Analysis of Specific Electric Conductivity of Thin Films of Polyaniline Doped with Sulfuric and Hydrochloric Acid

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Abstract **: This paper describes the specific electric conductivity of thin films of the polymer polyaniline, depending on the type of material that is used for doping the specified polymer. In our own laboratory, there were made four series of doped samples of polyaniline thin films of which two series were doped with sulfuric acid (PANI-H_2SO_4), and the other two were doped with hydrochloric acid (PANI-HCl). It is also significant that two series of the mentioned samples of thin films were obtained at room temperature (20˚C), and the other two at 0˚C. Next, the analysis of the specific electrical conductivity of all series was performed in order to demonstrate that the material that reaches the thin film affects its electrical conductivity.**

Keywords: **polymer, polyaniline, thin films, doping, sulfuric acid, hydrochloric acid, electrical resistance, specific electrical conductivity.**

1. Introduction

Polyaniline is one of the most important materials from the group of polymers, and therefore the most commonly used polymer for industrial purposes. Polyaniline, in the pure state, i.e. with no other impurities, is an insulator. Some polymers after certain modifications may become conductive. Conductive polymers exhibit electrical and optical properties of metals or semiconductors, while retaining good mechanical properties. One such material is polyaniline which can be converted into the conducting state by doping. As the theory of electrical conductivity of the polyaniline is not yet sufficiently clarified enough, in the work we have tried to obtain some specific indicators based on which certain clarifications for the conductivity of polyaniline would be given. Materials science studies the influence of the structure and processing of the material properties. Knowledge of this kind enables the prediction and production of new materials with desired properties. Materials science is interdisciplinary, while the majority of its theoretical background makes the physics of condensed matter and solid state physics. For the first time it appears in the early sixties of the 20^{th} century as a result of the synthesis of achieved discoveries in physics and empirical knowledge of chemistry and metallurgy. The development of new materials has enabled significant technological advances, and therefore the overall progress of the society as a whole. The physics, especially the physics of materials, has a permanent task to improve existing materials, or to find new materials of highly specific properties. Electrical conductivity of certain types of materials ranges from insulators to good conductors, from plastic to metal. The reason for the difference is the chemical structure. In plastics those are covalent bonds, long chains. Insulators, clearly, have no free carriers of electricity. 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 this structure can be transformed to a condition in which plastic becomes electrically conductive. The successful creation of new materials requires good understanding of the structure and physical processes

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that dominate those already existing materials, which form the basis for the creation of new materials. The most significant contribution to the early development of polymer physics was provided by P.J. Flory [1], [2]. A very important step was made by S.F. Edwards when he applied the sophisticated mathematical model of particle physics to the study of polymers [3].

It is known that the energy spectrum of electrons in metals and semiconductors is organized in bands and displayed within the first Brillouin zone. Band structure is the result of movement of nearly free electrons in a periodic potential of the crystal lattice of normal metals, or a consequence of approximations of strong bonds, that is tunneling of valence electrons between nearest neighbors for metals and semiconductors. Whether a material will be conductor, insulator, or semiconductor depends on the band occupancy (zone) by electrons and width of the forbidden energy band (energy gap) between the last valence band and the first higher band of allowed energies. The mechanism of conductivity by Variable Range Hopping (VRH) was developed to describe the conductivity in glass or non-crystalline systems such as for instance: amorphous semiconductors, amorphous alloys etc. This model showed good also for describing of conductivity in conductive polymers. In such systems, the concept of conducting and valence bands can be applied, but unlike crystals, such bands have a more complex structure of the distribution of density of the states N(E) [4]. Polymers are divided into industrial (synthetic) and natural. It is known that in the vast majority of cases, polymers are insoluble substances of low density, low production cost and high stability. They are easy to shape, do not reflect light, do not conduct heat nor electricity [5]. Thanks to these good qualities, a relatively small number of conventional synthetic polymers is among the most commonly used materials. The polymers are part of a wide range of different products. Because of their performances that successfully meet the needs of the users, polymers are constantly found in the focus of interest of materials science and its quest for improvements.

2. Material and Methods

This paper deals with the research on thin films of polyaniline which are doped with sulfuric acid (PANI-H_2SO_4) and hydrochloric acid (PANI-HCl). All the samples researched were synthesized in our own laboratory with the method of oxidative polymerization reaction. The process of obtaining and doping was carried out in a similar way as in the works [6] and [7]. Two polymerizations were made. The first polymerization of polyaniline (PANI-H_2SO_4) was carried out by chemical oxidation of aniline in aqueous solution (95%) of sulfuric acid (1M aqH_2SO_4), and the second polymerization (PANI-HCl) was done by chemical oxidation of aniline in 37% aqueous solution of hydrochloric acid (1 M aqHCl). In both cases was used ammonium peroxodisulphate $(NH_4)_2S_2O_4$ (APS) as an oxidizer. The thin films (PANI-HCl and PANI-H_2SO_4) were obtained by using a spin coater (Model P-6708D, Specialty Coating Systems, Indianapolis, IN) whose rotational speed can reach 8000 rpm/min. On the spin coater was attached a vacuum pump of the 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 disc with the diameter of 50 mm, an inkjet transparency film (insulator) was set with thickness of 0.08 mm on which were applied the mixtures PANI-HCl and PANI-H_2SO_4 in constantly the same amount of 400 μl. Thus we obtained thin films of doped polyaniline.

3. Experimental Results and Discussion

Using the mentioned method we obtained four series of polyaniline samples doped with sulfuric acid and hydrochloric acid:

Series 1 - polyaniline doped with sulfuric acid PANI-H_2SO_4) at 20°C,

Series 2 - polyaniline doped with hydrochloric acid (PANI-HCl) at 20°C,

Series 3 - polyaniline doped with sulfuric acid PANI-H_2SO_4) at 0°C,

Series 4 - polyaniline doped with hydrochloric acid (PANI-HCl) at 0°C.

From each series were made 16 films at various speeds of disc rotation (rpm). Films from number 1 to 8 of each series were obtained at different speeds, and the other 8 (from 9 to 16) at those same speeds, respectively. It is important to note that in order to obtain thin films from the prepared mixture the rotating disc of spin coater should be gradually accelerated. Table 1. shows maximum speeds of the rotating disc (rpm) at which they were obtained. After drying in a desiccator we have measured the electrical resistance of the film segment at a distance of 1cm, and on the basis of that data we have calculated the specific electrical conductivity of each sample of the thin film by the relation $\sigma = L \cdot G / S$ where $G = 1 / R$ and it is called conductance. The results for the four series based on experimental data are shown in Table 1.

Table 1. Results of the measurements of doped polyaniline films from all series

Number of samples	Rotational speed of disc (rpm)	Electrical resistance (kΩ)				Specific electrical conductivity (10^{-2} S/m)			
		Series 1	Series 2	Series 3	Series 4	Series 1	Series 2	Series 3	Series 4
1	600	6.07	6.47	4.92	1.43	1.65	1.55	2.03	6.99
2	700	7.64	6.55	6.23	1.78	1.31	1.53	1.61	5.62
3	800	14.76	8.31	6.58	2.33	0.68	1.20	1.52	4.29
4	1100	19.19	10.15	10.82	3.27	0.52	0.98	0.92	3.06
5	2000	25.01	13.47	11.26	3.57	0.40	0.75	0.89	2.80
6	2500	31.10	16.00	11.45	4.71	0.32	0.62	0.87	2.12
7	4000	92.90	16.88	12.28	5.4	0.11	0.59	0.81	1.85
8	6000	145.32	28.1	12.83	6.66	0.07	0.36	0.78	1.5
9	600	6.50	6.16	5.24	1.41	1.54	1.62	1.91	7.09
10	700	8.16	6.68	6.33	1.70	1.22	1.50	1.58	5.88
11	800	13.02	8.16	7.76	1.85	0.77	1.22	1.29	5.4
12	1100	19.96	10.1	11.28	2.77	0.5	0.99	0.88	3.61
13	2000	26.12	13.15	11.59	4.21	0.38	0.76	0.86	2.38
14	2500	31.70	16.24	12.38	4.30	0.31	0.62	0.81	2.33
15	4000	96.62	19.5	13.57	5.80	0.10	0.51	0.70	1.72
16	6000	153.53	25.9	13.76	7.32	0.06	0.39	0.73	1.36

The dependence of the specific electrical conductivity of thin films of PANI-H_2SO_4 and PANI-HCl, obtained at room temperature, from the rotation speed of disc is shown in Figure 1.

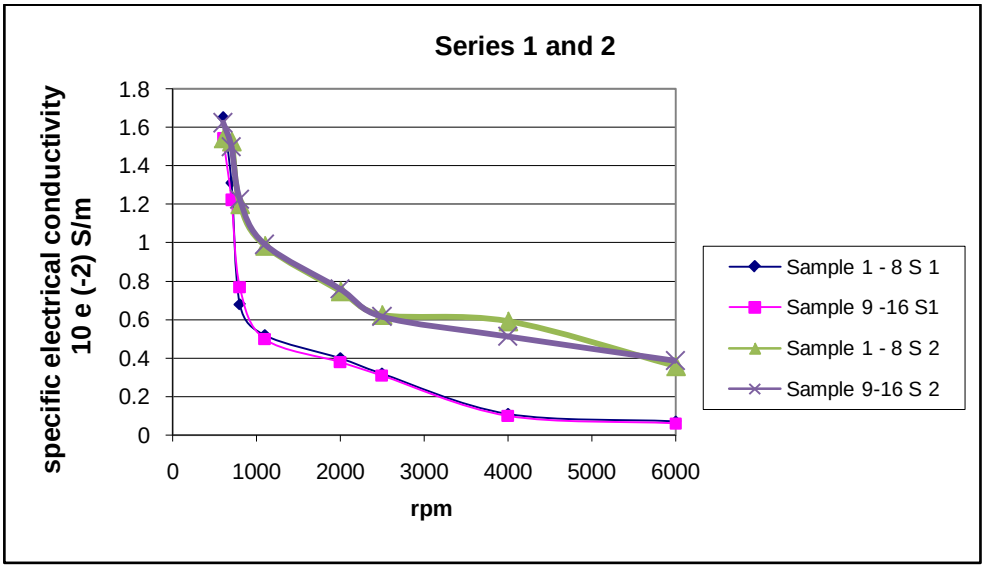

Figure 1. Change in specific electric conductivity depending on the speed of rotation for the thin films PANI-H_2SO_4 and PANI-HCl obtained at 20˚C.

From the image it can be seen that better electrical conductivity has the thin films obtained by doping polyaniline with hydrochloric acid (PANI-HCl) at 20°C (Series 2).

The dependence of the specific electrical conductivity of thin films of PANI-H_2SO_4 and PANI-HCl, obtained at 0°C, from the rotation speed of the disc is shown in Figure 2.

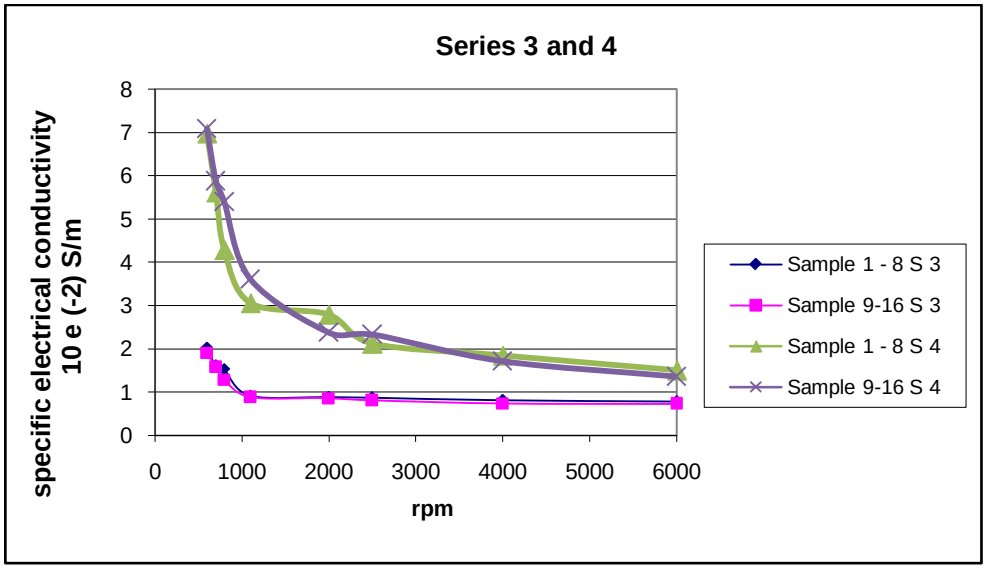

Figure 2. Change in specific electric conductivity depending on the speed of rotation for the thin films PANI-H_2SO_4 and PANI-HCl obtained at 0˚C.

In this case it can be noted that a better electrical conductivity has the thin films of polyaniline doped with hydrochloric acid (PANI-HCl) at 0˚C.

Next, we showed the dependence of the specific electrical conductivity of doped polyaniline thin films on the rotation speed of the rotating disc for all series (Figure 3.).

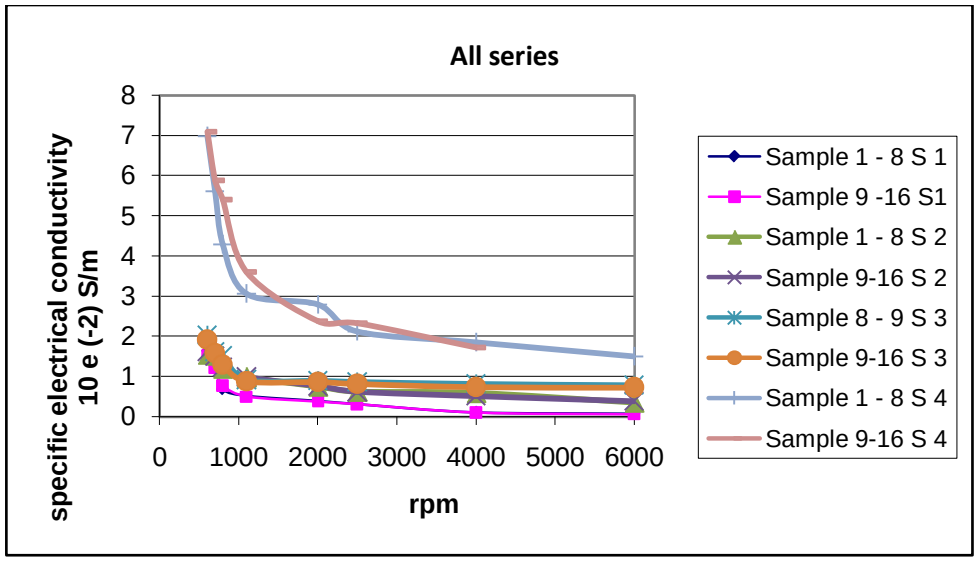

Figure 3. Change in specific electric conductivity depending on the speed of rotation for the thin films PANI-H_2SO_4 and PANI-HCl for all series.

It is obvious that the best electrical conductivity have samples of the series 4, i.e. the thin films of polyaniline doped with hydrochloric acid (PANI-HCl) at 0˚C.

The question is why is the electrical conductivity of thin films of PANI-HCl better than the conductivity of PANI-H_2SO_4?

The answer to this question is in the dimensions of the 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 doping polyaniline with hydrochloric acid, dissociation to cations and anions takes place:

$$HCl \rightarrow H^+ + Cl^-$$

while in doping with sulfuric acid the dissociation is something different:

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

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 the anions (SO_4^{2-}) are composed as molecules, but the particle is negatively charged. With increasing atomic number within a group in the periodic table, the ionic radius increases, because the principal quantum number has been increased that 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, i.e. with the increase in atomic number within a group.

So, in the second case because of the larger ion radius the anion SO_4^{2-} is less diffused in the polyaniline, while in the first case, the diffusion of non-metallic Cl^- was far better. As in the total conductivity participate both the positive and the negative ions then it is logical that the thin films doped with hydrochloric acid (HCl-PANI) will have better electrical conductivity.

The common graph (Figure 3.) shows that the best electrical conductivity has thin films of polyaniline doped with hydrochloric acid (PANI-HCl) at 0°C. This can be explained by Mott's model of conduction with the mechanism of Variable Range Hopping (VRH) [8]. Under this model, if the Fermi level is above the mobility threshold E_μ then the conductivity is described by Arrhenius's law of conduction band [9]:

$$\sigma(T) = C\ exp\left[\frac{-(E_\mu - E_F)}{k_B}\right].$$

If the Fermi level is below the mobility threshold then the states at the Fermi level are localized and electrons can not move freely but only by phonon-assisted hoping between localized states. According to N. Mott - such a mechanism of conduction should exist only at low temperatures. The connection between the hopping temperature T and density of the state at the Fermi level $N(E_F)$ is given by the relation:

$$T \sim \frac{1}{N(E_F)}$$

From the previous relation it can be seen that if the hopping temperature is lower then the density of states at the Fermi level is higher, and hence the conductivity of the sample is better which is in accord with the experimentally obtained results.

4. Conclusion

Based on the experimental results, comparing the electrical conductivity of samples obtained by doping thin films of polyaniline with sulfuric and hydrochloric acid (PANI-H_2SO_4 and PANI-HCl), obtained at 20°C, it can be concluded that a better electrical conductivity has the thin films obtained by doping polyaniline with hydrochloric acid (PANI-HCl). From Figure 2., as well as from the experimental data shown in Table 1., it is obvious that a better electrical conductivity has the thin films of polyaniline doped with hydrochloric acid (PANI-HCl) at 0°C, better than the samples obtained by doping with sulfuric acid (PANI-H_2SO_4) also at 0°C. Comparing all four series, it can be concluded that the best electrical conductivity have the thin films of polyaniline doped with hydrochloric acid (PANI-HCl) at 0°C. These experimental results can be successfully explained by the dimensions of resulting ions, which play an important role in the process of diffusion, as well as by Mott's model of conduction with the mechanism of Variable Range Hopping (VRH).

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