ABSTRACT

This paper presents the doping of thin films of polyaniline with phosphoric acid, that was carried out in order to determine how the material that reaches a thin film affects its electrical conductivity. In the very process of obtaining polyaniline (PANI) the doping was carried out with phosphoric acid (PANI-H₃PO₄). The doping was performed at room temperature (20°C) and at 0°C, and after that the thin films were made. Samples of films were obtained by the method of rotating disc at different speeds. The minimum rotation speed at which a thin film of polyaniline was obtained was 600 rpm and the maximum 6000 rpm. We made 4 series of thin films of doped polyaniline, each containing 8 samples. For each sample of film, from a particular series, we measured its electrical resistance, and on the basis of that the specific electrical conductivity was calculated. Based on the analysis of the experimentally obtained results it can be concluded that the electrical conductivity of thin films doped with phosphoric acid is lower than the electrical conductivity of thin films doped with sulfuric acid (PANI-H₂SO₄) and hydrochloric acid (PANI-HCl).

Keywords---- polymer, polyaniline, thin film, doping, phosphoric acid, electrical resistance, specific electrical conductivity.

I. INTRODUCTION

Polymers or plastics are substances composed of macromolecules. Most of these are organic macromolecules that are composed of many building blocks of the same type - monomers, which are linked together by a covalent bond. By adequate treatments and defined methods these can be transformed to a condition in which plastic becomes electrically conductive. It is known that polyaniline is in the group of conjugated polymers, and as such in its undoped state it does not conduct electric current, that is, it is an insulator. With various procedures, and one of them is the method of doping, polyaniline in a nonconducting state can be transformed into a conducting state. The most significant contribution to the early development of polymer physics was provided by P.J. Flory [1]. More recently, very intensive researches have been carried out in order to obtain polyaniline which would be a good conductor of electricity. It was first obtained in 1862, and had been 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], aroused 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 doping they can be converted to a conductive (metallic) form. 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 to 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, that is, such doped polyaniline can be dissolved by standard organic solvents such as chloroform or m-cresol [4]. Polyaniline doped with acids such as HCl, H₂SO₄, H₃PO₄ is not soluble in any organic solvent, while the undoped polyaniline (emeraldine base) is very well soluble in N-methylpyrrolidinone. Solubility is an important technological characteristic of polyaniline because it allows 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 applications [5]. The original use of polyaniline was for protection against corrosion and static electricity. More recently it is used for making organic light-emitting diodes (OLED) [6], field-effect transistors (FET), all-polymer integrated circuits [7], organic solar cells and memory elements [8]. To successfully create a new material assumes a good understanding of the structure and physical processes that dominate those already existing
materials that form the basis for the creation of new material.

II. MATERIAL AND METHODS

This paper deals with our researches on thin films of polyaniline which are doped with phosphoric acid (PANI-H₃PO₄). In our own laboratory, the polyaniline was first synthesized and then the doping with phosphoric acid was carried out. It is important to note that the doping was made by direct method in the process of polyaniline production. The polyaniline (PANI) was obtained by the method of oxidative polymerization reaction. Polymerization of polyaniline (PANI-H₃PO₄) was carried out by chemical oxidation of aniline in 85% aqueous solution of phosphoric acid. As an oxidizing agent there was used ammonium peroxide sulphate (NH₄)₂S₂O₄ (APS). The thin films (PANI-H₃PO₄) were obtained by using a spin coater (Model P-6708D, Specialty Coating Systems, Indianapolis, IN). On the spin coater there was attached a vacuum pump type D.V.P. Vacuum Technology s.r.l Italy and a compressor from the same manufacturer, 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 disc with the diameter of 50 mm, there was set a glass plate on which the mixture PANI-H₃PO₄ was spread in constantly the same amount of 200 µl. By changing the rotation speed of the spin coater we obtained thin films of varying thickness. The process of production and doping was carried out in a similar manner as in the referenced works [9] and [10]:

- In two containers (A and B) was put 93,3 ml of deionized water;
- 1M of H₃PO₄ was placed in each container, that is, 6,7 ml of 85% phosphoric acid;
- In the first container (A) was placed 8 ml (0,00884 mol) of aniline (C₆H₅NH₂);
- In the second container (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 from the mixture;
- 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.).
- Then the precipitate was rinsed with deionized water to completely remove the methanol, and filtration was conducted with filter paper;
- Before the polyaniline (PANI-H₃PO₄) doped with phosphoric acid was converted to solid state, we started the production of thin films.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Using the previously described method we conducted two syntheses of polyaniline samples doped with phosphoric acid (PANI-H₃PO₄). The first synthesis was conducted at room temperature of 20°C and the other was conducted in an identical manner only at the temperature of 0°C. For every synthesis there were made two series of doped thin films, so that from each series we made 8 thin films (Table 1). From four series we made a total of 32 thin films on the glass substrate.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Rotation speed of disc (rpm)</th>
<th>Electrical resistance (MΩ)</th>
<th>Specific electrical conductivity (10⁻³ S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Series 1</td>
<td>Series 2</td>
<td>Series 3</td>
</tr>
<tr>
<td>1</td>
<td>600</td>
<td>0.05</td>
<td>0.06</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>3</td>
<td>800</td>
<td>0.06</td>
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</tr>
<tr>
<td>4</td>
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<td>0.11</td>
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<tr>
<td>5</td>
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<tr>
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</tr>
<tr>
<td>7</td>
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<td>0.24</td>
</tr>
<tr>
<td>8</td>
<td>6000</td>
<td>0.31</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Table 1. Results of measurements for the doped films of polyaniline (PANI-H₃PO₄) of all series
The dependence of the specific electrical conductivity of the thin films doped with phosphoric acid (PANI-H₃PO₄), obtained at room temperature (20°C), on the rotation speed of disc is shown in Figure 1:

![Figure 1. The specific electrical conductivity of thin films of PANI-H₃PO₄, obtained at room temperature (20°C), depending on the speed of rotation of the disc.]

The dependence of the specific electrical conductivity of the thin films doped with phosphoric acid (PANI-H₃PO₄), obtained at 0°C, on the rotation speed of disc is shown in Figure 2:

![Figure 2. The specific electrical conductivity of thin films of PANI-H₃PO₄, obtained at temperature of 0°C, depending on the speed of rotation of the disc.]

Next, we showed the dependence of the specific electrical conductivity of the doped polyaniline thin films on the rotation speed of the disc for all series:

![Figure 3. The specific electrical conductivity of thin films of PANI-H₃PO₄, for every series, depending on the speed of rotation of the disc.]

Based on the Figures 1, 2, and 3, it is observed that the best electrical conductivity is found in the thin films of polyaniline doped with phosphoric acid (PANI-H₃PO₄) at 0°C. Also, the Figure 3 shows that all fitted curves have an exponential shape. From this we can conclude that the specific electrical conductivity of thin films doped with phosphoric acid can be shown by general formula \( y = a \cdot e^{-b\omega} \), where \( a \) and \( b \) are coefficients, and \( \omega \) is the speed of rotation of the disc. From the experimental data shown in Table 1 it is seen that the specific electrical conductivity of the thin films doped with phosphoric acid (PANI-H₃PO₄) for all series is of the order of magnitude of \( 10^{-3} \) S/m. In the earlier published works [9] and [10], which refer to the specific conductivity of thin films of polyaniline doped with hydrochloric acid (PANI-HCl), as well as of those doped with sulfuric acid (PANI-H₂SO₄), the specific electrical conductivity of these films is of the order of magnitude of \( 10^{-2} \) S/m. From this we can conclude that the specific electrical conductivity of the thin films doped with phosphoric acid (PANI-H₃PO₄) is lower than that of the films which were doped with hydrochloric and sulfuric acid by one order of magnitude, that is, 10 times lower. This fact can be explained by the dimension of ions that are used to dope the material, and their diffusion in the material. It is known that acids are compounds that dissociate in water, only to give positive hydrogen ions and negative ions of the acid residue. In the doping of polyaniline with hydrochloric acid, a dissociation to cations and anions takes place: \( HCl \rightarrow H^+ + Cl^- \), and in the doping of polyaniline with phosphoric acid: \( H_3PO_4 \rightarrow 3H^+ + PO_4^{3-} \). In both cases positive hydrogen cations are formed. The difference is in the negative anions, that are in the first case the anions of non-metal (\( Cl^- \)), and in the second case anions (\( PO_4^{3-} \)) are composed as molecules,
but the particle is negatively charged. With an increasing atomic number within a group in the periodic table, the ionic radius increases because the principal quantum number has been increased, which indicates how many electron shells are around the core. It is known that the valence electrons belong always to the last shell - the valence shell, as a result it is quite logical that the ionic radius increases with the increasing number of electron shells, that is, with the increase in atomic number within a group.

Thus, in the second case, because of the larger ion radius the anion $P_{3}O_{5}^{3-}$ is less diffused in the polyaniline, while in the first case, the diffusion of non-metallic $H_{3}O^{−}$ was far better. Since in the total conductivity participate both the positive and the negative ions, then, it is logical that the thin films doped with phosphoric acid (PANI-H$_3$PO$_4$) will have lower conductivity.

IV. CONCLUSION

Based on the obtained experimental results, calculations and graphs, the following conclusions can be drawn:

- Thin films of polyaniline doped with phosphoric acid (PANI-H$_3$PO$_4$) at 0°C have better specific electrical conductivity than films that are doped at room temperature of 20°C.
- The dependence of the specific electrical conductivity on the number of rotations of disc, for all series of samples of thin films, has an exponential shape.
- On the basis of the fitted curves, the specific electrical conductivity of thin films doped with phosphoric acid can be shown by general formula: $y = a \cdot e^{-b\omega}$, where $a$ and $b$ are coefficients, and $\omega$ is the speed of rotation of the disc.
- The specific electrical conductivity of thin films doped with phosphoric acid (PANI-H$_3$PO$_4$) is lower than the specific electrical conductivity of the films doped with hydrochloric and sulfuric acid by one order of magnitude, i.e. 10 times lower.

REFERENCES