Polyaniline/TiO₂/kaolinite: the composite material with high electrical anisotropy

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Abstract

Kaolinite-TiO₂ nanocomposite matrix (KATI) coated with polyaniline (PANI) layer has been prepared in powder form and pressed into tablets. The conductivity was studied in dependence on (1) wt.% of TiO₂ in KATI matrix and (2) thermal pre-treatment of KATI matrix. The anisotropy factor α, i.e. the ratio of in-plane conductivity and conductivity in the direction perpendicular to the tablet plane, was found to be very high for PANI/KATI tablet (α is of the order of 10³ - 10⁴) in comparison with pure PANI tablet (α is of the order of 10²). Structure has been studied using Raman spectroscopy, X-ray diffraction analysis, scanning electron microscopy and molecular modeling. The possibility of using the tablets as a load sensors have been tested and tablets pressed from composites containing calcined KATI seem to be promising material for this purpose.

Keywords:
A. composite materials;
B. chemical synthesis;
C. computer modelling and simulation;
D. electrical conductivity

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1. Introduction

Polyaniline (PANI), the most intensively studied conducting polymer, may exist in many oxidation and protonation states. The common green protonated emeraldine salt, formed during the polymerization of aniline in acidic environment, exhibits conductivity on a semiconductor level [1]. The conductivity is caused by polaronic structure which can be easily determined using Raman spectroscopy [2,3].

Nanocomposites based on PANI are studied and used in wide range of applications, like sensors, energy storage systems, electrostatic discharge protection materials, electrorheological fluids, and many others [4,5]. Ordering of polymer chains plays a key role...
in these systems [6-16]. PANI chains can be aligned, for example, using high pressure [17], blends with insulating polymers [13], mechanical orientation of PANI films [14], ordering of PANI particles in monomer mixture in an electric field [15]. Nanocomposites of PANI/layered inorganic matrix type (i.e. PANI/graphite [11] or PANI/phylllosilicate [18-21]) offer another possibility how to order the PANI chains along platy particles of layered matrices. In addition, the interaction between PANI chains and matrices improves and gives rise to properties, such as mechanical and thermal stability [19] or photosensitivity [22]. For a comprehensive review the reader is referred to [4].

Clay minerals with the layered structure (phylllosilicates) have been often used as matrices for such type of organo-inorganic composites [23-25]. The plate-like shape of phylllosilicate particles remains unchanged even after the surface modification and the powder particles of resulting nanocomposites exhibit the tendency to preferred arrangement even without any applied pressure. Therefore, pressing these nanocomposites into the tablets using high pressure will lead to a strong texture dramatically affecting the conductivity.

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 [7,26]. In the majority of articles dealing with the conductivity of tablets pressed from PANI/phylllosilicate composites the anisotropy is not discussed [17,18,27-30]. Moreover, the most used phylllosilicate in these works is the montmorillonite. Kaolinite (KLT) as a matrix for PANI is described only by Duran et al. [19], while Anakh and Çetinkaya [31] and Acar et al. [32] used KLT for the preparation of poly(2-ethyl aniline)/KLT and polypyrrole/KLT composites, respectively.

Present work is focused on structure and electrical conductivity of tablets pressed from PANI/KLT and PANI/KATI composites, where KATI means KLT covered by TiO$_2$ nanoparticles [33]. Raman spectroscopy, scanning electron microscopy, X-ray diffraction analysis and molecular modeling are used to study the structure of composites. The electrical conductivity is studied in dependence on thermal pre-treatment of KATI and amount of TiO$_2$ in KATI. The anisotropy factor $\alpha$ (i.e. the ratio of in-plane conductivity and conductivity in the direction perpendicular to the tablet plane) is determined for each sample. A possibility of using the tablets as a load senzors is also discussed.
2. Materials and methods

2.1 Samples preparation

Kaolinite/TiO\textsubscript{2} composites (KATI) were prepared from kaolinite SAK47 (Lasselsberger a.s.) with titanyl sulfate as a precursor. Samples denoted as KATI1X are composites dried at 105 °C and symbol X means the content of TiO\textsubscript{2} (2 for 20 wt.%, 4 for 40 wt.%, 6 for 60 wt.%). Samples denoted as KATI6X were calcined at 600 °C and meaning of the symbol X is the same as in KATI1X. More information about preparation of the composites can be found in [33].

Aniline, sulfuric acid and ammonium peroxodisulfate were purchased from Lach-Ner, Czech Republic, and used as received. 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 40 minutes (dark green color was observed). The solid was collected on a filter by rinsing with distilled water and subsequently dried at 40 °C in a kiln.

PANI/KATI1X, PANI/KATI6X and PANI/KLT composites were prepared using one-step process [28]. The anilinium sulfate and ammonium peroxodisulfate were added into water suspension containing 3 g of either KATI or KLT matrix. Polymerization of aniline was completed after 40 minutes, but the suspension was stirred for 6 hours. The solid was also collected on a filter by rinsing with distilled water and dried at same conditions as pure PANI. Prepared composites were pressed into tablets using LECO hand press (applied pressure 28 MPa) at room temperature, without any lubrication and binder. Diameter of each tablet was 32 mm. Thicknesses of PANI/KATI (both 1X and 6X), PANI and PANI/KLT tablets were 3.0 - 3.2 mm, 3.8 mm and 2.8 mm, respectively. Weight fraction of PANI in each sample calculated according to Duran et al. [19] is 27 wt. %.

2.2 Conductivity measurements

Two pairs of Cu contact electrodes have been used for the measurements of electrical conductivity in two perpendicular directions. Electrodes in each pair had different shape (see Fig. 1). Measuring instruments: DC POWER SUPPLY HY 5 3003 D-2, Programmable DC POWER SUPPLY BK PRECISION 9120, multimeter AGILENT 34401A, V-meter UNI-T UT802, pA-meter KEITHLEY 6487. Voltage U = 1 V was used for all measurements. For the measurement of conductivity in the direction parallel to the round surface of pressed tablet (i.e. conductivity in the direction perpendicular to the direction of pressing, see Fig. 1),
the tablet was placed between two curved electrodes. Each conductivity measurement was repeated four times. Then, the tablet was rotated about 90° and the measurement was again repeated four times. The conductivity value for each sample is presented as an average value obtained from all eight measurements.

The dependence of electrical current flowing through the tablet in the direction perpendicular to the round surface of tablet (i.e. in the direction of pressing, see Fig.1a) on mechanical load was used to study the possibility of using PANI/KATI tablets as load sensors. Twelve weights (124 g each) were used. Since the area of the round surface of tablet is $0.8 \times 10^{-3} \text{ m}^2$, each weight represents the pressure 1513 Pa. Experiment started after loading the tablet with two weights. Then, pairs of additional weights were added at definite time intervals (denoted as the loading part of measurement,). After reaching the maximum load (i.e. 1488 g or 18156 Pa), pairs of weights were again removed at the same time intervals (denoted as the unloading part of the measurement).

![Fig. 1.](image)

**Fig. 1.** (a) conductivities measured in the direction perpendicular and parallel to the flat round surface of tablet are denoted as $\sigma_\perp$ and $\sigma_\parallel$ respectively; (b) flat round electrodes for $\sigma_\perp$ measurement; (c) curved electrodes for $\sigma_\parallel$ measurement.

### 2.3. Structure characterization

Smart Raman Microscopy System XploRA™ (HORIBA Jobin Yvon, France) was used for the characterization of prepared samples. Raman spectra were acquired with 532 nm excitation laser source, with 50× objective and using 1200 gr./mm grating.

Images from the measurement on QUANTA 450 FEG (FEI) scanning electron microscope (SEM) were obtained using a secondary electron detector. Accelerating voltage used was 15 kV.

The X-ray diffraction patterns were recorded using Bruker D8 Advance diffractometer (Bruker AXS, Germany) equipped with fast position sensitive detector VÅNTEC 1. CoK$_\alpha$ irradiation ($\lambda = 0.178897$ nm) was used. Measurements of all samples were carried out in reflection mode in symmetrical Bragg-Brentano arrangement. In order to analyze the texture of tablets, diffraction patterns have been recorded from three diffraction planes defined by the
incident and diffracted beam: top round surface, outer curved surface and inner cutting surface. The inner cutting surface was carefully treated with brush before the measurements.

Molecular modeling in Accelrys Materials Studio (MS) was used to study the interaction energies between PANI chains and various KLT and TiO₂ surfaces in order to determine which part of the KATI composite the PANI chains prefer. Seven models of KLT and TiO₂ (anatase form) surfaces have been prepared according to the structures published in [34,35] and denoted as KLT(001), KLT(100), TiO₂(001), TiO₂(100), TiO₂(101), TiO₂(103), and TiO₂(112). The numbers in parentheses represent the Miller indices (see Table 1). Models of TiO₂ substrates have been built with one side protonated in order to study the interaction between PANI and protonated or unprotonated surfaces. Taking into account that the highest conductivity is exhibited by PANI/KATI14 sample, only KLT and anatase structures were studied. Models of calcined samples containing rutile and dehydroxylated KLT (see [33]) were not prepared.

Table 1
Sizes and crystallochemical formulae of KLT and TiO₂ substrates. The numbers in parentheses represent the Miller indices.

<table>
<thead>
<tr>
<th>substrate</th>
<th>size [nm]</th>
<th>crystallochemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>KLT(001)</td>
<td>5.1 × 5.4</td>
<td>Al₂₄₀Si₂₄₀O₆₁₀(OH)₄₆₀</td>
</tr>
<tr>
<td>KLT(100)</td>
<td>5.2 × 5.2</td>
<td>Al₂₃₈Si₂₅₂O₅₁₁(OH)₇₀₀</td>
</tr>
<tr>
<td>TiO₂(001)</td>
<td>4.9 × 4.9</td>
<td>Ti₆₇₆O₁₂₄₇(OH)₂₁₀</td>
</tr>
<tr>
<td>TiO₂(100)</td>
<td>4.9 × 4.7</td>
<td>Ti₃₅₀O₁₀₆₇(OH)₁₃₄</td>
</tr>
<tr>
<td>TiO₂(101)</td>
<td>4.9 × 4.9</td>
<td>Ti₄₁₆O₇₈₀(OH)₁₀₄</td>
</tr>
<tr>
<td>TiO₂(103)</td>
<td>4.9 × 5.3</td>
<td>Ti₃₆₀O₇₃₀(OH)₁₉₂</td>
</tr>
<tr>
<td>TiO₂(112)</td>
<td>4.8 × 4.9</td>
<td>Ti₃₃₃O₅₈₁(OH)₁₇₀</td>
</tr>
</tbody>
</table>

Initial models were prepared by placing the PANI chains (chemical formula C₄₈ H₄₂ N₈, length ~ 4.0 nm [36]) on the above mentioned substrates in various positions. Models containing PANI on protonated TiO₂ surface are denoted as PANI/TiO₂(101)OH, PANI/TiO₂(103)OH, etc. Also the models with PANI situated on octahedral KLT surface are denoted as PANI/KLT(001)OH, while PANI/KLT(001) means the PANI chain on tetrahedral surface. PANI/KLT(100)OH model contains fully protonated KLT edge. In PANI/KLT(100) model the KLT edge sets the uncovered aluminium atoms to PANI chains.

Initial models were optimized in MS Forcite module using Universal force field [37]. Smart algorithm was used with 500,000 iteration steps. Charges of atoms in PANI chain were assigned by Gasteiger method [38]. Gast_polygraph 1.0 parameter set containing enhancements for the treatment of four-valent nitrogen was used. Charges of atoms in KLT
and TiO$_2$ substrates were calculated using QEq method (QEq\_charged 1.1 parameter set) [39].

The interaction between the PANI chain and either KLT or TiO$_2$ substrate was quantified using the adhesion energy $E_{\text{ad}}$ calculated from optimized models

$$E_{\text{ad}} = (E_{\text{tot,PANI}} + E_{\text{tot, substrate}}) - E_{\text{tot}}$$ (1)

where $E_{\text{tot}}$ is the total potential energy of the model (i.e. PANI chain anchored on either KLT or TiO$_2$ substrate), $E_{\text{tot,PANI}}$ is the total potential energy of PANI chain and is $E_{\text{tot,substrate}}$ is the total potential energy of either KLT or TiO$_2$ substrate. These energies are expressed in the unit (kJ⋅mol$^{-1}$).

## 3. Results and discussion

### 3.1. Morphology of the materials

SEM analysis was used to study the morphology of prepared materials and the images can be seen in Figs. 2a-f.

![Fig. 2.](image_url) (a) pure PANI – disordered clusters are formed; (b) PANI/KLT – PANI does not fully cover the KLT particles, see the plain KLT surface on the right; (c) pure KATI14 – “collars” from TiO$_2$ encircling the KLT particles are clearly visible; (d) pure KATI64 – the morphology of KATI14 is preserved but one can see cracks on TiO$_2$ "collars"; (e) PANI/KATI14 – KATI14 is fully covered by PANI; (f) PANI/KATI64 – coverage is not full, see the plain surface of KATI64 on the right.
Pure PANI and PANI/KLT composite can be seen in Figs. 2a and b, respectively. Fig. 2b reveals that KLT is not fully covered by PANI (see the plain KLT surface on the right). The structure of PANI in PANI/KLT composite is also very similar to that of pure PANI, i.e. disordered clusters composed from smaller beads (compare Figs. 2a and 2b). As same as in our previous study [33], the SEM images show that TiO$_2$ nanoparticles grow preferentially on KLT edges and create a “collars” encircling platy KLT particles (Figs. 2c-f). Fig. 2b shows that PANI grows also on the edges of pure KLT (see the upper part of image) but not preferentially. For PANI/KATI14 composite the SEM analysis revealed the complete coverage of KATI14 by PANI layer (Fig. 2e).

In order to determine the interactions between PANI and TiO$_2$ or KLT surfaces, the molecular modeling was involved also in this study. Adhesion energies ($E_{ad}$) for PANI chains on KLT and TiO$_2$ substrates calculated using Eq. 1 are listed in Table 2.

### Table 2
<table>
<thead>
<tr>
<th>PANI-substrate $E_{ad}$ [kcal·mol$^{-1}$]</th>
<th>KLT(001)</th>
<th>KLT (100)</th>
<th>TiO$_2$(001)</th>
<th>TiO$_2$(100)</th>
<th>TiO$_2$(101)</th>
<th>TiO$_2$(103)</th>
<th>TiO$_2$(112)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O (Ti-O)</td>
<td>579</td>
<td>384</td>
<td>228</td>
<td>300</td>
<td>57</td>
<td>84</td>
<td>172</td>
</tr>
<tr>
<td>OH</td>
<td>390</td>
<td>431</td>
<td>625</td>
<td>616</td>
<td>426</td>
<td>404</td>
<td>275</td>
</tr>
</tbody>
</table>

The strongest $E_{ad}$ was obtained for the TiO$_2$(001)OH surface (2617 kJ·mol$^{-1}$), followed by TiO$_2$(100)OH with nearly the same $E_{ad}$ value (2579 kJ·mol$^{-1}$), leading to the order TiO$_2$(001)OH ≈ TiO$_2$(100)OH > KLT(001) > TiO$_2$(101)OH ≈ KLT(100)OH > TiO$_2$(103)OH > KLT(001)OH ≈ KLT(100) > TiO$_2$(100) > TiO$_2$(112)OH > TiO$_2$(112) > TiO$_2$(103) > TiO$_2$(101). Optimized models of PANI chain on TiO$_2$(001)OH and TiO$_2$(100)OH surfaces are shown in Fig. 3. One can see that PANI chain on TiO$_2$(001)OH and TiO$_2$(100)OH prefers the directions [110] and [012], respectively. This is caused by the tendency to find a position in which the distances between OH groups (d$_{OH-OH}$) become similar with the distances between NH groups (d$_{NH-NH}$) in PANI chains, which are ~ 0.56 nm. For TiO$_2$(001) and TiO$_2$(100) planes the d$_{OH-OH}$ in [110] and [012] directions are ~ 0.53 nm and ~ 1.21 nm, respectively. Nearly the same values of d$_{OH-OH}$ in case of [110] direction in TiO$_2$(001) plane and d$_{NH-NH}$ probably causes slightly stronger interaction between PANI and TiO$_2$(001)OH.
surface than between PANI and TiO$_2$(100)OH surface where the $d_{\text{OH-OH}}$ in case of [012] direction is twice the $d_{\text{NH-NH}}$.

![Image](image.png)

**Fig. 3.** Optimized models of PANI chain on TiO$_2$(001)OH and TiO$_2$(100)OH surfaces. Ti – light gray, O – red, H – white, C – dark gray, N – blue.

It is evident that PANI interacts preferentially with protonated TiO$_2$ surfaces, especially with TiO$_2$(001)OH and TiO$_2$(100)OH where the $E_{ad}$ is higher than for KLT. Surprisingly, the interaction of PANI with KLT(001)OH surface is weaker than with KLT(001) and KLT(100)OH but nearly the same as with KLT(100). Although the $E_{ad}$ is lower for KLT(001) than for TiO$_2$(001)OH and TiO$_2$(100)OH, the difference is only about 8% (see Table 2) and, therefore, PANI can be present on KLT(001) surface. In PANI/KLT samples the presence of PANI on KLT edges is also possible. The most important finding is that the $E_{ad}$ for KLT(100) and KLT(100)OH do not reach the $E_{ad}$ values for TiO$_2$(001)OH and TiO$_2$(100)OH surfaces. The presence of TiO$_2$ “collars” on KLT edges in KATI composites causes a more complete coverage by PANI than in case of pure KLT.

The growth of TiO$_2$ on KLT and the orientation of TiO$_2$ hkl planes against KLT have been already studied using computer simulations and for our previous results the reader is referred to [33] and [40]. Taking into account the strong adhesions found for KLT(100)/TiO$_2$(100) and KLT(100)/TiO$_2$(001) systems, two of the possible arrangements in PANI/KATI composites can be $KLT(100) \parallel TiO_2(100)OH \parallel PANI$ and $KLT(100) \parallel TiO_2(001)OH \parallel PANI$. However, this hypothesis is not supported by experimental analyses.

### 3.2. Raman spectra

Fig. 4 shows Raman spectra of PANI and TiO$_2$ in all prepared composites.
KLT substrates (and generally clays) are not visible in Raman spectra due to their fluorescence [41]. TiO$_2$ (anatase structure) has four main bands [42] but only the strongest one ($\sim 150$ cm$^{-1}$) is detectable in almost all Raman spectra with exception of PANI/KLT and PANI/KATI12 (see Fig. 4). The other bands are not clearly visible due to deformation vibrations of aromatic rings in range 200-800 cm$^{-1}$ [43]. Main band of TiO$_2$ is more or less visible for all calcined samples. For non-calcined samples this band is clearly visible only in the spectrum of PANI/KATI16 containing the highest amount of TiO$_2$.

The most information about protonation state gave “protonation band” corresponding to C-N$^+$ stretching vibration [44]. One can see that this band ($\sim 1320$ cm$^{-1}$) have the highest intensity for sample PANI/KATI14 which corresponds with the highest conductivity (see Table 3). PANI/KATI12 and PANI/KATI62 samples have similar Raman spectra with only small differences in protonation band and band of stretching vibration of >C=N- ($\sim 1498$ cm$^{-1}$) [44]. PANI/KATI12 sample exhibits higher protonation band than PANI/KATI62, which is also in good agreement with conductivity of these samples (see Table 3).
3.3. X-ray diffraction analysis

X-ray diffraction (XRD) patterns obtained from various surfaces of tablets (i.e. the flat round surface, the outer curved surface and the inner cutting surfaces) pressed from PANI/KLT, PANI/KATI1 and PANI/KATI6 composites are shown in Fig. 5a-c. In addition to the monitored phases kaolinite and anatase (denoted as KLT and A) two other phases quartz and muscovite (denoted as Q and M) have been identified. These minerals are commonly present in raw kaolin clay.

A wide set of low-intensity reflections forming a slight ripple in the range $2\theta = 11-19^\circ$ (Fig. 5b and c) arises from the longitudinally arranged PANI chains and in ideal case the angle $2\theta \sim 15^\circ$ corresponds to the situation when the planes of aromatic rings in PANI chains are parallel to the direction of pressing (i.e. perpendicular to the diffraction plane). However, no reflection at $2\theta \sim 15^\circ$ can be seen. There is only basal reflection of KLT ($2\theta \sim 14.4^\circ$) which will be discussed later. This suggests that aromatic rings in longitudinally arranged PANI chains are not oriented perpendicular to any diffraction plane, i.e. they are oriented randomly.

It is evident that the reason of high anisotropy factors (Table 3) has to be found in the space arrangement of matrices. Platy KLT particles oriented perpendicular to the direction of pressing (i.e. parallel to the flat round surface of tablet, see Fig. 1a) form a barrier limiting the flow of electric current while the conductivity $\sigma_\|\$ in the direction along this flat round surface (see Fig. 1a and Table 3) is significantly higher. One can see that reflections of KLT planes occur in the diffraction patterns obtained both from the flat round surfaces and outer curved surfaces (Figs. 5a and b).

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_|$ [$10^{-3}$ S/m]</th>
<th>$\sigma_|$ [S/m]</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI/KATI12</td>
<td>1.99</td>
<td>0.72</td>
<td>$10^4$</td>
</tr>
<tr>
<td>PANI/KATI14</td>
<td>4.39</td>
<td>2.76</td>
<td>$10^4$</td>
</tr>
<tr>
<td>PANI/KATI16</td>
<td>0.68</td>
<td>0.01</td>
<td>$10^3$</td>
</tr>
<tr>
<td>PANI/KATI62</td>
<td>2.75</td>
<td>0.22</td>
<td>$10^3$</td>
</tr>
<tr>
<td>PANI/KATI64</td>
<td>9.71</td>
<td>0.18</td>
<td>$10^3$</td>
</tr>
<tr>
<td>PANI/KATI66</td>
<td>3.50</td>
<td>0.03</td>
<td>$10^2$</td>
</tr>
<tr>
<td>PANI/KLT</td>
<td>2.15</td>
<td>0.03</td>
<td>$10^3$</td>
</tr>
<tr>
<td>PANI</td>
<td>16.98</td>
<td>0.03</td>
<td>$10^2$</td>
</tr>
</tbody>
</table>
Fig. 5. X-ray diffraction patterns of the flat round surfaces (a); the outer curved surfaces (b); and the inner cutting surfaces (c) for all PANI/KLT and PANI/KATI tablets. The sketches of all three surfaces are also provided. A-anatase, KLT-kaolinite, M-muscovite, Q-quartz.

This is caused by the encountering of KLT and KATI particles with the walls of pressing chamber during the pressing. Because these walls are stationary, the pressure spreading through the powder sample forces the KLT and KATI particles to take the positions parallel to these walls. This does not occur in the internal volume of powder sample and the above
mentioned reflections are not noticeable in the diffractogram of inner cutting surfaces (Fig. 5c).

Although the KLT reflections disappeared in the XRD patterns of PANI/KATI62 and PANI/KATI64, in the XRD pattern of PANI/KATI66 are clearly observable (Fig. 5a) suggesting that the presence of large amount of TiO$_2$ prevents the full transformation of KLT into metakaolinite. Since the KLT reflections of PANI/KATI66 can be found only in the XRD pattern of the flat round surface, it is probable that their visibility is the result of pressing.

3.4. Conductivity measurement

The in-plane conductivities ($\sigma_{\parallel}$), the conductivities in the direction perpendicular to the tablet plane ($\sigma_{\perp}$) and the anisotropy factors ($\alpha$) for all prepared samples are listed in Table 3. One can see that PANI/KATI14 sample exhibits the in-plane conductivity 2.76 S/m which is an order or two orders of magnitude higher than conductivities of other samples. This high conductivity corresponds well with the complete coverage of KATI14 by PANI layer (see Fig. 2e).

Since the exact $\alpha$ values can be affected by an error (due to the very small values $\sigma_{\perp}$), only the orders of magnitude are considered. The value $\alpha$ which is of order $10^2$ for pure PANI increases due to the addition of KLT and the tablet pressed from PANI/KLT composite exhibits the $\alpha$ of order $10^3$. Moreover, the presence of TiO$_2$ on KLT further increases the anisotropy and for PANI/KATI12 a PANI/KATI14 the value $\alpha$ is of order $10^4$. This is a maximum value reached for our PANI/KATI composites.

Further, it is evident that using the calcined KATI as a matrix results in the decrease of anisotropy as one can see from the comparison of $\alpha$ for PANI/KATI1X and PANI/KATI6X. This is caused by the partial loss of the KLT layered structure due to the transformation to metakaolinite during calcination. In case of PANI/KATI66 sample the transformation of KLT to metakaolinite is partially inhibited by the presence of large amount of TiO$_2$ (as mentioned in section 3.3. X-ray diffraction analysis) but, concurrently, this large amount of TiO$_2$ (i.e. 60 wt.%) causes the decrease of anisotropy ($\alpha$ values for PANI/KATI16 and PANI/KATI66 are lower than for other PANI/KATI samples). PANI/KATI66 exhibits the lowest $\alpha$ value (with exception of pure PANI) because in this sample both the transformation to metakaolinite and the large amount of TiO$_2$ play its role. In addition, the calcination causes the increasing size of TiO$_2$ crystallites [33] which may also contribute to the decreasing of $\alpha$. 

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The load test results are summarized in Table 4.

Table 4
The values of current obtained during the loading and unloading parts of the measurement. N, m and p represents the number of weights, the load and the pressure, respectively. I (%) shows the value of current (in percentage) relative to the value of current obtained for the highest load.

<table>
<thead>
<tr>
<th></th>
<th>PANI/KATI12</th>
<th>PANI/KATI14</th>
<th>PANI/KATI16</th>
<th>PANI/KATI62</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>m (g)</td>
<td>p (Pa)</td>
<td>I (μA)</td>
<td>I (%)</td>
</tr>
<tr>
<td>2</td>
<td>248</td>
<td>3026</td>
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<td>4</td>
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<td>744</td>
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<td>1132</td>
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<td>1954</td>
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<td>18156</td>
<td>2282</td>
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Because the load sensor has to respond to the same external loads identically, special attention has been paid to the values of current obtained for the same load in the loading and unloading part of the measurement. The current (I (μA)) was converted to percent (I (%)) and in order to evaluate the stability of response, differences between both I (%) values for the same load were calculated. An example follows. For 248g load the currents measured on PANI/KATI12 sample were 510 (loading part of the measurement) and 332 μA (unloading part of the measurement), i.e. 22.37 and 14.55 % of the highest current (2282 μA). The difference between these two values is 7.82 %. For the same load the currents measured on PANI/KATI62 sample were 156 and 159 μA, i.e. 25.6 and 26.07 % of the highest current.
(611 µA). The difference between these two values is 0.47 %. Although the PANI/KATI62 exhibits lower conductivity, its response to the same load is much more stable. Table 4 shows that the tablets pressed from PANI/KATI composites exhibit more stable response to the same load than tablets pressed from PANI/KLT and pure PANI. Moreover, it is evident that the responses of samples PANI/KATI6X are more stable than these of samples PANI/KATI1X. The average differences between the values I (%) for the same loads are as follows: 3.53% (PANI/KATI12), 43.9% (PANI/KATI14), 3.76% (PANI/KATI16), 2.15% (PANI/KATI62), 4.40% (PANI/KATI64), 1.82% (PANI/KATI66), 5.16% (PANI/KLT), and 15.24% (PANI).

4. Conclusions
Composites PANI/KATI containing PANI chains on KLT surface modified by nano-TiO₂ has been successfully prepared. Characterization of these composites using X-ray diffraction, scanning electron microscopy, Raman spectroscopy and molecular modeling revealed the arrangement of individual components. The most important finding is the role of TiO₂ which allows PANI to completely cover the surface of KATI particles. Electrical conductivity measurements showed significant anisotropic behavior of PANI/KATI composites. The highest reached anisotropy factor was $10^4$ (PANI/KATI12 and PANI/KATI14) representing an increase of two orders of magnitude compared with PANI and one order of magnitude compared with PANI/KLT. The possibility of using the tablets as load sensors was also tested. It was found that tablets containing dried KATI are not suitable as load sensors, while composites containing calcined KATI seem to be very promising material for this purpose.

Acknowledgement
This research has been funded by the Grant Agency of Czech Republic (project P108/11/1057). Authors wish to thank Tomáš Plaček for his significant assistance in preparation and characterization of the samples.

References