Reproducibility of Obtaining thin Films of Polyaniline by Direct Doping

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Abstract **- This paper presents the process of obtaining thin films of polymer polyaniline that has been doped directly in the production process. Samples of thin films were obtained using a rotating disk method at different speeds. Polyaniline synthesis (PANI) was performed at 0°C and room temperature of 20°C. Doping was made with hydrochloric acid (PANI-HCl). We have shown what were the important factors that had influence on obtaining reproducible patterns of about the same characteristics. As indicators of these properties we measured electrical resistance, on the basis of which was calculated specific electrical conductivity of the obtained samples of thin films of polyaniline from different series of production.**

Keywords **- polymer, polyaniline, thin films, doping, reproducibility, electrical resistance, specific electrical conductivity.**

1. Introduction

Polymers are substances composed of macromolecules. In most cases and these are organic macromolecules that are built of many (typically 10^{2-} $10^{6)}$ building blocks of the same type - the monomers, which are interconnected with covalent bonds. The bi-functional monomers provide chain and mesh macromolecules. Polymers are divided into saturated and conjugated. In saturated polymers, according to the Pauling model, there occurs a sp^3 hybridization, and all four valence electrons of the C atom participate in covalent bonds. In conjugated polymers the orbitals of L-shell of the C atom have the configuration sp^2p_z. This means that three of the four orbitals of L-shell of each C atom are hybridized and their electrons generate σ-bonds. Unhybridized p_z orbitals of adjacent C atoms in the chain overlap, thus creating a π-band with delocalized electrons, that is one π-orbital common to all C atoms. In conjugated polymers the orbitals of L-shell of C atoms have the configuration sp^2p_z. According to the method of generation polymers are divided into industrial (synthetic) and natural. Polyaniline belongs to the group of synthesized polymers. It was first synthesized in 1862 [1] and was already somewhat forgotten as it was not used for any important technological application. However, the discovery by MacDiarmid and associates in 1986, finding that a relatively simple chemical process can change it into the conducting state [2] arouses great interest in this material. All conjugated polymers in undoped state are insulators or semiconductors, but only some of them have the property that by the doping can be converted to the conductive (metallic) state. Doping achieves the final density of states at the Fermi level or the formation of new energy states (acceptor or donor) within the energy gap, which leads to moving of the Fermi level and increasing of the number of electrons (holes) in the conductive (valent) band and thus a large increase in conductivity [3]. Polyaniline is characterized by a very high degree of chemical stability which makes it very interesting for exploration and technological application. By doping polyaniline with functional protonic acids such as dodecylbenzenesulfonic acid (DBSA), camphorsulfonic acid (CSA) etc. we achieve its processability, and such doped polyaniline can be dissolved by standard organic solvents such as chloroform or m-cresol [4]. Polyaniline doped with acids such as HCl, H_2SO_4, H_2PO_4 is not soluble in any organic solvent, while the undoped polyaniline (emeraldine base) is very well soluble in N - methylpyrrolidone. Solubility is an important technological property of polyaniline because it allows for the production of thin polymer films. Polyaniline can also be made by simple synthesis methods in the form of nanofibers and nanotubes which indicates its great technological application [5]. More recently it is used for making organic light-emitting diodes (OLED) [6], field-effect transistors (FET) with all-polymer integrated circuits [7], organic solar cells and memory elements [8].

2. Material and Methods

The polyaniline material (PANI) to carry out research in this study was synthesized in our laboratory using the method of polymerization oxidation reaction. The polymerization of hydrochlorinated polyaniline was carried out by chemical oksidation of aniline in aqueous solution of hydrochloric acid (1 M aqHCl), where we used ammonium peroxydisulfate $(NH_4)_2S_2O_4$ (APS) as an oxidizing agent. Before the start of the synthesis we performed calibration of the pH meter type Greisinger GPHR 1400 pH / mV meter with two buffer solutions, one at a pH 7 and the other with pH value 4. Then using the pH meter we measured the acidity of the aqueous solution of hydrochloric acid in which the polymerization takes place and afterwards the controlled doping. For the synthesis we used deionized water and it was carried out at 0 ° C and at the room temperature of $20\ °C$. When obtaining the doped (hydrochlorinated) polyaniline it appeared that the order of the synthetic method was very important. Analyzing all the performed syntheses, the optimal results are obtained in the following order of procedures:

- In two containers (A and B) we put 94 ml of deionized water;

- 1 M of HCl was placed in each container that is 8.4 ml of 37% HCl, the pH value of the solution obtained amounted to pH = 0.19;

- In the first vessel (A) was placed 8 mL (0.00884 mol) of aniline $(C_6H_5NH_2)$. Aniline is a very weak base;

- The mixture is stirred until complete dissolution of the aniline or to obtain a light yellow transparent solution;

- In the second vessel (B) was placed 10.08 g (0.0442 mol) of APS, which was stirred until complete dissolution;

- Slowly, with continuous stirring, the contents of the container B is added into the vessel A;

- Shortly after stirring the mixture becomes dark blue, and shortly thereafter emerald green;

- The whole mixture was stirred for 24 hours with magnetic stirrer, then left to stand without being stirred for about 24 hours;

- After 24 hours of lying still on the bottom there was extracted emerald green precipitate;

- By decantation the precipitate is separated from the water in which the synthesis was carried out;

- After decanting the precipitate was washed with methanol until the liquid above the residue becomes transparent, to remove any unwanted polymerization products (oxidation products, oligomers, etc.).

Leaching was performed in a manner that methanol was poured into the container with the precipitate, then after sedimentation of the precipitate decantation is performed and again placing of new methanol. The procedure was repeated until above the sedimentary precipitate was only pure methanol left;

- Then the precipitate was rinsed with deionized water to completely remove the methanol and filtration was performed with filter paper;

- The resulting filtrate (emerald green colored) is released to dry in a digester for approximately 12 hours;

- Thereafter it was placed in a desiccator for further drying under reduced pressure to remove any remaining water from the resulting material. The drying in desiccator lasted for about 48 hours;

It is important to note that the doping was performed by direct method in the production process of polyaniline with 1M HCl (PANI-HCl). Before the doped polyaniline (PANI-HCl) was converted to solid state, we started the production of thin films.

Thin films of PANI-HCl were obtained using a spin coater (Model P-6708D, Specialty Coating Systems, Indianapolis, IN) with a maximum speed of rotation up to 8,000 revolutions/minute. On the spin coater was attached the vacuum pump type D.V.P. Vacuum Technology s.r.l Italy and a compressor from the same manufacturer (Figure 1) so that the entire process for obtaining thin films took place in a vacuum.

On the vacuum head of the spin coater which was made in the shape of a disk with the diameter of 50 mm is set inkjet transparency film (insulator) with thickness of 0.08 mm on which was applied mixture PANI-HCl in constantly the same amount of 600 μl. Finished films were dried in a desiccator for 7 days.

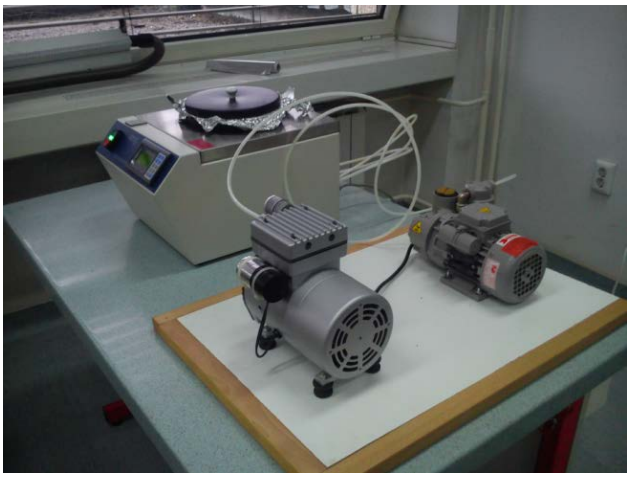

Figure 1: Apparatus used for the production of thin films of polyaniline.

3. Experimental Results and Discussion

Thin films PANI - HCl were obtained with spin coater (Model P-6708D, Specialty Coating Systems, Indianapolis, IN). This device offers control over the following parameters during the cycle: rotating speed from 100 - 8000 rpm, given that there are possibilities of programming three levels of rotation (RPM1 of 100-2000 rpm, RPM2 ≥ RPM1- 4000 rpm, RPM3 ≥ RPM2 - 8000 rpm); acceleration time of rotating disk (RAMP 1, RAMP 2, RAMP 3) of 1-30 seconds; deceleration time (RAMP 4) from 1-30 seconds; rotation length (TIME 1, TIME 2 TIME 3) up to 999 seconds. All these listed parameters are very important for obtaining high-quality film of polyaniline.

At speeds of disk rotation less than 600 rpm thin film can not be obtained, while at speeds higher than 6000 rpm obtained are films that are not conductive. After a series of failed attempts resulting films are of good quality at the speeds shown in Tables 1 and 2. In these tables in column 2 the first number represents RPM1, another number RPM2, and the third number RPM3. If we immediately programme the maximum speed of rotation (RMP3) then most of the sample material falls off from the substrate. Therefore, it is necessary to gradually accelerate the rotating disk from lower to higher speeds of rotation, namely from RPM1 to RPM3. Acceleration time of rotating disk for each level ie. RAMP1, RAMP2, RAMP3 for all our films was 20 seconds each. The length of disk rotation (TIME1, TIME2, TIME3), as well as the deceleration time to a completely stopped disk in all our experiments also was 20 seconds each.

Table 1. Results of the measurement for thin films obtained from Series 1 at 0 ° C

Sample number	Rotational speed (rpm)	Electrical resistance ($k\Omega$)	The specific electrical conductivity $\cdot 10^{-2}$ (S/m)
1.	200; 400; 600	1,43	6,99
2.	300; 5 00; 700	1,78	5,62
3.	400; 600; 800	2,33	4,29
4.	700; 900; 1100	3,27	3,06
5.	1000; 1400; 2000	3,57	2,80
6.	1500; 2000; 2500	4,71	2,12
7.	2000; 3000; 4000	5,40	1,85
8.	2000; 4000; 6000	6,66	1,50
9.	200; 400; 600	1,41	7,09
10.	300; 500; 700	1,70	5,88
11.	400; 600; 800	1,85	5,40
12.	700; 900; 1100	2,77	3,61
13.	1000; 1400; 2000	4,21	2,38
14.	1500; 2000; 2500	4,30	2,33
15.	2000; 3000; 4000	5,80	1,72
16.	2000; 4000; 6000	7,32	1,36

As described in chapter 2 we made two identical series of doping PANI-HCl. From each series were obtained 16 films (Series 1, Series 2). Films from number 1 to 8 of each series were obtained at different speeds, and the other 8 (9-16) at those same speeds, respectively. After drying in a desiccator we measured electrical resistance of the film segment at a distance of 1cm, and on the basis of that data we calculated the specific electrical conductivity of each sample of the thin film (Table 1). The specific electrical conductivity is a measure of the ability of a material to conduct electrical current. It can be determined if one knows the geometric characteristics and conductance of one part of the given material: $\sigma = l \cdot G / S$ where $G = 1 / R$ and it is called conductance.

Natural look of one of these films is shown in Figure 2.

Figure 2. Natural look of the obtained film of polyaniline.

Then we have shown graphically the dependence of the specific electrical conductivity on the maximum speed of rotation for the thin films from the Series 1 (Figure 3).

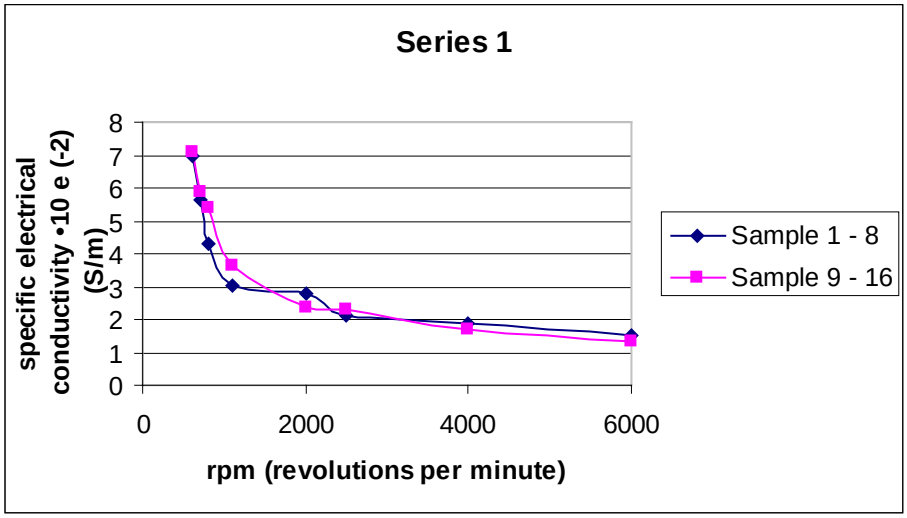

Figure 3. The change of the specific electrical conductivity of films from Series 1, depending on the speed of rotation

Thin films of Series 2 were obtained in the same manner as the films of Series 1 only this time the synthesis of samples PANI-HCl was performed at room temperature (20°C), whereas the synthesis of Series 1 was performed at 0°C. The measurement results for Series 2 are shown in Table 2. The dependency of the specific electric conductivity on the maximum speed of rotation for thin films from Series 2 is shown in Figure 4.

Table 2. Results of measurements for thin films obtained from Series 2 at room temperature (20°C).

Sample number	Rotational speed (rpm)	Electrical resistance ($k\Omega$)	The specific electrical conductivity $\cdot 10^{-2}$ (S/m)
1.	200; 400; 600	6.47	1,546
2.	300; 500; 700	6.55	1.527
3.	400; 600; 800	8.31	1.203
4.	700; 900; 1100	10.15	.985
5.	1000; 1400; 2000	13.37	.748
6.	1500; 2000; 2500	16.00	.625
7.	2000; 3000; 4000	16.88	.592
8.	2000; 4000; 6000	28.10	0,359
9.	200; 400; 600	6.16	1.623
10.	300; 500; 700	6.68	1,497
11.	400; 600; 800	8.16	1,225
12.	700; 900; 1100	10.10	0,990
13.	1000; 1400; 2000	13.15	.760
14.	1500; 2000; 2500	16.24	.616
15.	2000; 3000; 4000	19.50	.513
16.	2000; 4000; 6000	25.90	.386

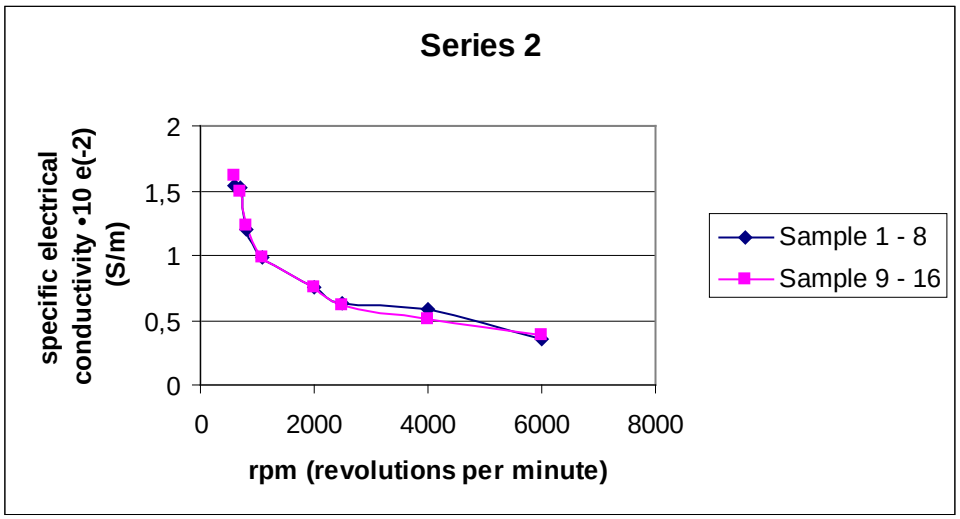

Figure 4. The change of the specific electrical conductivity of films from Series 2, depending on the speed of rotation

Using nonlinear method of least squares we fitted the experimentally obtained graphs (Figures 5 and 6). The mathematical form of the obtained curves is $y = a \cdot e^{-b\omega}$ where a and b are coefficients, and ω is the speed of rotating disk. For samples of Series 1 the coefficients are: a = 0.0786 and b = 0.4948. For samples from Series 2 the coefficients are: a = 0.0176 and b = 0.3611.

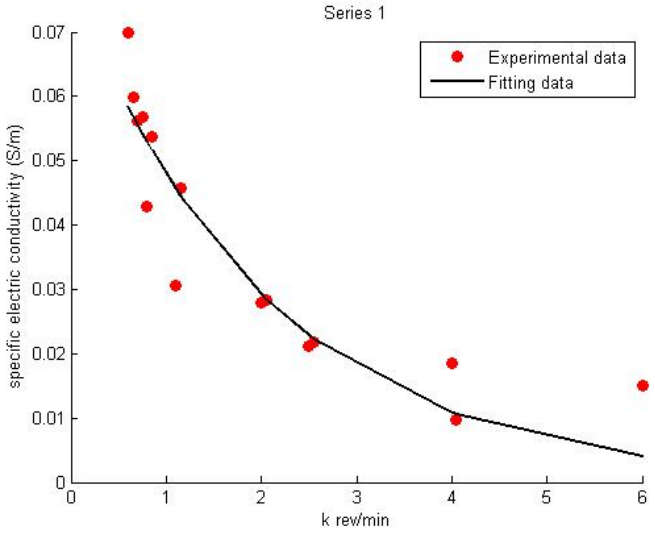

Figure 5: The fitted curve for Series 1

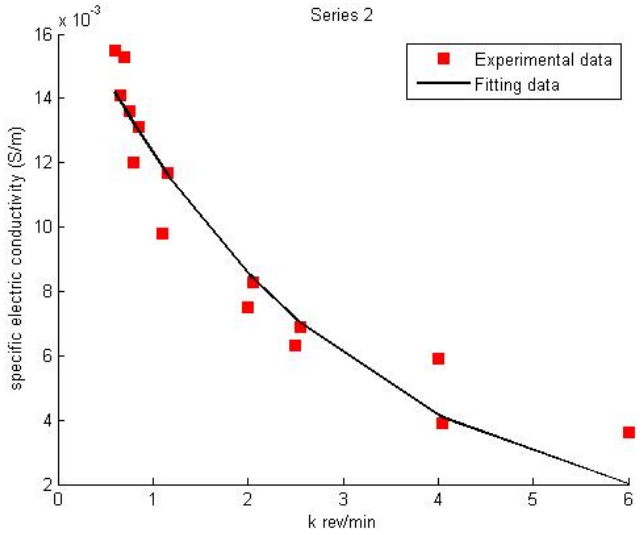

Figure 6: The fitted curve for Series 2

The recording of image of one sample (film) was performed with the microscope type Motic with the camera type Optica Microscopes Italy (Figures 7 and 8).

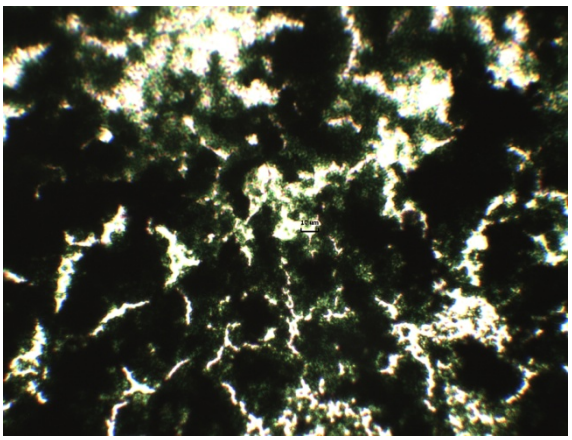

Figure 7. A 400 times enlarged part of the film surface

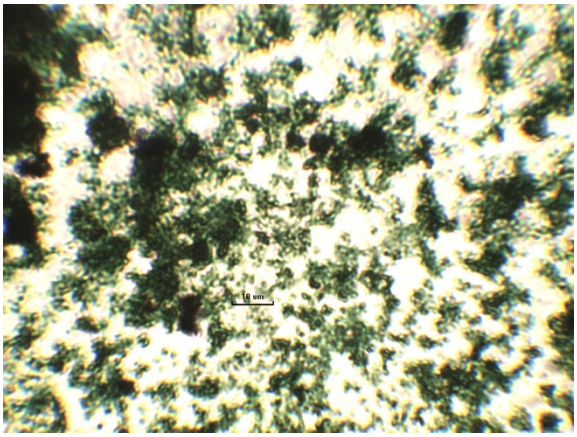

Figure 8. A 1000 times enlarged part of the film surface

It is known that the doping of polyaniline volume samples changes conductivity depending on the doping concentration [9]. From Table 1 and 2 and Figure 3 and 4 can be seen that the conductivity of

thin films of PANI-HCl also changes because undoped samples (films) do not conduct electricity. We have already said that polymers are substances made of macromolecules, and that macromolecules are built from many building blocks of the same kind - the monomers, which are interconnected with covalent bonds. Bi-functional monomers provide chain and mesh macromolecules which can be clearly seen from Figure 7 and 8. The mechanism of conductivity in these macromolecules can be described by a Variable Range Hopping (VRH) model [10]. The essence of this model is that the charge carriers can move around the localized states along and between the molecular chains. The frequency of hopping within a chain is greater than the frequency of hopping between the chains. The reason is that the movement between the chains is only possible in places where the chains close enough or where they are connected with a dopant e.g., a Cl^- ion.

4. Conclusion

Films of polyaniline obtained on higher speeds of rotating disk are thinner than those obtained at lower speeds. From the above tables, as well as from the shown graphs of conductivity it can be seen that thin films obtained at higher speeds of rotating disk have a lower specific electrical conductivity. Experimental dependency of the specific electrical conductivity on the rotating disk speed is given by exponential curve. The fitted exponential curve is generated by using the nonlinear method of least squares and its mathematical form is $y = a \cdot \exp(-b \cdot \omega)$, where a and b are coefficients whose value is in this paper accurately determined, and ω is the speed of the rotating disk. Films obtained at speeds greater than 6000 rev/min are not conductive. Also, comparing the films from Series 1 and Series 2 we can conclude that polyaniline films, which are obtained by synthesis at 0°C (Series 1) have better specific electrical conductivity. On the basis of microscopic analysis we can conclude that films of polyaniline are chain and mesh structures and that for their conductivity can be applied the Variable Range Hopping Model (VRH).

5. References

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