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Optical properties of heterogeneous nanosystems based on montmorillonite clay mineral and 5CB nematic liquid crystal

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Abstract

The effect of montmorillonite (MMT) clay modification with surfactant cations on the electrooptical properties of the LC–clay nanocomposites consisting of MMT and 4-pentyl-4′-cyanobiphenyl (5CB) nematic liquid crystal was investigated depending on the composite preparation method. We showed that only composites consisting of MMT modified with organic surfactants (alkylbenzyldimethylammonium chlorides with alkyl chain length C_{14}–C_{18}) display electrooptical memory effect and contrast. Adding a polar additive (acetone) to the mixture during the composite preparation considerably improves the homogeneity of the composites and their electrooptical performance. Using IR and Raman spectroscopy methods it was shown that in the LC-organoclay composites mutual interaction between the components takes place, which results in alignment of the near-surface layers of both organic and inorganic components of the composite. Due to such interaction, these systems display electrooptical contrast and memory effect. The LC–clay composites consisting of organophobic Na-MMT do not display electrooptical effect because of the absence of interaction between the components, which is confirmed by the IR and Raman spectroscopy data.

Keywords: LC–clay nanocomposites; Interface interactions; Electrooptical properties; Montmorillonite; 5CB; IR and Raman spectroscopy

1. Introduction

Nowadays, nanocomposites employing spatially confined liquid crystals are of great interest due to the prospects of their application in optoelectronic devices, photonic crystals, depolarizers, scattering displays, information storage and recording devices, and windows with adjustable transparency [1–5]. It has been shown that in such systems applied external electric field causes switching between the scattering and transparent states, and, under some conditions, these states can be retained after the field switching-off (so called 'memory effect'). For spherical aerosil particles, it has been found [6–8] that essential contribution to the memory effect is achieved due to formation of ordered branched network of the aerosil particles in the liquid crystal matrix. For anisometric particles of a clay mineral (∼1 nm thick lamellas), in addition to the effects of interparticle interaction, an important contribution can be gained from the influence of the clay surface on the alignment of adjacent LC layers, which can be controlled by application of a hydrophobizing organic modifier on the clay mineral [5,9–11].

IR and Raman spectroscopies have proven to be powerful tools for studying of interface interactions between the organic and inorganic components of the heterogeneous nanosystems. For example, authors of [12,13] have used FTIR spectroscopy to show the formation of hydrogen bonds of Si–OH$\cdots\pi$ type between the benzene rings of 5CB molecules and the surface silanol groups of aerosil particles in the heterogeneous system consisting of aerosil and 4-pentyl-4′-cyanobiphenyl (5CB) nematic LC. In similar system consisting of 8CB and aerosil nanoparticles, the authors of [14] have also shown the formation of CN$\cdots$HO–Si hydrogen bonds between the 8CB molecules and surface

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silanol groups of aerosil particles. In the composites consisting of 5CB filled with titanium dioxide (anatase) nanoparticles, the formation of CN···HO–Ti hydrogen bonds has been found [15]. Authors of [16] used FTIR spectroscopy to study the LC heterogeneous system consisting of 5CB confined to the channels of molecular sieves MCM-41. They have shown the formation of hydrogen bonds between the CN groups of the 5CB molecules and the surface OH groups in the channels of MCM. Similar phenomena have also been observed in the composites consisting of porous glasses filled with 5CB liquid crystal [17].

The purpose of the present work was to study the effect of modification of the montmorillonite (MMT) clay mineral with different organic surfactant ions on the electrooptical properties of the MMT+5CB heterogeneous LC–clay nanosystems depending on their preparation methods. In order to reveal the mechanisms leading to different electrooptical behavior of the obtained composites, we applied IR and Raman spectroscopies to investigate the inorganic–organic interface interactions in these hetero-systems at the molecular level.

2. Materials and experimental methods

As the initial clay mineral, we used purified natural MMT from the Askan deposit (Georgia). MMT is a layered aluminosilicate of 2:1 structural type with 'elastic' skeleton belonging to the smectite class. Theoretical formula of montmorillonite is $(OH)_4Si_8Al_4O_{20}\cdot nH_2O$. Na-form of MMT (Na-MMT, sample B1) was synthesized by repeated tenfold treatment of the natural MMT by 1 M NaCl solution at the ratio of liquid and solid phases 10:1, with subsequent washing with distilled water till negative reaction for chloride-ions. According to X-ray diffraction data, in the obtained Na-MMT the basal-plane spacing d_{001} equals to 1.24 nm, its cationic exchange capacity is 97.1 meq/100 g of the clay, and specific surface S_s makes up 580 m^2/g. This form of MMT is known to be organophobic.

In order to increase the chemical affinity of the MMT particles to 5CB molecules, as well as to ensure compatibility and mutual dispersancy of the components, we modified MMT with surfactant ions using interaction of the ion-exchangeable Na-MMT with water solutions of the appropriate salts. As organophilic modifier, we used octadecylbenzyldimethylammonium chloride (OBDM, $[C_{18}H_{37}N(CH_3)_2CH_2C_6H_5]^+Cl^-$, Armour Hess Co., England) with 99.5% purity (sample B2). As a reference material for preparation of the LC–clay composites, we also used Benton-27 (Baroid Division of the National Lead Company, USA), a hectorite clay mineral modified with alkylbenzyldimethylammonium chlorides with the alkyl radicals $C_{14}H_{29}$–$C_{18}H_{37}$ (sample B3).

The heterogeneous system MMT+LC was obtained by mixing the clay mineral (4.5 weight %) with nematic LC 5CB (nematic-to-isotropic phase transition temperature is 308 K) with the use of ultrasonic disperser UZDN-2T. In order to improve compatibility of the two components and to achieve better swelling and structure-forming effect of the organophilic MMT, as well as to achieve more homogeneous distribution of clay particles in 5CB environment, a small amount (not more than 1%) of acetone was added to the mixture.

For electrooptical measurements, the sample of the LC–clay composite was placed between two glass plates, internal surfaces of which were coated with thin electrically conducting indium–tin oxide (ITO) film. The thickness of the sample was controlled with the help of spacers placed between the plates ($d=20\ \mu$). The edges of the cell were hermetically sealed with epoxy glue. In our experiments we used a semiconductor laser APAV ($\lambda=635$ nm); an alternating voltage (U, V) (frequency $f=2$ kHz) applied to the cell varied from 0 to 80 V. We studied the optical transmission (T, %) of the cell as a function of the applied voltage U and evaluated the values of memory parameter M and contrast K using the formulae:

$$M = \frac{T_m - T_o}{T_{sat} - T_o} \times 100\% \quad (1)$$

$$K = \frac{T_{sat}}{T_o} \quad (2)$$

where T_0 is the initial optical transmission, T_m is the residual transmission, T_{sat} is the maximal optical transmission at U_{sat} (saturation voltage). One should note that sufficiently large K value is important for the information display devices.

The IR absorption spectra were measured at room temperature in the 380–4000 cm^{-1} region with Bruker IFS-88 FTIR spectrophotometer with resolution of 1 cm^{-1} and 64 scans for each spectrum. The clay mineral samples for IR measurements were prepared as emulsions in Nujol or Fluorolube. The LC–clay composite samples were flattened between the KBr windows. Raman spectra of powder clay samples and LC–clay composites were registered in the backscattering geometry with the use of FTIR Bruker IFS-88 FRA 106 spectrometer with 1 cm^{-1} resolution. The number of scans was 132. For excitation of the spectra, Nd:YAG laser was used with 1064 nm wavelength and 200 mW output power.

3. Results and discussion

3.1. Electrooptical properties of the composites

In their natural state, smectites are known to be highly hydrophilic, and such feature considerably prevents their mixing and dispersing with hydrophobic organic liquids, including LC. As a result, in the LC–clay composites based on Na-MMT (B1+5CB), we observed fairly instantaneous phase separation of the components, and the structure of