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STUDY OF PANI THIN FILM POLYMERIZATION

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Abstract: Polyaniline (PANI) is one of the most studied and applied conducting polymers because of the unique conduction mechanism and high environmental stability. PANI could be synthetized by chemical or electrochemical methods. For this study PANI thin films deposited on glass substrate were prepared by chemical bath deposition from anilinium sulfate (precursor) using ammonium peroxodisulfate as strong oxidizing agent. Prepared samples were dried in high voltage static electric field (0.6 - 2.7 kV/cm). The most important effect was the increase of PANI thin film conductivity. Results showed changes in the microstructure, morphology, and conductivity of PANI thin films in dependence on high voltage electrical field. Optical transmittance was studied by UV-VIS spectroscopy and Raman micro spectroscopy was used to study structural changes in PANI chains. Variances in the range 1480-1650 cm-1 was revealed in Raman spectra. The dependence of conductivity on electric field intensity showed the maximum for samples dried in field of intensity 1.0 kV/cm. This conductivity was 374 S/m. Presented results show the possibility to change the structure properties of PANI thin films using high voltage static electrical field.

Keywords: Polyaniline, conducting polymer, thin film, high voltage, Raman spectroscopy.

1. INTRODUCTION

Conducting polymer with unusual electrical and optical properties is polyaniline (PANI). PANI also has very good environmental stability and good redox reversibility [1,2]. Low cost and wide availability of aniline and its derivatives marked PANI as an ideal candidate in various applications such as electrochemical devices [3,4], light-emitting diodes [5], gas and pH sensing [6-9], and many others. Thin films from PANI polymer are frequently studied form of PANI on different substrates and with different techniques of preparations [10]. Many studies used glass slides, because they are transparent and chemically stable, e.g. Stejskal et al. used glass slide as a substrate for PANI thin films [11]. Our study shows the modification of the conductivity of PANI thin films by the postsynthetic high-voltage (HV) electrical field treatment in the range 0.6 – 2.7 kV/cm. Prepared samples were compared with the untreated sample (reference sample). Influence on PANI structure, optical and electrical properties was estimated by Raman spectroscopy, UV-VIS spectroscopy and conductivity measurements, respectively.

2. EXPERIMENTAL

2.1 PANI films preparation PANI thin films were coated on the glass slides (76 mm x 26 mm x 1 mm) which were washed in a soap solution, rinsed with distilled water, then with ethanol and dried. PANI thin film was coated on the only one side of the slide, because one side was covered by a scotch tape. PANI thin films were prepared by mixing two following solutions: 0.2 M aniline prepared in 0.5 M sulfuric acid, and 0.1 M ammonium peroxodisulfate dissolved in distilled water. The sulfuric acid has been used because it leads to much higher conductivity than aniline hydrochloride as we proved [12]. Before the polymerization and formation of PANI thin film the glass slide was attached by clips and was hanged on strings into the beaker. Polymerization process takes 20 minutes and then the glass slide with PANI thin film was removed from the beaker and rinsed with 0.2 M hydrochloric acid. All samples were dried in the DC HV field (MBS 601 – Tesla Brno). The intensities of the HV field were chosen 0.6, 1.0, 1.5, 2.0 and 2.7 kV/cm and prepared samples were denoted as P_0.6, P_1.0, P_1.5, P_2.0 and P_2.7 respectively. Reference sample (P_0) has been prepared at same conditions and let dried out of the field.

2.2 PANI films characterization Conductivity of the PANI thin films was measured by static applied voltage in DC regime using electrodes made of conductive rubber. These instruments were used: DC POWER SUPPLY HY 3003 D-2, V-meter UNIT_T UT802, pA-meter KEITHLEY 6487. To better understanding of this special apparatus see our work [13]. During and after repeated measurements, there was no visible damage of the PANI thin films caused by the electric current flowing the samples.

Raman spectra were acquired with 532 nm excitation laser source, with 100x objective and using 1200 gr./mm grating in the Smart Raman Microscopy System XploRATM (Horriba Jobin Yvon, France). CINTRA 303 (GBC Scientific Equipment) was used to measure UV-VIS spectra. The optical transmittance was measured at normal incidence at room temperature in the spectral range of 800-350 nm. Speed was 1000 nm/min with step size 0.427 nm, slit width was 2.0 nm.

3. RESULTS AND DISCCUSSION

Optical transmittance in dependence on wavelength for all prepared samples is shown in Figure 1. All prepared PANI thin films had the green color, what correspond to the conducting form of PANI (emeraldine salt) with chains lengths longer than 10-mer units [14]. During the HV treatment no color change was observed. From the spectra could by clearly observed, that the optical transmittances can be considered nearly the same. Maxima of the transmittance values with corresponding wavelengths are listed in Table 1.

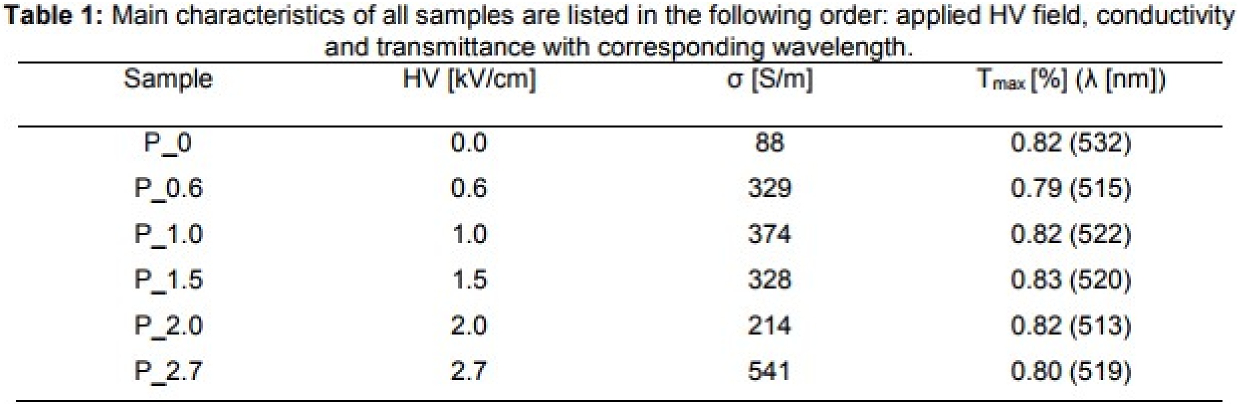

Table 1: Main characteristics of all samples are listed in the following order: applied HV field, conductivity and transmittance with corresponding wavelength.

Sample	HV [kV/cm]	σ [S/m]	T_{max} [%] (λ [nm])
P_0	0.0	88	0.82 (532)
P_0.6	0.6	329	0.79 (515)
P_1.0	1.0	374	0.82 (522)
P_1.5	1.5	328	0.83 (520)
P_2.0	2.0	214	0.82 (513)
P_2.7	2.7	541	0.80 (519)

Table 1 also summarizes the conductivity results in dependence on HV field intensity. Drying in the HV electric field leads to significant changes in the conductivity of the samples. Usage of the HV electric field up to 1 kV/cm leads to increase the conductivity, contrary to further increase of HV electric field to decrease the conductivity. Special case occurred for electric field of the intensity above 2 kV/cm, because the corona discharge has been observed. Corona discharge has significant influence on the conductivity of PANI thin film. The sample denoted as P_2.7 exhibits the highest conductivity (541 S/m). Unfortunately this increase of the conductivity was accompanied by the degradation of PANI chains [15]. If this special case with corona discharge left aside, the highest conductivity was observed for sample dented as P_1.0.

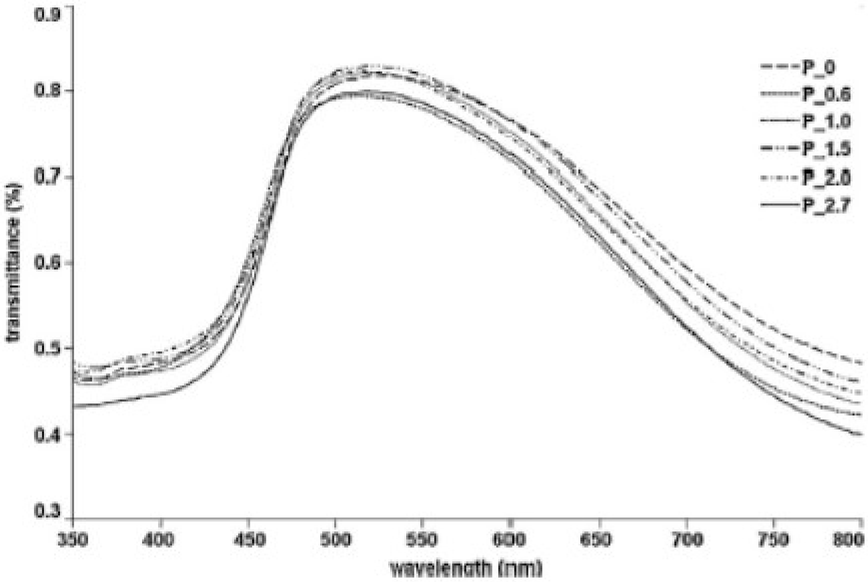

Figure 1: UV-VIS spectra for all prepared samples

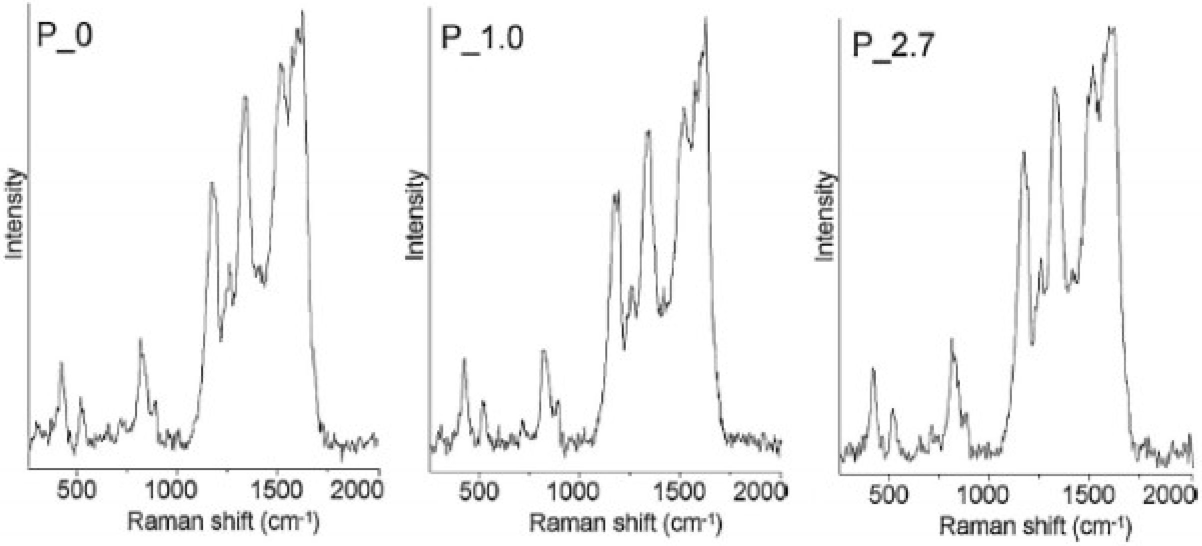

Figure 2: Raman spectra of samples P_0, P_1.0 and P_2.7¨

These findings corresponded to Raman spectra. Raman spectroscopy was used for characterization of all PANI thin films, because it is very valuable technique to characterize the protonation state of PANI and to determine the structural changes in PANI chains. In the further text the attention is paid to the comparison of the three interesting samples: reference sample P_0, and two samples P_1.0 and P_2.7. Their corresponding Raman spectra are shown in the Figure 2. All characteristic bands for PANI is clearly visible in reference sample (P_0) spectra, stretching mode in the phenyl rings (1626 cm-1), C=C stretching vibration in quinone (1595 cm-1), stretching vibrations of C=N and C=C in quinone (1515 cm-1), protonation band corresponding to stretching vibration of C-N+· (1318 cm-1), C-N stretching vibration of benzene, quinone (1260 cm-1), C-H bending vibration of semiquinone rings (1175 cm-1) and in the region 850-400 cm-1 are visible out-of-plane deformation vibrations of aromatic rings [16-22]. In this region any significant changes are not clearly visible. But sample P_2.7 exhibits significant changes in the spectra in the range 1400-1630 cm-1 . These changes corresponding to partially decomposed PANI chains [15,23]. This is understandable, because this sample was exposed to the corona plasma treatment. The P_1.0 is the sample treated with HV electric field with maximum conductivity and its Raman spectrum exhibited the narrower bands than reference sample (P_0). Also the wavenumbers of Raman bands are shifted to the higher wavenumbers in the spectrum of the sample P_1.0. These changes indicate higher degree of order in chain structure, so the corresponding increases of the conductivity.

4. CONCLUSIONS

Present study shows that the treatment with HV electrical field has the influence on conductivity of PANI thin films as well as its structure. Significant differences are observed for the conductivity of PANI samples treated with HV electric field contrary to reference sample. The highest conductivity of PANI thin film samples treated with HV electric field has P_1.0 sample (374 S/m). HV electric field above 2.0 kV/cm caused corona discharge what leads also to the very high conductivity of the sample P_2.7 (541 S/m). Raman spectroscopy is valuable technique to determine the structural changes of PANI thin films. Raman spectrum of P_2.7 sample shows changes, corresponding to partially decomposed PANI chains caused by the corona discharge. And also the P_1.0 exhibited some changes, the narrower bands and shifted wave numbers of Raman bands to the higher values. Less valuable information was obtained by the UV-VIS spectroscopy, because the differences in the optical transmittance are not significant and values remain nearly the same, which corresponds to the observation, that no changes in PANI thin films colors was occurred.

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