Specific Electrical Conductivity of Thin Films of Polyaniline Doped with Sulfuric Acid

Izet Gazdić1, Almedina Modrić-Šahbazović2, Suada Sulejmanović3
1,2 Department of Physics, Faculty of mathematics and natural sciences, University of Tuzla, BOSNIA AND HERZEGOVINA
3 Department of Physics, Faculty of mathematics and natural sciences, University of Sarajevo, BOSNIA AND HERZEGOVINA

ABSTRACT

This paper presents the specific electrical conductivity of thin films of polymer polyaniline which was doped with sulfuric acid. Polyaniline in the undoped state is an insulator and doping can convert it into a conductor of electrical current. Polyaniline material (PANI) which was the subject of the research in this study was synthesized in our laboratory with the method of oxidative polymerization reaction at 0°C and at room temperature of 20°C. Doping was carried out directly in the production process. From the thus obtained doped materials (PANI-H2SO4) were made thin films by the method of rotating disk at different speeds. Based on the measured electrical resistance of each film individually, we calculated specific electrical conductivity. It is shown that this conductivity depends on the temperature at which the doping is carried out with sulfuric acid, as well as on the speed of the rotating disk on which the individual thin films were obtained.

Keywords---- polymer, polyaniline, insulator, thin films, doping, sulfuric acid, electrical resistance, specific electrical conductivity, conductor.

I. INTRODUCTION

Macromolecular compounds formed by stringing basic substance molecules (monomers) into macromolecules with a large number of atoms (1000 and more) are referred to as polymers. The process of connecting into macromolecular substances, without the formation of by-products, is polymerization. The basic repeating structural unit of a polymer macromolecule is mer (in metals an atom). The number of molecules (monomers), of which a polymer molecule consists, determines the degree of polymerization. With the increasing degree of polymerization there occurs changing of the physical properties of polymers (viscosity, hardness, solubility, etc.). Each molecule is represented by the length of the chain consisting of specific members which by their chemical composition can be of the same or different type. Polyaniline belongs to a group of synthesized polymers. It was first synthesized in 1862 [1] and was almost forgotten as it had no important technological applications because it did not conduct electrical current. However, the discovery of MacDiarmid et al in 1986, that a relatively simple chemical process can transform it into a conductive state [2] started a sudden interest in this material. In the very beginning of the study on conducting polymers the main objective of the research was the understanding of fundamental processes in them, while today the main goal is improving the conductivity and its technological applications. This is especially evident after the discovery of a polymer LED (light emitting diode) in 1990 by Richard Friend [3]. Polymers are substances composed of macromolecules. Most of these are organic macromolecules that are composed of the same type of building blocks - the monomers, which are interconnected by covalent bonds. Each molecule is represented by the length of the chain consisting of specific members which by their chemical composition can be of the same or different type. Depending on the degree of order and density of mutual arrangement of chains a polymer can be:

- partially crystalline and
- completely amorphous.

Crystalline polymers have inside them loosely packed parts of the molecules that make up its amorphous phase. The crystal phase has a greater impact on the physical and mechanical properties. When switching from the amorphous polymer to the crystalline state, increased are the tensile strength, hardness and resistance to heat. Amorphous state of a system reduces its stiffness and makes it elastic. This phenomenon is used in production processes where it is necessary to provide good elasticity of material used. In terms of the states the polymers can exist...
in two states of matter: liquid and solid. They cannot have the gaseous aggregate state, because the vapor pressure is negligible and vapor decomposes. The discovery of conducting polymers began a new field of research on the border between chemistry and condensed matter physics. Conductive polymers paved the way for the improvement of fundamental understanding of physics and chemistry.

Polyaniline is characterized by a very high degree of chemical stability which makes it very interesting for exploration and technical application. It is available in the form of volume (bulk) or as a thin film, which is the subject of this paper. By doping it is converted to a conductive state. Polyaniline doped with acids such as HCl, H2SO4, H2PO4 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 feature of polyaniline because it enables the production of thin polymer films. It can be said that the polymers have a huge variety of properties. Small changes in the physical parameters (e.g., temperature) or a very mild chemical treatment can drastically change the properties of the polymer. This fascinating feature is typical of all soft matter, and by that term we mean: liquid crystals, polymers, detergents, colloidal beads and porous materials.

II. MATERIAL AND METHODS

Polyaniline doped with sulfuric acid (PANI-H2SO4) that was researched in this study was synthesized in our laboratory with the method of oxidative polymerization reaction. The process of obtaining and doping was carried out similarly as in the work listed under [4] in References. The polymerization of polyaniline was carried out by chemical oxidation of aniline in aqueous solution (95%) of sulfuric acid (1 M aq H2SO4), wherein the used oxidizer was ammonium peroxodisulphate (NH4)2S2O8 (APS). There have been several synthesis performed as follows:

- in two containers (A and B) was placed 94 ml of deionized water;
- 1M H2SO4 was placed in each container, that is 5.4 ml of 95% sulfuric acid;
- in the first vessel (A) was placed 8 mL (0.00884 mole) of aniline (C6H5NH2). Aniline is a very weak base;
- the mixture is stirred until complete dissolution of aniline to obtain transparent and light-colored solution;
- in another container (B) was placed 10.08 g of APS, which was stirred until complete dissolution;
- slowly, while stirring continuously, the contents of the container B is added into the vessel A;
- whole mixture was stirred for 24 hours with a magnetic stirrer (see Figure 1), and then left to stand without stirring for 24 h;
- after 24 hours in resting state of the mixture on the bottom of the container a green precipitate was formed;
- by decantation the precipitate is separated from the water in which the synthesis was carried out;
- after decanting the precipitate was rinsed with methanol until the liquid above the residue becomes transparent, to remove any unwanted polymerization products (Figure 2);
- then the precipitate was rinsed with deionized water to completely remove the methanol and a filtration was performed with filter paper;
- before the doped polyaniline (PANI-H2SO4) was transformed into solid state, we started the production of thin films.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Thin films of PANI-HCl were produced by using a spin coater (Model P-6708D, Specialty Coating Systems, Indianapolis, IN) whose rotational speed can reach 8000 revolutions/minute. On the spin coater was attached a vacuum pump type D.V.P. Vakuum 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 disk with the diameter of 50 mm, is set an inkjet transparency film (insulator) with thickness of 0.08 mm on which is applied the mixture PANI-H2SO4 in constantly the same amount of 400 µl.

In the process of obtaining thin films by Specialty Coating Systems we can control the following parameters:
- rotation speed of 100-8000 rev/ min, with the possibility of programming three levels (RPM1 of 100-2000 rev/min, RPM2 ≥ RPM1- 4000 rev/min, RPM3 ≥ RPM2- 8000 rev/min),
- acceleration time of rotating disk (RAMP 1, RAMP 2, RAMP 3) of 1-30 seconds,
- rotation length (TIME 1, TIME 2, TIME 3) up to 999 seconds,
- deceleration time (RAMP 4) from 1-30 seconds.

All these mentioned parameters are very important for obtaining a high-quality film of polyaniline doped with sulfuric acid. In order to obtain high quality films it is necessary first to set a lower speed of rotation, and then to accelerate the disk over specific time (200; 400; 600 revolutions/minute). As described in part 2 we made two identical series of doping PANI-H2SO4 at room temperature (20°C). From each series were made 8 films at different speeds of rotation disk (rpm). After drying in the desiccator we measured the electrical resistance of a part of the film at a length of 1cm, and based on this data we calculated the electrical conductivity for each sample of the thin film by the relation \[ \sigma = L/G/S \] where \( G = 1/R \) and is called conductance. The obtained results of these two series of experiments are shown in Table 1.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Rotational speed (rpm disk/ minute) -RPM</th>
<th>Electrical resistance (kΩ)</th>
<th>Specific electrical conductivity (10^2 S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Series 1</td>
<td>Series 2</td>
</tr>
<tr>
<td>1</td>
<td>200,400,600</td>
<td>6.07</td>
<td>6.5</td>
</tr>
<tr>
<td>2</td>
<td>300,500,700</td>
<td>7.64</td>
<td>8.16</td>
</tr>
<tr>
<td>3</td>
<td>400,600,800</td>
<td>14.76</td>
<td>13.02</td>
</tr>
<tr>
<td>4</td>
<td>700,900,1100</td>
<td>19.19</td>
<td>19.96</td>
</tr>
<tr>
<td>5</td>
<td>1000,1400,2000</td>
<td>25.01</td>
<td>26.12</td>
</tr>
<tr>
<td>6</td>
<td>1500,2000,2500</td>
<td>31.1</td>
<td>31.7</td>
</tr>
<tr>
<td>7</td>
<td>2000,3000,4000</td>
<td>92.9</td>
<td>96.62</td>
</tr>
<tr>
<td>8</td>
<td>2000,4000,6000</td>
<td>145.3</td>
<td>153.5</td>
</tr>
</tbody>
</table>

Table 1. Results of measurements for thin films PANI-H2SO4 obtained at 20°C

In exactly the same way was performed the doping of polyaniline with sulfuric acid (PANI-H2SO4) but now at 0°C. The entire process took place in containers with ice, with a constant temperature control. Of the material so obtained were made two series of samples of thin films (Series 3 and Series 4). The experimental results for these two series are presented in Table 2.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Rotational speed (rpm disk/ minute) -RPM</th>
<th>Electrical resistance (kΩ)</th>
<th>Specific electrical conductivity (10^2 S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Series 1</td>
<td>Series 2</td>
</tr>
<tr>
<td>1</td>
<td>200,400,600</td>
<td>4.92</td>
<td>5.24</td>
</tr>
<tr>
<td>2</td>
<td>300,500,700</td>
<td>6.23</td>
<td>6.33</td>
</tr>
<tr>
<td>3</td>
<td>400,600,800</td>
<td>6.58</td>
<td>7.76</td>
</tr>
<tr>
<td>4</td>
<td>700,900,1100</td>
<td>10.82</td>
<td>11.28</td>
</tr>
<tr>
<td>5</td>
<td>1000,1400,2000</td>
<td>11.26</td>
<td>11.59</td>
</tr>
<tr>
<td>6</td>
<td>1500,2000,2500</td>
<td>11.45</td>
<td>12.38</td>
</tr>
<tr>
<td>7</td>
<td>2000,3000,4000</td>
<td>12.28</td>
<td>13.57</td>
</tr>
<tr>
<td>8</td>
<td>2000,4000,6000</td>
<td>12.83</td>
<td>13.76</td>
</tr>
</tbody>
</table>

The dependence of the specific electrical conductivity for these two series (Series 3 and Series 4) on the rotation speed of the disk is shown in Figure 4.

![Figure 3. Change of specific electric conductivity depending on the speed of rotation for thin films PANI-H2SO4 obtained at 20°C](image.png)

The dependence of the specific electrical conductivity of thin films of PANI-H2SO4 obtained at room temperature on the speed of rotating disk is shown in Figure 3.
Figure 4. Change of specific electric conductivity depending on the speed of rotation for thin films PANI-H$_2$SO$_4$ obtained at 0°C

From the figures 3 and 4 we can see an exponential dependence of the specific electrical conductivity on the rotation speed of the disk for the samples of thin films of all series.

Using nonlinear method of least squares we made fitting of experimentally obtained graphics (Figures 5, 6, 7, 8).

Figure 5. Fitted curve for the PANI-H$_2$SO$_4$ obtained at 20°C (Series 1 and 2)

Figure 6. Fitted curve for the PANI-H$_2$SO$_4$ obtained at 20°C in the semi-logarithmic distribution (Series 1 and 2).

Figure 7. Fitted curve for the PANI-H$_2$SO$_4$ obtained at 0°C (Series 3 and 4).

Figure 8. Fitted curve for the PANI-H$_2$SO$_4$ obtained at 0°C in the semi-logarithmic distribution (Series 3 and 4).

From Figure 5 one can conclude that the experimental data for the PANI-H$_2$SO$_4$ obtained at 20°C make a good fit on the exponential function $y=0.0283\cdot\exp(-1.2675x)$. Figure 6 shows the same information but in a semi-logarithmic distribution where the exponential function is converted to a linear function (straight line). On the basis of that image one can better observe that the greater deviations from the line occur for higher values of rotating speed of the disk. Figures 7 and 8, respectively, show the same function but for the experimental data PANI-H$_2$SO$_4$ obtained at 0°C. The experimental results are fitted to a function $y = 0.0174 \cdot \exp(-0.2290\,x)$. In all mentioned functions, $x$ is the rotating speed of the disk (kilo rpm).

After that, we performed infrared spectroscopy (IR) of the material PANI-H$_2$SO$_4$ obtained at 20°C and 0°C. Infrared spectroscopy was performed on a PerkinElmer FT-IR System – Spectrum BX so that the infrared radiation is passed through a paste made from the powder mixture of PANI-H$_2$SO$_4$ and KBr at the ratio 1:9. After passing through the cuvette with an unknown compound, the intensity of the incident beam is reduced.
thus with a computer we obtain the dependence of the transparency coefficient on the reciprocal value of the wavelength in cm$^1$.

From the images 9 and 10 we can see that the dependence of both the PANI-H$_2$SO$_4$ at 0°C and the PANI-H$_2$SO$_4$ at 20°C, is almost the same. The only difference is that for the material PANI-H$_2$SO$_4$ obtained at 20°C there occurs additional peak at 1104 cm$^{-1}$, which indicates the additional C-O connection. After comparing the graphics obtained by infrared spectroscopy with the graphics obtained from database, there is a similarity of the PANI-H$_2$SO$_4$ at 0°C with a 86,995% 1,2,3,5-Tetrachlorobenzene, and of the PANI-H$_2$SO$_4$ at 20°C with a 90.445% Triethylene glycol monochlorohydrine.

IV. CONCLUSION

From the shown tables, as well as the graphical display of conductivity, it can be seen that films PANI-H$_2$SO$_4$ obtained at higher speeds of rotating disk have a lower specific electric conductivity. When disk rotation speeds are greater than 6000 rpm we can not get thin films that can conduct electricity. Also, by comparing films of all series it can be concluded that polyaniline films doped with sulfuric acid, which are obtained by the synthesis at 0°C (Series 3 and 4), have a greater specific electrical conductivity than those obtained at 20°C (Series 1 and 2) which is in line with the work [4]. Based on the experimentally obtained graphics and fitted functions it can be concluded in this paper too that the conductivity of thin films doped with sulfuric acid is given by relation $\sigma = a \cdot \exp(-b \cdot x)$ where x is the rotating speed of the disk (kilo rpm), and the constants a and b are correctly determined for each series of samples. The mechanism of conductivity in such materials can be described by the model of Variable Range Hopping - VRH [4] [5]. From the tables 1 and 2 and the figures 3 and 4 it can be seen that there exists a conductivity of thin films of PANI-H$_2$SO$_4$ and that it varies depending on the number of revolutions of the disk and the way of obtaining, whereas undoped samples (films) do not conduct electricity [6].

REFERENCES