PROPERTIES OF POLYANILINE/MONTMORILLONITE THIN FILMS IN DEPENDENCE ON PREPARATION TEMPERATURE

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Abstract

A simple method was used for the preparation of polyaniline/montmorillonite (PANI/MMT) nanocomposite thin films deposited on glass slides. Water solution of anilinium sulfate (as a precursor) was mixed with the ammonium peroxydisulfate (as an oxidizing agent) in presence of glass slide and an appropriate amount of MMT at different temperatures. Two following temperatures were used: 10°C and 20°C. Layered structure of the MMT significantly affects the ordering of PANI chains, i.e. the PANI nanostructure. PANI/MMT thin films contain no other components like additional polymeric carriers or binders. Present work is focused on how the change of temperature of preparation mixture affect the thickness, morphology and electrical conductivity of resulting PANI/MMT nanocomposite films. Raman spectroscopy, atomic force microscopy and conductivity measurement were used for the characterization of the samples.

Keywords:

polyaniline, montmorillonite, nanocomposite, thin film

1. INTRODUCTION

Nowadays, a growing interest in the use of polyaniline/phyllosilicate (PANI/MMT) nanocomposites is observed because of their uniquely high electrical conductivity, ease of synthesis and many potential applications in different fields such as energy storage devices [1], electronic and optical devices [2] or rechargeable batteries [3]. To the possible preparation methods belong electrochemical polymerization, mechanochemical intercalation, and in-situ oxidative polymerization [4]. The most common preparation route of polyaniline/phyllosilicate nanocomposites nowadays is the intercalation of the monomer into the interlayer space followed by polymerization [5]. Nanocomposites were prepared with organically pre-modified clays [6,7], and also several studies on synthesizing polyaniline/montmorillonite nanocomposite by a mechanochemical solid-state reaction can be found [8-10]. The novel properties arise from the arrangement of polymer chains on the surface and in the interlayer spaces of MMT (and other phyllosilicates) thus creating a high degree of structure ordering [11]. The MMT layers carry a negative layer charge and this causes the positive PANI chain to get attached to the MMT surface. The combination of PANI and MMT leads not only to the better electrical conductivity but also to the improved mechanical strength and thermal stability of resulting material.

Present study is focused on the dependence of PANI/MMT thin film conductivity and morphology on the temperature of reaction mixture.

2. MATERIALS AND METHODS

2.1 Materials

Na- MMT with basal spacing 1.24 nm and 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 purchased from Ankerpoort NV, Netherland. Aniline, ammonium peroxydisulfate and anilinium sulfate were used as received from Lach-Ner, Czech Republic. Microscope glass slides (76mm x 26mm x 1 mm) were used as substrates for PANI/MMT thin films.

2.2 Sample preparation

The glass slides were thoroughly washed in detergent solution, subsequently rinsed with distilled water, ethanol and dried. To prevent a formation of double side coating, one side of the glass slide was overlaid with scotch tape. Anilinium sulfate was used as a precursor for the preparation of PANI/MMT films on such treated glass slides. An appropriate amount of MMT (fraction < 5μm) was blended into a mix of two solutions (0.2 M aniline prepared in 0.5 M sulfuric acid and 0.1 M ammonium peroxydisulfate dissolved in distilled water). Glass slides were attached to clips with string, then hanging on a string they were dipped into a beaker with solution. During steady stirring a thin film was formed on the surface of glass slides. After several hours of polymerization the glass slides were withdrawn from the beaker and rinsed with 0.2 M hydrochloride acid to ensure the exchange of sulfate ions for chloride ions. Thereafter the samples were rinsed with ethanol and dried at 60°C. Two sets of glass slides with thin composite films differing in the preparation temperature were made. In the set PANI/MMT_10 the entire process of polymerization was carried out in a water bath with thermostat at 10°C. In the set PANI/MMT_20 the preparation process was performed at 20°C.

2.3 Structure and morphology

Raman spectra were recorded on Smart Raman Microscopy System XploRATM (Horiba JobinYvon, France). Laser 532 nm with 1% of laser signal and grating 1200 gr./mm were used for measurements. Both PANI glass slides were measured in 9 different points. In this paper the average spectra for both samples are presented. Atomic force microscopy (AFM), SolverNEXT (NT-MDT), was used for examining the thin film morphologies and surface character. The AFM was operated in contact mode using contact probe PPP-CONTR (Nanosensors). For the evaluation of the images IA P9 software (NT-MDT) was used.

2.4 Measurement of electrical conductivity

Homemade apparatus was used for the measurement of DC conductivity (Fig. 1). Voltage source DC POWER SUPPLY HY 3003 D-2 was used. 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. In all measurement static voltage of 1 V in the DC regime was used. The distance between linear Cu-electrodes was 3 mm. The apparatus was constructed in order to provide a perfect connection between the sample and Cu-electrodes. In addition, before use the Cu-electrodes were treated with special abrasive paste. The value of electric conductivity was obtained as an average of 300 values that were acquired during a 42 seconds-long measurements, each glass slide underwent 3 measurements in different regions of the sample.

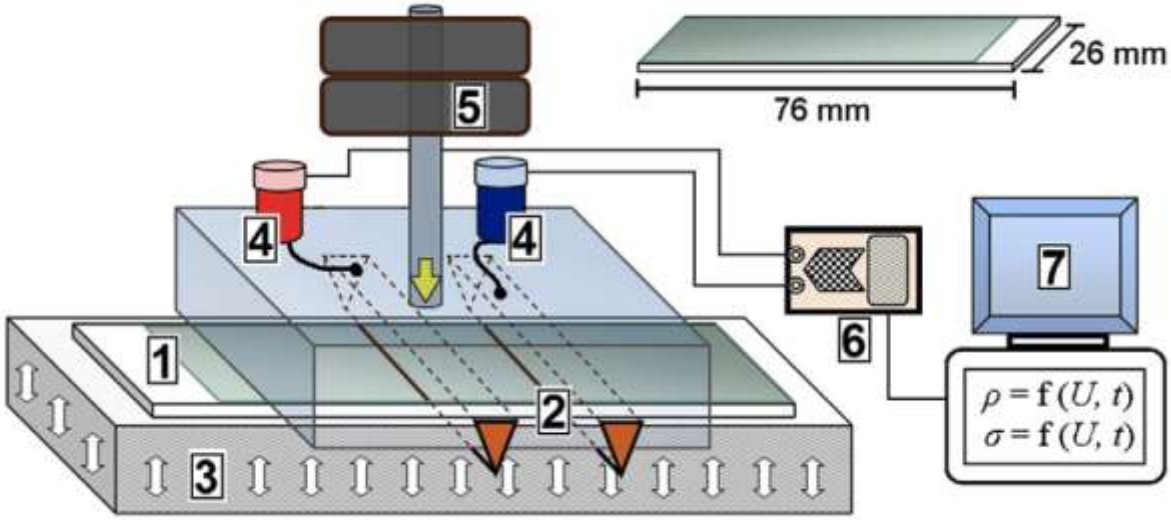

Fig. 1. Measuring device of DC conductivity. 1) sample - thin film on glass slide (glass slide dimensions in upper right corner); 2) Cu-electrodes (distance 3 mm); 3) flexible insulator; 4) voltage terminals; 5) weights to provide constant load; 6) measuring card; 7) PC + software

3. RESULTS AND DISCUSSION

The intercalation of anilinium ions into the MMT interlayer space during the preparation of nanocomposite was confirmed using the XRD analysis [12].

During analysis using Raman spectroscopy the PANI samples were measured in 9 different points. In these 9 points not the same protonation of the sample was observed and thus the average spectra were calculated and presented in the Fig. 2. The average spectra contain the same bands corresponding to the characteristic PANI spectrum. The bands of C=C and C-C stretching and C-H bending vibrations can be seen at 1599 and 1173 cm^{-1}, respectively [13]. Bands of out-of plane vibrations of aromatic rings can be found at 421 and 517 cm^{-1}, while a broad band at 815 cm^{-1} corresponds to the deformation vibrations of various substituted aromatic rings [14]. Two last bands are used for determination of the protonation state of PANI chains. The most important and characteristic band for the protonation state of PANI is band at 1334 cm^{-1} ($C\text{-}N^{+\bullet}$). Band at 1498 cm^{-1} corresponds to the C=N stretching vibration [15]. Fig. 2 clearly shows that the PANI/MMT_10 sample has more intensive band at 1498 cm^{-1} which means that the sample is less protonated. In the case of the PANI/MMT_20 sample this band is less intensive and the protonation band (1334 cm^{-1}) is more intensive, thus the sample is more protonated. In some measured points this difference in protonation state was more significant than in the average spectra.

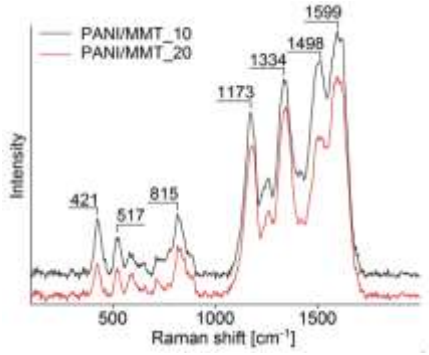

Fig. 2. Raman spectra of both PANI/MMT_10 and PANI/MMT_20 samples.

The final values of electrical conductivity are summarized in Table 1. By comparison of electrical conductivities of samples PANI/MMT_10 and PANI/MMT_20 we can state, that composites prepared at the higher temperature exhibited higher conductivity. This is a result of higher protonation of PANI/MMT_20 and thus a different structure of the thin layers.

Table 1. Film thickness (d), arithmetic mean value of roughness (R_a) and electrical conductivity (σ) are shown for samples prepared at 10°C and 20°C.

Sample	d [nm]	R_a [nm]	σ [$S.m^{-1}$]
PANI/MMT_10	360	101	268
PANI/MMT_20	508	289	1041

The AFM measurements show a significant difference in morphology of the samples (Fig. 3). Fig. 3a provides a closer look at the PANI/MMT_10. A relatively smooth layer with only small particles on the surface can be observed. The particles are separated from each other much more than in case of PANI/MMT_20 surface (Fig. 3b) on which a fairly large bulky particles of MMT and uneven surface can be seen.

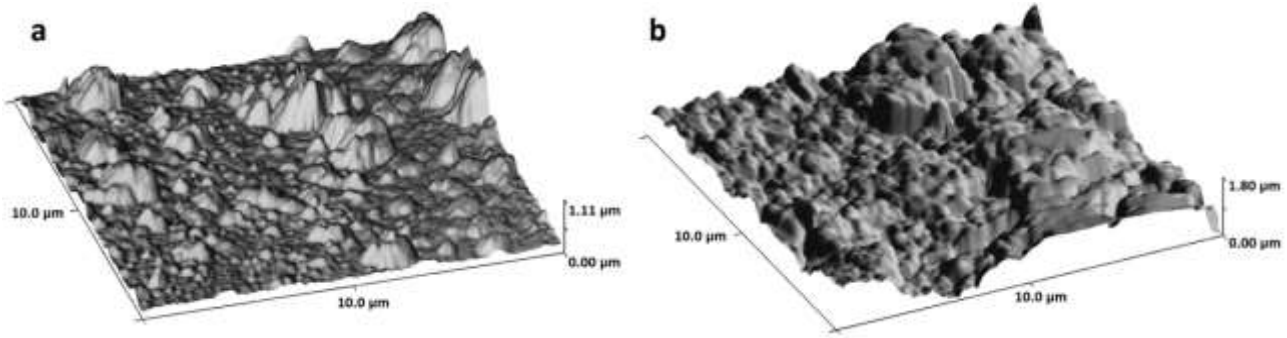

Fig. 3. AFM images of (a) PANI/MMT_10 on left, and (b) PANI/MMT_20 on right.

4. CONCLUSIONS

PANI/MMT are conductive composites which show interesting properties and can be prepared from available low cost materials. Thin layers of PANI/MMT nanocomposite were prepared on glass slides at 10°C and 20°C. Present data confirm the dependence of conductivity of PANI/MMT composite thin films on the temperature of reaction mixture. PANI/MMT nanocomposite thin film prepared at 20°C exhibited higher electrical conductivity than PANI/MMT thin film prepared at 10°C. This is caused by a higher protonation of PANI chains in the PANI/MMT_20 sample. However, the thickness and roughness of the surface is higher than for PANI/MMT_10.

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REFERENCES

[1] SHACKLETTE, L.W., CHANCE, R.R., IVORY, D.M., MILLER, G.G., BAUGHMAN, R.H. Electrical and optical properties of highly conducting charge-transfer complexes of poly(p-phenylene), *Synthetic Metals*, 1980, vol. 1, iss. 3, p. 307-320.

[2] NISHINO, H., YU, G., HEEGER, A.J., CHEN, T.A., RIEKE, R.D. Electroluminescence from blend films of poly(3-hexylthiophene) and poly(N-vinylcarbazole), *Synthetic Metals*, 1995, vol. 68, iss. 3, p. 243-247.

[3] KANATZIDIS, M.G. Coductive Polymers, *Chemical & Engineering News*, 1990, vol. 68, iss. 49, p. 36.

[4] GUPTA, R., RAKESH, A., MELVINE, A.A., PANDEY, A.C., PRAHASK, R. In-situ synthesis of polyaniline coated montmorillonite (Mt) clay using Fe^{+3} intercalated Mt as oxidizing agent, *Applied Clay Science*, 2014, vol. 95, p. 50-54.

[5] BEKRI-ABBES, I., SRASRA, E. Characterization and AC conductivity of polyaniline–montmorillonite nanocomposites synthesized by mechanical/chemical reaction, *Reactive and Functional Polymers*, 2010, vol. 70, iss. 1, p. 11-18.

[6] YANG, S.M., CHEN, K.H. Synthesis of polyaniline-modified montmorillonite nanocomposite, *Synthetic Metals*, 2003, vol. 135-136, p. 51-52.

[7] JIA, W., SEGAL, E., KORNEMANDEL, D., LAMHOT, Y., NARKIS, M., SIEGMANN, A. Polyaniline–DBSA/organophilic clay nanocomposites: synthesis and characterization, *Synthetic Metals*, 2002, vol. 128, iss. 1, p. 115-120.

[8] YOSHIMOTO, S., OHASHI, F., OHNISHI, Y., NONAMI, T. Synthesis of polyaniline–montmorillonite nanocomposites by the mechanochemical intercalation method*, Synthetic Metals*, 2004, vol. 145, iss. 2-3, p.265-270.

[9] OGAWA, M., HANDA, T., KURODA, K., KATO, C. Formation of Organoammonium-Montmorillonites by Solid-Solid Reactions, *Chemistry Letters*, 1990, vol. 19, p. 71-74.

[10] OGAWA, M., SHIRAI, H., KURODA, K., KATO, C., Solid-state intercalation of naphthalene and anthracene into alkylammonium-montmorillonites, *Clays and Clay Minerals*, 1992, vol. 40, iss. 5, p. 485-490.

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

[12] KULHÁNKOVÁ, L., TOKARSKÝ, J., MATĚJKA, V., PEIKERTOVÁ, P., VALLOVÁ, S., MAMULOVÁ KUTLÁKOVÁ, K., STÝSKALA, V., ČAPKOVÁ, P. Electrically conductive and optically transparent polyaniline/montmorillonite nanocomposite thin films*, Thin Solid Films*, 2014, vol. 562, p. 319-325.

[13] BERNARD, M.C., HUGOT-LE-GOFF, F.A. Quantitative characterization of polyaniline films using Raman spectroscopy: I: polaron lattice and bipolaron*, Electrochimica Acta*, 2006, vol. 52. iss. 2, p. 595-603.

[14] COLOMBAN, P., FOLCH, S., GRUGER, A. Vibrational study of short-range order and structure of polyaniline bases and salts, *Macromolecules*, 1999, vol. 32, iss. 9, p. 3080-3092.

[15] DA SILVA, J.E.P., DE TORRESI, S.I.C., DE FARIA, D.L.A., TEMPERINI, M.L.A. Raman characterization of polyaniline induced conformational changes, *Synthetic Metals*, 1999, vol. 101, iss. 1-3, p. 834-835.