MEASUREMENT AND EVALUATION OF THE ELECTRICAL CONDUCTIVITY OF PANI AND PANI/KAOLINITE/TITANIUM DIOXIDE PRESSED TABLETS – STUDY OF LOAD SENSOR

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Abstract

Polyaniline (PANI) is one of the widely studied conducting polymers due to its light weight, low cost, excellent environmental stability and reversible acid-base switching of its electrical conductivity. Present work is focused on PANI-based composites containing titanium dioxide (TiO_2). The layered silicate kaolinite was used as a carrier of TiO_2 nanoparticles (KATI). Pure PANI, PANI/kaolinite and PANI/KATI composite samples were prepared in powder form using simple one-step process. Pure PANI was prepared from aniline sulfate (precursor) and ammonium peroxodisulfate (oxidizing agent). PANI/kaolinite and PANI/KATI composites were prepared in a similar way but in the presence of kaolinite and KATI, respectively. Pressed tablets were prepared at room temperature under pressure 28 MPa. The dependence of electrical conductivity on mechanical load was used to study the possibility of using tablets as load sensors. The conductivity was recorded during loading and unloading the pellets with constant weights. It was found that PANI/KATI tablets exhibit more stable response to the loading and unloading than PANI/kaolinite tablets and pure PANI tablets. Measurements were repeated three times for each tablet during three days and no significant differences between the obtained results were found. Special attention has been paid to to the thermal pre-treatment of KATI composite and to the amount of TiO_2.

Keywords:

kaolinite, TiO_2, polyaniline, specific conductivity, sensor

1. INTRODUCTION

Polyaniline (PANI) belonging to the family of conducting polymers is well known for its interesting optical and electrical properties [1]. Due to the low cost of the preparation process, PANI is suitable for various practical applications like sensor [2], anticorrosive material [3], etc. For nanocomposites based on PANI or other conducting polymers the ordering of polymer chains is a crucial factor affecting the electrical conductivity [4,5,6]. Various methods how to align the chains were reported (mechanical orientation of thin films [7], ordering in electric field [6], compression using high pessures [8], etc.) including the use of different matrices [9,10]. Phyllosilicates are also used for this purpose [11,12] because their particles are flat and the compression results in a strong texture significantly affecting the resulting conductivity. In present work we used a pristine kaolinite (KLT) and KLT decorated with TiO_2 (KATI) nanoparticles [13] as a matrices for PANI. Powder composites were pressed into tablets and a possibility to use these materials as a load sensors was tested. Molecular modeling using empirical force field and scanning electron microscopy were used for the characterization of materials. It was found that TiO_2 is a crucial component of PANI/KLT/TiO_2 composite with respect to use of the material as a load sensor.

2. EXPERIMENTAL PART

2.1 Preparation of samples

PANI was prepared by oxidative polymerization of the solution of aniline by ammonium peroxodisulfate in the presence of sulfuric acid. All compounds were purchased from Lach-Ner, Czech Republic. After 40 minutes the dark green solid was collected on a filter by rinsing with 0.2 M hydrochloric acid and dried in a kiln at 40°C. PANI/KLT composite was prepared similarly in the presence of KLT SAK47 (Lasselsberger a.s.) in the reaction mixture. PANI:KLT ratio in resulting PANI/KLT composite is 1:1. Preparation of KATI is described in [13]. Briefly, $TiOSO_4$ used as a precursor was mixed with appropriate amount of KLT in order to obtain the desired amount of TiO_2 in resulting KATI composite. After hydrolysis the KATI powder was rinsed with distilled water and dried at 105°C. One half of the KATI was further calcined at 600°C for 1h. Calcination led to the better crystallinity of TiO_2 NPs [13]. KATI samples are denoted as follows. KATI1X are dried, KATI6X are dried and calcined, X means the content of TiO_2 in KATI composite (2 for 20 wt.%, 4 for 40 wt.%). PANI:KATI ratio in resulting PANI/KATI composite is 1:1. Therefore, the amount of TiO_2 in PANI/KATI composites is 10 wt.% and 20 wt.%, respectively. PANI/KATI composites were prepared in the same way as PANI/KLT. All prepared materials (m = 3 g) were pressed (p = 28 MPa) into round tablets (d = 31.8 mm) using LECO PR-36 hand press at room temperature. Thicknesses of PANI, PANI/KLT, PANI/KATI12, PANI/KATI14, PANI/KATI62, PANI/KATI64 tablets were 2.8 mm, 3.0 mm, 2.9 mm, 2.9 mm, 3.2 mm, 3.3 mm, respectively.

2.2 Characterization methods

Scanning electron microscope (SEM) QUANTA 450 FEG (FEI) was used for the visual observation of the samples. Images were obtained using a secondary electron detector. Accelerating voltage used was 15 kV. Molecular mechanics using Universal force field [14] in Materials Studio was involved in order to study the interaction between PANI and KLT or TiO_2 surfaces. Five substrates, TiO_2(001), TiO_2(100), TiO_2(101), KLT(001), KLT(100), have been built [15,16] and initial models were prepared by placing the PANI chains ($C_{48}H_{42}N_8$; length ~ 4.0 nm) on the top of the substrates. Models were optimized using Smart algorithm with 500.000 iteration steps. Atomic charges were assigned by Gasteiger and QEq methods [17,18]. Interaction energy (E_{int}) was calculated using the following equation

$$E_{int} = E_{tot} - (E_{tot,PANI} + E_{tot,sub}) \quad (1)$$

where E_{tot} is the total potential energy of the whole model, $E_{tot,PANI}$ is the total potential energy of PANI chain and is $E_{tot,sub}$ is the total potential energy of substrate (KLT or TiO_2). Energies are expressed in kJ mol^{-1}.

2.3 Electrical measurements

The dependence of electrical conductivity on mechanical load was studied using the apparatus displayed in Fig. 1. Voltage source DC POWER SUPPLY HY 3003 D-2 was used. Pressed tablets were placed between two round Cu electrodes polished before each measurement using a special abrasive paste. 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. Voltage U = 0.1 V was used for all measurements. Experiment started after loading the movable arm with two weights (124 g each). Taking into account that weights are placed at the end of the arm and the upper electrode is positioned in the middle of its length, a double force pushes the tablet (see Fig. 1). It means that for two weights the pressure is 6128 Pa and not 3064 Pa. Subsequently, additional pairs of weights were added at the same time intervals (5 minutes) during this “loading part” of the experiment until the maximum load (twelve weights, i.e., 1488 g and 36768 Pa) was reached.

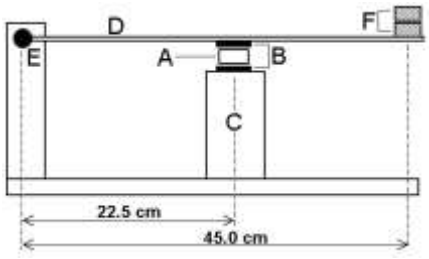

Fig. 1. Apparatus for the loading/unloading experiment. Tablet (A) is placed between two round Cu electrodes (B) attached to a solid easel (C) and movable arm (D). The arm is attached to the frame by the screw (E). Weights were placed on the end of the arm (F).

In the "unloading part" of the experiment pairs of weights were gradually removed at the same time intervals. Measurements were repeated three times for each tablet during three days and no significant differences between the obtained results were found. Experiments were performed at the temperature 22-23°C and relative humidity 50-60%. During the experiment the flow of current I (mA) was recorded. Subsequently, the conductivity σ (S m^{-1}) was calculated from the current. To determine the stability of response to increasing and decreasing load the highest conductivity value (measured at maximum load) was determined as 100% and conductivities for lower loads were expressed as a percentage of this highest value.

3. RESULTS AND DISCUSSION

Measurements of conductivity in dependence on the loading and unloading of PANI and PANI/KLT tablets (see Fig. 2) did not revealed any significant improvement in the stability of response for PANI/KLT in comparison with PANI. Increase and decrease of conductivity in case of PANI tablet is steeper than in case of PANI/KLT tablet but since the similar response to the same load during loading and unloading part is expected, none of these two tablets is suitable for practical use. Therefore, as an alternative to the KLT the KATI composite has been tested because the molecular modeling results showed stronger interaction between PANI and TiO_2 than between PANI and KLT. Interaction energies are listed in Table 1 and one can see that PANI prefers to adhere to the KLT(001) surface and not to the edge (i.e., KLT(100) surface). This problem can be solved by modifying the KLT particles. The main advantage of KATI composite lies in the fact that TiO_2 nanoparticles (NPs) grow preferentially on KLT edges (for more informations the reader is referred to [13]). So the KLT(100) surface, not appropriate for adhesion of PANI, is completely covered by TiO_2 NPs to which the PANI can be attached very easily (compare the interaction energies for TiO_2 and KLT(001) surfaces in Table 1).

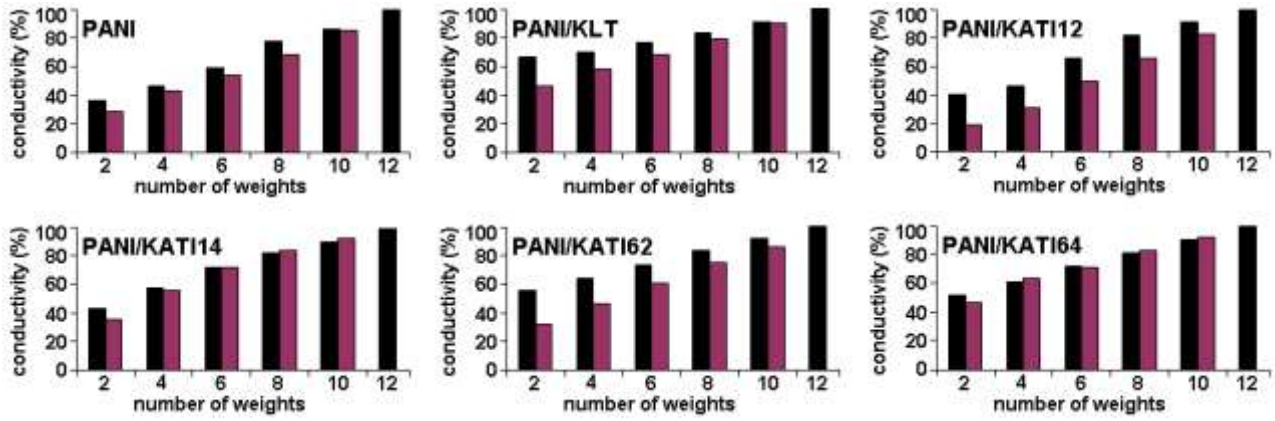

Fig. 2. Changes in conductivity of tablets in dependence on the number of weights. Data from loading and unloading part are black and violet, respectively.

Therefore, KATI composites have a larger surface area that can be covered by PANI than pure KLT. This area is larger after calcination because, as mentioned before, calcination causes an increase in the size of TiO_2 crystallites [13].

Table 1. Interaction energies between PANI and various KLT and TiO_2 surfaces. Tetrahedral and octahedral KLT(001) surfaces are denoted as KLT(001)-SiO and KLT(001)-OH, respectively.

mutual PANI-surface interaction energy (kJ mol^{-1})					
KLT(001)-SiO	**KLT(001)-OH**	**KLT(100)**	**TiO_2(001)**	**TiO_2(100)**	**TiO_2(101)**
-579	-390	-431	-625	-616	-426

Results of molecular modeling are confirmed by SEM analysis (Fig. 3). KLT edges are almost empty in PANI/KLT sample and KLT layers are clearly observable (Figs. 3a,b) while images of PANI/KATI (Figs. 3c,d) show the edges decorated with TiO_2 NPs and covered by PANI.

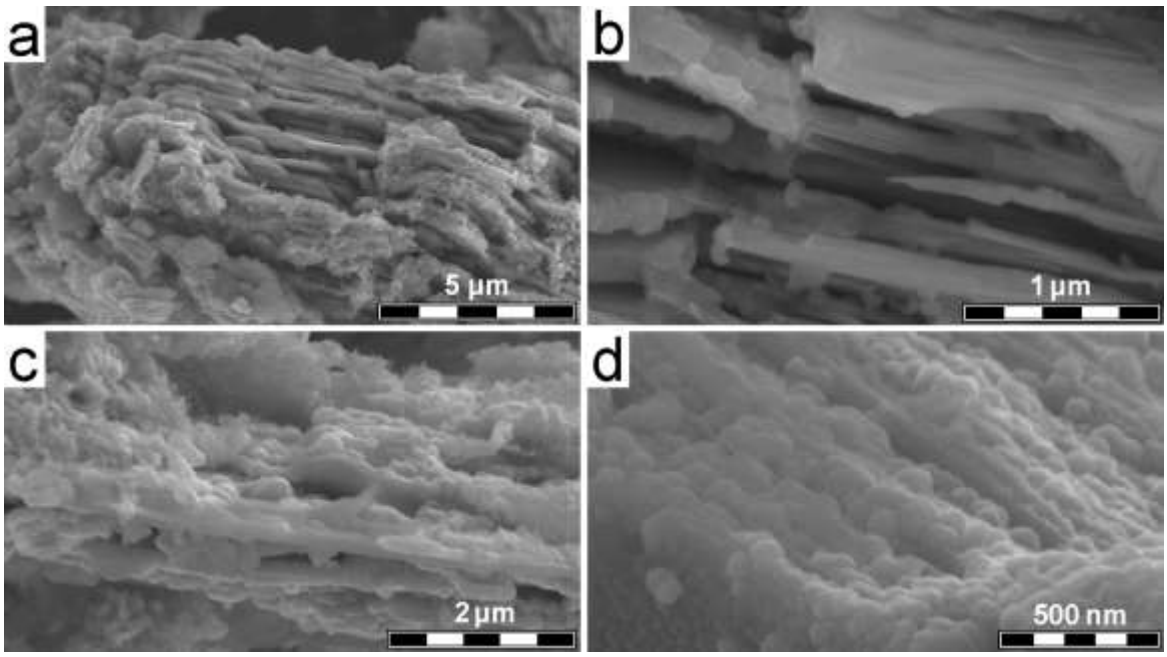

Fig. 3. SEM images of PANI/KLT (a,b) and PANI/KATI64 (c,d) composites.

Loading/unloading experiments with PANI/KATI composites were carried out under the same conditions as in case of PANI and PANI/KLT tablets. It was found that the use of KATI12 and KATI62 as a substrate does not lead to stable response (Fig. 2), probably due to the low amount of TiO_2. On the other hand, PANI/KATI14 and PANI/KATI64 samples exhibit very good stability in response to the same load during loading and unloading part (Fig. 2). The highest stability of response was found for PANI/KATI64 and data for this sample are listed in Table 2. Data for other samples are available upon request.

Table 2. Measured and calculated data for PANI/KLT64 tablet. Values of electrical current I (mA) and electrical conductivity σ (S m^{-1} and %) are listed for all the used loads.

number of weights (124 g each)										
2	4	6	8	10	12	10	8	6	4	2
current I (mA)										
10.975	12.830	15.131	17.238	19.168	21.138	19.370	17.366	15.072	13.327	9.949
electrical conductivity σ (S m^{-1})										
0.45	0.53	0.62	0.71	0.79	0.87	0.80	0.72	0.62	0.55	0.41
electrical conductivity σ (%)										
51.95	60.80	71.72	81.61	90.80	100	91.95	82.76	71.26	63.22	47.13

As one can see from Table 2 the differences between conductivity values are quite low for the same loads. The average difference is 1.82% while for PANI, PANI/KLT, PANI/KATI12, PANI/KATI14, and PANI/KATI62 the average differences are 5.03 %, 8.94 %, 15.45 %, 2.60 %, and 13.71 %. Poor stability of response observed in cases of PANI/KLT, PANI/KLT12, and PANI/KLT62 (i.e., the samples containing KLT with uncovered edges) suggests that the area of surface covered by PANI is an important parameter of the material. Also it can be said that TiO_2 is a crucial component of PANI/KATI composite because its absence or deficiency in the composite causes poor stability of response to the external load. Results also show that in order to obtain higher stability of response, calcined KATI composite is more suitable than dried KATI composite. A common feature of all samples is the growing difference between conductivity values in dependence on the decreasing load. The biggest difference is consistently observed for two weights (see Fig. 2). This difference is also apparent in case of PANI/KATI62 and PANI/KATI64 samples which otherwise exhibit good stability of response. However, this problem can be solved using small pressure applied constantly on the tablet.

4. CONCLUSIONS

The dependence of electrical conductivity on external mechanical load was used to study the possibility of using tablets pressed from PANI, PANI/KLT and PANI/KATI powders as a load sensors. After finding that PANI and PANI/KLT do not meet the requirement for stability of response to an external load, the KLT was replaced by KATI composite, i.e., KLT decorated with TiO_2 NPs. KATI composite calcined at 600°C and containing 40 wt.% of TiO_2 was found to be the most suitable for given purpose from all samples.

Our future work will be focused on increasing the stability of response by varying the proportions of the individual components of PANI/KATI composite.

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REFERENCES

[1] SAPURINA, I., STEJSKAL, J. The mechanism of the oxidative polymerization of aniline and the formation of supramolecular polyaniline structures, *Polymer International*, 2008, vol. 57, iss. 12, p. 1295-1325.

[2] MENEGAZZO, N., HERBERT, B., BANERJI, S. BOOKSH, K.S. Discourse on the utilization of polyaniline coatings for surface plasmon resonance sensing of ammonia vapor, *Talanta*, 2011, vol. 85, iss. 3, p. 1369-1375.

[3] GONCALVES, G.S., BALDISSERA, A.F., RODRIGUES, L.F., MARTINI, E.M.A., FERREIRA, C.A., Alkyd coatings containing polyanilines for corrosion protection of mild steel, *Synthetic Metals*, 2011, vol. 161, iss. 3-4, p. 313-323.

[4] LIU, Y.D., CHOI, H.J. Electrorheological fluids: smart soft matter and characteristic, *Soft Matter*, 2012, vol. 8, iss. 48, p. 11961-11978.

[5] ROZLÍVKOVÁ, Z., TRCHOVÁ, M., ŠEDĚNKOVÁ, I., ŠPÍRKOVÁ, M., STEJSKAL, J. Structure and stability of thin polyaniline films deposited in situ on silicon and gold during precipitation and dispersion polymerization of aniline hydrochloride, *Thin Solid Films*, 2011, vol. 519, iss. 18, p. 5933-5941.

[6] WU, X., QI, S., HE, J., DUAN, G. High conductivity and low percolation threshold in polyaniline graphite nanosheets composites, *Journal of Materials Science*, 2010, vol. 45, iss. 2, p. 483-489.

[7] COSTOLO, M., HEEGER, A.J. Anisotropic conductivity in polyaniline and image processing applications, *Synthetic Metals*, 2000, vol. 114, iss. 1, p. 85-90.

[8] PROKEŠ, J., VARGA, M., KŘIVKA, I., RUDAJEVOVÁ, A., STEJSKAL, J. The influence of compression pressure on transport properties of polyaniline, *Journal of Materials Chemistry*, 2011, vol. 21, iss. 13, p. 5038-5045.

[9] FANG, F.F., CHOI, H.J., AHN, W.S. Electroactive response of mesoporous silica and its nanocomposites with conducting polymers, *Composites Science and Technology*, 2009, vol. 69, iss. 13, p. 2088-2092.

[10] SHAKIRI, S., LIEW, S.Y., THIELEMANS, W., WALSH, D. A., CUMMINGS, C.Y., RASSAEI, L., EDLER, K.J., BONNÉ, M.J., MARKEN, F. Electrochemical characterisation of layered polyaniline-nanocellulose composite films, *Journal of Solid State Electrochemistry*, 2011, vol. 15, iss. 11-12, p. 2675-2681.

[11] BEKRI-ABBES, I., SRASRA, E. Solid-state synthesis and electrical properties of polyaniline/Cu-montmorillonite nanocomposite, *Materials Research Bulletin*, 2010, vol. 45, iss. 12, p. 1941-1947.

[12] TOKARSKÝ, J., STÝSKALA, V., KULHÁNKOVÁ, L., MAMULOVÁ KUTLÁKOVÁ, K., NEUWIRTHOVÁ, L., MATĚJKA, V., ČAPKOVÁ, P. High electrical anisotropy in hydrochloric acid doped polyaniline/phyllosilicate nanocomposites; Effect of phyllosilicate matrix, synthesis pathway and pressure, Applied Clay Science, 2013, vol. 80-81, p. 126-132.

[13] MAMULOVÁ KUTLÁKOVÁ, K., TOKARSKÝ, J., KOVÁŘ, P., VOJTĚŠKOVÁ, S., KOVÁŘOVÁ, A., SMETANA, B., KUKUTSCHOVÁ, J., ČAPKOVÁ, P., MATĚJKA, V. Preparation and characterization of photoactive composite kaolinite/TiO_2, *Journal of Hazardous Materials*, 2011, vol. 188, p. 212-220.

[14] RAPPÉ, A.K., CASEWIT, C.J., COLWELL, K.S., GODDARD, W.A., SKIFF, W.M. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations, *Journal of American Chemical Society*, 1992, vol. 114, iss. 25., p. 10024-10035.

[15] HOWARD, C.J., SABINE, T.M., DICKSON, F. Structural and thermal parameters for rutile and anatase, *Acta Crystallographica B*, 1991, vol. 47, iss. 4, p. 462-468.

[16] NEDER, R.B., BURGHAMMER, M., GRASL, T., SCHULTZ, H., BRAM, A., FIEDLER, S. Refinement of the kaolinite structure from single-crystal synchrotron data, *Clays and Clay Minerals*, 1999, vol. 47, iss. 4, p. 487-494.

[17] GASTEIGER, J., MARSILI, M. Iterative partial equalization of orbital electronegativity: a rapid access to atomic charges, *Tetrahedron*, 1980, vol. 36, iss. 22, p. 3219-3228.

[18] RAPPÉ, A.K., GODDARD, W.A. Charge equilibration for molecular dynamics simulations, *Journal of Physical Chemistry*, 1991, vol. 95, iss. 8, p. 3358-3363.