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Highly anisotropic conductivity of tablets pressed from polyaniline-montmorillonite nanocomposite

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ABSTRACT

Polyaniline-montmorillonite nanocomposite was prepared from anilinium sulfate (precursor) and ammonium peroxodisulfate (oxidizing agent) using simple one-step method. The resulting nanocomposite obtained in powder form has been pressed into tablets using various compression pressures (28–400 MPa). Electrical conductivities of tablets in two perpendicular directions, i.e. direction parallel with the main surface of tablet ($\sigma_{=}$) and in orthogonal direction ($\sigma_{\perp}$), and corresponding anisotropy factors (i.e., the ratio $\sigma_{=}/\sigma_{\perp}$) have been studied in dependence on compression pressure used during the preparation. Polyaniline-montmorillonite nanocomposite was characterized using X-ray diffraction analysis, raman spectroscopy, transmission electron microscopy, thermogravimetric analysis and molecular modeling which led to the understanding of the internal structure. Measurement of hardness performed on pressed tablets has been also involved. Taking into account the highest value of anisotropy factor reached ($\sigma_{=}/\sigma_{\perp} = 490$), present study shows a chance to design conductors with nearly two-dimensional conductivity.

1. Introduction

In conducting polymer systems the nanostructure and chains alignment are the crucial factors affecting their properties. Ordering of polymer chains can be achieved by various methods such as mechanical orientation of polyaniline (PANI) chains using blends with insulating polymers, using electric field or high pressure [1–3]. Hybrid PANI/phyllosilicate nanocomposites offer the promising way of PANI chains alignment due to the inclusion of phyllosilicate particles into polymeric matrix and due to the intercalation of polymeric chains into the phyllosilicate layered structure. In addition, the interaction of PANI chains with phyllosilicate structure leads to improved thermal, mechanical and anticorrosive properties [4–6]. Among various phyllosilicates the montmorillonite (MMT) represents the most convenient layered structure suitable as a matrix for conducting polymers because (1) MMT structure is easily expandable (i.e., able to accommodate polymeric chains in the interlayer space) and (2) thanks to a low layer charge of MMT layers the conductivity of PANI chains is not significantly reduced in PANI/MMT nanocomposite.

Dependence of conductivity on pressure for PANI and its derivatives has been investigated by several authors [7–9]. Results obtained in these studies showed that the dependence can be strongly affected by many factors, like acid doping of PANI, the synthesis pathway, and use of PANI derivatives. In spite of many studies focused on conductivity of PANI/phyllosilicate nanocomposites [4–6,10–15], the dependence of conductivity on compression pressure used for the preparation of tablets from these materials has not been studied yet. In present work we investigate how various compression pressures (28–400 MPa) affect the electrical conductivity of tablets prepared from PANI/MMT nanocomposite. Also, the internal structure of PANI/MMT nanocomposite is studied using combination of X-ray diffraction analysis, thermogravimetric analysis, transmission electron microscopy, raman spectroscopy, and molecular modeling. The main aim of our work is reaching very high anisotropy in order to obtain the two-dimensional conductivity.

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2. Experimental

2.1. Preparation of the samples

Aniline, sulfuric acid and ammonium peroxodisulfate were purchased from the Lach-Ner company (Czech Republic) and used as received. Commercially available Na-MMT Portaclay® (The mineral company Ankerpoort NV, Netherland) having structural formula (Si_8) $(Al_{2.85}Mg_{0.71}Ti_{0.02}Fe^{3+}_{0.42})$ O_{20} $(OH)_4$ with layer charge ~0.7 el. per unit cell was used to prepare PANI/MMT composites. Portaclay® is a light gray fine powder having, according to the informations provided by the supplier, relative density 2.6 and pH of 5% solution in water at 20 °C in the range 9,10. Size fraction <40 μm was used during for preparation of the samples. Specific surface area calculated from BET isotherm is 31 $m^2 g^{-1}$.

Pure PANI powder was prepared by oxidative polymerization of the solution of aniline by ammonium peroxodisulfate in acidic environment (sulfuric acid). Time of the polymerization was 60 min (dark green color indicating the formation of emeraldine salt was observed). The green solid was collected on a filter by rinsing with distilled water and dried at 40 °C in a kiln.

PANI/MMT composites were prepared using one-step process. The anilinium sulfate and ammonium peroxodisulfate were added into water suspension of MMT. Polymerization of aniline was completed after 60 min, but the suspension was stirred for 6 h to ensure that the largest possible amount of PANI enters the interlayer space of MMT. The green solid was also collected on a filter by rinsing with distilled water and dried at the same conditions as pure PANI.

Prepared PANI and PANI/MMT powders (3 g of powder for each tablet) were pressed into square tablets using ZWICK 1494 press (applied pressures 28, 50, 100, 200, 300, and 400 MPa) at room temperature, without any lubrication and binder. Parameters of the controlled pressing were as follows. Loading speed was 1.0 $mm \cdot min^{-1}$ and using final pressure the sample was compacted for 10 min. Unloading speed was 0.1 $mm \cdot min^{-1}$. Size of each square tablet was 28 × 28 mm.

2.2. Characterization methods

2.2.1. X-ray powder diffraction

X-ray diffraction (XRD) measurements have been carried out in order to characterize the degree of preferred orientation of MMT flat particles in PANI/MMT nanocomposite samples. The XRD patterns were recorded under CoKα irradiation (λ = 1.789 Å) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a VÅNTEC 1 detector.

2.2.2. Transmission electron microscopy

PANI and PANI/MMT samples in powder form were dispersed in water and ultrasonicated for 5 min. One drop from each dispersion was placed on the Cu mesh covered by carbon membrane and both samples were dried at room temperature. The morphology of samples was observed on a a transmission electron microscope (TEM) JEOL 2010HC (JEOL Ltd. Japan). Accelerating voltage was 160 kV.

2.2.3. Thermogravimetry analysis

Simultaneous thermogravimeter-differential scanning calorimeter (TG–DSC) STA 409 EP (Netzsch) equipped with a high-sensitive analytical balance was used for measuring the mass change of the samples (30 mg in weight) as a function of time or temperature. The sample carrier system contains the type S thermocouples (Pt 10% Rh-Pt) to measure the temperature and the temperature difference. All samples were heated up to 1000 °C in the crucibles (α-Al_2O_3) in a dynamic atmosphere of dry air with a flow rate of 100 $cm^3 \cdot min^{-1}$. Heating rate was 10 °C·min^{-1}.

2.2.4. Hardness measurement

To compare mechanical properties of PANI and PANI/MMT composites the indentation hardness (HIT) was measured using Zwick ZHU 2.5, whereas 5 mm steel ball was used as an indentor.

2.2.5. DC conductivity measurement

Special measuring cell was constructed for measurement of DC conductivity (see Supplementary material, Fig. S1a). Attached DC voltage source (DC POWER SUPPLY HY 3003 D-2) was stabilized with a tolerance of 10^{-3} (i.e. the precision was 2.000 ± 0.001 V) and annexed with the endurance of several tens of seconds to min. Great attention was paid to fix the contact area of the sample with flat Cu electrodes. These electrodes were polished before each measurement using a special abrasive paste. Electric current passing through the sample has been measured in two perpendicular directions, in the tablet plane and in orthogonal direction to the tablet plane (see Supplementary material, Fig. S1b), and the mean value of electric current was used to calculate the conductivity. Multimeter AGILENT 34401A and V-meter UNI-T UT802 were used for the calibration. All parameters necessary for the measurement were specified and controlled using computer equipped with PCI-6221 board. Data were registered and processed in the homemade software prepared in labview environment.

2.2.6. Molecular modeling

Molecular modeling was carried out in materials studio modeling environment (MS). The MMT crystal structure was built using the structure data published by Méring and Oberlin [16] and Tsipursky and Drits [17]. The model of MMT substrate was built under periodic boundary conditions as a supercell with the formula $(Al_{46}Mg_{16}Fe^{3+}_{10})$ (Si_{144}) O_{360} $(OH)_{72}$ and with the total negative layer charge −16 el. This charge, arising from the substitutions in octahedra, was compensated by Na^+ cations and/or PANI chains (prepared as dimers with charge +4 el.) in the interlayer space. Set of initial models with five different Na^+/PANI ratios (8/0, 6/1, 4/2, 2/3, 0/4) and various numbers of water molecules was prepared. Atomic charges in MMT structure were assigned using the charge equilibration (QEq) method allowing prediction of charge distributions based on atomic ionization potentials, electron affinities and atomic radii [18] while for charges of PANI and water molecules the Gasteiger method was

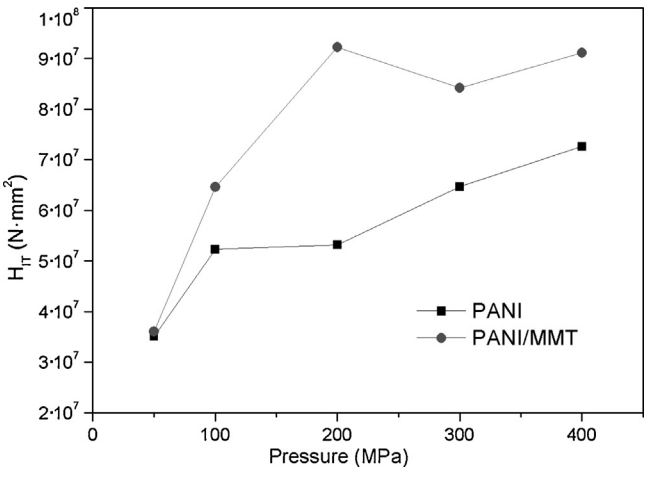

Fig. 1. Comparison of hardness in dependence on pressure used for the preparation of PANI and PANI/MMT tablets.