LIQUID CRYSTAL MATERIALS ORIENTATION USING NEW APPROACH

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Abstract: It is well known that the liquid crystal (LC) mesophase is actively used in display technique and biomedicine devices. Unfortunately, the switching time of the devices based on the LCs is not fast enough; thus, it is very important to find novel perspective ways to obtain the good switching time of the LC dipoles used in these devices. Initial orientation of the LC molecules influences the dynamic parameters, for example, the switch-on and switch-off characteristics and the diffraction efficiency of the final devices. Among the different methods and approaches to find the optimized orientation of the inertial LC molecules a nanotechnology approach has shown the best results. This approach allows increasing the transparency, to decrease the resistivity and the number of the functional layers in the sandwich LC structures. Thus, it results in a decrease in the applied bias voltage. The effect is based on the fact that the ITO coating can be considered as the conducting layer and as the orienting (alignment) layer simultaneously. In the current paper, we continue our steps in the direction to find the best way of the LC molecules orientation. It is proposed to consider the LC media sensitization process as the method to change the surface relief when this relief is prepared from the polymeric orienting materials doped with the carbon nano-objects. Based on the solid fullerene-doped polyimide thin films and other organics it can be shown that the content of the fullerenes influences the wetting angle significantly. The fullerene concentration is correlated with the different surface relief view applied in the aligning of the LC molecules. The switching of the LC can be improved; furthermore the novel relief depended on the fullerene content can be used for the optical limiting of the laser irradiation.

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Keywords: Liquid crystal orienting layers, surface relief, fullerenes, wetting angle

I. Introduction

It is well known that at present time the extensive development of optoelectronics, laser and display technologies, solar energy and gas storage systems, biomedicine devices, etc. has stimulated detailed investigations aimed at increasing the performance of active elements and devices. An important aspect of this matter is the development, synthesis, and characterization of new organic materials doped with nano-objects, such as fullerenes, carbon nanotubes, etc. Among the different class of the organic materials, liquid crystals (LC) have a special place. An important property of liquid crystals is their orienting ability, which is used in the creation of electro-optical composite materials. Liquid crystals can orient particles suspended in them and can act as molecular matrices, which can be easily controlled by a different external field, such as electrical, magnetic, thermal, acoustic, etc. Moreover, because of the interaction between the matrix and the particles suspended in it, the later become sensitive to the external field, with the result that the orientation of the liquid-crystal matrix also changes (de Gennes, 1974; Lee, 1993; Ouskova, 2011; Nawel Ould-Moussa, 2013; Kamanina, 2005).

It should be mentioned that the initial orientation of the LC molecules influences the dynamic parameters of the final devices based on this electro-optical mesophase. Thus, one of the key tasks is to find the perspective orienting layers, which can place the LC molecules in the planar, homeotropic or tilted positions according to the needs of the optoelectronic schemes. Different types of materials (oxides, polymers, etc.) and techniques (rubbing technique, oxides deposition, polymer network organization, polymers UV irradiation, printing of the relief by the holographic grating applying, surface relief creating by the surface electromagnetic wave treatment, etc.) have been applied in order to obtain the most suitable surface relief orienting the LC molecules (Zharkova, 1994; Kamanina, 1998; Wang, 1998; Tsoi, 2003; Vasilyev, 2007; Kamanina, 2016).

In the current paper about the novel approach, evidence is shown in order to discuss the alternative way for the LC molecules alignment on a solid surface. The main idea is based on the fact that the sensitization process of the body of the LC mesophase directly influences the surface relief due to the fullerenes or carbon nanotubes skeleton creating conditions which modify the surface topography. The last one can be tested via measurement of the wetting angle changes.

II. Experimental conditions, materials and results

It should be noted that to modify the properties of the solid organic thin films applied as the orienting layers a glass substrate was used. Fig.1*a*,*b* shows the general view of the pure glass substrate (Fig.1,*a*) and the sandwich structures of the LC cell or of the LC electro-optical modulator (Fig.1,*b*).

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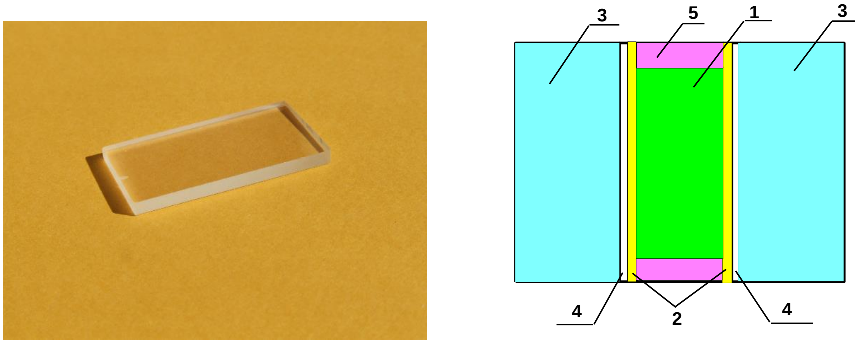
Figure 1: Generally used glass substrate (*a*) and construction of the LC modulator (*b*) with the layers: 1- LC mesophase, 2 – orienting (alignment) layers, 3 – used glass substrate, 4 – conducting layers, 5 – spacers to develop the gap before the LC filling in the cell.



a *b*

Source: Author

One can see that the orienting layers are the important part of the LC device sandwich construction. These layers should be treated with different approaches in order to obtain the orienting relief for the LC molecules.

Because the main idea of this paper is based on the fullerene or carbon nanotubes skeleton influence on the materials surface, the following model can be considered, which is presented in Fig.2*a*,*b*.

Figure 2: Model of the solid organic film sensitized with fullerenes, which skeleton modify the surface (*a*) and the possible variant of the LC molecules orientation on this skeleton-based relief (*b*).

a *b*

Source: Author

The OCA 15EC device purchased from LabTech Co. (Saint-Petersburg-Moscow, Russia) was applied in order to support the change of the wetting angle at the modified surfaces. The measured wetting angle reveals the surface relief evident. The obtained experimental data are shown in Table 1. The previously obtained results (Kamanina, 2018a; Kamanina, 2018b) and recent ones are presented. The PI - polyimide, PMPS - poly(methyl phenyl silane), PVA – polyvinyl alcohol, NPP – N-(4-nitrophenyl)-(L)-prolinol, PNP – 2-(n-prolinol)-5-nitropyridine, PBMA - poly(butyl methacrylate) materials have been used as the model matrixes for the doping process. The fullerenes C_{60}, C_{70} and carbon nanotubes are applied as the intermolecular acceptors. Fullerene powder with a purity of 97% and single wall carbon nanotubes (SWCNTs), type #704121, with the diameter placed in the range of 0,7-1,1 nm, were purchased from Alfa Aesar and Aldrich Co., respectively. It is important to mention that the poly(methyl phenyl silane) polymer systems were carefully investigated for the optical limiting evidence in the paper by Zyev (2013), as well as the poly(butyl methacrylate) compounds synthesis and properties have been presented recently in the paper by Pozdnyakov (2018).

Indeed, other polymer compounds can be considered, which can extend the data shown in Table 1.

Analyzing the data shown in Table 1, one can suggest that the wetting angle is significantly changed. It can be coincided with the fact that part of the fullerene or the nanotubes molecules as the effective acceptors interact with the donor fragment of the conjugated organic materials, for example, as has been shown in the paper by Kamanina (2008) for the polyimide donor fragment and fullerenes C_{60} and

C_{70}. It predicts the development of the intermolecular charge transfer process and increased composite dipole moment.

Table 1: Wetting angle change at the different doped with nano-objects organic thin films

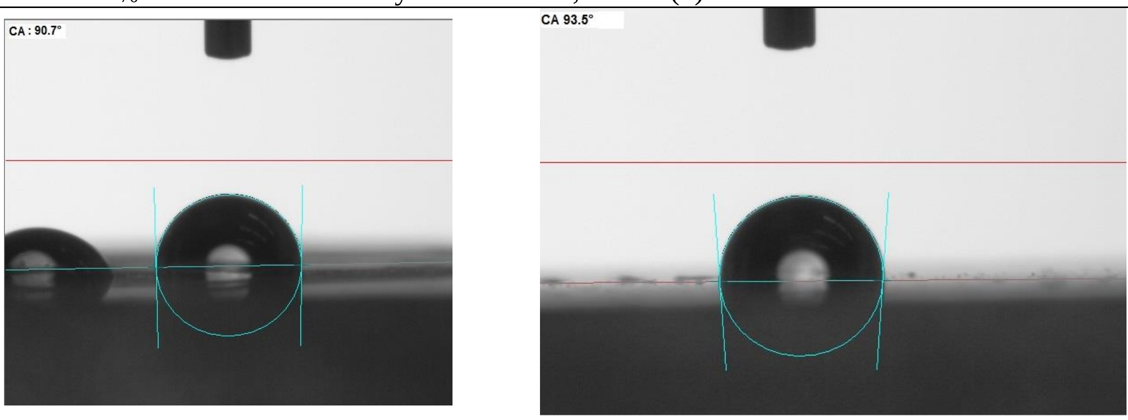
Materials	Content of the sensitizer, wt.%	Type of the sensitizer	Organic thin film thickness, microns	Wetting angle *before* sensitization, °	Wetting angle *after* sensitization, °	Ref.
PI	0,5	C_{70}	3	72	89	Kamanina, 2018a
PI	1,0	C_{70}	3	72-73	103	"-"
PMPS	0,83	C_{60}	4	75	81	Kamanina, 2018b
PVA	0,1	C_{60}	50	40	83	current
PVA	1	CNTs	50	39-40	82	current
NPP	1	C_{60}	3	97	102	current
PNP	1	C_{70}	3	90-91	94	current
PBMA	0,34	C_{60}	2,5	54	61	current

Source: Author

But, additional part (some excess part) of the fullerenes or the nanotubes does not participate in such interaction and simply fills the free volume between polymer lamellas. Frame (skeleton) of the fullerenes or the nanotubes may be quite feasible in order to protrude above the surface of the thin solid polymer films by changing the topology of the surface and creating the relief for the LC molecules orientation. In this case the wetting angle can be considered as a good indicator of this surface relief change.

Some demonstration of the wetting angle change is shown in Fig.3. These are the randomly selected data for the conjugated organic materials with the smallest and the largest change in the surface wetting angle obtained during the sensitization process. For example, for the 2-(n-prolinol)-5-nitropyridine system the smallest wetting angle change was found. It should be taken into account that the PNP system is the donor-acceptor compound that can reveal the intermolecular charge transfer complex formation process.

Figure 3: The wetting angle of the studied organics based on pure PNP (*a*) and when the content of the fullerene C_{70} inside the matrix body has been of 1,0 wt.% (*b*)



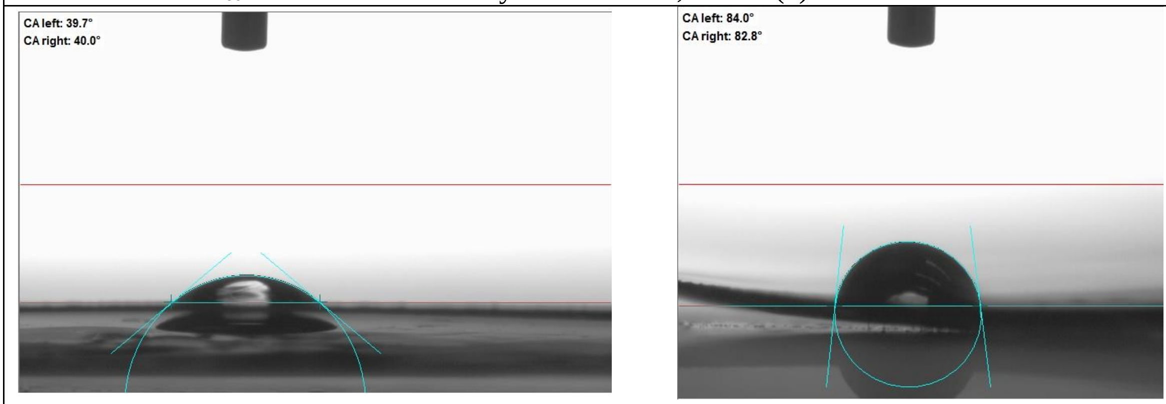
a *b*

Source: Author

In this case, the fullerene C_{70} has been used with the content of the sensitizer of 1 wt.% in the PNP conjugated materials.

From the other side, one can consider the results for the PVA matrix when the content of the fullerene C_{60} was only 0,1 wt.%. A two-fold increase of the wetting angle can be seen. It is good coinciding with the fact that PVA compound is not the donor-acceptor system and cannot reveal the intermolecular charge transfer process, which can accept the fullerenes as the effective acceptors. Thus, an increase in number of the fullerene molecules can organize the network, which skeleton influences on the surface relief. For the PVA materials some data of the wetting angle change are shown in Fig.4.

Figure 4: The wetting angle of the studied organics based on the pure PVA (*a*) and when the content of the fullerene C_{60} inside the matrix body has been of 0,1 wt.% (*b*)



a *b*

Source: Author

Thus, it is a really interesting phenomenon that sensitization of the body of the organics conjugated materials directly influences on the surface properties. One can see that the wetting angle for the PVA doped only with the 0,1 wt.% of fullerenes C_{60} can change the wetting angle from 39-40 degrees up to 83-84 degrees.

This tendency permits us to apply this fact in order to consider it a novel way for the LC molecules orientation process. Moreover, due to the reason that the fullerenes can change the transparency of the doped LC mesophase and the refractive index, the obtained results possibly can be added to the additional mechanism in the optical limiting process due to the scattering from these modified surfaces. Thus, if organic materials, including LC ones, sensitized with fullerenes or nanotubes are supposed to be used for the attenuation of the laser irradiations in the optoelectronic schemes, in addition to reverse saturable absorption, absorption by the intermolecular charge transfer complex, as well as the influence of the thermal factor, it is necessary to take into account the reflection from the modified surfaces, as is shown in the current paper.

Conclusion

To summarize the obtained results and the proposed qualitative models, one can suggest the following aspects: 1). The sensitization process of the organics differently influences the surfaces of the polymer solid thin films. It is dependent on the presence or absence of the initial donor-acceptor interaction in the model polymer matrix. 2). The model matrix system with an initial donor-acceptor interaction requires the doping of the matrix at the different concentrations to observe the effect of surface changes. From one side, some part of the doping agents (sensitizers) will be included in the intermolecular charge transfer process; from the second side, the extra nano-objects, which are not involved in the process of complexation, will be involved in the surface modification procedure. 3). The model matrix system without an initial donor-acceptor interaction requires the doping of the matrix at the higher concentrations to observe the effect of surface changes. But, this process will depend on the fact how affectively the dopant (sensitizer) will fill the free volume inside the polymer matrix. 4). Structuration of the organic material body provokes the change of their surface features. From one side it can be considered as the novel aligning layer for the LC molecules orientation; from the other side, it permits to use the structured polymers as the separate elements in the different complex optoelectronic schemes, for example, for the optical limiting realization.

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