Mol. Cryst. and Liq. Cryst., 2001, Vol. 367, pp. 463-474
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Structure of Filled Liquid Crystals Studied by Acoustic Methods

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The measurements of ultrasound velocity and absorption of the aerosil suspensions in nematic liquid crystal (LC) 5CB were carried out in the regime of linear acoustic for the aerosil concentrations of (0-6) volume % and sound frequencies of 1-120 MHz. The sound velocity decreases with the increase of aerosil fraction in the mixture. It shows structuring of aerosil as separated aggregates. Proceeding from the data of absorption in frame of the model of rigid spheres the aggregate parameters (size of aggregates, aggregation rate and volume fraction of aerosil in aggregate) were calculated.

Keywords: liquid crystal; aerosil; suspension; acoustic; structure

INTRODUCTION

Filled LCs- suspensions of small solid particles in liquid crystalline matrix - are exciting objects of investigation. First materials of this type were suggested in 70th when Chen et al. [1] considered "ferromagnetic" LC- suspension of needlelike ferromagnetic particles in the nematic liquid crystal. In such suspensions LC was involved with the magnetic particles in the process of reorientation in a weak magnetic field. In the

beginning of 90th Eidenschink and de Jeu [2] suggested new system containing aerosil as filling material. Primer particle of aerosil could be roughly considered as porous sphere with the diameter of about 100 Å. Each from the particles generate orientational defect in the LC. In the macroscopic scale it results in the strong light scattering. Application of the electric field leads to orienation of LC molecules and, as result, to the clearing up the suspension layer. The unique property of such suspensions is pronounced memory effect, which consists in the essential residual transparency after removing the electric field [3]. Efficiency of the memory depends on the chemical structure of LC molecules, surface state of the aerosil particles and parameters of the applied field [4-5]. The study of intrinsic properties of filled LCs is a subject of great interest during last years [6-8].

The properties of filled liquid crystals are tightly connected with the structural organization of solid phase in LC matrix. In spite of great actuality, this question is studied rather poor. Direct observation of the aerosil structure was carried out only in the mixtures with polymeric LC by means of AFM method [9]. In [10] the size of aerosil inclusions in liquid crystal was evaluated by neutron scattering technique. In our studies the acoustic technique was chosen whose capabilities were earlier demonstrated for the aerosil suspensions in various isotropic liquids [11-13]. To our opinion, this technique is much more informative then the other methods of investigation of the structuring in suspensions. The obtained results are compared with the corresponding results earlier obtained with the other methods.

EXPERIMENTAL

Sample

As a host it was used liquid crystal 4-pentyl-4'-cyanobiphenyl (5CB) by Merck having nematic mesophase in the 18°-35°C temperature interval.

In the first experiments we used hydrophilic aerosil A300 by Degussa. However, the mixture 5CB-A300 was hard for investigation because of the intensive phase separation. That is why in the following experiments the hydrophobic aerosil R812 by Degussa was used as a filling material. The majority of surface OH groups of R812 particles are substituted by CH_3 fragments, which diminish separation of the aerosil in a mixture. A density of OH groups is 0.3 nm^{-2} compared with 5 nm^{-2} for the non-modified aerosil [10]. Before preparing samples the aerosil was dried for 2h at 120°C in order to remove water adsorbed on its surface. The suspensions were prepared immediately before experimental studies. The LC and aerosil were mixed using ultrasonic disperser. The intensity and frequency of sonification were 4000 W/m^2 and 22 kHz, respectively. A series of suspensions with different concentration of aerosil (0.35, 2.5, 4, 5, and 6 vol. %) were prepared.

Method

The sound velocity c was measured by means of impulse-phase method whereas sound absorption coefficient α by impulse method. Both parameters were measured in the frequency range of 5-120 MHz.

The principle scheme of the used set up is presented in Fig.1. For the sake of simplicity, in Fig.1 it is omitted electronic part providing generation of the transmitted signals as well as amplification and measurements of the received signals. The studied material is located in an acoustic chamber with the hollow frame filled with circulating water for the temperature stabilization. The temperature was stabilized with the accuracy of 0.1 °C. In the bottom part of the acoustic chamber is located receiving piezocrystal P1. A transmission piezicrystal P2 is mounted in the upper part of the chamber. Both P1 and P2 are connected with the cylindrical delay lines made from the fused quartz. The delay

lines prevent superposition of the investigated impulse with the other impulses reflecting from the chamber walls and passing through the

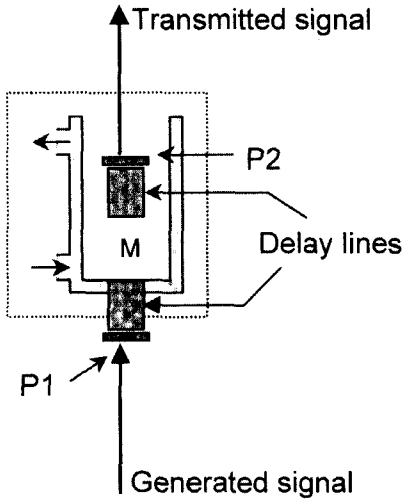

FIGURE 1 Acoustic camera for the acoustic data measurement.

studied material. The distance between delay lines is an acoustic distance l. A change of the acoustic distance $\Delta l=l_1-l_2$ leads to 20 the change of the amplitude of the received signal $\Delta A=A_1-A_2$. In tern, Δl and ΔA are connected with the coefficient of sound absorption as [14]

$$\alpha = \frac{\Delta A}{20ge\Delta l} \tag{1}$$

All measurements were carried at ΔA being proportional to Δl, i.e. in the region of linear acoustic. It means sound wave passing through investigated system did not destroy its structure.

An interference in the acoustic volume appears if $\tau>t$, where τ is impulse duration and $t=2L/c$. This interference causes pulsation of the amplitude of the received signal when l is altered. In this case $\Delta l=n\lambda/2$,

where n is pulsation number, λ is sound wavelength. Hence, c could be calculated as

$$c = \frac{2\Delta l}{n} f \tag{2}$$

The described principle of c and α measurement is common for the investigated frequency range. However two different chambers with different size of the delay lines and piezosensors were used for the measurements within 1-10 and 10-120 MHz, respectively.

RESULTS AND DISCUSSION

Dependence of the sound velocity on the volume fraction of aerosil in the suspension is presented in Fig.2. The velocity C monotonously decreases with the increase of aerosil concentration φ. Decreasing rate

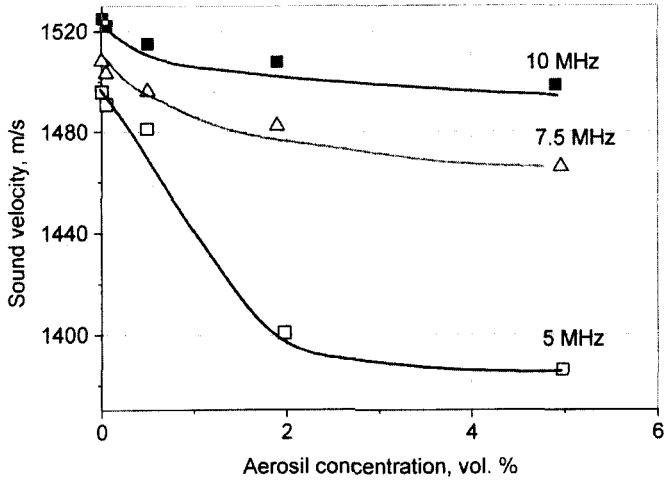

FIGURE 2 Dependence of the sound velocity on the volume fraction of aerosil in the suspension.

grows with the frequency decrease and is especially strong for the frequencies below 10 MHz. One can see substantial difference comparing with the data for aerosil suspension in dodecane [13]; in the last case dependence $c(\varphi)$ goes through a minimum, while in the case of 5CB-aerosil mixture monotonously decreases. The grow of $c(\varphi)$ was assigned to the formation of 3D skeleton of aerosil phase and passing of the sound wave through such a rigid network.

The suggested explanation is a wide accepted notion in the colloid science. For example, same explanation was given for the system air-snow in [15]. So, it is not detected continuos aerosil network in the 5CB-R812 system in the studied frequency range and the structure of separated aerosil inclusions should be accepted for the following consideration.

The frequency normalized value of sound absorption of pure LC,

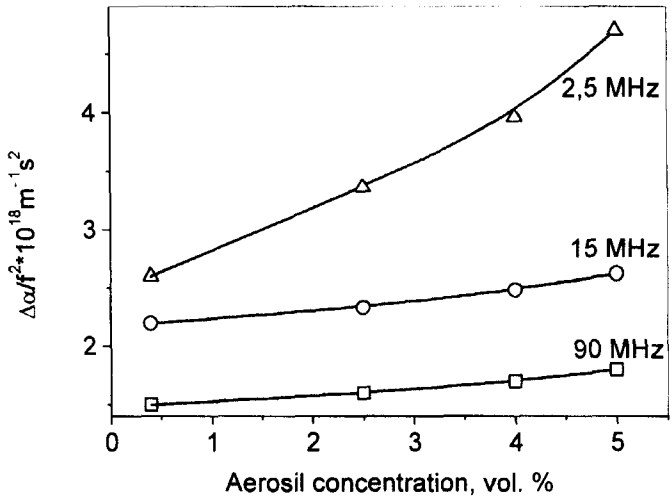

FIGURE 3 The redundant sound absorption *vs* aerosil concentration.

$\frac{\alpha_{LC}}{f^2}$, as well as of the suspension, $\frac{\alpha_s}{f^2}$, has wide relaxation region within 5-70 MHz. Insertion of aerosil in LC leads to additional absorption of the sound wave. The redundant absorption $\frac{\Delta\alpha}{f^2} = \frac{\alpha_s}{f^2} - \frac{\alpha_{LC}}{f^2}$ could be roughly considered as a linear function of the concentration of aerosil up to φ=5 vol. % (Fig.3).

It is evidence of the additive contribution of each aerosil aggregate to the sound absorption in the absence of effective interaction between aggregates [11,13]. This result agrees well with the concentration behavior of sound velocity discussed above. Parameters of the aggregates can be estimated using values of $\frac{\alpha_{LC}}{f^2}$ and $\frac{\alpha_s}{f^2}$ measured for the sound frequency out of the regions of relaxation. Let

$$R_a = r_p N_{pa}^{\alpha} \tag{3}$$

where N_p is a number of particles in an aggregate, r_p is a radius of a primer aerosil particle, α is a constant. The mean value of α obtained from the computer simulation of aggregates as equal rigid globes is 0.429 [16]. From Eq. (3) the volume fraction of aerosil in aggregate φ_{pa} can be derived:

$$\varphi_{pa} = \left(\frac{r}{R_a}\right)^{3-\frac{1}{\alpha}} \tag{4}$$

Relationship between φ and φ_{pa} is described as

$$\varphi = \varphi_{pa}\varphi_a \tag{5}$$

where φ_a is a volume fraction of aggregates in the suspension.

For the determination of N_p we used the equation

$$\frac{\alpha_s}{f^2} = \frac{\alpha_{LC}}{f^2}\left(1 + 3N_p\varphi\right) \tag{6}$$

earlier obtained empirically for the suspensions of aerosil in various isotropic liquids [12]. A correctness of this equation in case of studied system was checked additionally.

To the end, using equation [14]

$$L = 2R_a \sqrt[3]{\frac{0.74}{\varphi}} \tag{7}$$

the averaged distance between aggregates can be estimated.

So using the system of equations (3)-(7) one can calculate radius of aggregates R_a, number of particles in aggregate N_p, interaggregate distance L, volume fraction of aerosil in aggregate φ_{pa} as well as aggregates in the suspension φ_a at various aerosil concentrations and temperatures.

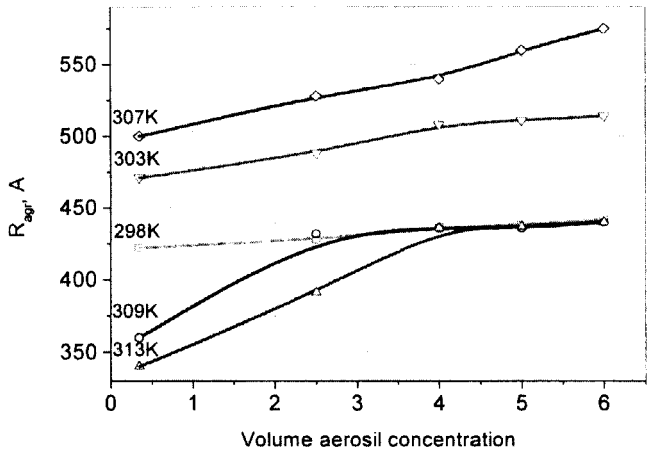

FIGURE 4 Aerosil aggregate size *vs* aerosil concentration.

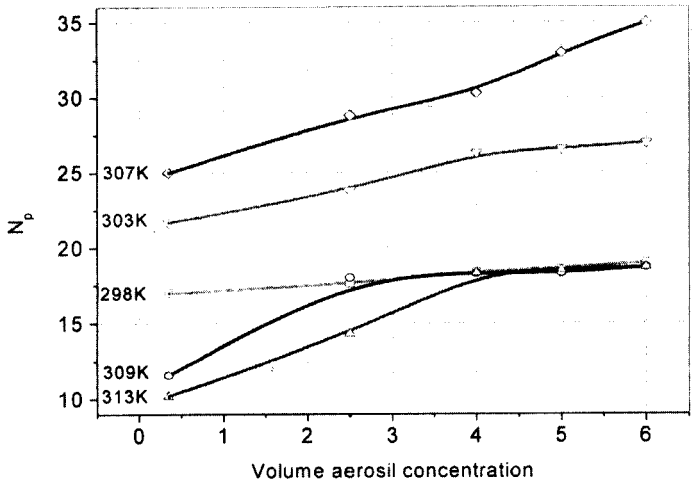

FIGURE 5 Number of aerosil particles in the aggregate *vs* aerosil concentration in the suspension.

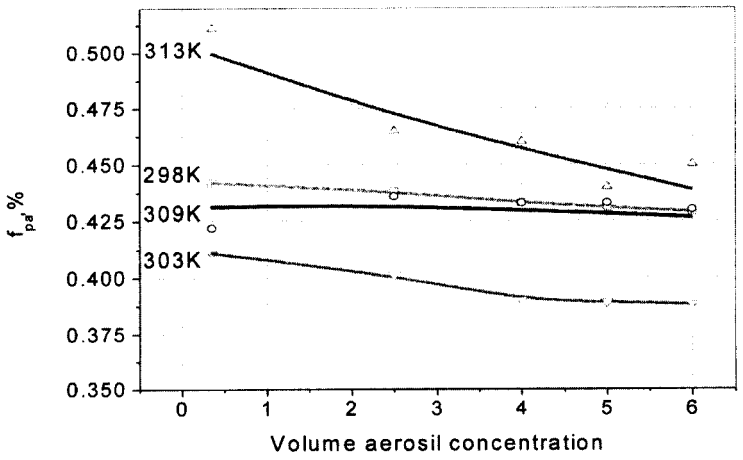

FIGURE 6 Volume part of the solid phase in the aggregate *vs* aerosil concentration in the suspension.

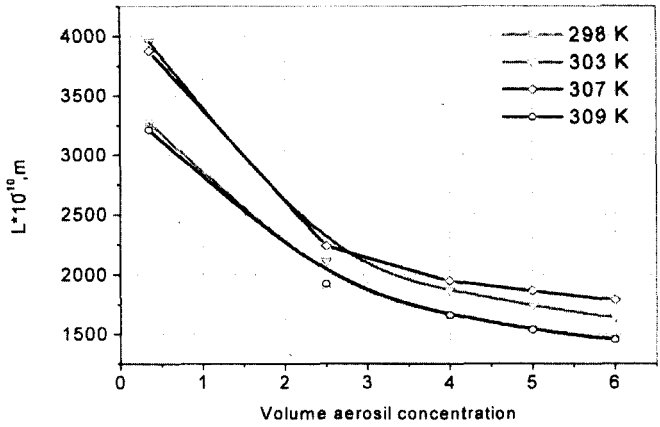

FIGURE 7 Distance between the aggregates *vs* aerosil concentration.

Dependencies $R_a(\varphi)$, $N_p(\varphi)$, $\varphi_{pa}(\varphi)$ and $L(\varphi)$ at various temperatures of the nematic and isotropic phase are presented in Fig.4-7, respectively. They are calculated using values of $\frac{\alpha_{LC}}{f^2}$ and $\frac{\alpha_s}{f^2}$ at 100 MHz. The estimated values of the aggregate parameters R_a, N_p, and φ_{pa} are of the order of 50 nm, 20 and 0.4, respectively. The size of aggregate, R_a, and rate of aggregation, N_a, quazilinerly increase with the increase of aerosil concentration (excepting temperatures near the phase transition), whereas aerosil fraction in aggregate, φ_{pa}, changes not essentially. The interaggregate distance, L, is of the order of several hundreds nm. L decreases with the increase of φ. The obtained values are in great agreement with the corresponding values for the aerosil suspension in LC polymer obtained in [14] by AFM technique. As one can see from Fig.4, 5, the values of R_a and N_p slightly grows with the temperature increase in mesophase. The aggregates exist even in isotropic phase at $T-T_c<5^{\circ}C$. At $\varphi<5\%$ they are appreciably smaller then that below

melting point T_c, whereas at φ>5% the values of R_a and N_p in isotropic phase are estimated to be same as at the deep temperatures of mesophase. It apparently shows a structure of aerosil is the most strongly influenced by LC matrix at the small aerosil fraction in the suspension. At the concentrations φ>5% the steric factors seem to be very important for the structural organization of the system.

CONCLUSIONS

Acoustic methods could be effectively used for the study of the structural peculiarities of the system LC-aerosil. The results obtained for the system LC 5CB-aerosil R812 with the volume fraction of aerosil 0-6 % could be interpreted in frame of the aggregate structure of aerosil phase. The aggregate parameters (size, aggregation rate, aerosil fraction) as well as the interaggregate distance could be estimated using formalism developed for the colloidal systems. Good consent with the data obtained with the other methods is detected.

Acknowledgement

The presented studies were supported by INTAS foundation (grant No 97-1315). Authors are thankful to Prof. Yu. Reznikov for the fruitful discussions.

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