

ORIGINAL PAPER

TEXTURE AND ELECTRICAL CONDUCTIVITY OF PELLETS PRESSED FROM PANI
AND PANI/MONTMORILLONITE INTERCALATE

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ABSTRACT

Polyaniline/montmorillonite (PANI/MMT) intercalate pressed into pellets using the pressure 28 MPa has been prepared in order to achieve two-dimensional conductivity which is close to pure PANI, however with improved mechanical and thermal stability (due to the presence of silicate). Structure-conductivity relationship has been investigated using X-ray diffraction analysis and diffraction patterns obtained from two perpendicular planes revealed the strong texture. The structural anisotropy led to the anisotropy in conductivity, which is much stronger for PANI/MMT than for pure PANI pellets. Anyway, the in-plane conductivity is of the same order for both PANI/MMT and pure PANI pellets. The anisotropy factor, that means the ratio of in-plane conductivity and conductivity in the direction perpendicular to the pellet plane, was 328 (PANI/MMT pellet) and 6.7 (pure PANI pellet), respectively.

KEYWORDS: clay; composite; conducting polymer; structure-property relations; synthesis and processing

1. INTRODUCTION

Hybrid nanocomposite materials based on conducting organic polymers are of interest in a wide range of applications in many fields, such as electrochromism, electroluminescence, sensors and energy storage systems (for review see for example (Lira-Cantú and Gómez-Romero, 2009)). In conducting polymer systems, chains alignment plays a key role (Cromack et al., 1991; Ou et al., 2003; Quadrat et al., 1998; Špírková et al., 1999; Costolo and Heeger, 2000; Wu et al., 2010; Adams et al., 1996; Cao et al., 1993; Shariki et al., 2011; Stejskal et al., 1997). Ordering of polymer chains can be achieved by various methods such as: mechanical orientation of polyaniline (PANI) films (Adams et al., 1996) using blends with insulating polymers (Cao et al., 1993; Shariki et al., 2011), ordering of PANI particles in monomer mixture in an electric field (Stejskal et al., 1997) or by using high pressure (Prokeš et al., 2011). Hybrid nanocomposites: PANI/phyllsilicate (Wu et al., 2000; Duran et al., 2009; Yoshimoto et al., 2004; Bekri-Abbes and Srasra, 2010) or PANI/ graphite (Wu et al., 2010) offer another way of PANI chains ordering due to the

inclusion of platy particles of layered inorganic structures into polymeric matrix. In addition the interplay of PANI chains with inorganic materials can result in improved properties of nanocomposite, such as thermal and mechanical stability (Duran et al., 2009) or photovoltaic properties (Cuentas-Gallegos et al., 2005), etc. (for review see (Lira-Cantú and Gómez-Romero, 2009)).

Thanks to unique properties, clay minerals (phyllsilicates) have been widely employed as matrix for organo-inorganic composite materials (Lagaly et al., 2006; Ogawa and Kuroda, 1995; Lerf and Čapková, 2003). Layered structure of phyllsilicates offers a chance to intercalate the organic guest species including polymer chains into the interlayer space and to create high degree of structure ordering. In addition, the interaction of guest species with negatively charged layers of phyllsilicates can lead to new properties of these hybrid structures (Simha Martynková et al., 2007; Klika et al., 2007; Klika et al., 2009). Intercalation of conducting polymers into layered structure of phyllsilicates is expected to lead to nanocomposites with high degree of polymer ordering and with enhanced thermal and mechanical

stability and gas barrier properties compared to pristine polymers (Alexander and Dubois, 2000).

Phyllosilicates, as well as all layered crystal structures, exhibit platy crystallites. Intercalation and surface modification preserves the plate-like shape of modified clay particles, which tend to preferred orientation of powder particles even by free filling of measuring cells without any pressure. Preparing pellets using pressure will lead to texture in nanocomposite structure, which is expected to dramatically affect electrical characteristics. Although the design of functional units based on these nanocomposites has to take into account this effect of texture, only few works focused on this topic can be found (Hutchison et al., 1996; Semakov et al., 2010). In the majority of articles dealing with PANI/phyllosilicate composites (and including measuring of pressed pellets conductivities) the anisotropy is not discussed. Applied pressure – conductivity or PANI content – conductivity relationships are commonly presented but authors do not pay an attention to the conductivities of pellets in different directions (Prokeš et al., 2011; Wu et al., 2000; Kazim et al., 2012; Oyharcabal et al., 2012; Bober et al., 2010; Do Nascimento et al., 2006).

In the present work, montmorillonite (MMT) as a typical representative of smectite group of phyllosilicates has been chosen as a matrix for intercalation of conducting PANI. MMT exhibits relatively small layer charge and easy expansion of interlayer space and consequently easy intercalation of large guest molecules. Present work is focused on the texture – electrical conductivity relationship, using X-ray diffraction analysis of texture together with directional conductivity measurements. Directional analysis of structure and conductivity was carried out for pressed pellets from pure PANI and PANI/MMT intercalate.

2. MATERIALS AND METHODS

2.1. MATERIALS

Na-MMT Portaclay® (The mineral company Ankerpoort NV, Netherland) with basal spacing 1.24 nm was used in this study. Aniline, sulfuric acid and ammonium peroxydisulfate were purchased from Lach-Ner, Czech Republic, and used as received.

2.2. SAMPLE PREPARATION

PANI powder was prepared using simple oxidative chemical polymerization of the solution of aniline in concentrated sulfuric acid by strong oxidizing agent at room temperature. The method is based on the mixing of two solutions: a) aniline solution in sulfuric acid (0.5 M) which serves as cationic source, and b) solution of ammonium peroxydisulfate (0.2 M) in distilled water which serves as an oxidizing agent. After the mixing of both solutions the polymerization of the aniline proceeds. This was signaled by the dark green colour of the

reaction mixture. The time of the polymerization was 40 minutes. The green solids were collected on a filter by rinsing with distilled water and subsequently dried at 40 °C in a kiln.

PANI/MMT powder has been prepared using simple one-step process by the oxidative polymerization of anilinium sulfate with ammonium peroxydisulfate in aqueous suspension of MMT at room temperature. The MMT was suspended in freshly prepared aqueous reaction mixture containing aniline solution in sulfuric acid and 0.2 dm³ solution of ammonium peroxydisulfate. The polymerization of aniline was completed within 40 minutes and the suspension was stirred still for 6 hours. The green solids were collected on a filter by rinsing with distilled water and subsequently dried at 40 °C in a kiln. Prepared PANI/MMT samples contained ~ 56 wt.% of PANI. During this one-step process the PANI chains were intercalated into the interlayer space of MMT structure. In the interlayer space of the pristine MMT, Na⁺ cations have been exchanged for cationic PANI chains. This process led to the increase of the basal spacing from 1.24 nm to 1.31 nm (see further in section 3.1 *Structure analysis and texture characterization*).

Pressed pellets of pure PANI and PANI/MMT composite were prepared using LECO handpress (applied pressure 28 MPa) at room temperature, without any lubrication and without any binder. Portion of each powder sample before pressing was 3.0 g. Pellets diameter was 32 mm but thicknesses of pellets were not the same – 2.7 mm for PANI/MMT and 4.2 mm for pure PANI – due to the different densities and compressibilities of PANI/MMT nanocomposite and pure PANI. The duration of pressing for each pellet was measured by stopwatch and recorded.

2.3. X-RAY DIFFRACTION ANALYSIS

The X-ray diffraction patterns were recorded using Bruker D8 Advance diffractometer (Bruker AXS, Germany) equipped with fast position sensitive detector VANTEC 1, with CoK_α irradiation ($\lambda = 0.1789$ nm). All measurements were carried out in reflection mode in symmetrical Bragg-Brentano arrangement. In order to analyze the texture in pressed pellets, diffraction patterns have been recorded for two positions of pellets with respect to the diffraction plane (diffraction plane is defined by the incident and diffracted beam). For that purpose the pellets have been cut and the cutting plane has been carefully treated with brush before the diffraction measurements. X-ray diffraction patterns were recorded from pellet surface and cutting plane, respectively. Diffraction geometry is illustrated in Figure 1. In the first position, the pellet surface is perpendicular to the diffraction plane (i.e. normal to the surface of pellet lies in the diffraction plane; see Fig. 1a). In the second position the pellet surface is parallel to the diffraction plane and, therefore, the

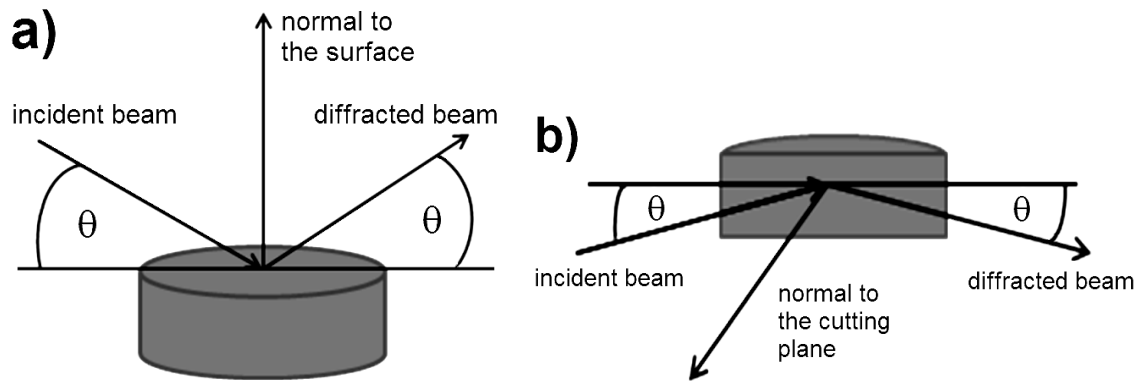


Fig. 1 Illustration of diffraction geometry for texture (preferred orientation) investigation in pellets.

cutting plane is perpendicular to the diffraction plane (i.e. normal to the cutting plane lies in the diffraction plane; see Fig. 1b).

2.4. CONDUCTIVITY MEASUREMENTS

Conductivity measurements have been carried out in three mutually perpendicular directions: (1) perpendicular to the pellet plane, i.e. in the direction of pressing (denoted as σ_{\perp}) and (2) in the pellet plane, i.e. perpendicularly to the direction of pressing (denoted as $\sigma_{\parallel 1}$ and $\sigma_{\parallel 2}$). Last two values were averaged and the resulting value is denoted as $\sigma_{\parallel av}$. For the schematic illustration of conductivity measurements see Figure 2. Two-point flat probe method has been used for DC conductivity measurements with contact Cu electrodes, where the special shape of curved surface of Cu electrodes has been designed for measurements in the direction perpendicular to the direction of pressing while the flat round Cu electrodes were used for the measurement in the direction of pressing. Measuring instruments: DC POWER SUPPLY HY 3003 D-2, Programmable DC POWER SUPPLY BK PRECISION 9120, multimeter AGILENT 34401A, V-meter UNI-T UT802, pA-meter KEITHLEY 6487.

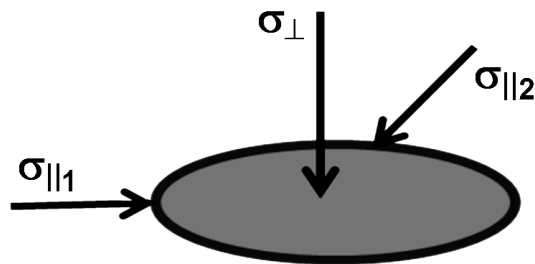


Fig. 2 Schematic illustration of conductivity measurements in three perpendicular directions.

3. RESULTS AND DISCUSSION

3.1. STRUCTURE ANALYSIS AND TEXTURE CHARACTERIZATION

As one can see in Figure 3, the platy silicate particles in pellets are preferentially oriented with their 001 plane parallel to the flat pellet surface. Consequently, in the diffraction arrangement displayed in Figure 1a we can record preferentially the diffraction lines from $00l$ basal plane of MMT. Corresponding pattern is in Figure 3a. The asymmetric broaden peaks at $2\theta \sim 23^\circ$, 31° and 41° correspond to hk - bands typical for smectites. The diffraction pattern from the cutting plane (in the arrangement displayed in Fig. 1b) is in Figure 3b. Comparing diffractions patterns in Figures 3a and 3b, respectively, one can see in Figure 3b the strong decrease of basal reflection with respect to hk - bands in case of diffraction on cutting plane, which means the presence of strong texture in the pellets.

Analysis of X-ray diffraction patterns (see Figs. 3a and 3b) revealed following important structural features of PANI/MMT pellets.

1. Strong preferred orientation in the sample – texture type $00l$. Typical attributes of this texture are: strong intensity for $00l$ reflection at $2\theta = 6.5^\circ$ in comparing with the intensity of hk - band characterizing the periodicity in silicate layer planes at $2\theta \sim 23^\circ$ for diffraction arrangement in Figure 1a. On the other hand by diffraction arrangement displayed in Figure 1b we can observe dramatic change of $00l/hk$ band intensity ratio (compare Fig. 3b with Fig. 3a).
2. First basal reflection $00l$ at $2\theta \sim 6.5^\circ$ corresponds to the basal spacing 1.31 nm, what indicates the change of interlayer structure of pristine MMT after one step composite preparation. The relatively sharp $00l$ profile in comparison with other PANI/clay intercalates (see for example (Kulhánková et al., 2012)) indicates that MMT was fully intercalated by PANI chains. Intercalation of PANI has significant effect on the in-plane conductivity of pellets, as will be discussed further.

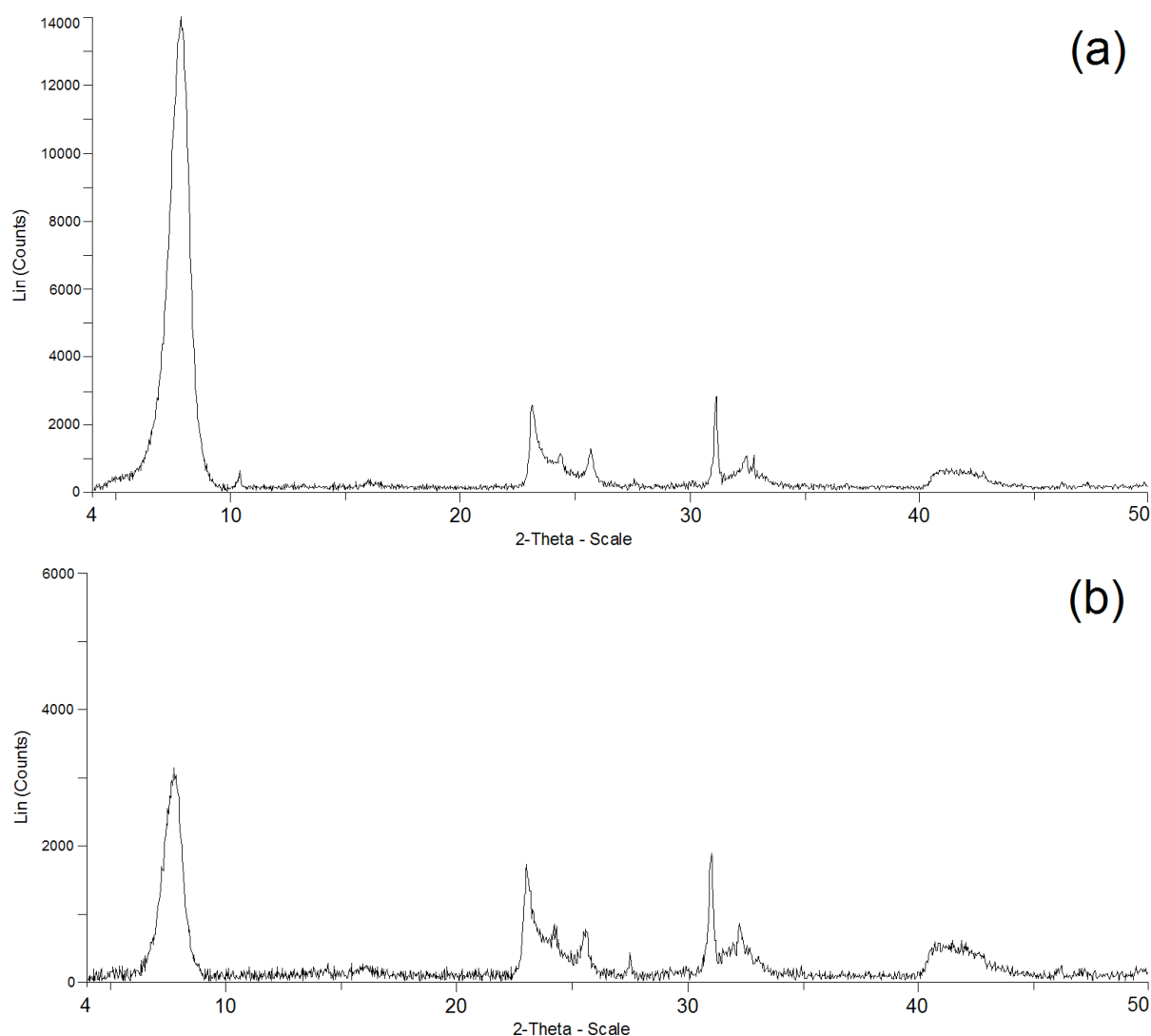


Fig. 3 (a) Diffraction pattern of pressed pellets from PANI/MMT intercalate recorded from diffraction plane perpendicular to the pellet plane (see arrangement in Figure 1a); and (b) diffraction pattern recorded from cutting plane (see arrangement in Figure 1b).

3. In the 2θ range of $14\text{--}18^\circ$ we can observe also an inkling of very small broaden peak of pure PANI component occurring between silicate plates.

Diffractograms of the pellet surface plane and the cutting plane for the pure PANI pellet is in Figures 4a and 4b, respectively. The difference in both diffractograms is evident and indicates the strong texture in pure PANI pellets. That means the morphology of pure PANI particles is also strongly anisotropic. The flakes, ribbons and nanorods have been reported in (Laslau et al., 2012), where the PANI chains are parallel with rods and ribbons axis or with the flake planes. Consequently in the diffractogram of pellet plane we can record preferentially the reflections from planes parallel to chains, and consequently the peaks at 0.60, 0.44 and 0.35 nm correspond to periodicity in stacking and ordering of PANI chains in planes parallel to flake planes or in

planes forming a low angle with the flake planes. On the other hand, the diffractogram of the cutting plane (see Fig. 4b) exhibits one strong peak at 0.74 nm corresponding to the periodicity in planes perpendicular to flake plane/ribbon plane. Peaks corresponding to tilted planes at 0.60 and 0.35 nm are observable on both patterns. Laslau et al. (2012) investigated the structure of PANI powder samples in capillary using synchrotron diffraction. In spite of different experimental conditions - capillary (Laslau et al., 2012) versus the flat textured sample (our work) – there is quite good agreement in peaks at ~ 0.35 , 0.44 and 0.60 nm.

3.2. CONDUCTIVITY MEASUREMENT

Results of DC conductivity measurements are summarized in the Table 1, where σ_{\perp} is the conductivity in direction perpendicular to the pellet

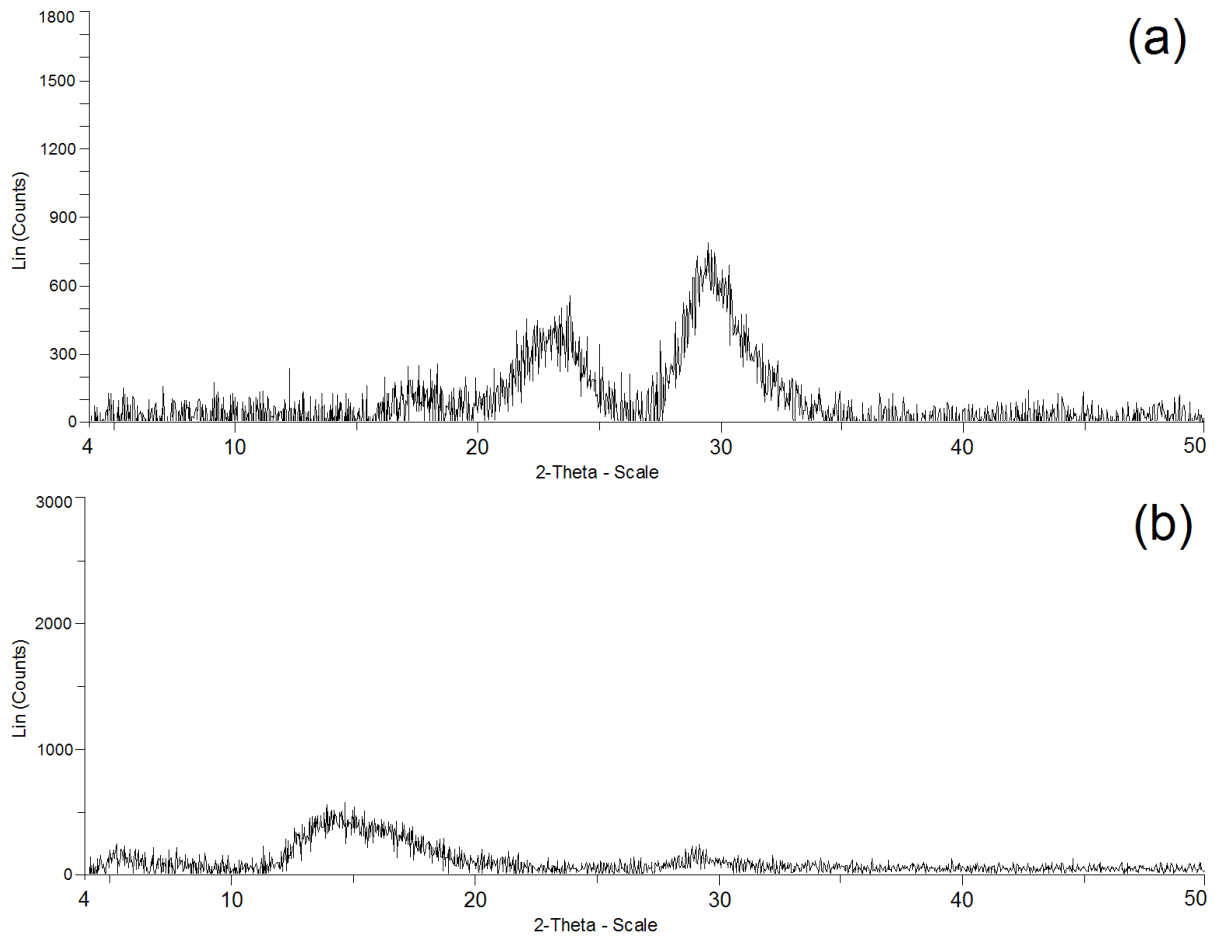


Fig. 4 (a) Diffraction pattern of pressed pellets from pure PANI recorded for diffraction plane perpendicular to the pellet plane (see arrangement in Figure 1a); and (b) diffraction pattern recorded from cutting plane (see arrangement in Figure 1b).

Table 1 DC conductivities in three perpendicular directions for two pellets pressed from PANI/MMT powder in two different pressing times (see the time in parentheses) and one pellet pressed from pure PANI powder. The values of anisotropy factor (expressed as $\sigma_{||av}/\sigma_{\perp}$ ratio) are listed in the bottom row.

directions	conductivity $1 \cdot 10^{-3}$ [S·cm ⁻¹]		
	PANI/MMT (20 min)	PANI/MMT (17 min)	PANI (22 min)
σ_{\perp}	0.0149	0.0380	1.0370
$\sigma_{ 1}$	4.8904	4.6179	7.3118
$\sigma_{ 2}$	4.8904	4.6341	6.5591
$\sigma_{ av}$	4.8904	4.6260	6.9355
	anisotropy factor [-]		
$\alpha = \sigma_{ av}/\sigma_{\perp}$	328.2	121.7	6.7

plane, $\sigma_{||1}$ and $\sigma_{||2}$, respectively, are the conductivity values in the pellet plane in two perpendicular directions (for an arrangement see Fig. 2) and $\sigma_{||av}$ is an average of $\sigma_{||1}$ and $\sigma_{||2}$ values. Value α is the anisotropy factor, a dimensionless $\sigma_{||av}/\sigma_{\perp}$ ratio.

Values in first two columns of Table 1 correspond to PANI/MMT intercalate exposed to the

pressure 28 MPa for 20 min (in the first column) and for 17 min (in the second column). Conductivity values of pure PANI pellet pressed at 28 MPa for 22 min is in the third column for comparison. One can see that for pressing pellets from PANI/MMT powder the shorter time was needed than for pressing pellets from pure PANI. This is caused by better structural

ordering of PANI chains in PANI/MMT powder than in pure PANI powder.

Results of conductivity measurements can be summarized as follows.

1. It is evident, that the strong texture revealed for all samples by diffraction measurements manifests itself by the strong anisotropy in conductivity.
2. The longer pressing time allows better arrangement of MMT layers in the direction perpendicular to the direction of pressing. This fact leads to a lower σ_{\perp} conductivity and consequently to the stronger anisotropy, as one can see comparing first and second columns in the Table 1.
3. While for the PANI/MMT composite the strong texture and anisotropy was expected, because of the morphology of clay particles, the pure PANI pellets exhibit quite remarkable anisotropy as well.
4. While in the direction perpendicular to the pellet plane the conductivity σ_{\perp} is about 100 times lower for PANI/MMT composite than for pure PANI, the $\sigma_{\parallel av}$ values for composite and pure PANI are of the same order ($1 \cdot 10^{-3}$). This agreement in in-plane conductivity for PANI/MMT and pure PANI is the consequence of the fully intercalated structure of MMT, confirmed by X-ray diffraction.
5. Present values of conductivity for pure PANI σ_{\perp} and $\sigma_{\parallel av}$ are lower than values published by (Stejskal et al., 2002 and Prokeš et al., 2011) $\sim 5.1 \text{ S} \cdot \text{cm}^{-1}$. On the other hand, (Kazim et al., 2012) reported preparation of pellets pressed from PANI/MMT composite under the pressure $\sim 490 \text{ MPa}$ and found the conductivity an order of magnitude lower ($1.6 - 7.4 \cdot 10^{-4} \text{ S} \cdot \text{cm}^{-1}$). However, the comparison is difficult as the previously published results have been obtained using pellets pressed at much higher pressure (700 MPa in (Prokeš et al., 2011 and Stejskal et al., 2002), 490 MPa in (Kazim et al., 2012)). In addition, (Stejskal et al., 2002 and Prokeš et al., 2011) carried out the measurement using van der Pauw four-point method which represents different experimental configuration than in our work.

4. CONCLUSIONS

Present study showed the relationship between structure and conductivity of pressed pellets of PANI/MMT and PANI analyzing the texture in samples. The main result of this work is the conclusion, that the in-plane conductivity $\sigma_{\parallel av}$ of PANI/MMT composite and pure PANI pellets is nearly the same. This is promising result as to future practical applications, as it means that we can get a functional unit of PANI/MMT composite with the two-dimensional conductivity, which is the same as

for pure PANI. The main advantage of PANI/MMT composite is the high anisotropy factor $\alpha = \sigma_{\parallel av} / \sigma_{\perp}$ (328.2 for PANI/MMT and 6.7 for pure PANI), which means the better chance for design of two-dimensional conductor. In addition, this PANI/MMT functional unit will be more mechanically and thermally stable than pure PANI, thanks to the presence of silicate layers.

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