattering becomes stronger, while on-state transmittance becomes smaller. Such angular worsening of the on-state transmittance is known as off-axis haze of PDLC.

Per last years the problem of the off-axis haze suppression in PDLC has been intensively studied [4-7]. The simplest way consists in setting of polarizer in front of PDLC film with polarization direction perpendicular to the light incidence plane [4]. Indeed, light of this polarization (s-wave) is not sensitive to changes of light incidence angle. However, polarizer decreases brightness of PDLC film at least in twice that makes this method not very attractive. The other solution [5] suggests to replace isotropic polymer by anisotropic one with ordinary and extraordinary refractive indices approximately equal to  $n_{LC}^{o}$  and  $n_{LC}^{e}$ , respectively. The serious problem of this method is selection of anisotropic medium and its proper alignment in PDLC.

The most common and realistic decision consists in selection of isotropic polymer with the refractive index satisfying inequality

$$n_{LC}^{o} < n_{p} < n_{LC}^{e}, \tag{1}$$

where  $n_{LC}^{e}$  is the extraordinary refractive index of LC [6,7]. When (1) is true, then peak of maximal transmittance for PDLC is shifted away from normal incidence so that range of viewing angles with sufficiently high onstate transmittance becomes broader.

In this paper we propose the modified version of the last approach. Instead of choosing polymer with proper optical parameters we suggest to modify optical properties of polymer, which is already optimized for the formation of PDLC with the selected LC. The refractive index of polymer can be continuously varied by doping it with nanoparticles (NP) having refractive index substantially higher than that of polymer. This method is based on the earlier ascertained fact that, in the course of phase separation of LC-P-NP mixtures, the nanoparticles are mainly absorbed by polymer changing its optical properties. The effectiveness of this method is experimentally demonstrated.

#### **Experimental part**

We used traditional materials: nematic liquid crystal mixture E7 from Merck and optical adhesive NOA65 provided by Norland Inc. (USA) for making PDLC [8]. Nematic mixture E7 consists of three cyanobiphenyls (5CB-51%, 7CB-25%, 80CB-16%) and n-pentylcyanoterphenyl (5 CT-8%). This mixture is characterized by relatively broad mesomorphic region (from  $-10^{\circ}$ C to 58°C) and optical anisotropy (refractive indices are  $n_{LC}^{\circ}=1.5216$ ,  $n_{LC}^{e}=1.7462$ ) [8].

Norland optical adhesive NOA65 is a mixture of three monomer constituents: trimethylolpropane diallyl ether, trimethylolpropane tristhiol, isophorone diisocianate ester and photoinitiator. In the initial state it is transparent (refractive index  $n_p$ =1.524), liquid (density is  $\rho = 1.12$  g/cm<sup>3</sup>) and viscous (1200 cps at 20°C) mixture. NOA 65 becomes hard under the action of UV light due to accurately balanced chemical reaction [9].

As filler for PDLC we used several types of inorganic NP with different refractive indices of their materials. They are SiO<sub>2</sub> NPs (size 10-20 nm, refractive index  $n_{SiO_2}$  =1.46) and Sb<sub>2</sub>O<sub>5</sub> NPs (size 7-11 nm,

 $n_{Sb_2O_3}$  =1.7). NP of silica and antimony pentoxide were provided by Nissan Chem. Inc. (USA) in the form of dispersions in alcohol medium.

We mixed components thoroughly for the preparation of composites. The range of filler's concentrations in the mixture was varied from 0 to3 vol.%. In all samples the volume concentration of LC was 63 %. Such amount of LC is optimal for PDLC morphology [3, 10]. The alcohol presented in NP colloid was removed by intensive stirring. The complete removing of alcohol was achieved by applying a vacuum to the suspension at  $10^{-2}$  Torr over 0.5 h.

To obtain desirable PDLC films we placed the drop of mixture between two glass slides having transparent ITO electrodes in the inner side. The cell gap was maintained by 20  $\mu$ m spacers. Then the cells were irradiated with the full spectrum of a high pressure mercury lamp (100 mW/cm<sup>2</sup>, 20 min), in order to provide photopolymerization and corresponding phase separation of components.

We used typical setup, which test the optical transmittance of a laser beam through the tested sample [11]. The sample is powered by a sine-like voltage signal 0-200 V (f=2 kHz) synthesized by computer and, subsequently, amplified. Using this set up one can determine the sample transmittance

 $T = \frac{I_{out}}{I_{in}}$  ( $I_{in}$  and  $I_{out}$  are the intensities of the probe beam before and after

passing through the sample) as a function of the applied voltage U.

Angular dependences of the transmittance at the voltage corresponding to saturation of T(U) curve were measured by means of sample rotation on 0, 15, 30, 45 50, 60, and 70 degrees.

#### **Results and discussion**

The T(U) curves for pure PDLC and PDLC doped with 1 vol.% of inorganic nanoparticles of Sb<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub> (Sb<sub>2</sub>O<sub>5</sub>-PDLC and SiO<sub>2</sub>-PDLC, respectively) are presented in Fig. 1. Qualitatively, all dependences are rather similar: *T* rises with the increase of driving voltage *U* until reaching saturation level  $T_s$ . At the same time, saturation transmittances are different and reached at different values of applied voltage. In the following measurements of angular characteristics the applied voltage corresponded to saturation state of all samples.

Fig. 2 shows dependences of  $T_s$  vs. incidence angle  $\Theta$  for pure PDLC and PDLC doped with different types of NPs. The light is polarized in the incidence plane so that it is maximally sensitive to the changes in the incidence angle. One can see that in case of pure PDLC and SiO<sub>2</sub>-PDLC samples  $T_s$  monotonically decreases. In contrast, for Sb<sub>2</sub>O<sub>5</sub>-PDLC  $T_s$  changes slowly and non-monotonically going through maximum. In the range of 0°-50° the transmittance  $T_s$  changes inessentially, while for the higher angles it does not decrease abruptly as in the case of other samples (Fig. 2). In other words,

 $T_s(\Theta)$  curve considerably flattens that is the evidence of the substantial suppression of the off-axis haze.



Fig. 1. T (U) dependences for pure PDLC and PDLC doped with NPs. 1 -  $\varphi_{LC}$  = 63 vol.%,  $\varphi_{NP}$  = 0 vol.%, polymer - the rest; 2 -  $\varphi_{LC}$  = 63 vol.%,  $\varphi_{NP}$  = 1 vol.% (SiO2 NP), polymer - the rest; 3 -  $\varphi_{LC}$  =63 vol.%,  $\varphi_{NP}$  =1 vol.% (Sb2O5 NP), polymer - the rest.



Fig. 2. The saturation transmittance  $T_{\rm S}$  for pure PDLC and PDLC doped with NPs as a function of light incidence  $\Theta$ . The light is p-polarized. 1 - pure PDLC ( $\varphi_{NP} = 0$ ); 2 -  $\varphi_{SiO_2} = 1$  vol.%; 3 -  $\varphi_{Sb_2O_3} = 1$  vol.%. For all cases  $\varphi_{LC} = 63$  vol.%, the rest is polymer content.

According to Fig. 3 the shape of  $T_s(\Theta)$  curve for Sb<sub>2</sub>O<sub>5</sub>-PDLC composite is rather sensitive to concentration of NP. The increase of NP concentration leads to better flattening of  $T_s(\Theta)$  curve, but, simultaneously, to lowering of sample transmittance for small angles of light incidence. Thus, concentration of NP should be well optimized to obtain samples with acceptable electrooptic contrast and angular characteristic.



# Fig. 3. The saturation transmittance $T_{S}$ vs. incidence angle $\Theta$ curves for PDLC doped with different amount of Sb2O5: 1 - $\varphi_{NP}$ = 1 vol.%, 2 - $\varphi_{NP}$ = 3 vol.%. For all cases $\varphi_{LC}$ = 63 vol.%, the rest is polymer content.

To explain the observed suppression of the off-axis haze let us remind results recently obtained [10, 12].

1. The addition of small amount of NP to LC-P mixtures (less than 5 vol.%) before polymerization does not change PDLC morphology of these samples.

2. In the course of the photoinduced phase separation the nanoparticles are mainly absorbed by the formed polymer matrix. In contrast to the pure polymer *P* we shell mark NP modified polymer as  $\tilde{p}$ .

3. The small amount of NP (less than 5 vol.%) changes refractive index of polymer rather than its optical uniformity.

The above means that NP vary refractive properties of polymer changing the refractive index balance of LC and modified polymer  $\tilde{P}$ . The changes in refraction can be qualitatively analyzed using the refractive indices diagram (Fig. 4). The refractive index of SiO<sub>2</sub> NP is close to polymer refractive index. So particles of this sort practically do not influence refractive index of polymer. This explains why  $T_s(\Theta)$  curves for PDLC and SiO<sub>2</sub>-PDLC are of similar shape and close each to other. For both these systems, at  $\Theta$ =0,  $n_P \cong n_{LC} = n_{LC}^{\circ}$ so that light transmittance is high. With  $\Theta$  increase,  $n_{LC}$  grows approaching  $n_{LC}^{\circ}$  at grazing incidence. This causes growing of the refractive index mismatch,  $n_{LC} - n_P$ , and so light scattering in PDLC. Besides, light scattering grows because of lengthening of light pass in the composite layer. Consequently, light transmittance should demonstrate fast monotonic decrease that fully corresponds to experimental observation (curves 1, 2 in Fig 2).

Refractive index of antimony pentoxide is considerably higher than  $n_p$  (close to  $n_{LC}^{e}$ ). So, doping of PDLC with  $\text{Sb}_2\text{O}_5$  NP leads to an increase in the refractive index of the polymer phase  $\tilde{p}$  so as  $n_{LC}^{e} < n_{\tilde{p}} < n_{LC}^{e}$ . Since  $n_{\tilde{p}}$  does not match  $n_{LC}^{e}$ ,  $T_s$  at the normal incidence is not so high as in the case of PDLC and SiO<sub>2</sub>-PDLC composites.



Fig.4. The refractive indices diagram for the nanoparticles, polymer and LC.

The mismatch of  $n_p$  and  $n_{LC}$  changes non-monotonically with a grow of  $\Theta$  it decreases, vanishes at some light incidence angle  $\Theta_c \neq 0$  and finally grows. The scattering tendency determined by the non-monotonic refractive index mismatch superposes with the scattering trend connected with the light pass grow with the incidence angle. In result,  $T_s(\Theta)$  should be non-monotonic: maximal transmittance should be shifted away from the normal incidence to the angle  $\Theta_c \neq 0$ . Simultaneously, range of angles corresponding to relatively high transmittance should become broader. This explains well result for Sb<sub>2</sub>O<sub>5</sub>-PDLC composite (curve 3 in Fig. 2).

# Conclusions

In summary, modification of polymer's refractive properties by inorganic nanoparticles may be applied to suppress off-axis haze of PDLC. Using this approach it is not needed to find polymer with appropriated refractive properties. Instead, refractive index of any polymer can be modified by insertion of NP with high refractive index in PDLC to meet condition (1) required to suppress off-axis haze.

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# References

- 1. Liquid Crystals Applications and Uses / Edited by B. Bahadur. -Singapore: World Scientific, 1990. – Vol.1, 604 pp.
- 2. Chigrinov V.G. Liquid crystal devices: Physics and Applications. Boston-London: Artech-House, 1999.- 357 pp.
- Bouteiller L., Le Barny P. Polymer-dispersed liquid crystals: Preparation, operation and application // Liq. Cryst.-1996.- Vol. 21.-Đ.157-174.

- West J. L., Fredley D. S., Carrell J. C. Haze-free polymer dispersed liquid crystals utilizing linear polarizers // Appl. Phys. Lett. – 1992. – Vol. 61, No.17. – P. 2004-2005.
- Doane J. W., West J. L., Tamura-Lis W., and Whitehead J. B. Polymer dispersed liquid crystals for haze-free, wide-angle view light shutters // Pacific Polymer Preprints I. – 1989. – P. 245-246.
- Wu B.-G., West J. L., and Doane J. W. Angular discrimination of light transmission through polymer-dispersed liquid-crystal films // J. Appl. Phys. – 1987.- Vol. 62, No. 9. – P. 3925-3931.
- 7. Drzaic P., Konynenburg P. V., US Patent 5,156,452 (1992).
- Bhargava R., Wang S.-Q., and Koenig J. L. FTIR Imaging Studies of a New Two-Step Process To Produce Polymer Dispersed Liquid Crystals // Macromolecules. – 1999.-Vol. 32.-P. 2748-2760.
- 9. Norland Products Inc., P.O. Box 145, North Brunswick, NJ 08902.
- Dolgov L. O., Yaroshchuk, O. V. Electrooptics of the Suspensions of Monodispersed Non-Organic Particles in Liquid Crystals // Mol. Cryst. Liq. Cryst.-2004.-Vol. 409.- P. 77-89.
- Zakrevska S., Zakrevskyy Yu., Nych A., Yaroshchuk O., Maschke U. Electro-optics of LC-aerosil-photopolymer composites // Mol.Cryst.Liq.Cryst. -2002.- Vol. 375. – P. 467-480.
- 12. Yaroshchuk O.V., Dolgov L. O., Kiselev O. D. Electro-optics and structural peculiarities of liquid crystal-nanoparticles-polymer composites // Accepted to Phys. Rev. E.