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 ($\sigma_{\parallel}$) and in orthogonal direction ($\sigma_{\perp}$), and corresponding anisotropy factors (i.e., the ratio $\sigma_{\parallel}/\sigma_{\perp}$) 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 ($\sigma_{\parallel}/\sigma_{\perp} = 490$), present study shows a chance to design conductors with nearly two-dimensional conductivity.

Keywords: composites, layered compounds, chemical synthesis, high pressure, electrical properties

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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/phyllsilicate nanocomposites offer the promising way of PANI chains alignment due to the inclusion of phyllsilicate particles into polymeric matrix and due to the intercalation of polymeric chains into the phyllsilicate layered structure. In addition, the interaction of PANI chains with phyllsilicate structure leads to improved thermal, mechanical and anticorrosive properties [4-6]. Among various phyllsilicates 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/phyllsilicate 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.

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 $(\text{Si}_8)(\text{Al}_{2.85}\text{Mg}_{0.71}\text{Ti}_{0.02}\text{Fe}^{3+}_{0.42})\text{O}_{20}(\text{OH})_4$ 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 $< 40 \mu\text{m}$ was used during for preparation of the samples. Specific surface area calculated from BET isotherm is $31 \text{ m}^2 \cdot \text{g}^{-1}$.

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 minutes (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 minutes, but the suspension was stirred for 6 hours 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 $1.0 \text{ mm} \cdot \text{min}^{-1}$ and using final pressure the sample was compacted for 10 minutes. Unloading speed was $0.1 \text{ mm} \cdot \text{min}^{-1}$. Size of each square tablet was $28 \times 28 \text{ mm}$.

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 $\text{CoK}\alpha$ irradiation ($\lambda = 1.789 \text{ \AA}$) using the Bruker D8 Advance diffractometer (Bruker AXS) equipped with a VANTEC 1 detector.

2.2.2 Transmission electron microscopy

PANI and PANI/MMT samples in powder form were dispersed in water and ultrasonicated for 5 minutes. 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 transmission electron microscope (TEM) JEOL 2010 HC (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 (Pt10%Rh-Pt) to measure the temperature and the temperature difference. All samples were heated up to 1000 °C in the crucibles (α -Al₂O₃) in a dynamic atmosphere of dry air with a flow rate of 100 cm³·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 indenter.

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 minutes. 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 (Al₄₆ Mg₁₆ Fe³⁺₁₀) (Si₁₄₄) O₃₆₀ (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 used [19]. All models have been optimized using Universal force field able to parameterize atoms both in organic (PANI) and inorganic (MMT) part of the structure [20]. A Smart algorithm was used for the geometry optimization with 500 000 iteration steps. Interlayer distance for each model optimized in MS/Forcite module has been calculated using MS/Reflex module under the same conditions as in the experiment (i.e., 2θ range: 5-50°; $\text{Co}_{\text{K}\alpha}$ irradiation ($\lambda = 1.78897 \text{ \AA}$), Bragg-Brentano geometry) and compared with experimental data in order to find the most probable interlayer structure.

3. Results and discussion

3.1. Thickness, dimensional stability, homogeneity and hardness of tablets

In dependence on applied pressures, i.e., 28, 50, 100, 200, 300, and 400 MPa, various thicknesses of tablets (d_0) were obtained (see Supplementary material, Table S1). With respect to the portion of powders (3 g for each tablet) and densities of PANI ($1.46 \text{ g}\cdot\text{cm}^{-3}$) and PANI/MMT ($1.99 \text{ g}\cdot\text{cm}^{-3}$) measured by He pycnometer, theoretical thicknesses should be 2.6 mm and 1.9 mm, respectively. Table S1 shows that this values have not been reached even at a pressure of 400 MPa. However, the thicknesses d_0 measured immediately after the compaction ($d_0(\text{PANI}) = 2.708 \text{ mm}$, $d_0(\text{PANI/MMT}) = 2.039 \text{ mm}$) are very close to these values. Thicknesses were further measured after 40 days (see values d_{40} in Table S1) in order to estimate the dimensional stability of tablets.

It is evident that PANI/MMT tablets have higher dimensional stability than PANI tablets for pressures 28-200 MPa. Significant expansion of PANI/MMT tablets (i.e. higher Δd values) can be observed only when the pressure is 300 and 400 MPa.

Lengths of edges ($a_0 = 28 \text{ mm}$) did not change significantly during 40 days. Differences Δa were of order of $1 \cdot 10^{-2} \%$ for all tablets.

In order to find whether the PANI and MMT are homogeneously distributed in pressed PANI/MMT tablets, simple experiment was performed. Each PANI/MMT tablet was broken into 10 pieces, these pieces were weighted, calcined at 1000 °C for 3 h, and, finally, the weight loss (WL) of each piece of each tablet was measured. No significant differences

between WL of pieces were found for each tablet and this fact suggests that PANI/MMT tablets can be considered homogeneous. For illustration, the WL values for ten pieces of tablet compressed by pressure of 28 MPa are provided (see Supplementary material, Table S2). Although the WL is slightly higher for smaller pieces with lower weights, all WL values are very similar. The average WL value $\sim 42\%$ was obtained for all PANI/MMT tablets. Comparison of hardness of PANI tablets and PANI/MMT tablets is shown in Fig. 1 and clearly demonstrates the increased hardness of PANI/MMT composite. Taking into account that indenter can meet either PANI or MMT particle, the hardness was measured repeatedly at 10 different points on the surface and the average values are presented.

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

3.2 Structure analysis

Visual observations of powder materials were carried out using TEM. It can be clearly seen that pure PANI powder (Fig. 2a) is composed from a rod-shaped grains. Length and diameter of grains is about 200 nm and 50 nm, respectively. Such shaped grains tend to arrange parallel to one another under external pressure. The total volume of powder is thus reduced and this seems to be the reason of the significant decrease in thickness of the pure PANI tablets pressed at high pressures (see Supplementary material, Table S1). Fig. 2b shows that PANI/MMT powder is much more dense than pure PANI powder. MMT layers can be clearly distinguished as a dark elongated bodies bounded and surrounded by PANI.

Fig. 2. TEM images of (a) pure PANI, and (b) PANI/MMT powders. MMT particles can be distinguished as a dark elongated bodies.

XRD pattern of PANI tablets showed the typical diffractogram of amorphous polymeric samples, keeping the same profile for the whole pressure range 28-400 MPa (see Supplementary material, Fig. S2). One can see that the diffraction patterns are very noisy and all peaks are quite broad. On the other hand, the XRD pattern of PANI/MMT composite tablets exhibits the strong texture (Fig. 3), i.e. the strong preferred orientation of platy MMT particles with their basal plane 001 parallel to the main surface of tablet (see Supplementary material, Fig. S3). Increasing preferred orientation of MMT particles in dependence on increasing pressure in composite samples manifests itself with increasing intensity of 001 diffraction line for MMT (Fig. 3).

Fig. 3. X-ray diffraction profile of 001 basal reflection of MMT in PANI/MMT composite, illustrating the increase of peak intensity due to increase of preferred orientation of MMT particles with increasing pressure.

Moreover, as one can see in Fig. 3, the preferred orientation of MMT particles reached maximum at 300 MPa and increase in pressure does not lead to higher degree of orientation. Diffraction analysis of 001 peak position also showed the following increase of the MMT interlayer distance in PANI/MMT composite. While the pristine MMT has the interlayer distance 1.245 nm, in tablets pressed from PANI/MMT composite the interlayer distances in MMT are ~ 1.295 nm.

For PANI/MMT composites, the expansion of MMT interlayer distance is considered as an evidence of intercalation of PANI by many authors [4,5,13,21,22]. In our study, molecular modeling was used to support the results of XRD analysis. Results of the modeling showed that the value $d_{001} = 1.295$ nm may correspond not only to various amount of PANI chains in the MMT interlayer space but also to the MMT interlayer space without PANI if containing ~ 13.4 wt.% of water (Fig. 4).

Fig. 4. Dependencies of amount of water and PANI in the MMT interlayer space on the d_{001} values as calculated from the optimized models. Real sample (2.4 wt.% of water; $d_{001} = 1.295$ nm) is displayed as the bold cross.

However, TG/DTA of PANI/MMT sample (Fig. 5) revealed that the amount of water in the MMT interlayer space is ~ 2.4 wt.%. This value helped us to eliminate all implausible models. Taking into account all known experimental data (i.e. d_{001} value and amount of interlayer water) and molecular modeling results (Fig. 4) the situation in the real PANI/MMT sample seems to be an average of model having $d_{001} = 1.296$ nm and containing two PANI chains (i.e. 9.4 wt.% of PANI) and 38 water molecules (i.e. 4.4 wt.% of H₂O) and model $d_{001} = 1.294$ nm and containing three PANI chains (i.e. 14.1 wt.% of PANI) and 5 water molecules (i.e. 0.6

wt.% of H₂O). Therefore, content of the interlayer space in real PANI/MMT sample can be estimated at 2.5 wt.% of water and 11.7 wt.% of PANI. Molecular modeling also showed that Na⁺ ions in the MMT interlayer space are not fully exchanged by PANI chains. Taking into account that ideally 2.5 PANI chains are present in the MMT interlayer space, only ~ 40 % of Na⁺ ions were exchanged.

Fig. 5. Thermal analysis of (a) pure MMT and (b) PANI/MMT samples.

Amount of PANI chains in the interlayer space, calculated from optimized models, can be compared with results of TG/DTA (Fig. 5b). While temperatures up to 200 °C results in the loss of adsorbed water (endothermic process with maximum at 94.5 °C and weight loss 6.4 wt.%), exothermic process with maximum at 459.1 °C and weight loss 28.98 wt.% is observed in the range 200-650 °C. This process can be attributed to the gasification of organic matter. The expected amount of PANI in the MMT interlayer space (i.e., 11.7 wt.%,

calculated from models) suggests that approximately two-fifths of the total amount of PANI in the PANI/MMT composite are intercalated into MMT.

The sum of the weight losses measured by TG/DTA is 39.4 wt.%. This value agrees well with the weight loss determined after calcination of tablets during the test of homogeneity (see Supplementary material, Table S2).

In addition, there is one more fact proving, at least indirectly, the presence of PANI in the MMT interlayer space. Temperature maximum of loss of hydroxyl groups for MMT (Fig. 5a) and PANI/MMT (Fig. 5b) is 679.4 °C and 710.2 °C, respectively. Higher temperature observed in case of PANI/MMT sample suggests the presence of barrier, missing in pristine MMT, that prevents the constitutional water to leave the MMT interlayer space. This barrier are very probably the remnants of PANI chains and products of the gasification.

3.3. DC conductivity of pressed tablets

Results of conductivity measurements are summarized in the Table 1, where we compare the conductivity of PANI and PANI/MMT tablets in two directions: $\sigma_{\parallel}$ is the in-plane conductivity in direction parallel to the main surface of tablet and $\sigma_{\perp}$ is the conductivity in orthogonal direction, i.e., in the direction of pressure (see Supplementary material, Fig. S1b). Anisotropy factor α , defined as the $\sigma_{\parallel}/\sigma_{\perp}$ ratio, describes the degree of anisotropy of conductivity and, therefore, the tendency to the two-dimensional conductivity.

Table 1

Conductivities and anisotropy factors in dependence on pressure used for the preparation of tablets.

pressure (MPa)	PANI tablets			PANI/MMT tablets		
	$\sigma_{\parallel}$ (S/m)	$\sigma_{\perp}$ (S/m)	anisotropy $\alpha = \sigma_{\parallel}/\sigma_{\perp}$	$\sigma_{\parallel}$ (S/m)	$\sigma_{\perp}$ (S/m)	anisotropy $\alpha = \sigma_{\parallel}/\sigma_{\perp}$
28	0.69	0.10	7	0.49	0.001	490
50	4.67	0.18	26	0.07	$<10^{-3}$	-
100	3.40	0.04	80	0.09	$<10^{-3}$	-
200	2.13	0.03	63	0.04	$<10^{-3}$	-
300	1.04	0.02	52	0.04	$<10^{-3}$	-
400	3.50	0.01	350	0.03	$<10^{-4}$	-

Comparing values for PANI and PANI/MMT one can see a different course of conductivity with increasing pressure. In case of PANI, the in-plane conductivity $\sigma_{\parallel}$ exhibits maximum for tablets pressed at 50 MPa, while for PANI/MMT the in-plane conductivity decreased with increasing pressure. Electrical anisotropy observed in case of PANI tablets is caused by the shape of PANI grains. The grains are elongated as revealed by TEM (see Fig. 2a) and it can be expected that the texture formed during preparation of tablets will also be reflected in the electrical properties. Anisotropy of PANI/MMT tablets confirms the preferred orientation of MMT(001) planes parallel to the main surface of tablet. In the direction perpendicular to the surface the silicate layers form a barrier reducing the flow of current, i.e. the MMT serves as an insulator in this direction (see Supplementary material, Fig. S3, for the illustration). In case of PANI/MMT tablets, the $\sigma_{\perp}$ values for pressure ≥ 50 MPa are lower than $1 \cdot 10^{-3}$ S/m and, therefore, affected by measurement errors. Consequently, the α values were not calculated. Anyway, the anisotropy of PANI/MMT tablet pressed at 28 MPa is very high ($\alpha = 489$) and for other tablets the α values also in the order of hundreds can be estimated. It can be concluded that in order to achieve a significant anisotropy of electrical conductivity the compression pressure higher than 28 MPa is not required.

4. Conclusions

PANI/MMT composite is an interesting conductive material which can be prepared from widely used and cheap precursors. Tablets pressed from PANI/MMT powder composite exhibit higher hardness and lower conductivity than PANI within the range 28-400 MPa. In spite of this lower conductivity, the anisotropy factor is very high and, therefore, PANI/MMT tablets offer a chance to design two-dimensional conductors. Taking into account the similarity of the conductivities obtained for PANI/MMT tablets prepared at pressures of 50 to 400 MPa, we can conclude that nearly two-dimensional conductors can be prepared without use of extremely high pressure.

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Supplementary material

Fig. S1. (a) Experimental apparatus for electrical measurement. A) sample (tablet); B) Cu-electrodes; C) flexible insulator; D) weights to ensure a constant load; E) soft underlay; F) measuring card; G) DC voltage source; H) PC + software. (b) Two directions of conductivity measurements. Tablets were pressed in the direction parallel to $\sigma_{\perp}$.

Fig. S2. X-ray diffraction patterns of PANI tablets pressed at 28-400 MPa.

Fig. S3. Schematic illustration of preferred orientation of platy silicate particles in PANI/MMT pressed tablets. The degree of orientation depends of pressure.

Table S1

Thicknesses of PANI and PANI/MMT tablets measured after preparation (d_0) and after 40 days (d_{40}). The difference value (Δd) is given as a percentage.

	PANI			PANI-MMT		
pressure (MPa)	d_0 (mm)	d_{40} (mm)	Δd (%)	d_0 (mm)	d_{40} (mm)	Δd (%)
28	4.304	4.422	2.74	2.876	2.883	0.24
50	4.272	4.358	2.01	2.806	2.814	0.29
100	3.228	3.301	2.26	2.361	2.364	0.13
200	2.865	2.899	1.19	2.203	2.207	0.18
300	2.727	2.777	1.83	2.087	2.126	1.87
400	2.708	2.792	3.10	2.039	2.126	4.27

Table S2

Weights of pieces of PANI/MMT tablet (compressed by pressure 28 MPa) before (m_{dry}) and after ($m_{\text{calc.}}$) calcination. WL – weight loss.

piece No.	m_{dry} (g)	$m_{\text{calc.}}$ (g)	WL (%)
1	0.656	0.385	41.33
2	0.476	0.279	41.40
3	0.359	0.210	41.37
4	0.355	0.209	41.22
5	0.274	0.160	41.72
6	0.252	0.147	41.56
7	0.229	0.132	42.39
8	0.216	0.126	41.61
9	0.083	0.048	42.33
10	0.070	0.040	42.53