PACS numbers: 61.30.Pq, 68.37.Hk, 78.20.Ci, 78.20.Jq, 81.07.-b, 81.16.-c, 82.70.Dd

Nanoparticles-Doped PDLC: Electrooptics and Structural Peculiarities

O. Yaroshchuk, L. Dolgov, and A. D. Kiselev^{*}

Institute of Physics, N.A.S.U., Prospekt Nauky, 46, 03028 Kyyiv, Ukraine *Chernihiv State Technological University, Shevchenko Str., 95, 14027 Chernihiv, Ukraine

Structural peculiarities and electrooptic performance of polymer dispersed liquid crystals (PDLC) doped with a small amount of inorganic colloid nanoparticles (NPs) are considered. As shown, during the phase separation, the NPs are mainly involved by polymer and serve as nuclei of polymerization. The absorbed NPs change the refractive index of polymer thus affecting the refractive-index mismatch between the polymer and LC. This modifies light-scattering characteristics of PDLC. By optimization, NPs-doped PDLC composites with the improved viewing-angle characteristics and the electrooptic contrast typical for conventional PDLC can be obtained.

Розглянуто структурні особливості й електрооптику капсельованих рідких кристалів (КРК) з малим вмістом неорганічних кольоїдних наночастинок. Показано, що під час фазової сепарації наночастинки в основному захоплюються полімером і є зародками полімеризації. Поглинуті наночастинки змінюють показник заломлення полімеру й у такий спосіб впливають на різницю показників заломлення полімеру й рідкого кристалу. Це змінює характеристики світлорозсіяння КРК. Завдяки оптимізації, порівнюючи із традиційними КРК, можна отримати наповнені наночастинками КРК з покращеною характеристикою огляду й типовим електрооптичним контрастом.

Рассмотрены структурные особенности и электрооптика капсулированных жидких кристаллов (КЖК) с малым содержанием неорганических коллоидных наночастиц. Показано, что во время фазовой сепарации наночастицы в основном захватываются полимером и служат зародышами полимеризации. Поглощенные наночастицы изменяют показатель преломления полимера и так влияют на разность показателей преломления полимера и жидкого кристалла. Это изменяет характеристики светорассеяния КЖК. Благодаря оптимизации, по сравнению с традиционными КЖК, могут

489

быть получены наполненные наночастицами КЖК с улучшенной характеристикой обзора и типичным электрооптическим контрастом.

Key words: polymer dispersed liquid crystal, doping, structure, electrooptics.

(Received October 13, 2004)

1. INTRODUCTION

The heterogeneous liquid crystal (LC) systems form a separate class of composite materials, which is attractive for both science and technological applications. Some of these materials demonstrate strong light scattering that can be effectively controlled by applying external fields. The well-known examples of such composites are polymer dispersed liquid crystals (PDLC) [1, 2] and filled LC [3-5]. The reasons for light scattering in these systems differ. The PDLC composites scatter light because of the refractive index mismatch between LC and P, two adjacent droplets and within the droplets of LC [2]. A strong decrease of the light scattering in the field on state is caused by the unidirectional alignment of LC within the drops and matching the refractive indices of LC and polymer. On the other hand, it is commonly accepted that intense light scattering in filled LC is caused by the orientational defects generated by the particles of filler in LC media. In the field on transparent state, LC alignment leads to removal of these defects. Both PDLC and filled LC have advantages and disadvantages well discussed in the corresponding literature.

In a given work, we consider some hybrid of these systems—threecomponent composite 'LC–Nanoparticles (NPs)–Polymer (P)'. Our aim is to show that this composite has important advantages and can be regarded as a robust material for LC applications. We shall also propose the model of phase separation in the LC–P–NPs system that provides a good explanation of the electrooptic data.

2. MATERIALS AND METHODS

As NP filler, we used several types of colloidal monodispersed NPs:

1) Antimony pentoxide (Sb_2O_5) NPs with sizes of 7–11 nm;

2) Silica (SiO₂) NPs with the sizes of 10-20 nm.

The Sb_2O_5 and SiO_2 NPs were obtained from Nissan Chemicals Industries Ltd. (USA) as colloidal dispersions in methanol with a particles' content of 35 wt.% and 30 wt.%, respectively. All these objects were chosen because of substantial difference in their refractive indices¹.

490

 $^{^{1}}$ Initially, we also used colloidal TiO₂ NPs (from ANP Ltd., Korea). These particles, however, react with components of pre-polymer composition giving rise to a yellowing effect. Since this effect causes light adsorption, we abandoned the further use of these particles.

As a liquid crystal, nematic mixture E7 from Merck was used. As a photopolymerizing material, we employed UV curable adhesive No. 65 from Norland Inc. (USA). Both E7 and Norland's photopolymer No. 65 have been widely used before for preparation of LC–Polymer composites [6, 7].

For the composite preparation, we mixed all the components. The intensive mixing caused evaporation of alcohol. The complete removing of alcohol was achieved by applying a vacuum to the suspension at 10^{-2} Torr over 0.5 h.

We operated with volume concentrations of NPs, ϕ_{NP} , and polymer, ϕ_P for the reasons discussed later in the subsequent section. The ϕ_{NP} and ϕ_P concentrations were calculated as

$$\phi_{\rm NP} = \frac{m_{\rm NP} / \rho_{\rm NP}}{m_{\rm NP} / \rho_{\rm NP} + m_{\rm P} / \rho_{\rm P} + m_{\rm LC} / \rho_{\rm LC}} \text{ and } \phi_{\rm P} = \frac{m_{\rm P} / \rho_{\rm P}}{m_{\rm NP} / \rho_{\rm NP} + m_{\rm P} / \rho_{\rm P} + m_{\rm LC} / \rho_{\rm LC}},$$

where $m_{\rm NP}$, $m_{\rm P}$, and $m_{\rm LC}$ are masses, while $\rho_{\rm NP}$, $\rho_{\rm P}$ and $\rho_{\rm LP}$ are densities of corresponding phases. In the present experiments, concentration of NPs was kept relatively low ($\varphi_{\rm NP} = 1-2.5 \text{ vol.}\%$), while polymer concentration was varied within a wide range ($\varphi_P = 5-50 \text{ vol.}\%$) to optimize electrooptic performance of new composites.

The drop of mixture was placed between two glass slides having transparent ITO electrodes in the inner side. Then the cell was pressed and glued with epoxy glue. The 20 μ m spacers set the cell thickness. Finally, the cells were irradiated with a mercury lamp (100 mW/cm², 20 min), to provide photopolymerization and corresponding structuring of polymer phase.

The electrooptic characteristics were measured by the homemade measuring system previously described in Ref. [8]. In this set up, LC cell is powered by a sine like voltage signal 0-200 V synthesized by computer and, subsequently, amplified. The system allowed us to vary intensity (voltage *U*) and frequency *f* of the applied voltage. Optical part of the set up consists of laser ($\lambda = 635$ nm, polarized irradiation) and photodiode detecting light transmitted through the specimen within the cone 2.

Using this set up we can determine the specimen transmittance $T = I_{out}/I_{in}$ (I_{in} and I_{out} are the intensities of the probe beam before and after passing through the specimen) as a function of the applied voltage.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Morphology

It is well known that morphology of LC–P composites strongly depends on the concentration of polymer phase. In case of phase separation of LC–Prepolymer mixture with $\phi_P = 1-10$ vol.%, polymer forms rigid network (polymer network liquid crystal (PNLC) morphology) [9]. At $\phi_P = 30-50 \text{ vol.}\%$, polymer forms porous matrix filled with LC (PDLC morphology)[1, 2].

In the LC-NPs-P mixtures with a small content of polymer, phase separation also leads to the formation of polymer network. This network stabilizes LC-NPs suspension. These stabilized suspensions are robust materials quite attractive for the LC related applications [10].

In the present paper, we are focused on the LC-NPs-P composites with a high content of polymer ($\phi_P = 30-50 \text{ vol.}\%$) capable to form PDLC morphology. The amount of NPs in these composites is low ($\phi_{NP} = 1-2.5 \text{ vol.}\%$) to minimize deformation of PDLC structure formed by P and LC.

Our study of morphology of LC–NPs–P composites is aimed to answer two questions. (1) To what extend a small amount of NPs influences morphology of LC–P composites? (2) How NPs are distributed in LC–NPs–P composites?

To answer the second question, LC–NPs–P specimens were kept in hexane to dissolve and remove LC. The specimens were carefully weighed before and after extraction of LC phase to clear whether NPs are also removed. As we obtained, the specimen lost the weight less then the weight of LC contained in the composite. By observation in polarizing microscope, we also investigated content of the extracted phase. In these experiments, the signs of NPs have not been detected as well. This allows us to conclude that during phase separation NPs are mainly involved with the polymer phase. Moreover, they can serve as the germs of polymerization. To answer the first question, the solid remainder obtained after extraction of LC was studied by means of SEM method. Observing SEM images, one can conclude that small amount of NPs does not distort PDLC morphology of LC–P composites (see Fig. 1).



Fig. 1. SEM image of PDLC ($\varphi_P = 40 \text{ vol.}\%$).

Thus, roughly speaking, by insertion of NPs, LC–P system is transformed to the LC– \tilde{P} system, where \tilde{P} is a particle-modified polymer. The properties of polymer \tilde{P} may substantially differ from the properties of pure polymer depending on particle's material, size and aggregation rate. What is most important for the present research, embedded NPs may modify optical uniformity of polymer \tilde{P} . The calculations show that when the diameter of spherical particles or its aggregates is above 300 nm the polymer loses optical uniformity, *i.e.* polymer becomes opaque. By contrast, for d < 100 nm, even 15 vol.% NPs loading does not affect polymer's uniformity. The latter was checked by preparation of P–NPs composites with a varying content of NPs. It was obtained that both P–SiO₂ NPs and P–Sb₂O₅ NPs probes remain transparent up to the 5 vol.% loading. So, even at $\varphi_{\rm NP} = 5$ vol.%, the aggregation rate of NPs is low.

When the uniformity of polymer is preserved, the imbedded NPs modify refractive index of polymer. In a good approximation, refractive index of modified polymer \tilde{P} linearly depends on NPs concentration:

$$n_{\tilde{p}} = (n_{\rm P} \varphi_{\rm P} + n_{\rm NP} \varphi_{\rm NP}), \qquad (1)$$

where $\varphi_{\rm P}$ and $\varphi_{\rm NP}$ are the volume fractions of polymer and NPs [11]. This method is frequently used to enhance refractive index of polymer, which typically does not exceed 1.7. Inserting NPs with a high $n_{\rm MNP}$ enables us to increase this value by factor two and more [12].

For PDLC specimens, modification of $n_{\rm P}$ may result in the substantial modification of scattering characteristics, mainly because of the refractive index mismatch between LC and polymer. Thus, adding NPs modifies $n_{\tilde{p}}$ and, as a result, scattering properties of PDLC.

Since the refractive index of modified polymer is a linear function of $\varphi_{\rm NP}$, independently on the kind of particles, we operate with the volume concentrations of components. Taking into account that NPs are mainly involved with a polymer phase, serving as building blocks for polymer skeleton, we compare only specimens with equal volume of \tilde{P} and equal volume of LC. As we believe, these specimens will be of very similar morphology.

3.2. Electrooptic Performance

Figure 2 shows T vs. U curves for the LC-P (1) and LC-P-NPs (2, 3) composites of PDLC morphology. For NPs-containing specimens, one can observe some increase of the controlling voltage. It might be caused by the modification of dielectric permittivity of polymer phase that, in turn, may reduce the effective electric field applied to the LC drops. By adding NPs, the initial transmittance trends toward the slight increase, but this dependence is not very clear. At the same time, it is clearly seen that adding NPs may considerably reduce the speci-



Fig. 2. T-U curves for the non-doped and NPs doped PDLC composites. $1 - \phi_P = 40 \text{ vol.}\%$; $2 - \phi_P = 39 \text{ vol.}\%$, $\phi_{NP} = 1 \text{ vol.}\%$ (SiO₂ NPs); $3 - \phi_P = 39 \text{ vol.}\%$, $\phi_{NP} = 1 \text{ vol.}\%$ (SiO₂ NPs); $3 - \phi_P = 39 \text{ vol.}\%$, $\phi_{NP} = 1 \text{ vol.}\%$ (Sb₂O₅ NPs).



Fig. 3. T_s vs. φ_{NP} curves for NPs doped PDLC. $\varphi_P + \varphi_{NP} = 40$ vol.%. 1—SiO₂ NPs; 2—Sb₂O₅ NPs.

men transmittance in the saturation state, T_s . This decrease is stronger for Sb₂O₅ NPs. Figure 3 shows that T_s monotonically decreases with the NPs concentration.

The results for the T_s can be easily explained in terms of the refractive index mismatch. When LC within the drops is aligned along the electric field, the refractive index mismatch between LC and P is a decisive factor of light scattering. For the convenience sake, let us consider the refractive indices diagram of the components of our composites (Fig. 4). First, second, and third columns in this diagram refer to LC, P (\tilde{P}), and NPs. It is seen that the ordinary refractive index of E7 ($n_{\rm LO}^{\circ}=1.52$) is very close to the refractive index of pure polymer



Fig. 4. The refractive indices diagram explaining the role of the refractive index mismatch in the light scattering by LC–NPs–P composites.

 $n_{\rm P} = 1.524$. This explains highly transparent state of LC–P composites in the field on state at the normal viewing. Adding NPs to the polymer phase enhances mismatch between the refractive indices of LC, $n_{\rm LC}^{\circ}$, and the modified polymer, $n_{\tilde{p}}$. As a result, T_s decreases. The more particles are added, the larger is the distance between $n_{\rm LC}^{\circ}$ and $n_{\tilde{p}}$ in the diagram that explains the concentration behaviour presented in Fig. 3.

Figure 5 presents data for the contrast ratio $CR = \frac{T_{sat}}{T_0}$ in the LC–P

and LC-P-NPs series of composites. In these series, the concentration of polymer is varied to determine the proportion of components maximizing *CR*. The LC-P-NPs series contain SiO_2 and Sb_2O_5 NPs, respectively. The volume concentration of NPs in these series is the same.



Fig. 5. *CR* vs. φ_{P} curves for LC–P and LC–NPs–Polymer composites. $1-\varphi_{NP}=0$; $2-\varphi_{NP}=1$ vol.% (SiO₂); $3-\varphi_{NP}=1$ vol.% (Sb₂O₅).

From these data several conclusions can be drawn.

1. The *CR* vs. φ_P curves for all series are non-monotonic and go through the maximum, which is mainly determined by the minimization of T_0 . Poor contrast at low φ_P is explained by the non-developed PDLC structure more similar to PNLC (LC–P specimens) or PNLC filled with small amount of NPs (LC–P–NPs specimens). In turn, abrupt decrease of *CR* at $\varphi_P > 50$ vol.% may be caused by the reduction of size and concentration of LC drops and lowering the refractive index mismatch between LC and P (\tilde{P}), because of enhanced content of LC in polymer and vice versa.

2. The maximal value of CR is somewhat smaller for the NPs containing series. Within the latter series, the maximum for Sb₂O₅ NPs series lies lower than for the SiO₂ series. However, these differences are rather weak, because of low concentration of NPs in the composites.

3. The *CR* vs. φ_P curves for the LC–P–NPs series are shifted to the lower concentrations as compared to the curve for the LC–P–NPs series. This may imply that NPs serve as building blocks for the polymer phase thus increasing the total volume of the modified polymer, \tilde{P} . This is in a good agreement with our previous conclusion about the preferential involvement of NPs with polymer.

Finally, let us consider angular characteristics of new composites. Figure 6 represents T_s as a function of the incidence angle α of the testing laser beam. The light is p polarized. The T_s vs. α curves are presented for the LC-P composite and for the composites with varying content of Sb₂O₅ NPs. As it can be seen for LC-P composite, T_s rather steeply drops with α . This means that specimen becomes hazy and *CR* falls. The off-axis haze in the field on state is an intrinsic problem of PDLC. Similarly to the effects discussed above it is also connected with the refractive index mismatch. As α increases, the refractive index of LC changes from $n_{\rm LC}^{\circ}$ at $\alpha = 0^{\circ}$ to $n_{\rm LC}^{\circ}$ at $\alpha \to 90^{\circ}$ (Fig. 4). This enhances the mismatch between $n_{\rm LC}$ and $n_{\rm P}$, and, as a result, light scattering of PDLC composites. The off-axis haze of PDLC can be reduced by choosing the polymer with the refractive index satisfying the following condition:

$$n_{\rm LC}^{o} < n_{\rm P} << n_{\rm LC}^{e}$$
 (2)

Typically, the difference $n_{\rm P} - n_{\rm LC}^{o}$ does not exceed 0.01 [13].

Figure 6 shows that doping with NPs reduces value of T_s at $\alpha = 0$. The $T_s(\alpha = 0)$ vs. $\varphi_{\rm NP}$ plots were earlier shown in Fig. 3. It is very important that, in parallel with decrease of T_s , NPs-adding flattens angular dependence of T_s . This means that, since NPs are absorbed by polymer, condition (2) is met. It is advantageous to work with NPs having high $n_{\rm NP}$ to minimize particles concentration. This idea may be considered as a novel method to reduce the 'off-axis haze'. According to this method,



Fig. 6. The on-state transmittance T_s of the Sb₂O₅ NPs doped PDLC as a function of angle of the light incidence α . The light is *p*-polarized. $1 - \phi_{NP} = 0$; $2 - \phi_{NP} = 0.6 \text{ vol.}\%$; $3 - \phi_{NP} = 0.9 \text{ vol.}\%$; $4 - \phi_{NP} = 1.2 \text{ vol.}\%$; $\phi_P + \phi_{NP} = 40 \text{ vol.}\%$.

it is not necessary to select polymer with $n_{\rm P}$ satisfying the non-equality (2); by adding NPs, one can adapt the polymer most suitable for the formation of PDLC structures with the given LC.

By optimizing the concentrations, one can select the LC-P-NPs composites, which are most attractive for the electrooptic LC applications. For instance, compared to LC-P specimens, Sb_2O_5 NPs containing composites ($\phi_{NP} = 1 \text{ vol.}\%$) show similar switching contrast (Fig. 5), but improved viewing angle curve (Fig. 6). According to formula (1), adding of 1 vol.% of Sb_2O_5 NPs to LC-P composite increases refractive index of polymer phase only in 0.002. This is, however, enough for the drastic change the electrooptic characteristics.

4. CONCLUSIONS

In summary, NPs-doped PDLC represents a new class of heterogeneous LC media, which is very attractive for applications. Retaining electrooptic contrast typical for PDLC, these composites have improved viewing angle characteristic. It is realized by modifying the polymer refractive index with NPs mainly involved with polymer phase at the phase separation of LC-P-NPs mixtures. We believe that the doping of polymer phase with inorganic NPs may lead to other improvements of PDLC, such as enhancement of thermal stability, reduction of LC content in polymer. In addition, it may also result in interesting effects, such as colouring and photochromism, modification of dielectric and photoconductive properties, *etc.* This altogether creates an interesting field for future studies.

ACKNOWLEDGEMENT

This work was carried out within the framework of the project 'Ordering Regularities and Properties of Nanocomposite Systems' of the N.A.S. of Ukraine.

REFERENCES

498

- 1. Liquid Crystals Applications and Uses (Ed. B. Bahadur) (Singapore: World Scientific: 1990).
- 2. P. S. Drzaic, Series on Liquid Crystals (World Scientific: 1995), vol. 1—Liquid Crystals Dispersions, ch. 3.
- 3. M. Kreuzer, T. Tschudi, and R. Eidenschink, Mol. Cryst. Liq. Cryst. 223: .219 (1992).
- 4. A. Glushchenko, H. Kresse, V. Reshetnyak, Yu. Reznikov, and O. Yaroshchuk, Liq. Cryst., 23, No. 2: 241 (1997).
- 5. M. Boxtel, R. Janssen, D. Broer, H. Wilderbeek, and C. Bastiaansen, *Advanced Materials*, **12**: 753 (2000).
- 6. J.-J. Wu and C.-M. Wang, *Physics Letters*, A232: 149 (1997).
- 7. R. Bhargava, S.-Q. Wang, and J. Koenig, Macromolecules, 32: 2748 (1999).
- 8. O. Kovalchuk, S. Zakrevska, O. Yaroshchuk, and U. Maschke, *Mol. Cryst. Liq. Cryst.*, **368**: 129 (2001).
- 9. Y. Fung, D.-K. Yang, S.Ying, L.-C. Chien, S. Zumer, and J. Doane, *Liquid Crystals* 19: 797 (1995).
- 10. L. Dolgov and O. Yaroshchuk, Colloid and Polymer Sci. (to be published).
- 11. N. Kambe, S. Kumar, S. Chiruvolu, B. Chaloner-Gill, Y. Blum, D. McQueen, and G. Faris, *MRS Proceed.*, **676**: Y8.22 (2001).
- 12. W. Caseri, Macromol.Rapid Commun. 21: 705 (2000).
- 13. P. Drzaik and P. H. van Konynenburg, US Patent 5.156.452 (1992).