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Langmuir and Langmuir-Blodgett films based on stearic acid, barium stearate and carbon nanotubes

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Langmuir films and Langmuir-Blodgett multilayers based on fatty acid (stearic acid, barium stearate) mixed with carbon nanotubes have been prepared and investigated by isothermal compression (for Langmuir films) and X-ray diffraction (for Langmuir-Blodgett multilayers). An irreversible modification has been observed in the case of Langmuir films doped by carbon nanotubes, due to reordering of the nanotubes in the film matrix.

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Keywords: Langmuir film, Langmuir-Blodgett multilayers, Carbon nanotubes, Stearic acid, Barium stearate

1. Introduction

The carbon nanotubes have been discovered by Iijima in 1991 [1]. After this discovery, a lot of research on the structure and properties of these new nanocarbon objects has been carried out [2-4]. Free-standing films of polymer/nanocarbon composites have been reported [5]. Recently, the investigations have been extended to the understanding of their properties related especially to the modification of the resistivity when the nanotubes are in contact with various organic molecules [6]. From the theoretical point of view, various topological indices for carbon nanotubes have been developed as numerical descriptors, widely used for establishing the relationship between the structure of nanotubes and their physico-chemical properties [7-11]. Theoretical investigation of hydrogen adsorption by carbon nanotube bundles has been done by Ganji and Mousavi [12].

The way was opened toward applications of carbon nanotubes in the detection and measurements of various concentrations of organic and inorganic substances both in liquid or gas phase.

The preparation of barium-stearate and copper-stearate multilayers has been reported in a previous paper [13]. Magnetic particles in multiwall carbon nanotubes have been investigated [14].

In this paper we report the results obtained in the preparation of Langmuir and Langmuir-Blodgett (LB) films based on stearic acid and barium stearate with the addition of carbon nanotubes.

2. Experimental

Ordered layers with various compositions have been prepared by the LB method using the system KSV 5003. The system is provided with double trough and is fully controlled and monitored by a computer. Room temperature depositions have been carried out. The formation prosess of the Langmuir layers in the KSV system with double trough has been studied by the continuous recording of the compression-decompression curves (π-A curves). Various parameters as pH of the substrate solution, the room humidity and room temperature have been monitored. A sequential recording of the data has been introduced. A special computer program has been implemented with the purpose to process the π-A curves.

The carbon nanotubes are from Alpha Aesar. SDB is from Merck, benzene is of p.a. purity, Stearic acid and Barium stearate are from Fluka.

The X-ray diffraction data have been recorded at grazing incidence with a BRUKER D8 ADVANCE diffractometer provided with copper target, scintillation counter, Göbell mirror and Asymmetric Channel-cut (ACC) Ge (220) for getting a parallel monochromatic beam. The measurements were conducted in the following conditions: entry slit 0.6 mm, Soller slits in the diffracted beam, exit slits 0.6 /0.6 mm, angular step 0.025° (2θ), measuring time per step 73 s.

2.1 Preparation of the solutions with nanotubes

The solutions have been prepared in benzene. The substances have been weighted carefully to get various concentrations of nanotubes in the fatty acid matrix. The carbon nanotubes are usually obtained as bunches of individual tubules, sometimes entangled. The main problem is the dispersion of the nanotubes as separate entities. After a series of testings we have found an appropriate dispersion medium for nanotubes the commercial tensioactive sulfonate of dodecyl-benzene (SDB). Thus, new mixture of barium stearate with nanotubes and a small amount of SDB has been prepared. The solution was ultrasonicated for 30 minutes in a sonication bath at 37 kHz. The solution was used in the same day of preparation but after several hours of storage.

2.2 Substrate preparation

Glass substrates have been used for LB deposition.

The substrates were carefully cleaned in isopropylic alcohol mixed with acetone (1:1), in ethylic alcohol and then washed in bidistilled water.

2.3 The samples

The following samples have been prepared:
-Langmuir films based on pure stearic acid;
-Langmuir films based on carbon nanotubes mixed with stearic acid (concentration ratio: 1/10);
-Langmuir-Blodgett multilayers (3-7 layers) based on pure barium stearate;
-Langmuir-Blodgett multilayers (3-7 layers) based on carbon nanotubes mixed with barium stearate (concentration ratio: 1/10).

All the LB multilayers have been prepared on glass substrates.

3. Measurements and results

3.1 The pression-area curves of the Langmuir films

The compression curves have been measured for both types of films (with and without carbon nanotubes). The measurements were made in several runs. Compression up to deposition surface tension was followed immediately by decompression and after reaching the initial point a new compression was started. The recorded curves are shown in Fig. 1 and 2. The compression and decompression was achieved by moving the teflon barrier on the water surface with a speed of 10 mm per minute.

The difference in the behaviour of the Langmuir layers with nanotubes and those without nanotubes consists in the pronounced irreversible effect of hysteresis in the film with nanotubes. We suggest that the nanotubes suffer probably a reordering effect and better implantation into the fatty acid layer. Thus a new stable configuration is reached and this one is preserved for the following compression-decompression runs. This surprising effect could be used in the preparation of films with controlled properties and good stability for chemical and biochemical sensors.

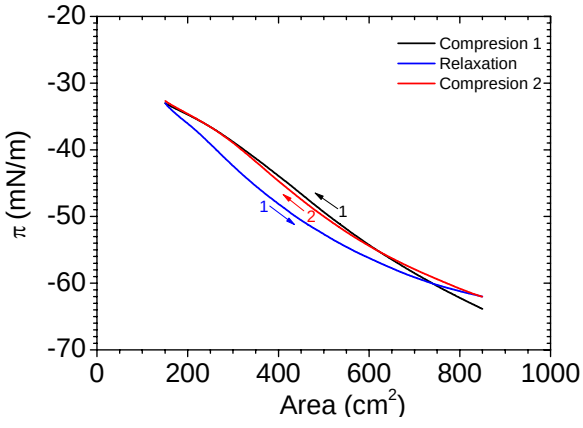

Fig. 1. Pressure-area diagrams for the Langmuir films with barium stearate without carbon nanotubes. Hysteresis phenomenon is clearly observed.

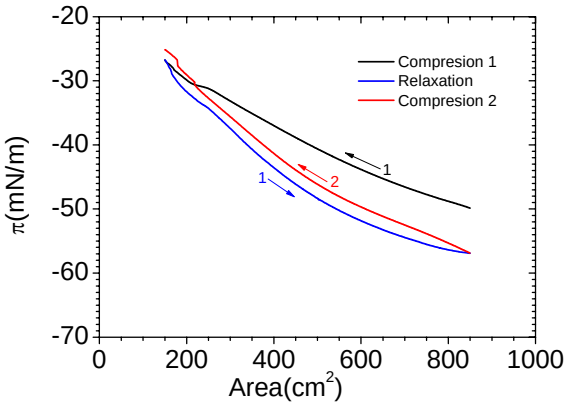

Fig. 2. The pressure-area diagram for the barium stearate film with carbon nanotubes. An irreversible effect is observed during the back and forth runs.

3.2 X-ray diffraction

The X-ray diffraction diagrams (Fig. 3, 4 and 5) of the multilayers exhibit narrow peaks with decreasing intensity as a function of the order of diffraction (I to X). This is a proof for the good ordering of the layers in the multilayer packing. From the position of the diffraction maxima we have calculated the interlayer distance. The result is d=40.569 Å, in good agreement with the data from literature. In the case of the barium stearate multilayers two ordered, crystalline, phases have been observed [15]. The major phase with the packing periodicity of 48.425 Å and a minor phase with the packing periodicity of 40.853 Å.

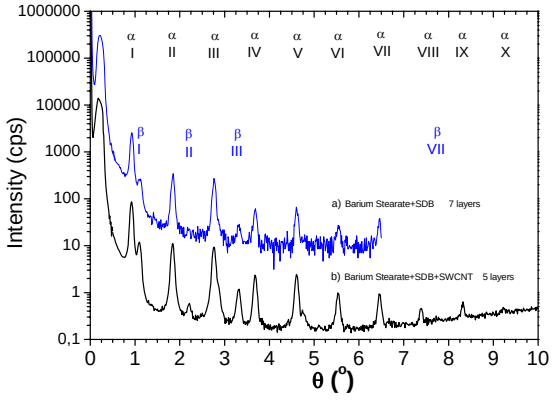

Fig. 3. X-ray diffraction diagram on multilayers deposited on glass a) barium stearate, d^{alfa} = 47.900 Å, d^{beta} = 40.058 Å (7 layers - using 4 ml of the solution: 0.05 g Ba stearate+0.05 g SDB+16 ml benzene) b) barium stearate + functionalized carbon nanotubes, d^{alfa} = 47.982Å, d^{beta} = 40.160 Å (5 layers – using 0.4 ml from the solution: 0.05 g Ba stearate + 0.005 g carbon nanotubes+0.05 g SDB + 16 ml benzene).

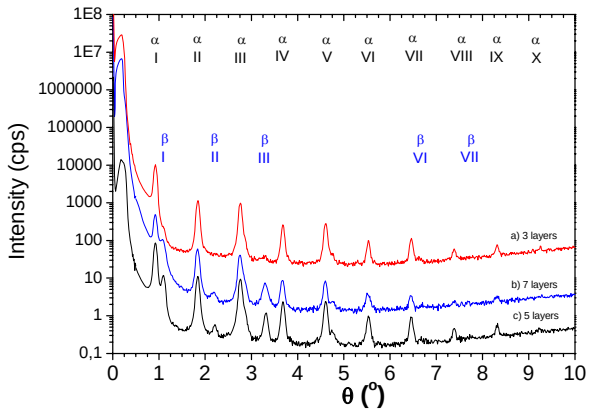

Fig. 4. X-ray diffraction diagram of the LB multilayers of barium stearate+carbon nanotubes a) d^{alfa} = 47.97 Å, d^{beta} = 40.000 Å (3 layers – 0.4 ml solution: 0.05 g Ba stearate + 0.005 g carbon nbanotubes + 0.05 SDB + 16 ml benzene) b) d^{alfa} = 48.272 Å, d^{beta} = 40.562 Å (7 layers – 0.4 ml solution: 0.05 g Ba stearate + 0.005 g carbon nanotubes + 0.05 g SDB + 16 ml benzene) c) d^{alfa} = 47.982 Å, d^{beta} = 40.160 Å (5 layers – 0.4 ml solution: 0.05 g Ba stearate + 0.005 g carbon nanoitubes + 0.05 g (SDB) + 16 ml benzene).

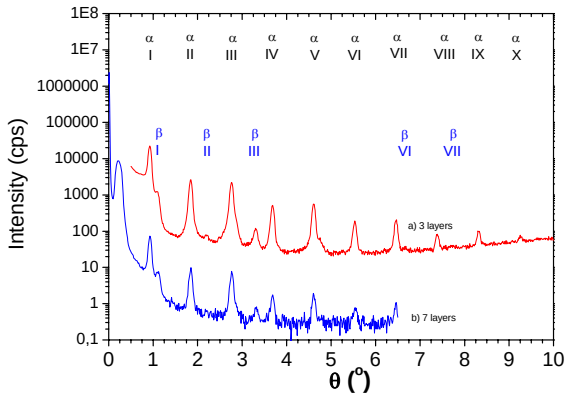

Fig. 5. X-ray diffraction diagram on multilayers deposited on glass substrates: a) barium stearate + SDB, d^{alfa} = 47.900 Å, d^{beta} = 40.058 Å (3 layers - 4 ml solution: 0.05 g Ba stearate + 0.05 g SDB + 16 ml benzene) b) barium stearate + SDB, d^{alfa} = 47.959 Å, d^{beta} = 40.115 Å (7 layers –0.4 ml solution: 0.05 g Ba stearate + 0.005 g carbon nanotubes + 0.05 g SDB + 16 ml benzene).

4. Discussion

Thin ordered films on the water surface have been prepared and investigated. The major finding is related to the influence of the compression-decompression cycles on the ordering of molecules in films. In the case of the simple barium stearate films, the decompresion curve ends very close to the intial point that of the compression startup. It is a significant difference in the case of carbon nanotube-doped layers, where the decompression curve ends at a much lower surface-pressure value than in the case of the simple layers.

This lead us to the suggestion that the carbon nanotubes suffer a process of inclusion in the barium stearate matrix with strong bonds thus ensuring an improved stability of the films. This unusual property may be useful in the development of chemical and biochemical sensors with low aging effect.

Regarding the carbon nanotubes it is remarkable the dispersion effect of SDB. Nevertheles, during preparation, ultrasonication is helpful for getting an advanced dispersion. The research is in progress.The ability of these complex Langmuir-Blodgett films to detect specific gases and pollutants in liquids has been recently tested. The results are rewarding and will be reported in a next paper.

5. Conclusions

Langmuir films based on stearic acid and barium stearate with and without carbon nanbotubes have been prepared in LB trough. During compression-decompression run, the films without carbon nanotubes show a hysteresis effect. The initial state is recovered.

In the case of the films with carbon nanbotubes, we have discovered through repeated compression–decompression runs, an irreversible effect which was attributed to the introduction of the nanotubes in the ordered films followed by strong interaction and very good stability. The stabilization of the films with carbon nanotubes makes the films useful for sensor devices.

Thin ordered multilayers based on barium stearate template with carbon nanotubes have been prepared by a wet method: Langmuir–Blodgett method. The structural properties of the multilayered films have been investigated. No significant differences between the film with nanotubes and that without nanotubes were observed on the X-ray diagrams. This is a proof for a good homogeneity of the films. Further research aims to demonstrate the sensing properties against substances in liquid or gaseous phase.

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