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LIQUID CRYSTAL/COPOLYMER-CLAY NANOSTRUCTURED SYSTEMS: CONTRIBUTION TO THE CONDUCTIVITY OF THE ELECTRODE POLARIZATION

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Conductivitatea electrică a unor noi sisteme nanocompozite cristal lichid-montmorillonit este determinată folosind spectroscopia de impedanță. Se obține dependența acesteia de frecvență, temperatură şi tensiunea electrică de polarizare. Rezultatele referitoare la influenta tensiunii alternative permit obtinerea mai multor informații asupra mecanismului de conducție față de cele obținute anterior din influența frecvenței şi a temperaturii. Un rol important il are polarizarea la interfața electrod-proba, atât în curent continuu cât şi în curent alternativ. Este examinat de asemenea efectul polarizării la electrod asupra conductivității electrice în funcție de parametrii mai sus mentionați.

The electrical conductivity of new nanocomposite systems liquid-crystal/montmorillonite clay is performed using impedance spectroscopy. The dependence of the electrical conductivity on the frequency, temperature and bias voltage is obtained. The results referring to the alternative voltage influence allow getting more information on the conduction mechanism than the previous ones obtained under frequency and temperature influence. An important role has the polarization at the electrode-sample interface, both in continuous and alternative current. The electrode polarization effect on the electrical conductivity in dependence on the above mentioned parameters is also examined.

Keywords: Nanocomposite, impedance spectroscopy, electrode polarization, bias voltage.

1. Introduction

More than one hundred years has past since the discovery of liquid crystals [1, 2] and their study is in continuous expansion. New methods of investigation have been proposed [3] and special attention is paid to liquid crystals composites, due to their properties and applications [4, 5, 6, 7].

In the last decade new liquid crystal/montmorillonite clay nanocomposites with improved electro-optical properties have been obtained. The particles in dispersions form internal interfaces with large specific surface, making possible to

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stabilize different director configurations and consequently to better control the properties of the composite. For a good interaction with the liquid crystals (LCs), the clay particles should have on their surface compatible functional groups. Thus, surfactants [8, 9] or modifications of the montmorillonite by hydrophobic organic substances [10] have been used.

We have recently examined the electrical properties of a nanocomposite containing a known nematic liquid crystal doped with new polymer-clay mixture [11]. The latter (Cloisite-type clay) was modified by copolymerization of maleic anhydride and divinyl benzene and the nanocomposite has intercalated structure. I-V characteristics raised under dc, led to the conclusion that there can be many types of conduction mechanisms (Schottky, Poole-Frenkel, Mott) because of their nonlinear appearance (Fig. 3 of ref.[11]). In many cases the analysis of I-V characteristics as obtained for different systems with LC [12-17] shows that experimental data can not be approximated by equations characteristic to the above mentioned effects.

In this contribution new measurements of the electrical conductivity as function not only on the frequency and temperature but also on the applied voltage are presented and the conduction mechanism of the ac electrical conductivity in the case of a nanocomposite system containing a nematic liquid crystal doped with rather new polymer-clay mixture is studied.

2. Experimental

The systems to be investigated were obtained by the polymer-clay nanocomposite dispersion (5% in weight) in the nematic liquid crystal 5CB (Merck) [18]. Transition temperatures of the bulk liquid crystal are:

$$Cr \xrightarrow{296.9\text{ K}} N \xrightarrow{308.4\text{ K}} I$$

where *Cr* means the crystalline state, *N* – the nematic and *I* - the isotropic one.

The polymer-clay nanocomposite was obtained as previously described [11,19] starting from Na-Cloisite (Sothern Clay Product Inc.) dispersed in a mixture of solvents (methyl ethyl cetone and heptane) by adding maleic anhydride (MA) and divinyl benzene (DVB) [19] and letting them react at 70°C with azoisobutytironitrile (AIBN) as initiator. Finally the functionalized copolymer clay nanocomposite (DVB-MA-clay) has intercalated structure according to its XRD pattern. The nanocomposite to be investigated was noted 5CB/ DVB-MA-clay.

The samples for dielectric measurements were sandwiched between two parallel plane electrodes, at a distance of 50 μm (kept by quartz wire spacers).

The equipment to measure the complex dielectric function was a high-resolution Alpha analyzer (Novocontrol) in the frequency domain between 1 and

10^6 Hz. The temperature was controlled to within 0.2 °C. The electrodes consisted of polished circular plates coated with gold.

The temperature dependence of the impedance and its derived physical quantities was evaluated from 306.1 K to 321.1 K. The electric polarization voltage U_{CC} was between 0 V and 40 V. The alternative voltage is set to 0.05 V.

The dielectric data were processed using WinFIT software from Novocontrol. The conduction effects were treated as usually by adding a conductivity contribution $\sigma_0/\varepsilon_0(2\pi f)^x$ to the dielectric loss. σ_0 is related to the dc conductivity of the sample. The parameter x ($0<x\leq 1$) describes for $x<1$ non-Ohmic effects in the conductivity.

3. Results and discussion

3.1. Dependence of the electrical conductivity on the dc voltage

Fig. 1 presents the conductivity dependence on the dc voltage, at some fixed temperatures.

The conductivity curves (Fig. 1) thus obtained by the impedancemeter show an upward trend in the low voltage region, a maximum (for the voltage around 2V), and asymptotically decline, at relatively high voltages. The presence of this maximum and the two branches indicate changes in the conduction mechanism. This behavior can not be explained on the basis of only one of the above mentioned effects since in these cases both the I-V characteristics curves and their slopes must be strictly monotonically increasing and this requirement is not fulfilled here.

The I-V characteristics previously determined [11], show a change in the slope of the curve, situated around 2 V, which is consistent with the results in the ac regime: the I-V characteristic slope is numerically equal to the ac electrical conductivity at sufficiently low frequencies.

We can speculate that at the contact surface between the electrode and the sample the adsorbed molecules of the liquid form a compact monolayer (Helmholtz layer) which prevents or limits the electric charge transfer between the electrode and the sample. Under the dc voltage, the space charge formed by the ions accumulation is extended, which further limits the electric charge transfer of other ions coming from the sample volume toward electrodes. Higher the polarization voltage greater the size of the space charge layer. It results a current increase less than that corresponding to the applied voltage. This behavior means a drop in the electrical conductivity of the sample.

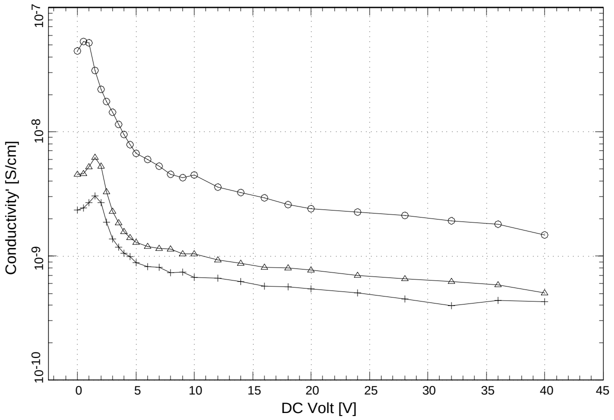

Fig. 1. The electrical conductivity dependence on the bias voltage, at different temperatures: 321.1K (O); 312.1K (Δ); 306.1 K (+).

3.2. Frequency dependence of the dielectric constant and the electrical conductivity

The ac conductivity *σ(ω)* is a complex function. Thus associated with the real part there is also an imaginary component; the latter determines the real part of the frequency-dependent permittivity. Figs. 2 and 3 show representative dependencies on the frequency of the ac conductivity and of the permittivity.

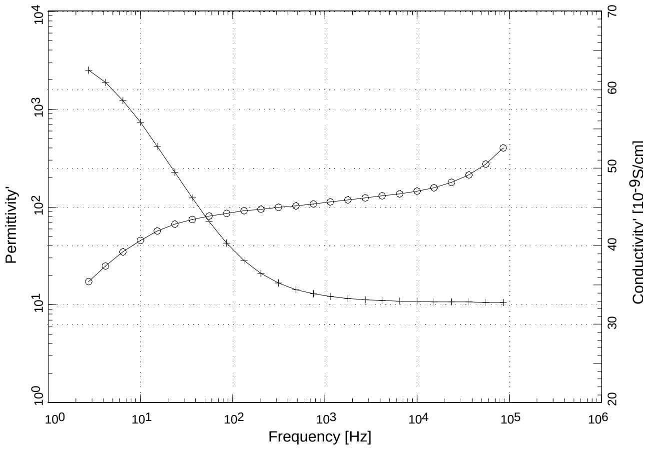

Fig. 2. The electrical conductivity (o) and the permittivity (+) dependence on the frequency, at a temperature of 321.1 K and at U_{cc}=0 dc voltage.

In materials with mobile ions the electrode polarization effects and the ionic conductivity overlap at low frequencies in the spectrum of complex functions $\varepsilon^*(\omega)$, $\sigma^*(\omega)$, $M^*(\omega)$. The ac electrode polarization effect is manifested by increase of the dielectric permittivity, well above the normal values, compared with the bulk at lower frequencies. In this case the effective dielectric constant is derived from the movement and accumulation of ions at the electrode interface region. [20, 21, 22, 23].

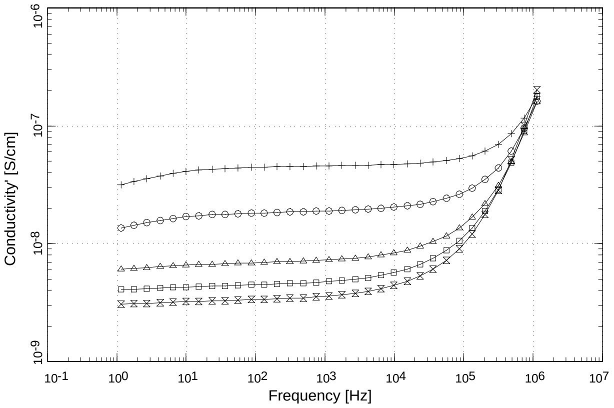

Fig. 3. The electrical conductivity dependence on the frequency, at the temperatures: 321.1 K (+), 318.1 K (O); 315.1 K (Δ), 312.1 K (□), 309.1 K (X). The dc voltage is U_{cc}=0.

The accumulation of charge carriers at the electrode-sample interface leads to a lower conductivity and the redistribution of the local electric field. In the interface region the intensity of the electric field increases and in the volume region the intensity of the electric field decreases. This process occurs dynamically and is specific to the ion electrical charge transport in the ac regime.

3.3. Temperature dependence of the electrical conductivity

Figure 4 shows the increase of the electrical conductivity with increasing temperature, over a certain dc voltage, because of increased concentration of mobile charge carriers or of increased mobility.

The majority of the liquid crystals (LCs) are insulators, with the bulk electrical conductivity obeying the Arrhenius law [24]:

$$\sigma_{dc} = \sigma_{00}(T)\exp\left(-\frac{W_A}{k_B T}\right) \tag{1}$$

with σ_{00} a material-dependent parameter, W_A is the activation energy.

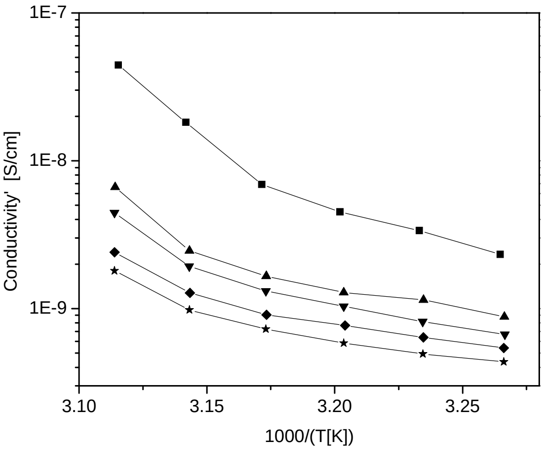

Fig. 4. The electrical conductivity dependence on the temperature, at the dc voltage: U_{cc}= 0 V (■), 5 V (▲), 10 V (▼), 20 V (♦), 36 V (ξ); at the frequency f=133 Hz.

From Fig. 4 one can observe that the conductivity values are far from being situated on a straight line, obeying Arrhenius law. Instead, the dependence of the conductivity on the temperature is curved as expected e.g. in the case of obeying Vogel-Fulcher-Tamman law. In fact, the considered system is a complex one and this complexity can be seen in conductivity behavior as well. Extracting dc conductivity from σ' is not straightforward: in the case of some montmorillonite samples [25] the conductivity expression contains two terms, one due to dc conductivity and the second one due to the power law.

3.4. Electric conductivity dependence on the frequency and dc voltage

High-frequency parts of ac conductivity and permittivity spectra are governed by ion movements in the bulk of the electrolyte, while the low-frequency part is governed by so-called “electrode polarization” effects, as shown in Fig. 5, also a representative one. Since the ions are blocked at the electrode-sample interface, there is an accumulation or a depletion of ions near the electrodes, leading to the formation of space-charge layers. The voltage drops rapidly in these layers, which implies a huge electrical polarization of the material and almost the absence of the electric field in the bulk sample at low frequencies. The build-up of electrical polarization and the drop of the electric field in the bulk are reflected in an increase in the ac permittivity and a decrease in the ac conductivity with decreasing frequency [20-23].

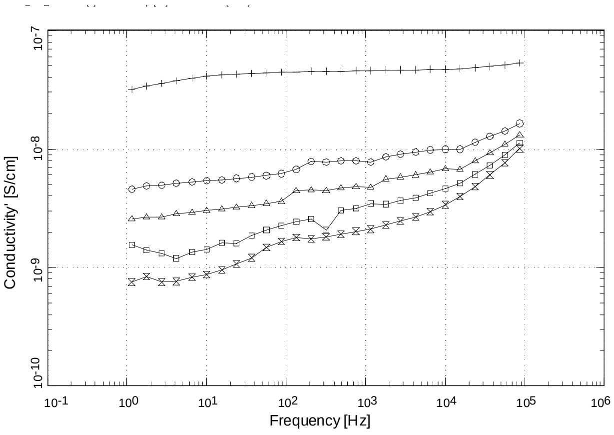

Fig. 5. The electrical conductivity dependence on the frequency, for the dc voltage: U_{cc}= 0 V (+); 5 V (O); 10 V (Δ); 20 V (□); 36 V (X).

The conductivity increases in the high-frequency region (Fig. 5). This can be attributed to the ionic conduction due to complex sample composition.

The conductivity spectra in the low-frequency regime (i.e. below 100 MHz) can be well described by Jonscher type power laws [26,27]:

$$\sigma(\omega) = \sigma_{dc} + K_1 \omega^{1-N} \tag{2}$$

$$\sigma^*(\omega) = \sigma_{dc}\left(1 + \left(i\omega / \omega_p\right)^{1-N}\right) \tag{3}$$

Typically, the exponent N has values in the range $0.1 < N < 0.4$.

dc conductivity σ_{dc} and the characteristic frequency ω_p, are related by the Barton-Nakajima-Namikawa (BNN) equation [28]:

$$\frac{\sigma_{dc}}{\omega_p} = \varepsilon_0 \varepsilon_{R,\infty} \tag{4}$$

Fitting our electrical conductivity curves with the exponent function (type Jonscher power law) we got the N values between 0.14 (at 306.1 K) and 0.035 (at 321.1 K) namely the obtained values fit well the above range.

4. Conclusions

Liquid crystal/copolymer-clay nanostructured samples are materials with ion mobility in which the electrode polarization effects and the ionic conductivity overlap, at low frequencies. The electrode polarization is produced by the space charge region at the electrode-liquid interface. The accumulation of charge carriers at the interface leads to lower conductivity and the redistribution of the local electric field. The electrode polarization occurs specifically in the dc and the ac regime. The ionic conduction is manifested by increasing conductivity at low frequency.

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