

## RAMAN MICROSPECTROSCOPY AS A USEFUL TOOL FOR THE POLYMER/CLAY NANOCOMPOSITES CHARACTERIZATION

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### Abstract

During the last decade, interest in conducting polymer/clay nanocomposites increased, mostly due to their very good physical, chemical, and mechanical properties, which can be significantly enhanced in various ways compared to pristine polymers. One of the most studied conducting polymers is polyaniline (PANI) which has unique electrical and optical properties, and, in addition, its interaction with clay structure leads to improvement of resulting electrical conductivity. In this study, the clay mineral montmorillonite (MMT) was used. Raman spectroscopy is nondestructive technique and coupled with an optical microscope has a potential to determine the chemical composition and possible inhomogeneity of the sample. Moreover, Raman spectroscopy is very sensitive to changes in the structure of polymers in terms of its protonation state. Aim of the study was the characterization of PANI/MMT nanocomposites prepared in three different forms (powders, layers, and tablets) by Raman microspectroscopy. In addition, after calcination of the prepared samples at 1300 °C, the transformation of PANI to the few-layer graphene was observed. Above that, Raman microspectroscopy was used to creation of the Raman spectral maps which reveal the distribution of the formed few-layer graphene.

**Keywords:** Raman microspectroscopy, polyaniline, montmorillonite, graphene, calcination

### 1. INTRODUCTION

Polyaniline (PANI) is one of the most studied conducting polymers because of unique electrical and optical properties, good redox reversibility and high environmental stability [1-2]. Due to its low cost, PANI could be useful in many applications such as sensors, antistatic and/or anticorrosive coatings, and many others [3]. According to intended application, several different forms of PANI can be prepared (thin films, powders, tablets) but whatever the form is, the most desirable feature is regular ordering of PANI chains leading to increased conductivity. Ordering of chains can be achieved by various methods, one of which is intercalation of PANI into interlayer space of phyllosilicates [4-6]. One advantage of phyllosilicate use is the plate-like shape of phyllosilicate particles which remains unchanged even after the surface modification and the particles in resulting nanocomposites exhibit the tendency to preferred arrangement [7]. Pressing these nanocomposites into the tablets further improves the texture of the sample [8]. Montmorillonite (MMT) is easily expandable layer silicate and has been chosen as the most convenient silicate matrix for the preparation of PANI/MMT nanocomposites. For PANI as conducting polymer and its possible application is also very important to know the protonation state of prepared samples.

Aim of the study was to prepare PANI and nanocomposites PANI/MMT samples in form of powder, thin film, and tablet and characterize them by Raman microspectroscopy, which is nondestructive and very sensitive technique suitable for detection of structural changes in polymers chains, especially for evaluation of PANI protonation state. Moreover, the PANI/MMT thin film and tablet were calcined at 1300 °C to prove the formation

of graphene in the samples. Raman spectral imaging was used in selected areas to determine not only the carbon form, but also the distribution of graphitic structure/few-layered graphene in samples.

## **2. EXPERIMENTAL**

### **2.1. PANI samples preparation**

Aniline, sulfuric acid and ammonium peroxydisulfate 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 peroxydisulfate in acidic environment (sulfuric acid). The green solid was collected on a filter by rinsing with 0.2 M hydrochloric acid and subsequently dried at 40 °C in a kiln.

Same simple oxidative chemical polymerization of the solution of aniline in concentrated sulfuric acid by strong oxidizing agent at room temperature was used for preparation PANI thin films. Quartz glass slide which was carefully washed in a soap solution, rinsed with distilled water, then with ethanol and dried was used and PANI thin film was deposited onto its surface by their rinsing into the reaction mixture.

Afterwards, PANI powder (3 g of powder for one tablet) was pressed into square tablets using ZWICK 1494 press at room temperature, without any lubrication and binder. Parameters of the controlled pressing were as follows. Loading speed was 1.0 mm·min<sup>-1</sup> and using final pressure (400 MPa) the sample was compacted for 10 min. Unloading speed was 0.1 mm·min<sup>-1</sup>.

### **2.2. PANI/MMT nanocomposites preparation**

PANI/MMT nanocomposites were prepared using one-step process. The anilinium sulfate and ammonium peroxydisulfate were added into water suspension of MMT (Commercially available Na-MMT Portaclay<sup>®</sup>, The mineral company Ankerpoort NV, Netherlands). Polymerization of aniline was completed after 60 min, but the suspension was stirred for 6 h to ensure that the largest possible amount of PANI enters the interlayer space of MMT. The green solid was again collected on a filter by rinsing with 0.2 M hydrochloric acid and dried at the same conditions as pure PANI sample.

Same type of quartz glass slide with same pre-treatment was used as substrates for PANI/MMT thin film. The preparation of PANI thin film was similar, when reaction mixture was mixed together with appropriate amounts of MMT. After several hours of polymerization and formation of thin film, the glass slide was removed from the mixture and rinsed with 0.2 M hydrochloric acid and dried.

PANI/MMT nanocomposite was used for the tablet preparation, which was similar as described in Chapter 2.1 and again pressure 400 MPa was used.

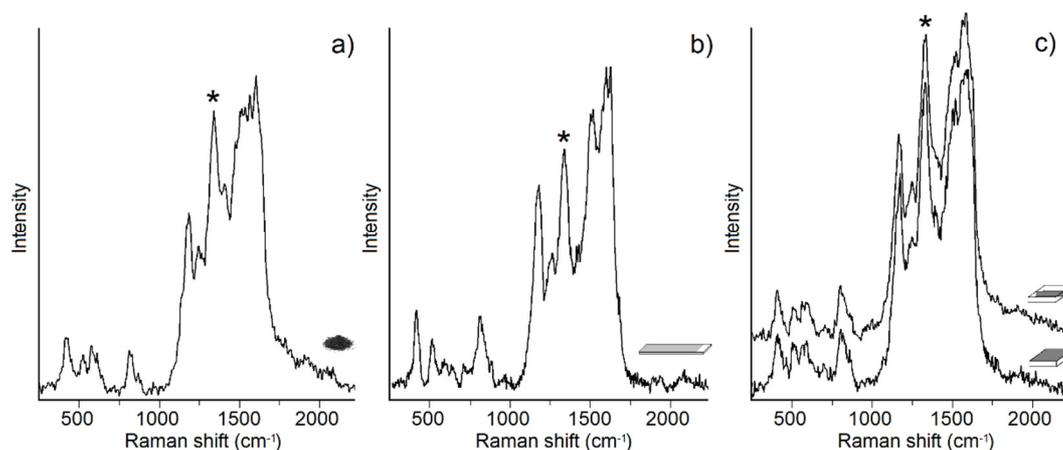
Moreover, PANI/MMT thin film and PANI/MMT tablet were calcined in the electric resistance tube furnace (CLASIC CZ Ltd., Czech Republic) at the temperature 1300 °C (for 1 hour). The temperature was controlled by Pt-13%Rh/Pt thermocouple placed near the sample. Heating and cooling rate was 5 °C·min<sup>-1</sup>. In order to avoid oxidization of the samples, protective Ar atmosphere was used.

### **2.3. Raman microspectroscopy**

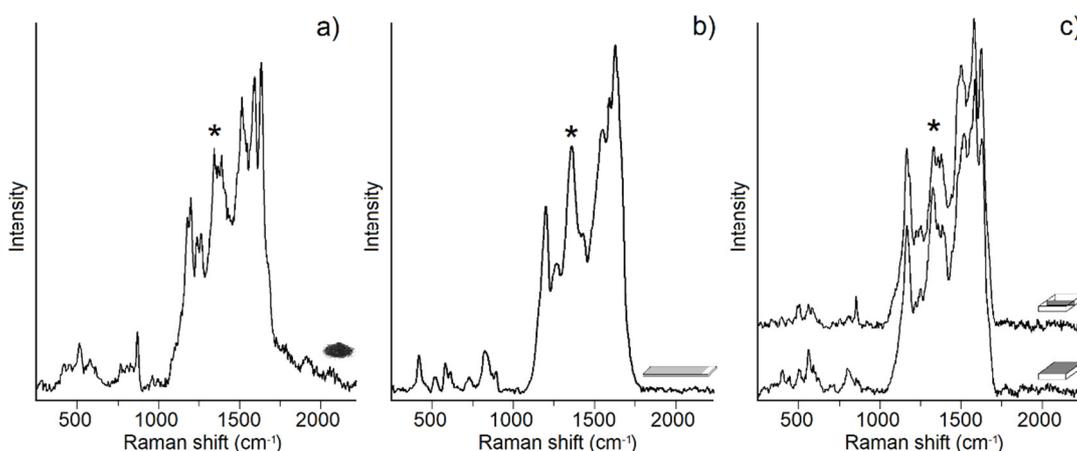
Raman spectra of all prepared samples were measured using a Smart Raman Microscopy System XploRA<sup>™</sup> (HORIBA Jobin Yvon, France). Spectra were acquired with 532 nm excitation laser source (20 - 25 mW). The intensity was reduced to the 10 % of the initial laser beam. Grating was set to 1200 grooves/mm and 100× objective for thin film and 50 × objective for powder and tablet measurement were used. Recording of the spectral maps was performed in selected regions with 1 μm step. Raman spectral maps were generated with respect to the intensity of 2D band which was used as an identifier of the presence of graphitic structure. Raman spectra and spectral maps were processed in LabSpec software which is part of XploRA<sup>™</sup> device.

### 3. RESULTS AND DISCUSSION

Since the Raman microspectroscopy allows measurements in very small area (laser spot has diameter  $\sim 500$  nm), several different points of each sample were measured and average spectra were created. Spectra of PANI powder, thin layer, and tablet (measured both on surface and in internal volume of the tablet) show characteristic bands of PANI (see **Figure 1**) with small differences. The most important band corresponds to the protonation state of PANI (also called protonation band - stretching vibration of C-N<sup>+</sup>) and it is located at  $1345\text{ cm}^{-1}$  (asterisk in **Figure 1**) [9]. Its intensity in spectra of all three types of sample confirmed protonation state of PANI. However, in the case of thin film, its intensity is the lowest (comparing with bands above  $1500\text{ cm}^{-1}$ ) in comparison with other two samples. There are also differences in region above  $1500\text{ cm}^{-1}$  which corresponds to changes in the benzene/quinone ratio in PANI chains [7]. Description of other PANI bands can be found in e.g. [7] and [9]. Spectra of tablet measured on the surface and in the internal volume are almost the same and there are not any significant differences in comparison with PANI powder which means that pressing does not affect the PANI structure.



**Figure 1** Average Raman spectra of the PANI powder (a), thin film (b) and tablet from the surface and the internal volume (c)

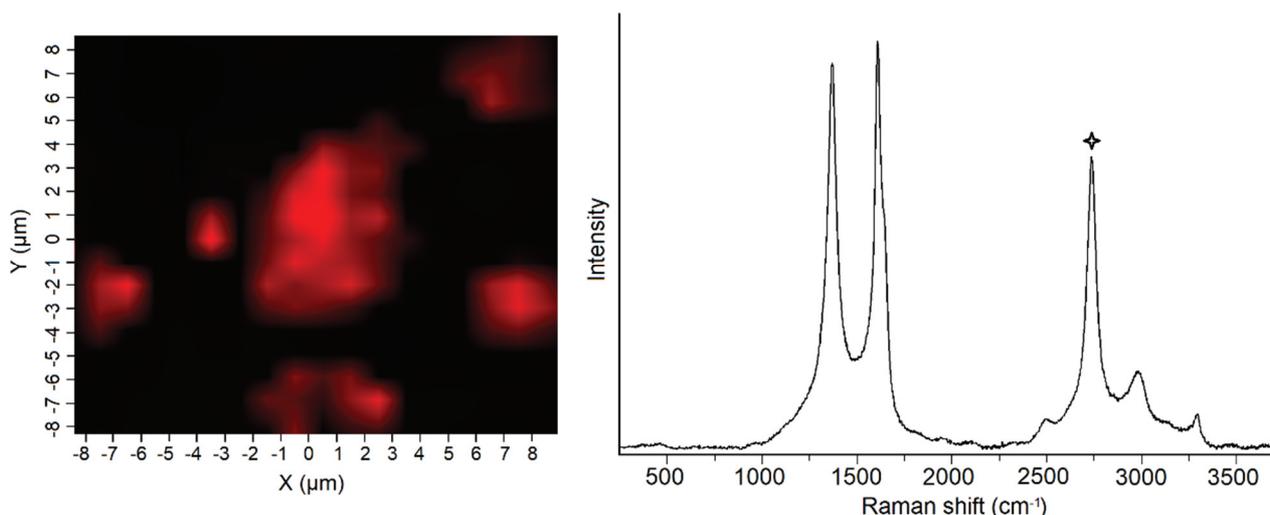


**Figure 2** Average Raman spectra of the PANI/MMT powder (a), thin film (b) and tablet from the surface and internal volume (c)

Average Raman spectra of all three types of PANI/MMT nanocomposites (powder, thin film, and tablet) show also the main characteristic bands of PANI (see **Figure 2**). Bands corresponding to the MMT are not visible

due to the high fluorescence of the clay [10]. The most significant difference is visible in protonation band of PANI (asterisk in **Figure 2**) and as well in region above  $1500\text{ cm}^{-1}$ . In case of PANI/MMT powder and tablet, significant decrease in the protonation band intensity was found when compared with PANI powder and tablet (**Figure 1**). On the contrary, the intensity in case of PANI/MMT thin film does not significantly change in comparison with PANI thin film (**Figure 1**). Decrease in the intensity could be connected with the presence of MMT. PANI chains are distributed in the interlayer space of MMT and as well on the surface of the MMT particles. Comparison of PANI/MMT (tablet) spectra from surface and internal volume clearly shows that average intensity in spectra measured on the surface is higher than average intensity in spectra measured in the internal volume. From Raman measurement can be concluded that MMT negatively affects protonation state of PANI, but the situation can differ in interlayer space of MMT particles where the PANI chains are stretched along the MMT layers [4].

Our previous study showed that calcination of PANI/MMT nanocomposite at  $1400^{\circ}\text{C}$  led to the formation of graphene while calcination at  $1200^{\circ}\text{C}$  not [8]. Therefore,  $1300^{\circ}\text{C}$  was used in this study and both thin film and tablet were calcined. Raman spectral maps were created for resulting samples. In case of calcined thin film, mostly the amorphous carbon (black areas in **Figure 3**) was detected. It corresponds to complete burning of PANI (no PANI bands were detected). Though, in some points were recorded spectra with graphitic structure. Raman spectral imaging was applied in selected areas (see **Figure 3**) for better distinguishing of these points.

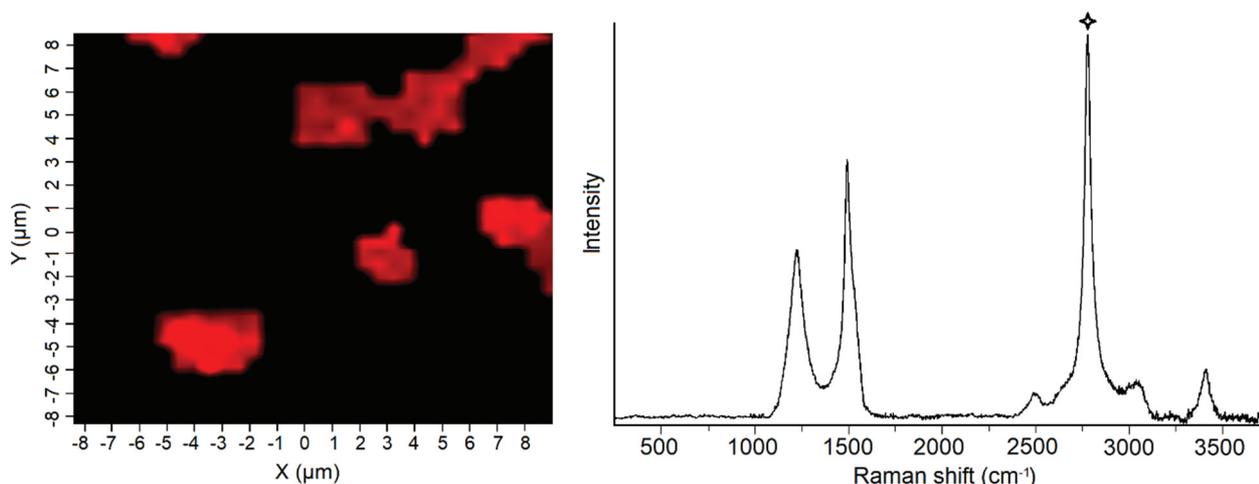


**Figure 3** Raman spectral map of chosen area on surface of calcined PANI/MMT thin film with Raman spectrum corresponding to the red areas in Raman spectral map

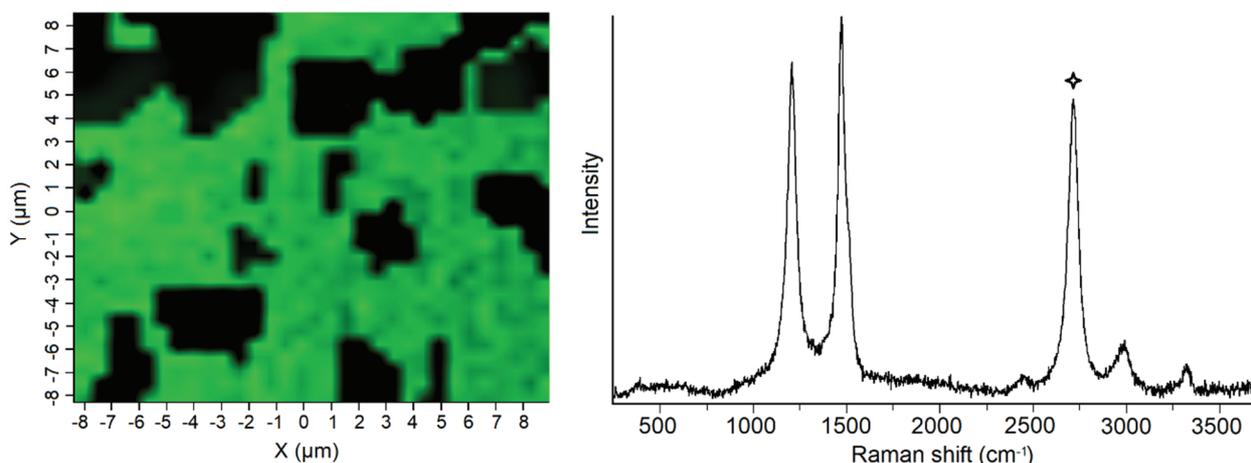
Raman spectral map shows areas (red color in **Figure 3**) where the graphitic structure was detected. The graphitic structure is confirmed by presence of 2D band (cross in spectrum in **Figure 3**) at  $\sim 2700\text{ cm}^{-1}$  which is always observed in Raman spectra of graphite samples. 2D band is connected to the second order of zone-boundary phonons, sometimes referred to as an overtone of the D band [11]. In ideal case of single-layered graphene, the 2D band should have the intensity four times higher than intensity of G band (graphitic band at  $1577\text{ cm}^{-1}$ ). The third most significant band is called D band (disorder band) and is located at  $1343\text{ cm}^{-1}$  and originates from disordered carbon atoms, thus, it cannot be found in spectra of the very well-ordered graphite and graphene [12]. These results suggest that the prepared carbon material is not pure graphite nor graphene and its distribution is inhomogeneous.

Raman spectra obtained from the surface of calcined PANI/MMT tablet revealed only the amorphous carbon (data not shown). However, in case of internal volume of calcined PANI/MMT tablet (see **Figures 4** and **5**), spectra of some areas (red color in **Figure 4**) exhibit 2D band with intensity higher than intensity of G and D

bands (see cross in **Figure 4**) which suggests presence of few-layer graphene. Unlike the **Figure 3**, black areas in **Figure 4** do not correspond only to amorphous carbon, but mainly to graphitic structure with intensity of 2D band lower than G band. These areas are highlighted in green in **Figure 5**. Only very small area corresponds to the amorphous carbon in comparison with Raman spectral map of thin layer. Thus, PANI/MMT tablet was proven as good precursor for the graphene formation during calcination. Detection of few-layered graphene only in the internal volume of tablet suggests importance of intercalation, and for non-intercalated PANI at least sandwiching between MMT particles.



**Figure 4** Raman spectral map of area in internal volume of calcined PANI/MMT tablet with Raman spectrum corresponding to the red areas in Raman spectral map



**Figure 5** Raman spectral map of area in internal volume of calcined PANI/MMT tablet with Raman spectrum corresponding to the green area in Raman spectral map

#### 4. CONCLUSION

Three types of PANI and PANI/MMT samples were prepared (powder, thin film, and tablet) and characterized by Raman microspectroscopy. Raman microspectroscopy confirmed protonation form of PANI in all samples. In case of nanocomposites PANI/MMT, the protonation state of PANI was lower than in case of pure PANI samples. However, PANI/MMT nanocomposite in form of thin film and tablet show potential to form few-layer graphene after calcination to 1300 °C. In case of PANI/MMT tablet, the formed graphene was better (higher intensity of 2D band) than in case of PANI/MMT thin film (lower intensity of 2D band). Thus, Raman

microspectroscopy is proven to be very useful tool for the PANI structure characterization and identification of carbon forms, and, in addition, allows creation of spectral maps, which serves for better understanding of distribution of carbon forms in selected areas.

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