

PREPARATION AND CHARACTERIZATION OF CONDUCTING COMPOSITE FROM ANILINIUM-MONTMORILLONITE INTERCALATE

¹DAVIDOVÁ Markéta, ¹KULHÁNKOVÁ Lenka, ²TOKARSKÝ Jonáš, ¹ŘEHÁČKOVÁ Lenka, ¹RITZ Michal, ¹MATĚJKA Vlastimil

¹VSB - Technical University of Ostrava, Faculty of Materials Science and Technology, Ostrava, Czech Republic, EU

²VSB - Technical University of Ostrava, CEET, Nanotechnology Centre, Ostrava, Czech Republic, EU

<https://doi.org/10.37904/nanocon.2022.4581>

Abstract

The main purpose of this work is to explore the possibilities of preparing conducting composite containing graphite or graphene from anilinium/montmorillonite intercalates. The use of only a precursor (without polymerization) is a fundamental difference compared to earlier research devoted to the preparation of graphite/graphene-silicate composites from polyaniline/montmorillonite intercalates. Therefore, the preparation procedure tested in this study represents another way to obtain an electrically conductive material, the electrically conductive component of which is formed *in situ*. Four different concentrations of anilinium sulfate solution were used to prepare these intercalates (0.2M; 0.4M; 0.6M; 0.8M). Montmorillonite was added to these solutions, and after 7 days of intercalation, the solutions were filtered and the resulting intercalates were dried. From each sample, one tablet was pressed, and the electrical conductivity of these tablets was measured before and after their calcination in argon atmosphere at 1300 °C. Electrical conductivity of the calcined samples crushed to powder was also measured. For the analysis of uncalcined samples, X-ray diffraction analysis was used. Calcined samples were analyzed using X-ray diffraction analysis and Raman spectroscopy. These analyses in combination with electrical conductivity measurements revealed that conducting composite can be prepared using the method described above.

Keywords: Graphite, montmorillonite, anilinium sulfate, electrical conductivity, calcination

1. INTRODUCTION

Composites containing graphite or graphene as conductive component are of interest to researchers mainly because of their high electrical conductivity [1,2]. The most common method of preparation is the use of ready-made graphite or graphene, which are commercially available, and their application to the selected matrix [1- 4]. However, graphite or graphene can also be prepared *in situ*, from a suitable precursor. The starting material in these cases can be, for example, SiC [5]. Phyllosilicate matrices intercalated with organic substances can also be used for this purpose [6,7]. Calcination of intercalates produces graphite or graphene in the resulting composite. In this work, the clay mineral montmorillonite (MMT) was used as a matrix. This most conventional layered silicate has a great ability to expand and accept other molecules into the interlayers to form an intercalate. The aim of this work was to use a simple organic molecule for the preparation of electrically conductive composite. Inspiration was taken from the article by Čapková et al. [7] in which the graphene was prepared from the polyaniline/MMT intercalate. The same precursor, aniline, was used in this work. However, it was only intercalated into the interlayers of MMT, the polymerization step was omitted here, and the preparation was thus generally easier. Taking into account that one of the reasons for the successful transformation of polyaniline into graphite and graphene was stated to be the arrangement of polyaniline chains on the surface of MMT, we were interested in the behavior of a similar intercalate in which anilinium polymerization was not performed.

2. MATERIALS AND METHODS

2.1. Materials and preparation of the samples

Na-montmorillonite (MMT) was purchased from Ankerpoort NV, The Netherlands. Basal spacing of the MMT is ~ 1.193 nm and the crystallochemical formula $(M_{0.5})(Al, Mg)_2(Si)_4O_{10}(OH)_2$ with a layer charge ~ 0.7 el. per unit cell. Aniline and sulfuric acid were used as received from Lach-Ner, Czech Republic. By addition of aniline to an aqueous sulfuric acid solution, solutions of anilinium sulfate were prepared. For the preparation of different concentrations of samples, different amounts of aniline were used. Then MMT was added to each sample and the suspensions were allowed to intercalate for 7 days. The final products were collected on filters by washing them with distilled water. Filter cakes were dried for 24 h at 40 °C. The prepared samples were denoted as 0.2An_MMT, 0.4An_MMT, 0.6An_MMT and 0.8An_MMT. To press the samples into square-shaped tablets, a table hydraulic press was used without using any binders or lubricants. The pressed tablets were calcined in a high-temperature tube resistance furnace (CLASIC CZ, spol. s.r.o., Czech Republic) equipped with a Pt-13% Rh/Pt thermocouple. In a tube, an inert atmosphere ($>99.9999\%$ Ar) was maintained under a constant overpressure of $1.06 \cdot 10^5$ Pa. The process included controlled heating and cooling within a temperature range of 25–1300 °C at a rate of 5 °C min⁻¹. The tablets were exposed to the target temperature of 1300 °C for 1 h. The Ar atmosphere was replaced four times during the process: at 900 °C, at 1100 °C, at the beginning and at the end of the 1 h interval at 1300 °C. The rate of each replacement was 5 dm³·min⁻¹, and each replacement took 5 min. The internal volume of the tube was 2.26 dm³.

2.2. Characterization methods

XRD analysis was performed on a Miniflex600 powder diffractometer (Rigaku, JP) with a DTex/Ultra 1D detector. The samples were measured in reflex mode, ranged from 5 to 80° 2Theta, with a step of 0.02° and a step time of 5° min⁻¹. During the measurement, a Co tube was used. Before measurement, the samples were ground to a fine powder. The Raman spectra were measured on the DXR SmartRaman dispersive Raman spectrometer (ThermoScientific, USA) with a CCD detector using a 180-degree measurement technique. The wavelength of the excitation laser was 780 nm, the grating was 400 lines mm⁻¹, the aperture 50 μm, the exposure time 1 s, and the number of exposures 250. An empty sample compartment was used for background measurement. The spectra were corrected for fluorescence (by a polynomial function of the 6th order).

2.3. Conductivity measurements

For DC conductivity measurement, we constructed a special measuring apparatus using DC POWER SUPPLY HY 3003 D-2, programmable DC POWER SUPPLY BK PRECISION 9120, pA-meter KEITHLEY 6487. The DC conductivity of the uncalcined tablets has been measured in two perpendicular directions, in the tablet plane (σ_{\leftrightarrow} ; **Figure 1**) and in an orthogonal direction to the tablet plane (σ_{\downarrow} ; **Figure 1**). Flat Cu electrodes were used for the measurements. The tablets of samples 0,2An_MMT and 0,4An_MMT after calcination were broken. Therefore, to measure the DC conductivity, these samples were first crushed into fine powder. In this case, the conductivity was denoted as σ_{pow} . The samples were then measured on a special measuring apparatus intended to measure powder samples. To estimate the effect that this crushing had on electrical conductivity, the electrical conductivity of samples 0.6An_MMT and 0.8An_MMT was measured first in tablets and then in crushed powder.

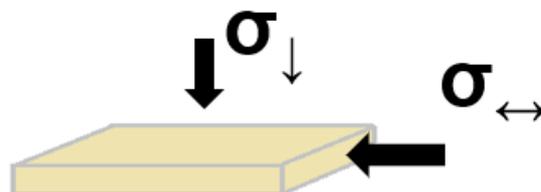


Figure 1 Directions of conductivities measured

3. RESULTS AND DISCUSSION

The profile of the (001) basal diffraction line of pure MMT and 0.2An_MMT XRD is shown in **Figure 2**. The shape of (001) diffraction line registered for pure MMT is of a diffuse character with a nonsharp maximum, which proves the disorder of the MMT particles. The intercalation of anilinium to interlayers of MMT caused the arrangement of MMT particles, which was manifested by a narrowing of the peak and an increase in its intensity. In all uncalcined samples, the presence of a peak at around 8.4° 2Theta proving intercalation in the MMT interlayers (**Figure 3**). However, in the XRD pattern of 0.8An_MMT (**Figure 3d**), additionally an intensive peak at around 6.5° 2Theta appears. This peak belongs to pure anilinium sulfate, which is confirmed by the XRD pattern of 0.8An_sulfate (**Figure 3e**). The comparison of these two patterns shows that the anilinium is located not only in the MMT interlayer space, but also on the surface of the MMT particles.

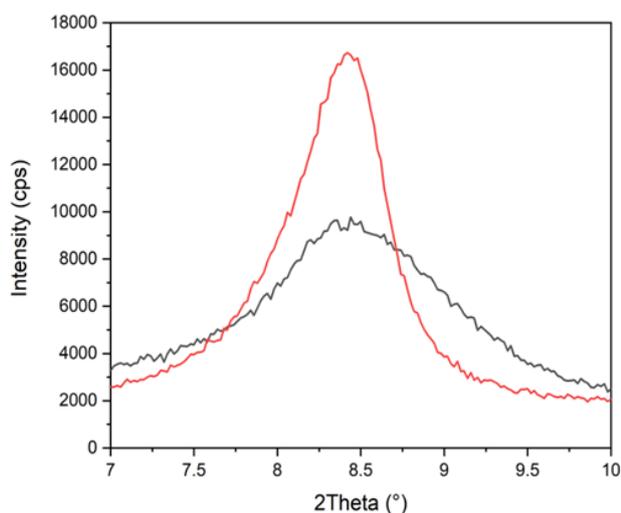


Figure 2 XRD patterns of pure MMT (black) and 0.2An_MMT (red)

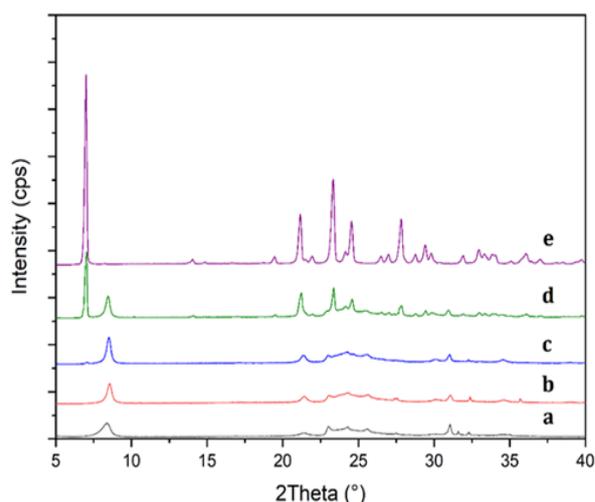


Figure 3 XRD patterns of uncalcined samples; a) 0.2An_MMT, b) 0.4An_MMT, c) 0.6An_MMT, d) 0.8An_MMT, e) 0.8An_sulfate

In the case of calcined samples (**Figure 4**), the diffraction line (001) is missing due to dehydroxylation of the MMT structure. Furthermore, the calcination of the intercalates led to the formation of cristobalite (PDF card No. 01-076-0941), mullite (PDF card No. 01-079-1457) and graphite (PDF card No. 03-065-6212).

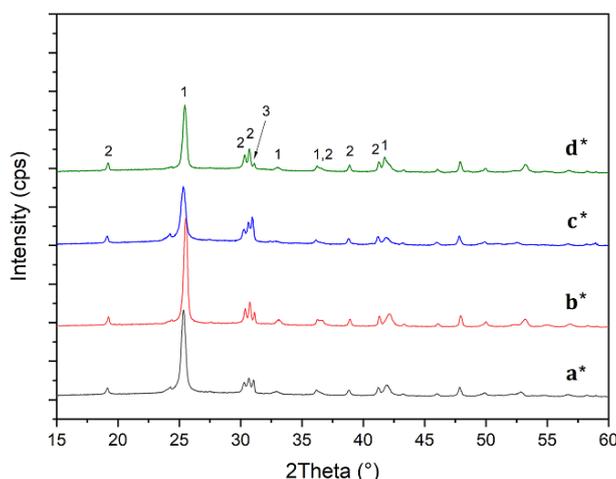


Figure 4 XRD patterns of calcined samples; a*) 0.2An_MMT, b*) 0.4An_MMT, c*) 0.6An_MMT, d*) 0.8An_MMT. 1 ... cristobalite, 2 ... mullite, 3 ... graphite

Raman spectra of the calcined samples are shown in **Figure 5**. The graphitic band confirming the orderliness of the carbon structure ($\sim 1590\text{ cm}^{-1}$) and the disorder band (shows defects in the samples; $\sim 1315\text{ cm}^{-1}$) appear in all spectra. The fact that disorder bands are more intensive than graphitic bands show the predominance of defects in the carbon structure [7-9]. In the spectra of sample 0.8An_MMT the peak of the band around 1600 cm^{-1} is divided to 1606 and 1579 cm^{-1} . The peak of 1606 cm^{-1} can prove the presence of aromatic rings bonded to nitrogen [10]. Also, a strong band at 2613 cm^{-1} can be observed in the spectra of 0.8An_MMT. This band is attributed to the 2D overtone of graphite [11]. The highest intensity of this band can be seen in spectrum of the 0.8An_MMT originally containing anilinium not only in the MMT interlayer space.

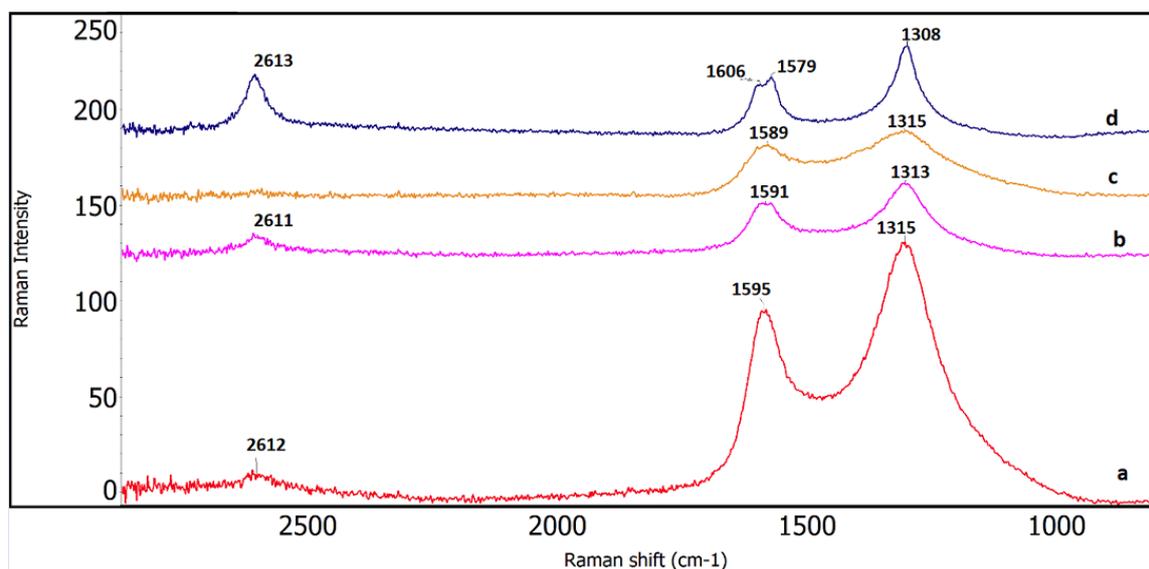


Figure 5 Raman spectra of calcined samples; a) 0.2An_MMT, b) 0.4An_MMT, c) 0.6An_MMT, d) 0.8An_MMT

The conductivities measured for the uncalcined samples (**Table 1**) showed very low values. This result was expected because in these samples, there is no ingredient that could provide electrical conductivity. Electrical conductivities of calcined samples are also listed in the **Table 1**. For these samples, a huge effect of calcination on conductivity can be seen. When comparing the electrical conductivities of samples measured in powder form and in tablet form, significantly higher σ_{pow} value can be observed for the 0.8An_MMT sample. This electrical conductivity is about twenty times higher in comparison with conductivity measurements of the 0.8An_MMT sample in tablet form. By pressing into tablets, the MMT particles were arranged in such a way that they had the function of an insulator [7]. Since the arrangement was disrupted when the sample was crushed, the flow of electric current was less restricted. This crushing together with the highest amount of anilinium and its location not only in the MMT interlayer space led to the highest electrical conductivity obtained for the 0.8An_MMT sample.

Table 1 Electrical conductivities of uncalcined and calcined samples

Sample	uncalcined		calcined		
	$\sigma_{\perp} (\text{S}\cdot\text{m}^{-1})$	$\sigma_{\leftrightarrow} (\text{S}\cdot\text{m}^{-1})$	$\sigma_{\text{pow}} (\text{S}\cdot\text{m}^{-1})$	$\sigma_{\perp} (\text{S}\cdot\text{m}^{-1})$	$\sigma_{\leftrightarrow} (\text{S}\cdot\text{m}^{-1})$
0.2An_MMT	$4.009\cdot 10^{-7}$	$1.018\cdot 10^{-4}$	2.574	X	
0.4An_MMT	$1.632\cdot 10^{-7}$	$3.145\cdot 10^{-5}$	11.652		
0.6An_MMT	$1.304\cdot 10^{-7}$	$2.601\cdot 10^{-5}$	5.651		
0.8An_MMT	$9.159\cdot 10^{-8}$	$1.839\cdot 10^{-5}$	53.210	0.069	2.642

4. CONCLUSION

In this work, an effort was made to synthesize conducting composite from An_MMT intercalate. Samples with four different concentrations of anilinium sulfate were prepared. Subsequently, the samples were calcined at 1300 °C. The XRD analysis of uncalcined samples revealed the anilinium intercalated into the MMT interlayers in all samples. In the case of the highest concentration (sample 0.8An_MMT), the anilinium was found also outside the MMT interlayer space. Raman spectroscopy and XRD analysis of calcined samples proved the presence of graphite. The formation of graphite was also confirmed by electrical conductivity, which in calcined samples was several orders of magnitude higher than in uncalcined samples. The highest conductivity correlates with the largest amount of anilinium and its presence outside the MMT interlayer. The graphite thus formed is probably located on the surface of the silicate grains, as was observed earlier [12], whereby contributes to the conductivity achieved. The question of the presence of graphene in the MMT interlayer and the number of layers of graphite formed will be the subject of further study. The present results confirm that the electrically conductive composite can be prepared from the intercalate without the need to polymerize the anilinium.

ACKNOWLEDGEMENTS

This work was supported by the Czech Republic Ministry of Education, Youth, and Sports project (SP2022/61).

REFERENCES

- [1] RAMÍREZ, C., F.M. FIGUEIREDO, P. MIRANZO, P. POZA, M.I. OSENDI, Graphene nanoplatelet/silicon nitride composites with high electrical conductivity. *Carbon*. 2012, vol. 50, pp. 3607-3615.
- [2] MUÑOZ-FERREIRO, C., A. MORALES-RODRÍGUEZ, T.C. ROJAS, E. JIMÉNEZ-PIQUÉ, C. LÓPEZ-PERNÍA, R. POYATO, A. GALLARDO-LÓPEZ. Microstructure, interfaces, and properties of 3YTZP ceramic composites with 10 and 20 vol% different graphene-based nanostructures as fillers. *J. Alloys Compd*. 2019, vol. 777, pp. 213-224.
- [3] ŁUKASZEWICZ, M., P. GŁUCHOWSKI, B. CICHY, W. STRĘK. Persistent photoconductance in graphene ceramics. *Phys. Pro cedia*. 2015, vol. 76, pp. 155-159.
- [4] BELMONTE, M., A. NISTAL, P. BOUTBIEN, B. ROMÁN-MANSO, M.I. OSENDI, P. MIRANZO. Toughened and strengthened silicon carbide ceramics by adding graphene-based fillers. *Scripta Mater*. 2016, vol. 113 pp. 127- 130.
- [5] MIRANZO, P., C. RAMÍREZ, B. ROMÁN-MANSO, L. GARZÓN, H.R. GUTIÉRREZ, M. TERRONES, C. OCAL, M. I. OSENDI, M. BELMONTE. In situ processing of electrically conducting graphene/SiC nanocomposites. *J. Eur. Ceram. Soc*. 2013, vol. 33, pp. 1665-1674.
- [6] C. XU, G. NING, X. ZHU, G. WANG, X. LIU, J. GAO, Q. ZHANG, W. QIAN, F. WEI. Synthesis of graphene from asphaltene molecules adsorbed on vermiculite layers. *Carbon*. 2013, vol. 62, pp. 213–221.
- [7] ČAPKOVÁ, P., V. MATĚJKA, J. TOKARSKÝ, P. PEIKERTOVÁ, L. NEUWIRTHOVÁ, L. KULHÁNKOVÁ, J. BEŇO a V. STÝSKALA. Electrically conductive aluminosilicate/graphene nanocomposite. *Journal of the European Ceramic Society*. 2014, vol. 34, no. 12, pp. 3111-3117.
- [8] CALIZO I., GHOSH S., BAO W., MIAO F., LAU C.N., BALANDIN A.A. Raman Nanometrology of Graphene: Temperature and Substrate Effects. *Solid State Communications*. 2009, vol. 149, pp. 1132-1135.
- [9] ZHOU Z., GU H., WANG C., ZHANG J., LV M., HE R. Study on the Synthesis and Surface Enhanced Raman Spectroscopy of Graphene-Based Nanocomposites Decorated with Noble Metal Nanoparticles. *Colloids and Surfaces A*. 2013, vol. 430, pp. 103-109.
- [10] M. BADAWI, H., W. FÖRNER a S. A. ALI. A comparative study of the infrared and Raman spectra of aniline and o-, m-, p-phenylenediamine isomers. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2013, vol. 112, pp. 388-396.
- [11] MALARD, L.M., M.A. PIMENTA, G. DRESSELHAUS a M.S. DRESSELHAUS. Raman spectroscopy in graphene. *Physics Reports*. 2009, vol. 473, pp. 51-87.
- [12] TOKARSKÝ, J., K. MAMULOVÁ KUTLÁKOVÁ, P. PEIKERTOVÁ, L. ŘEHÁČKOVÁ, M. KORMUNDA, P. MATĚJKOVÁ, S. ŠTUDENTOVÁ a L. KULHÁNKOVÁ. Polypyrrole/montmorillonite and polypyrrole/ghassoul intercalates as a source of graphite and multi-layer graphene: Preparation of nanocomposites exhibiting strongly anisotropic electrical conductivity. *Materials Research Bulletin*. 2021, vol. 142, 111429.