THIN POLYANILINE FILMS: STUDY OF THE THERMAL DEGRADATION

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Abstract

Conductive polyaniline (PANI) is nowadays in the forefront of the interest because of its very good electrical conductivity combined with other beneficial properties such as light weight and low cost. Not only PANI in the powder form, but also PANI thin films are widely investigated, because they can be used in wide field of applications, for example as sensors or antistatic and anticorrosive coatings. This work deals with the morphological and structural changes of PANI films after their exposure to higher temperatures. PANI was prepared from anilinium sulfate by its chemical polymerization using ammonium peroxodisulfate. During the polymerization process, PANI films were coated on glass slides. Changes, caused by exposition of PANI thin films to elevated temperatures (80, 100 and 120°C), were studied by Raman microscopy and atomic force microscopy. Thanks to these methods the morphological and structural changes in PANI thin films were revealed. It was observed that the increasing of temperature influences the color of PANI thin films, which passes from green (room temperature) to blue color (120°C). The color change and differences in Raman spectra may indicate the transition of PANI to its nonconductive form.

Keywords: Polyaniline film, conducting polymer, Raman microscopy, atomic force microscopy, thermal degradation

1. INTRODUCTION

Conductive polymers are nowadays extensively studied, because they have wide use in many applications. Polyaniline (PANI) which is one of the most common conductive polymers is in the forefront of the interest because of its good electrical conductivity combined with other beneficial properties such as light weight, low cost, excellent environmental stability and reversible acid-base switching of its electrical conductivity [1]. These properties are used in many applications such as anticorrosion and antistatic coatings [2], electrodes for batteries [3], sensors [4-6], etc. PANI exists in two basic forms, the blue pernigraniline form which converts during polymerization to the green protonated emeraldine form [7].

Many physicochemical properties of PANI are also studied by using thin polymer layers. Any surface in contact with reaction mixture becomes coated with thin PANI film, thickness of the film depends on the reaction conditions [8]. The possible arrangement of PANI polymer onto the glass slide is shown in Fig. 1.

For the practical utilization of PANI film, it is very important to know the stability of PANI film under the various conditions as well as its degradation mechanism. This study is focused on the effect of thermal treatment on the morphology and structural changes of thin PANI films produced in situ on glass slides.

Two experimental techniques, Raman spectroscopy and atomic force microscopy (AFM), were used in this study. Raman spectroscopy provides information about molecular vibrations, which are specific to the chemical bonds and symmetry of molecules. Such kind of information can be used for sample identification or to determine the changes in the sample structure.
In this study the AFM was used for observation of the changes in the surface topography of the thin PANI films caused by their exposition to elevated temperatures. AFM provides 3D images of the surface topography characterized by high resolution, which even enable imaging of single atoms. Its outstanding advantage is its ability to acquire an image of almost any type of surfaces, including polymers, ceramics, composites, glass, and biological samples.

2. EXPERIMENTALS

2.1 Preparation of thin polyaniline film

PANI thin films were prepared using simple oxidative chemical polymerization of the solution of aniline in concentrated sulfuric acid by strong oxidizing agent at room temperature. The method is based on the mixing of two solutions: i) aniline solution in sulfuric acid which serves as cationic source, and ii) solution of ammonium persulfate in distilled water which serves as an oxidizing agent. After the mixing of both solutions the polymerization of the aniline proceeds what is signalized by the green color of the reaction solution, the time of the polymerization was 35 minutes. PANI thin films were deposited onto the surface of the glass slides by their rinsing into the reaction mixture.

The prepared thin PANI films were exposed to three different temperatures 80, 100 and 120°C in oven (Memmert, model 100-800). One glass slide with PANI thin film was left as a control sample without exposure to elevated temperature.

2.2 Raman spectroscopy

Raman spectra of the thin PANI films were measured using a Smart Raman Microscopy System XploRA™ (HORIBA Jobin Yvon, France). Raman spectra were acquired with 532 nm excitation laser source, 100x objective and using 1200 gr./mm grating in the range from 80 to 2000 cm⁻¹.

2.3 Atomic force microscopy

The surface topography of the sample before and after the thermal treatment (120°C) was studied using atomic force microscope SolverNext (NT-MDT) operated in semicontact mode, the PPP-NCHR probe (Nanosensors) was used.

3. RESULTS AND DISCUSSION

The change in color PANI films as a result of their thermal treatment at 80, 100 and 120°C is evident in Fig. 2. It can be seen that the color change in samples B, C, D depends on the temperature. The green color
of control sample A, converts to blue color of the sample D, which was exposed to 120°C, whereas the blue color may indicate the presence of deprotonated form of PANI or aniline oligomers [9].

Registered Raman spectra of PANI thin films, sample A, B, C and D, are shown in Fig. 3. Raman spectrum of the PANI thin film, which was not exposed to high temperature shows characteristic band for C-C stretching vibration of the benzenoid ring at 1621 cm\(^{-1}\) and characteristic band for stretching vibration of >C=N- at 1498 cm\(^{-1}\) [10]. Band at position 1600 cm\(^{-1}\) corresponds to C=C stretching vibration in the quinonoid ring [11]. The presence of the benzenoid and quinonoid characteristic bands depends on the laser excitation wavelength [12]. The band at 1335 cm\(^{-1}\) provides information about ‘protonation band’ characteristic of the C-N\(^{+}\) stretching mode [10]. The band at 1172 cm\(^{-1}\) corresponds to the C-H bending vibration of the semiquinonoid rings [13]. Band at 810 cm\(^{-1}\) corresponds to benzene ring deformations. Remaining two bands at positions 425 and 516 cm\(^{-1}\) correspond to out-of-plane deformations of the rings [15].

After the PANI thin films exposure to elevated temperatures the Raman spectra shows changes which are the most evident at Raman spectrum of the PANI thin film exposed to 120°C. The band at 1621 cm\(^{-1}\) is shifted to 1615 cm\(^{-1}\) and its intensity decreased with the temperature. To the contrast intensity of the band at position 1590 cm\(^{-1}\) increased with the temperature. New band appears at position 1556 cm\(^{-1}\), which may be assigned to N-H deformation vibration in semiquinonoid structures [15]. Band at 1470 cm\(^{-1}\) is dominating to all spectrum and is assigned to C=N from quinonoid ring. Intensity of the bands at 1324 cm\(^{-1}\) as well as at 1262 cm\(^{-1}\) drastically decreases, which may be due to decrease in number of quinonoid rings in the structure [9]. New band with maxima centered at 1220 cm\(^{-1}\) is caused due to the presence of C-N stretching vibration. Decrease in intensity of the band appearing at 1164 cm\(^{-1}\) which corresponds to the deformation vibrations of the C-H groups on the quinonoid ring, confirms the decrease in the number of this groups. Broad structural band at positions 745, 778 and 813 cm\(^{-1}\) corresponds to vibrational modes of substituted aromatic rings [9]. Bands at 418 and 530 cm\(^{-1}\) correspond to out-of-plane deformations of the rings [14].

The character of the samples surfaces studied using AFM revealed no significant changes in surface topography after heating of the samples. Comparing to the 3D images the surface of the heated PANI layer seems to be smoother.
Fig. 4 AFM images of PANI films A – room temperature and B – 120°C.

CONCLUSIONS

Although the AFM did not prove significant changes in the morphology of the surface of the PANI thin film after exposure to 120°C, Raman spectroscopy found out structural changes. Amount of the quinonoid rings in the PANI thin film decreased with the temperature increasing, whereas less number of the quinonoid rings means that PANI converts to the PANI base, which is the nonconductive form of the PANI. This conclusion is confirmed by color change of the samples under heat treatment.

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LITERATURE


