ENHANCEMENT OF ELECTRICAL CONDUCTIVITY AND STABILITY OF POLYPYRROLE BY INTERCALATION INTO MONTMORILLONITE

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Abstract

Natural phyllosilicate montmorillonite (MMT) was intercalated by electrically conducting polymer polypyrrole in order to obtain nanocomposites with enhanced electrical conductivity and stability in comparison with pure polypyrrole (PPYR). Samples in powder form were prepared via oxidative polymerization of pyrrole in aqueous solution using $FeCl_3$ as oxidizing agent. Two nanocomposites MMT/PPYR_1 and MMT/PPYR_2 containing 32 wt.% and 45 wt.% of PPYR, respectively, were prepared and characterized. Composition of the samples was studied using elemental analysis and X-ray fluorescence spectroscopy, and amount of PPYR in each nanocomposite was calculated from results of thermogravimetric analyses. Intercalation rate was monitored by X-ray powder diffraction. Raman spectroscopy was used to characterize the polypyrrole in the samples. Electrical measurements performed over 700 days revealed the course of changes in conductivity. Comparison of conductivities of fresh samples showed enhancement of the conductivity and its preservation in the case of nanocomposites. The enhancement was observed throughout the whole testing period, the nanocomposites constantly exhibited higher conductivity compared to PPYR.

Keywords: Polypyrrole, montmorillonite, intercalation, conductivity, stability

1. INTRODUCTION

Polypyrrole (PPYR) belongs to the family of electrically conductive polymers with π-conjugated structure. Although the pure PPYR itself is suitable for various practical applications, e.g. sensors [1], attention is paid to tuning the conductivity by preparation of PPYR-based nanocomposites. Natural layered phyllosilicate montmorillonite (MMT) whose interlayer cations are exchangeable via intercalation proces is very suitable for this purpose. These nanocomposites exhibit increased conductivity in comparison with pure PPYR [2,3]. Stable conductivity is an important factor for practical applications, and, in the case of pure PPYR samples, temperature and time dependence of conductivity has been studied [4,5]. However, these experiments are still rare in papers devoted to MMT/PPYR nanocomposites. Effect of thermal ageing on AC conductivity of chemically prepared Fe-MMT/PPYR was studied by Zidi et al. [6], and effect of ageing under ambient conditions (60 days) on DC conductivity of electrochemically prepared PPYR mixed with caprolactam-modified MMT was reported by Liu and Tsai [7]. Present work describes chemical synthesis of pure PPYR and two MMT/PPYR nanocomposites and their characterization. Pure unmodified Na-MMT was also characterized for comparison. Attention was paid to determination of PPYR amount in the nanocomposites, but the main goal of the experiment was to monitor the changes in conductivity of the nanocomposites and the PPYR over a long-time horizon of 700 days.

2. MATERIALS AND METHODS

Pyrrole (C_4H_5N; ≥ 98 %, reagent grade) and ferric chloride ($FeCl_3$) were used as received. Crystallochemical formula of the Na-MMT Portaclay® is $(Al_{2.85}Mg_{0.71}Ti_{0.02}Fe^{3+}_{0.42})(Si_8)O_{20}(OH)_4$ with negative layer charge -0.69 el. per unit cell. Size fraction < 40 µm was used. Pure PPYR was prepared via oxidative polymerization of 0.05 mol of pyrrole by 0.1 mol $FeCl_3$ in 250 ml of water. MMT/PPYR_1 and MMT/PPYR_2 nanocomposites were prepared similarly via oxidative polymerization of pyrrole (n = 0.025 or 0.05 mol) by $FeCl_3$ (n = 0.05 or 0.1 mol) in 250 ml of MMT aqueous dispersion (m = 4 g). After 6 h, black solids were collected on filters by rinsing with distilled water and dried for 24 hours at 40 °C. Samples were stored in closable plastic vessels in the dark at an average room temperature of 25 °C.

Thermogravimetric (TG) analysis was performed using Netzsch STA 409 EP thermogravimeter. Samples were heated up to 800 °C (10 °C/min) in dry air with a flow rate 100 cm^3/min. Elemental analysis was performed using Vario EL Cube Elementar Analyzer with sulfanilic acid as a standard. Chlorine was determined by titration. Chemical composition was also determined by X-ray fluorescence spectroscopy (XRFS) using SPECTRO XEPOS spectrometer equipped with 50 W PdX-ray tube. Intercalation was controlled by Bruker D8 Advance diffractometer equipped with detector VÅNTEC 1. X-ray powder diffraction (XRPD) patterns were obtained in reflection mode under CoKα radiation (λ = 1.7889 Å). Raman microspectroscopy was performed using Raman microscope XploRA™, Horiba Jobin Yvon, equipped with 785 nm excitation laser source, with 50× objective and using 600 gr/mm grating. Acquisition time was set to 30 s with ten repetitions. Electrical measurements of powder samples (V ~ 60 mm^3; height of column ~ 5 mm) were performed using home made device equipped with measuring card PCI-6221. Electric current passing through the sample between two polished Cu electrodes under the constant voltage U = 1 V (DC voltage source HY3003D) was measured for 600 s and the mean value was used to calculate the conductivity. Each measurement was repeated five times in order to obtain average conductivity value.

3. RESULTS AND DISCUSSION

3.1. Composition of samples

XRFS analysis revealed increasing Cl content in MMT/PPYR nanocomposites compared to pure MMT (**Table 1**). This finding together with decrease in amount of other analytes and increase in LOI values suggests expected increase in PPYR amount in the nanocomposites.

Table 1 Composition of samples according to XRFS analysis. LOI - loss on ignition.

sample	Al_2O_3 (wt.%)	Cl (wt.%)	Fe_2O_3 (wt.%)	MgO (wt.%)	SiO_2 (wt.%)	SO_3 (wt.%)	LOI (wt.%)
MMT	19.4±2.3	0.02±0.01	3.81±0.75	3.22±0.54	56.7±1.4	0.68±0.12	11.9
MMT/PPYR_1	13.0±2.0	3.39±1.13	3.18±0.07	2.47±0.37	41.5±6.3	0.23±0.07	34.2
MMT/PPYR_2	10.2±1.6	5.71±0.86	2.56±0.39	2.32±0.35	30.5±4.6	0.08±0.01	43.7

TG analysis in temperature range 30-800 °C (**Table 2**) showed four temperature intervals of weight loss for pure MMT. The first two intervals can be attributed to loss of water adsorbed on MMT surface and loss of water in the MMT interlayer space, respectively. No weight loss was detected in the third interval. Weight loss in the last interval is caused by dehydroxylation of the MMT [8]. Total weight loss of the MMT was 7.8 wt.%. In the case of PPYR sample, two temperature intervals of weight loss were observed (**Table 2**). The first one corresponds to loss of water, and the second one can be attributed to PPYR degradation. This observation agrees with previously reported experiments [2]. Total weight loss of the PPYR was 90.6 wt.%. Weight losses of the nanocomposites in the first two intervals were similar to the MMT. However, unlike the MMT, significant weight loss was observed in the third interval (**Table 2**). This can be attributed to the decomposition of PPYR in the nanonocomposite. Since the weight loss in the last interval is higher in comparison with pure MMT, simultaneous dehydroxylation of MMT and additional decomposition of PPYR can be expected.

Table 2 Weight losses of MMT, PPYR, and MMT/PPYR nanocomposites according to TG analysis. Only two intervals of weight loss were observed for PPYR.

sample	$\Delta m_{30\text{-}110°C}$ (wt.%)	$\Delta m_{110\text{-}200°C}$ (wt.%)	$\Delta m_{200\text{-}580°C}$ (wt.%)	$\Delta m_{580\text{-}800°C}$ (wt.%)
MMT	3.8	1.0	0.0	3.0
PPYR	4.4		86.2	
MMT/PPYR_1	2.1	1.4	32.1	8.1
MMT/PPYR_2	3.1	1.5	44.9	3.2

Rough estimation of the PPYR amount in the nanocomposites according to the third interval in **Table 2** was refined by calculation using the following formula [9]:

$$\Delta m_{MMT/PPYR} = w_{PPYR} \cdot \Delta m_{PPYR} + (1 - w_{PPYR}) \cdot \Delta m_{MMT} \tag{1}$$

where $\Delta m_{MMT/PPYR}$ is the residue of MMT/PPYR nanocomposite after heating (wt.%), w_{PPYR} is the proportion of PPYR (wt.%), Δm_{PPYR} is the residue of PPYR after heating (wt.%), and Δm_{MMT} is the residue of MMT after heating (wt.%). Calculated amount of PPYR, i.e., 31.9 wt.% and 44.7 wt.% for MMT/PPYR_1 and MMT/PPYR_2, respectively, is not only very close to the initial estimation but is also in good agreement with data obtained from elemental analysis (**Table 3**).

Table 3 Elemental analysis of MMT/PPYR nanocomposites

sample	C (wt.%)	H (wt.%)	N (wt.%)	S (wt.%)	Cl (wt.%)
MMT/PPYR_1	18.49±0.06	2.226±0.014	5.318±0.008	0.156±0.005	4.17±0.14
MMT/PPYR_2	28.22±0.03	2.710±0.002	8.157±0.019	0.120±0.002	5.59±0.08

Elemental analysis confirmed presence of all elements contained in PPYR (**Table 3**). Small amount of S originates from the MMT as revealed by XRFS (**Table 1**). Total amount of C, H, N, and Cl for MMT/PPYR_1 and MMT/PPYR_2, i.e., 30.20 wt.% and 44.67 wt.%, respectively, agrees well with PPYR amounts obtained from TG analysis using Eq. (1). While the C/N ratio in PPYR is ideally equal to 3.43, values 3.48 and 3.46 were found for MMT/PPYR_1 and MMT/PPYR_2, respectively. This result shows successful polymerization.

3.2. Monitoring the intercalation

Original MMT sample exhibits asymmetric shape of (*001*) basal reflection having FWHM = 0.94 °2θ. Quite regular arragement of part of the MMT layers with d_{001} = 12.569 Å (**Figure 2a**) corresponds with presence of hydrated Na^+ cations in the MMT interlayer space [10], however, another part of the MMT layers exhibits less regular arrangement (6.0-7.5 °2θ in **Figure 2a**). Significant increase in basal distances observed for nanocomposites suggests that the intercalated structure was successfully prepared (**Figure 2a**). Finding that basal distance of the MMT/PPYR_1 (d_{001} = 17.631 Å; FWHM = 1.17 °2θ) is higher than basal distance of the MMT/PPYR_2 (d_{001} = 15.315 Å; FWHM = 1.50 °2θ) led to repeated preparation of both nanocomposites, however, the same result was obtained. It can be explained by rapid reaction of pyrrole with $FeCl_3$, which in the case of MMT/PPYR_2 with higher content of these compounds in the reaction mixture leads to disorder in arrangement of MMT layers and to lower intercalation. The explanation is supported by both lower intensity of (*001*) basal reflection and higher FWHM value of the MMT/PPYR_2. XRPD analyses of prepared nanocomposites were performed three times during the experiment: 1 day, 303 days, and 700 days after preparation. No significant differences were found, d_{001} values varied only in tenths of angstrom. For illustration, basal reflections of the MMT/PPYR_1 nanocomposite are shown in **Figure 2b**.

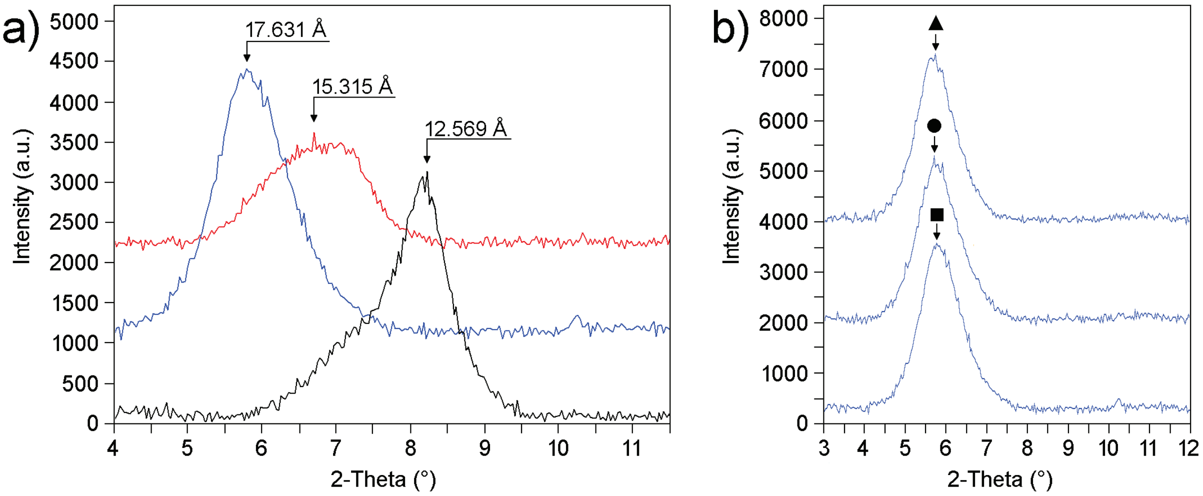

Figure 1 (a) XRPD profiles of *(001)* basal reflections for pure MMT (black), MMT/PPYR_1 (blue), and MMT/PPYR_2 (red) measured 1 day after preparation. (b) Comparison of (*001*) basal reflections for MMT/PPYR_1 over time. ■ 1 day, d_{001} = 17.631 Å; ● 303 days, d_{001} = 17.801 Å; ▲ 700 days, d_{001} = 17.714 Å.

3.3. Electrical conductivity and Raman spectroscopy

Electrical measurements of fresh samples performed one day after preparation showed enhancement of the conductivity in the case of nanocomposites (σ_{PPYR} = 21.7±1.5 S/m, $\sigma_{MMT/PPYR\_1}$ = 49.1±6.5 S/m, $\sigma_{MMT/PPYR\_2}$ = 41.1±5.2 S/m; see **Figure 2**). Although the decrease of initial conductivities is obvious for all samples throughout the whole testing period, MMT/PPYR_1 and MMT/PPYR_2 nanocomposites constantly exhibited higher conductivity compared to pure PPYR. After 700 days, conductivities σ_{PPYR} = 0.7±0.03 S/m, $\sigma_{MMT/PPYR\_1}$ = 21.2±1.7 S/m, and $\sigma_{MMT/PPYR\_2}$ = 24.1±4.7 S/m were obtained (**Figure 2**). Concerning preservation of the conductivity, the PPYR exhibits only 3 % of the original value after 700 days, while the MMT/PPYR_1 and MMT/PPYR_2 nanocomposites exhibit 45 % and 54 %, respectively, after the same time period.

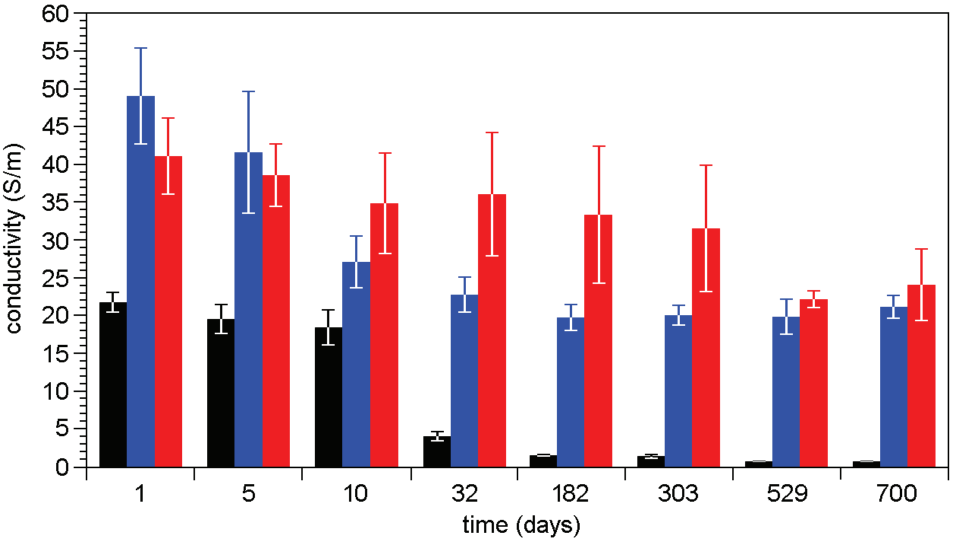

Figure 2 Changes in electrical conductivity of pure PPYR (black), MMT/PPYR_1 (blue), and MMT/PPYR_2 (red) monitored over a long time horizon of 700 days

A drop below 50 % of the original conductivity was recorded on both PPYR and MMT/PPYR_1 samples between the 1st and the 32nd day. While the conductivity of the PPYR further decreased, the conductivity of the MMT/PPYR_1 sample was preserved until the end of the experiment (32nd - 700th day; **Figure 2**). Average value calculated from five mean conductivities during this period is 20.7±1.2 S/m. Conductivity of the MMT/PPYR_2 sample was relatively stable from the 10th to the 303rd day (**Figure 2**), and the average value calculated from four mean conductivities of the MMT/PPYR_2 during this period is 33.9±1.7 S/m.

Raman spectra, measured in the 1st and the 700th day, are shown in **Figure 3**. All characteristic bands of PPYR are present [11,12], however, MMT bands are not visible due to the MMT fluorescence. The spectra of fresh samples (the 1st day; **Figure 3a**) showed that the pure PPYR sample is less conductive compared to MMT/PPYR_1 and MMT/PPYR_2 samples, because band of C=C and C-C stretching related to oxidation state of the polymer (marked with ▼in **Figure 3**) is shifted to the highest wavenumbers [11,12]. The lowest wavenumber of this band detected for the sample MMT/PPYR_1 indicate the highest conductivity. Also, the more intensive band of C-H in-plane deformation vibrations in radical cation units in protonated polypyrrole (marked with ★) in comparison with band of C-H in-plane deformations in the neutral units of polypyrrole base (marked with ✦) is connected to the better protonation of the sample MMT/PPYR_1 (see **Figure 3a**) [11,12]. This is in good agreement with electrical measurements (**Figure 2**).

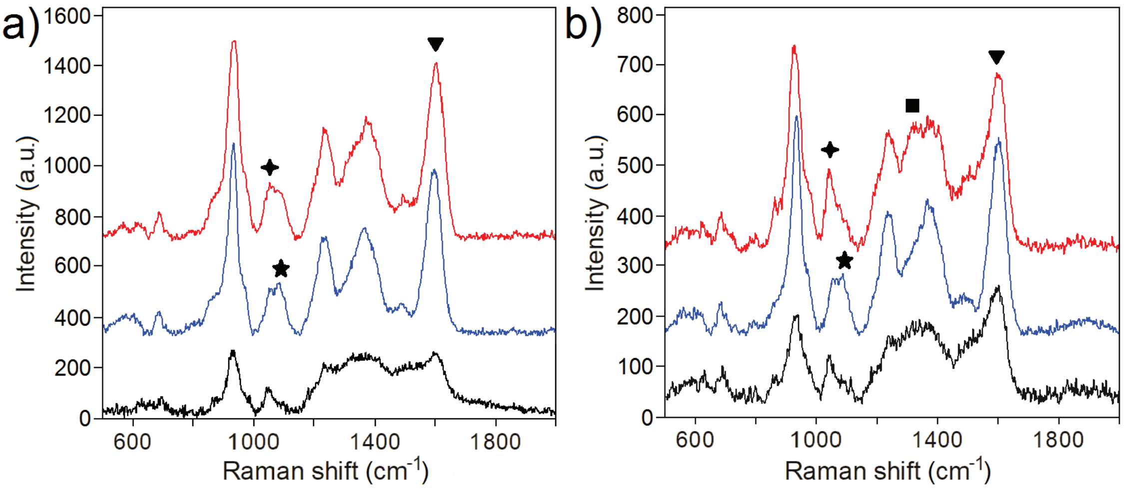

Figure 3 Raman spectra of pure PPYR (black), MMT/PPYR_1 (blue), and MMT/PPYR_2 (red) measured 1 day after preparation (a) and 700 days after preparation (b)

Raman spectra measured after 700 days (**Figure 3b**) are noisier and their overall intensities are lower compared to spectra from the 1st day. The band ★ is still more intensive than the band ✦ in spectrum of the MMT/PPYR_1 (**Figure 3b**), and the band of neutral C-C ring stretching vibrations related to of reduced units (denoted as ■ in **Figure 3b)** appeared in spectrum of the MMT/PPYR_2. This should indicate the highest conductivity of the MMT/PPYR_1 sample [11,12], however, the wavenumber of the band ▼ is higher compared to spectrum of the MMT/PPYR_2 sample (**Figure 3b**) suggesting lower conductivity. Conductivity can be, therefore, considered equal, which agrees with electrical measurements (**Figure 2**).

4. CONCLUSION

Two nanocomposites MMT/PPYR_1 and MMT/PPYR_2 containing 32 wt.% and 45 wt.% of PPYR, respectively, were succesfully prepared by intercalation of MMT. Composition and structure of the nanocomposites and pure components, i.e., PPYR and MMT, were studied using XRFS, TGA, elemental analysis, XRPD, and Raman spectroscopy. Electrical conductivity of the samples was monitored over 700 days, and higher conductivity of the nanocomposites and significantly lower decrease in the conductivity compared to pure PPYR were observed. After 700 days, the conductivity of MMT/PPYR_1 and MMT/PPYR_2 decreased by 55 % and 46 %, respectively, while the conductivity of pure PPYR decreased by 97 %. Stable conductivity is important for practical applications. Conductivity of the MMT/PPYR_1 was stable between 32nd and 700th day, i.e., for 668 days, and the average conductivity during this period was $\sigma_{average}$ = 20.7±1.2 S/m. For the MMT/PPYR_2, the stability in conductivity was observed between 10th and 303rd day day, i.e., for 293 days, and the average conductivity during this period was $\sigma_{average}$ = 33.9±1.7 S/m.

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