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**Abstract.** A liquid crystalline composite (LC-composite) based on synthesized borosiloxane (BS) and 5 wt. % liquid crystal (LC) 4-cyano-4'-N-heptylbiphenyl was obtained and investigated. The microstructure of the obtained composite was characterized by the method of polarization optical microscopy (POM). It is shown that the LC in the composite is contained as a separate phase, which is not miscible with BS. The phase is represented by spherical micro droplets with sizes from 1 to 50 microns. The introduction of the LC into the BS matrix leads to the clouding of the initially transparent BS. This phenomenon is associated with the difference in the refractive indices of the LC and BS, which leads to light scattering on the micro droplets of the LC component. It was established that the BS matrix and the LC composite have self-healing properties after surface damage. The time of self-healing of surface damage at room temperature and normal conditions was about 1.5 - 2 hours. The obtained LC composites may be interesting as promising materials for flexible multilayer biocompatible electronics and electro-optical devices with self-healing properties.

## 1. Introduction

The development of electronic and electro-optical technology goes in several directions at once, aimed at increasing the functionality and energy efficiency of modern high-tech devices. There are traditional developments aimed at miniaturizing the working elements of devices, including optical ones. One example in this direction is research in the field of liquid crystal devices - microresonators, where the working element is a liquid microcapsule (LC) with a radius of only 10 - 15 microns [1-3]. In the direction of the development of flexible electronics technologies, including flexible displays, global brands (Sony, Samsung, Xiaomi, and others) are moving from experimental development to commercial products [4]. Relatively new trends for research and development are the directions of biocompatible and self-healing electronics and display equipment [5 - 8]. Interesting examples of developments are smart phone display [6], artificial biocompatible electronic skin [7], and supercapacitors [8], which have self-healing properties.

Materials based on borosiloxane (BS), attract the attention of developers and researchers due to a complex of unique properties. BS is the common name of organosilicon compounds containing the

$R_n$Si-O-B group, where R is a hydrocarbon radical, n = 1 - 3. BS is the reaction product between organosiloxanes and boron-oxygen compounds. These elastic-plastic materials have the properties of a viscous fluid over a long time period but as an elastic solid over a short time period. In the previous works of the authors [9-15], new materials based on BS and LC for electro-optical and electronic devices were obtained, investigated and patented. At the same time, as reported in the scientific literature, BS is a promising material for various systems with self-healing properties, including biocompatible [16]. Flexible conductive composites based on BS and carbon nanotubes with self-healing properties were obtained in work [17], and borosiloxane self-healing coatings to protect the metal from corrosion were investigated in work [18]. One of the approaches to the creation of self-healing materials is the creation of multilayer composites [19], containing one or several functional layers, which allow to carry out of the self-healing process after damage. Consideration of orientation effects in such systems was described in the paper [20-22]. Thus, BS is of interest as a promising material for flexible biocompatible electronics and electro-optical engineering, which can be used both by itself and as a functional layer with self-healing properties, for example, in multi-layer systems based on liquid crystals dispersed in a polymer PDLC [23]. In addition, one of the promising materials for self-healing are phthalocyanins with asymmetric structure containing expanded alkyl or alkoxyl substituents [24–29].
Therefore, the aim of the work was to obtain a new LC-composite based on synthesized BS and to study the self-healing properties of these materials.

## 2. Experimental part

In this work BS was synthesized by mechanical stirring in a glass beaker of hydroxy terminated polydimethylsiloxane (PDMS) with average molecular weight 20,000 g/mol with crushed boric acid (BA) taken in an amount of 2 wt. %. The samples were formed from the synthesized BS in the form of films by coating onto a polymer substrate, followed by keeping for 24 hours at room temperature. The process of obtaining BS was characterized using rotational viscometry on a viscometer Viscotester E (Thermo Scientific, Germany) at room temperature . To do this, immediately after mixing PDMS with BA, the spindle of the rotational viscometer was placed in a sample beaker and the viscosity was measured as a function of time. As the viscosity increased, spindles were replaced from L2 to L4, which made it possible to measure in the range from $1.5 \cdot 10^2$ to $6 \cdot 10^6$ mPa·s.
The introduction of the nematic LC 4-cyano-4'-N-heptylbiphenyl (figure 1) into BS was fulfilled by mechanical stirring at room temperature. LC was introduced into the BS in the state of the mesophase at a concentration of 5 wt. %. Samples in the form of films were obtained from the LC-composites.

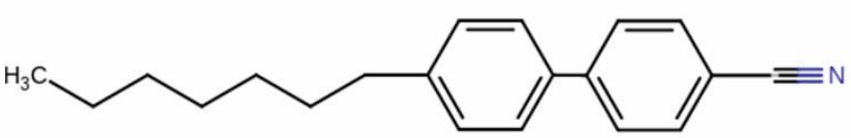


**Figure 1.** Structural formula of the nematic LC 4-cyano-4'-N-heptylbiphenyl.

Mechanical damage to the films was made using a metal needle in the shape of the Latin alphabet letters "S" and "H", according to the first letters of the English word "Self-Healing".
A POLAR 3 microscope (Altami, Russia) was used to study by polarization optical microscopy (POM). Investigations were carried out in transmitted unpolarized light and in crossed polarizers.

## 3. Results and discussion

### *3.1. Obtaining of the BS-matrices*

The initial PDMS is a clear liquid with a viscosity of about 2000 mPa·s. It is shown that the viscosity of PDMS slightly changes with increasing or decreasing temperature, while the introduction of BA leads to a 250-fold increase in viscosity, converting the initially viscous flowable fluid into an elastic-

plastic mass. Rotational viscometry was used to analyze the processes occurring during BS synthesis (figure 2).

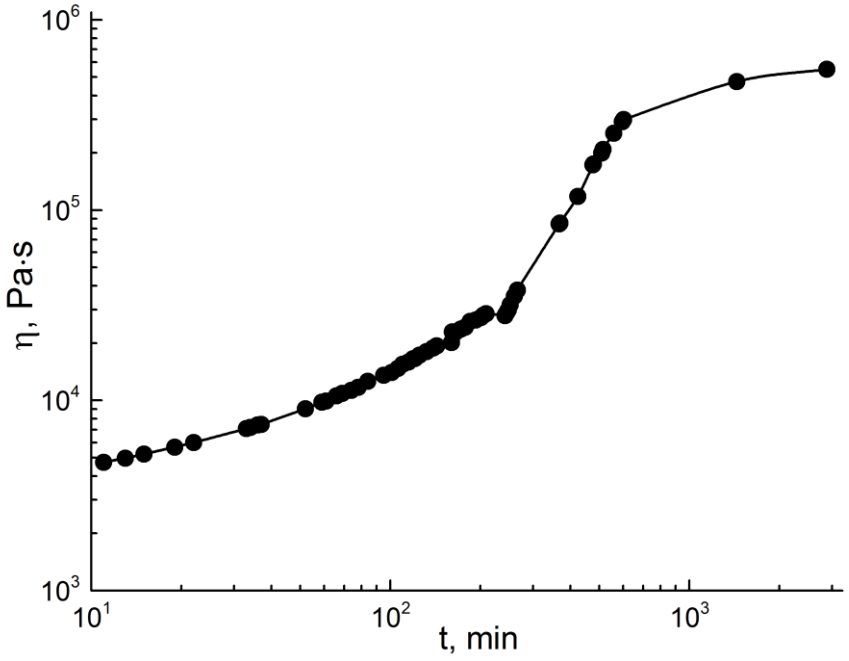


**Figure 2.** Dependence of the viscosity of the reaction mixture on the reaction time in log–log plot at room temperature.

The figure shows that the viscosity of the BS increases over time, reaches the plateau and then stops to grow. This happens within 24 hours. The dependence curve is S-shaped with an inflection point in the region of 6 hours from the moment of preparation of the mixture. Such an S-shaped character of viscosity change is characteristic of three-dimensionally crosslinkable systems, such as various resins, gels, rubbers, etc. [27]. However, for BS, obtained in this way, it is characteristic that it is not crosslink into a completely solid elastic state, but continues to have some fluidity. The nature of crosslinks of these materials is dynamic, donor-acceptor bonds can reversibly break and form again. This property gives to the BS characteristics of elastic solids with fast exposure and the properties of liquids at slow.

The BS samples were obtained by coating of a freshly prepared mixture of PDMS with BA onto a polymer substrate. The samples are transparent rubber-like polymer films with self-adhesion properties.

By POM method, it was shown that in the initial BS matrix, which is visually optically transparent, there are particles with sizes from 2 to 20 μm, which are absent in the original PDMS (figure 3(a)). These particles are birefringent in crossed polarizers. Apparently, these particles are unreacted BA (figure 3(b)).

The introduction of the LC in the BS-matrix results in a homogeneous milky-white sample. The clouding of the initial transparent BS matrix apparently deals with the difference in the refractive indices of LC and BS. The microstructure of the obtained composite was characterized by the POM method. It is shown that the LC in the composite is predominantly contained as a separate phase, which is not miscible with BS. The phase is represented by spherical microdroplets with sizes ranging from 1 to 50 μm (figure 3 (c) and 3 (d)).

### *3.2. Analysis of the self-healing properties of the BS-matrix and LC composite*

It should be noted that the nature of damage of materials may be different. It can be accompanied only by an increase in the surface area of a sample, as in the case of, for example, a surface defect or scratch, and a loss of mass, as in the case of breakdown (through hole).

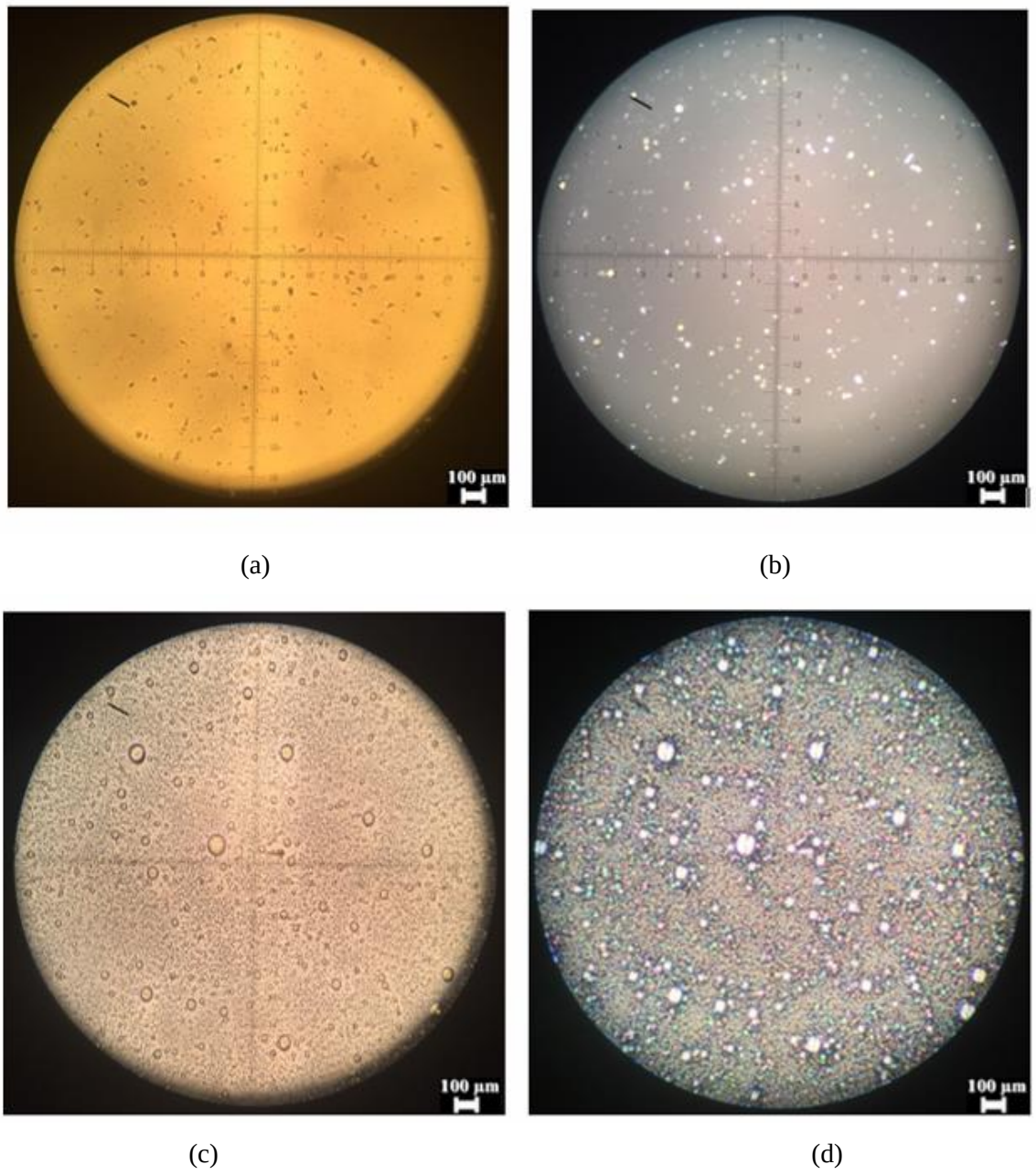


**Figure 3.** Microphotographs of BS (a), (b) and LCD composite (c), (d) at room temperature in transmitted non-polarized light (left) and in crossed polarizers (right).

In this work, damage is modeled, accompanied by an increase in the surface area of the samples, without loss of the total mass, by applying surface scratches. It should be noted that the BS is scratched like a polymer film. It breaks brittle and collapses locally. Samples of the BS films and the LC composite after causing damage were left at room temperature. A photo fixation of changes was made every 30 minutes (figure 4).

It is clearly seen that over time, the letters disappeared as a result of a spontaneous healing process. So the traces of the inscriptions on the samples were almost gone after 1.5 - 2 hours. Moreover, the inscription on the LC composite disappeared earlier than on the BS, which, apparently, is explained by the fact that a certain amount of LC dissolves in the BS-matrix and plasticizes it, thereby increasing its plastic properties.

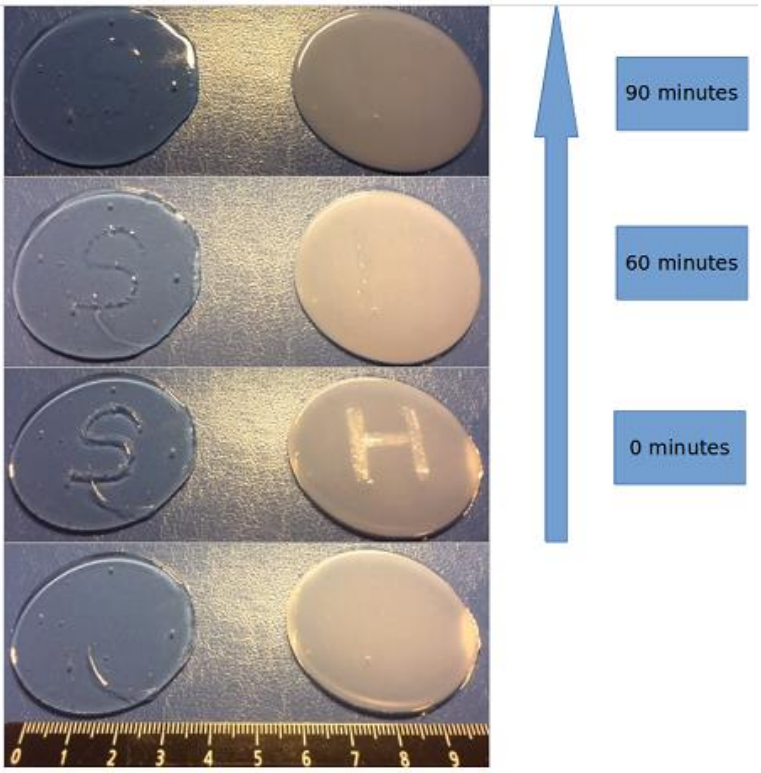


**Figure 4**. Samples of BS (left) and LC composite based on it (right): before (lower photo) and after surface damage (3 upper photos).

The mechanism of self-healing of bonds after damage is caused by a recovery of destroyed non-covalent bonds in BS. This property is apparently due to the molecular structure of BS, where donor – acceptor bonds B – O and hydrogen bonds can be either easily destroyed or easily restored. Thus, the brittle destruction of BS and composites based on it can occur many times without changing of the material`s characteristics and a molecular weight of the molecules, since there is no destruction of the covalent bonds.

## 4. Conclusions

It was shown that the introduction of the LC into the BS matrix does not lead to a noticeable effect on the mechanical properties of LC composites, however, the time for self-healing of surface damage is reduced. Using the POM method, it was shown that the LC in the matrices is in the form of a separate phase in the form of spherical droplets, which may allow to use of functional optical characteristics of the LC, for example, when developing miniature electro-optical devices, such as microresonators. The obtaining LC composites may also be of interest as promising materials for flexible multilayer biocompatible electronics and electro-optical devieses, such as, for example, PDLC films, with self-healing properties.

## 5. Acknowledgments

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