Technology of manufacturing and a physical properties of a dispersed microencapsulated liquid crystals.

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Abstract: The paper describes the technology of ultra-fine powder production; the powder consists of plastic spherical microcapsules containing a liquid crystal. The average size of the capsules is about ~ 10 micrometers, wall thickness ~ 0.1 micrometer. Some electrooptical properties of the produced microcapsules have been studied. It is proposed to use these microcapsules to manufacture flexible film liquid-crystal indicators.

Key Words: Microencapsulated Liquid Crystals, PDLC, Flexible Displays.

1 Introduction

Despite evident advantages, the polymer-dispersed liquid crystals (PDLC) still have not been widely spread due to a number of technological problems. We suppose some of these problems can be solved with the aid of a microencapsuling (MC) technology, i. e. the manufacturing of disperse polymer microcapsules filled with the liquid crystal (LC), followed with the production polymer films based on them. The microencapsulating improves significantly the technological and functional properties of various products and considerably widens the area of their application. With the aid of this technology, many challenges can be solved, for example, the toxicity and volatility of the products can be decreased, density can be changed, color, odor, and taste can be hidden, and the content of the MC core can be protected from the ambient action [1]. That is why at the very beginning of the PDLC investigations, some authors tried [2] to use this technology to produce the PDLC. The method of this task solution on the state-of-the-art technological level is described below.

2 Microencapsulating technology

2.1 Basic method of MC

The original technology of so-called "block-polymerization" [3] has been used for the LC microencapsulating. It is based on the method of polycondensation on the phase boundary in the "oil-in-water" system, when one component of the future shell lies in the future core, and the other – in the disperse medium. The basic procedure used here was the microcapsules synthesis; according to this procedure, polyethylenpolyamine (PEPA) in the water phase and polyisocyanate (PIC) in the organic phase are used to obtain the urea-resin shell. The polycondensation reaction on the phase boundary is fast at the room temperature (20-25 ^{o}C) [1]. This technology guarantees the stable production of the microcapsules within the range of 1 – 100 micrometers, with the shell thickness of 0.1 – 10 micrometers, correspondingly. The limitations for the core material properties (water insolubility and no chemical reaction with the shell material) are satisfied for most LC. One more advantage of this technology is the effect of autostabilization of the core content, i.e. no extra stabilizing admixtures are needed.

2.2 Synthesis of the microencapsulated LC

The synthesis of the MC LC contains two stages: the preparation stage and synthesis itself. The preparation stage also contains two parts: preparation of the water phase wherein LC is emulsified, and preparation of the organic phase, the future core of the microcapsules. The amount of the LC and PIC has been calculated to produce the MC wall of the assigned thickness.

To produce the microcapsules, 0.02% solution of a complex emulsifier was poured into the reactor; a special mixer mixed it for at least 30 minutes at the speed of 200 rpm. Then, the revolution speed was increased up to such a value to avoid foam formation. In 10 – 15 minutes of the mixing, the solution of PIC in LC was injected (with the assigned speed) into the reactor. Then the reaction mixture was mixed again to emulsify the organic phase in the water phase, the mixing intensity being increased gradually. The stable microemulsion readiness was checked visually – every 2 minutes the samples were taken on an object-plate. When the emulsion droplets size was ~ 10 micrometers and less, the mixing intensity was not increased anymore.

When the stable emulsion pattern is observed for ~20 minutes and the mixing speed was stable, we injected the needed amount of the 10-% solution of PEPA. The sampling was done periodically and the microcapsules formation was observed simultaneously with the control of the reaction medium pH. As the water medium pH was > 7, the primary formation of the shell was over, and the process of its formation turned to the diffusion mode. Upon this, the reaction mixture was mixed for 10 minutes again, and then it was poured into a sealed vessel and shaken for at least one hour. Then, the water suspension of the microcapsules was held for ~ 1 week with periodical mixing until the pH is 7 – 8. By this moment, the process of the shell formation was over. The MC was washed from the reaction medium and dried.

3 Physical properties of the microencapsulated LC

The study of the produced samples of a microencapsulated nematic included the definition of geometrical characteristics of the capsules and electrooptical characteristics of a thin layer in the microcapsules coated onto a substrate. Well examined nematic LC 4-n-pentil-4'-cyanobyphenil was used for all tests.

Fig. 1 shows the microphotos of the microcapsules filled with a nematic liquid crystal, set on the glass substrate. The shots of one region have been made with a polarization microscope. On the top –the polarizer and analyzer are co-axial, on the bottom they are crossed. The images on the top shot allow to estimate the capsules shape and size. Most of them are spherical, several have stuck to each other. The bottom image enables to see the sizes of the cavities filled with the liquid crystal, since the light passed through the cavities with nematic obtained the elliptic polarization (in general case).

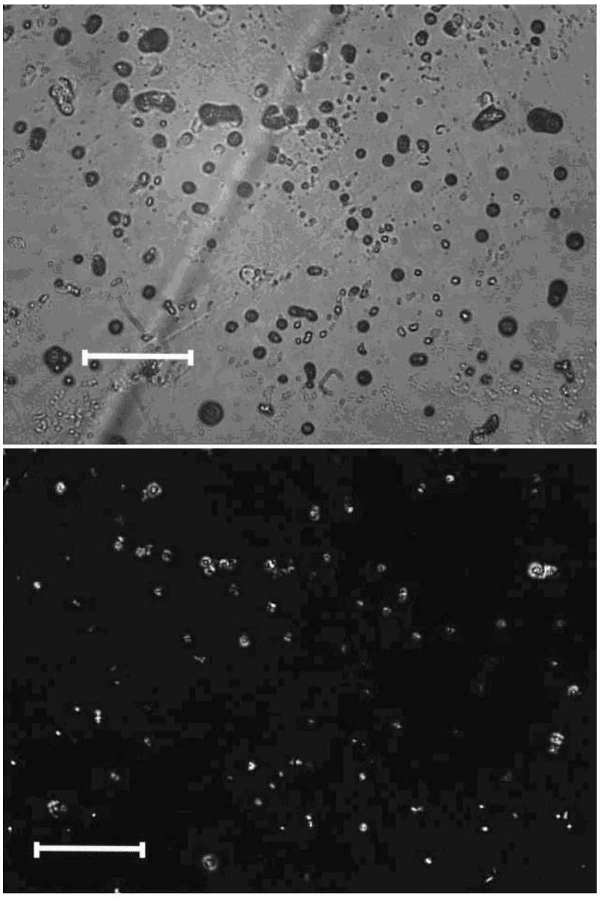


Fig. 1. Microphotos of the capsules, scale of 0.1 mm

The preliminary experiments were performed with a cell filled with the concentrated aqueous suspension. The cell consisted of two thin pieces of glass, one side of them was coated with a transparent electric-conductive layer. The glasses were set with the conductive layers facing each other, at the distance of 0.01 mm. Alternative voltage of various amplitude and frequency ranging from 10 Hz to 20 MHz were applied to the electrodes.

Fig. 2 shows the microphotos of the sample obtained for the frequency of 10 Hz at two values of the voltage between the electrodes – 2 V and about 30 V (the maximum voltage of the observation). Dark spots on the left microphoto correspond to the regions without capsules. Fig. 3 presents a blown-up fragment of the sample for the frequency of 10 Hz, voltage of 2 V (1), voltage of 25 V (2); frequency of 10 kHz – 0 V (3), and 30 V (4). The arrow points the position of one capsule with the liquid crystal.

The hairlines on the top, Fig. 2, designate the cross sections used to measure the samples transparency. Fig. 4 shows the obtained plots of relative transparence distribution for 10 Hz, Fig. 5 – the same for 10 kHz. The distance (in pixels) is measured from the top edge. Maximum values of contrast registered in these measurements reach 10 (for example, in Fig. 4, for the region near 130^{th} pixel). The vision-field averaging of the contrast values equal approximately to 1 : 3, regardless the frequency.

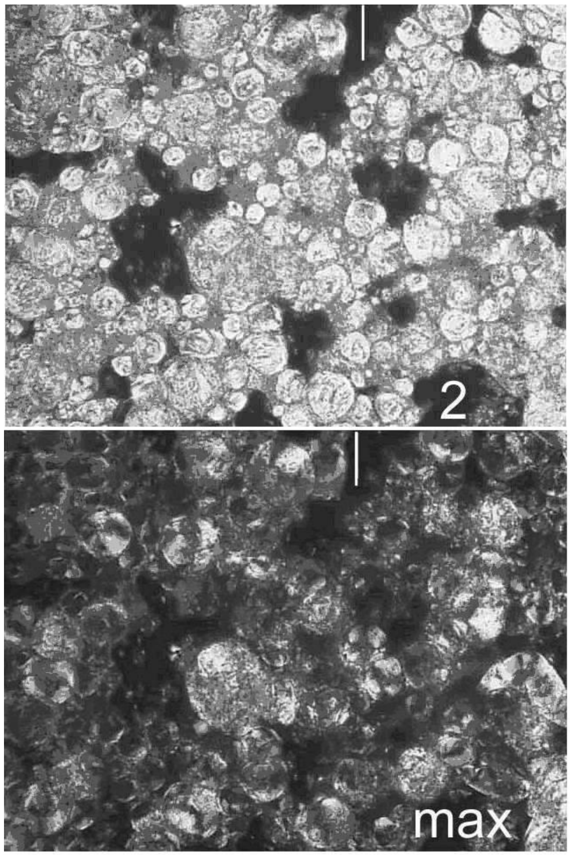
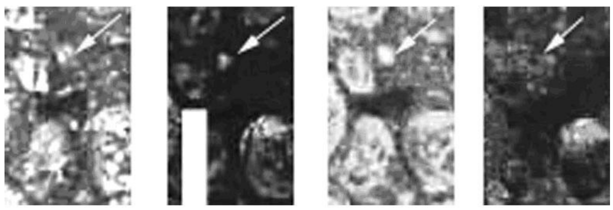


Fig. 2. Samples microphotos at 10 Hz



1 2 3 4

Fig. 3. Fragment of the sample microphoto at 10 Hz: 1 – 2 V, 2 – 25 V, at 10 kHz: 3 – 0 V, 4 – 30 V

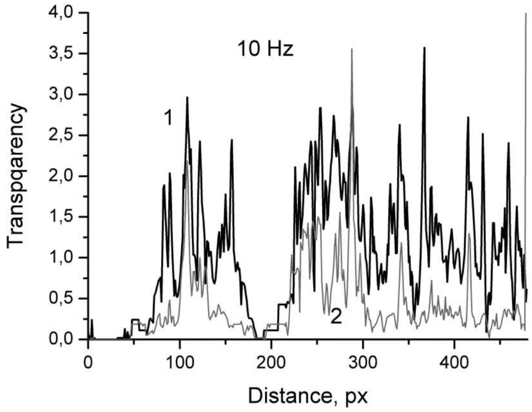


Fig. 4. Distribution of the sample transparency at 10 Hz, 2 V (1) and 30 V (2)

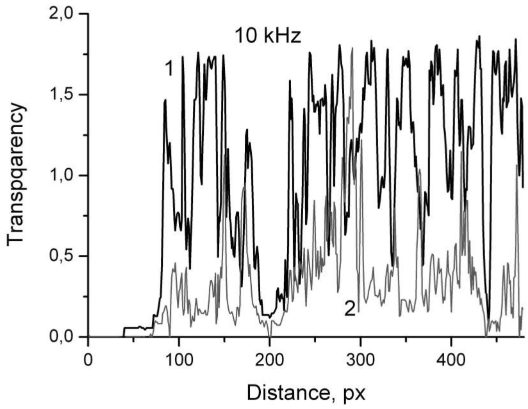


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Fig. 5. Distribution of the sample transparency at 10 Hz, 0 V (1) and 30 V (2).

4 Conclusions

1. The MC technology enables to produce the disperse LC-containing microcapsules from 1 to 100 micrometers size, with the shell thickness from 0.1 to 10 micrometers. This technology provides stable results because it is based on such easily-controlled parameters as the initial concentration of the substances and mixing speed. This has been confirmed by the results of the existing experimental manufacturing of the microencapsulated material.
2. No regular structure is observed inside the capsule. This circumstance does not facilitate to obtain a broad dynamic range for obtained samples, but determines a direction of further researches: a sophistication of technology of MC manufacturing and research of gears of interaction of a material of a shell, LC and additional doping components.
3. Maximum values of contrast registered in these measurements reach 1:10 for standalone microcapsule and 1:3 - for vision-field average. The low values of average contrast can be improved by a further sophistication of technology of deposition and packing of MC in a polymer film.
4. The transparency changes, as the voltage is applied, at the threshold below or comparable to the pure NLC, which is a positive feature of the studied samples. Normally, the threshold voltage rise in the capsules with the solid matrix, and the increase is considerable.

Hence, the possibility of production of the electrooptical materials based on the microencapsulated LC has been demonstrated. Actually, the microencapsulating technology is the transition from the classical LCD (PDLC) to the electronic ink technology (EInk), and allows to combine the advantages of both technologies, and, what is the most important, to use the common technological background. Further improvement of the MC technology will include the improvement of their electrooptical characteristics and will enable to increase considerably the contrast range and performance of the LCD (incl. flexible) on the ground of the disperse microencapsulated liquid crystals.

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