

Determination of the surface free energy of thin films of polyaniline doped with sulfuric acid

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Abstract: The aim of this study is to estimate the surface free energy of thin films of polyaniline doped directly in the production process with sulfuric acid, by measuring the contact angle. Synthesis of polyaniline (PANI) was performed at 0°C and at room temperature 20°C. Samples of thin films were obtained by the method of rotating disc at different speeds. Thereafter, the contact angle was measured between ethylene glycol and the film, and distilled water and the film. Based on the angle we calculated polar, disperse and total free surface energy. It was also proved that the free surface energy depends on the rotational speed at which the film was created, but also of the temperature at which the solution was synthesized. We also measured dynamic contact angle.

Keywords: polyaniline, thin films, doping, contact angle, surface free energy.

I. Introduction

Polyaniline is among the materials referred to as electrically conductive polymers. It is known since 1860 as "aniline blackness" that was used as a coloring agent for cotton. It was first produced and analyzed by Runge in 1834. It is amorphous substance, stable in air at up to 300 ° C and insoluble in most organic and aqueous solutions. Polyaniline is built by repeating the different number of benzene and quinone units making the basic structure of a chain of eight aniline molecules. For polyaniline there are three main oxidation states: leucoemeraldine, emeraldine and pernigraniline. Emeraldine condition is stable form of the polymer, and the protonated emeraldine is its only conductive form. Each of these forms is of different color, leucoemeraldine is yellow, emeraldine green and pernigraniline purple blue. Because of the simple and inexpensive synthesis, stability and a wide range of potential applications polyaniline is the most studied conductive polymer lately. Polyaniline can be synthesized in various ways, and its properties depend on the ways and conditions of preparation. Doping the volume samples of polyaniline makes changes in conductivity, depending on the doping concentration [1]. The synthesis is carried out by oxidation of aniline in aqueous or non-aqueous media by chemical or electrochemical method [2,3,4]. The advantage of chemical synthesis in comparison to the electrochemical one is simplicity of processes and the possibility of production of large quantities of polyaniline and it is therefore a primary commercial method in production of particulate mass, dispersions and coatings. The oxidation is carried out with chemical oxidizing agent in solution. The most commonly used one is ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The acidity of the medium is necessary ($\text{pH} < 3$) for solvation of aniline in water and avoiding occurrence of branched products [2,5]. By doping with acids (HCl, H_2SO_4 , H_2PO_4 ,...) achieved is a final density of states at the Fermi level and the formation of new energy states (acceptor or donor) within the energy gap, which leads to movement of the Fermi level and the increase of the number of electrons (holes) in the conductive (valent) band and hence the large increase in conductivity as well [4]. Polyaniline is characterized by a very high degree of chemical stability that makes it very interesting for the exploration and technical applications.

Surface appearances are the phenomena that occur at the border of phases (solid-liquid, liquid-gaseous and solid-liquid- gaseous), but they can also take place on the borders of two liquids that do not mix with each other. At molecules in the interior of a phase the forces from other molecules act from all sides, but they are compensated and the resultant force is zero. However, those molecules that are found at the phase border are not surrounded from all sides by particles of the same phase, and have not all the forces compensated. There are equivalent molecules to the left and right side and in the interior that compensate their forces, but from the top does not work equal attractive force. So there occurs an excess force, which results in surface free energy. If the resultant force is less than zero, the molecules are oriented toward the interior of the liquid, and if it is greater than zero, the force acts outwardly. As a result of the surface free energy on the surface of the phase there occurs a surface tension. This is the force exerted perpendicular to the surface of the liquid. It seeks to reduce the surface area, and thus reduce the total energy content. The higher cohesive forces within a liquid or gas the higher is the surface tension.

Energy of the matter and surface tension are proportional, so that liquids tend to reduce the surface free energy, which can be achieved by creating a geometric body with a minimum surface area, ie, a sphere or

geometric body as similar as possible to a sphere. Surface tension depends on its characteristics, but also on the characteristics of the substance with which it is in contact, their mutual adhesion forces, and on the temperature. If temperature increases the kinetic energy of the particles also increases, they move faster, bonds between molecules get weaker and thus the surface tension decreases. Conversely, if the temperature decreases, there will be less forces in action, and more uncompensated energy, which will increase the surface tension. The surface tension of solids is usually much greater than that of liquids, because the bonds between their particles are much stronger as compared to those in the liquid. Also electrostatic attractive forces between ions, are larger than the attractive forces between molecules. That is why ionic crystals have the highest surface tension. Of all materials, mercury has the largest surface tension. The shape occupied by liquid droplets on the surface of a certain solid body talks about the degree of wetting this matter by that liquid. The angle which is obtained by pulling tangent from the triple point (solid-liquid-gas) to the edge of the drop is called the contact angle of wetting, and is marked with θ (Figure 1). When wetting is complete then $\theta = 0^\circ$, ie. $\cos\theta$ approaching 1. In full non-wetting the contact angle $\theta = 180^\circ$, and $\cos\theta$ value is -1. Lower values of the contact angle mean better spillage or better wetting by the fluid, and vice versa, higher values assume lower wettability.

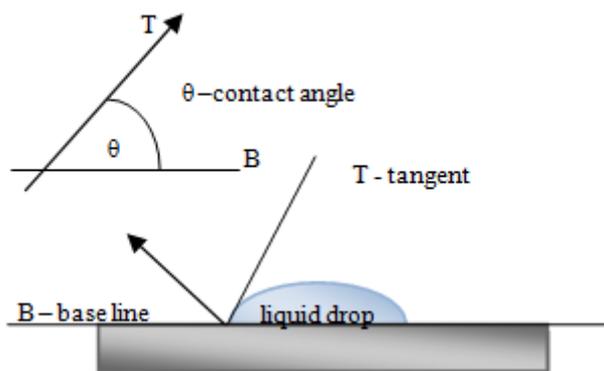


Figure 1: The contact angle at the border of three phases

When measuring static contact angle one should be very cautious and very careful in order to obtain as accurate experimental results as possible. It is known that the contact angle decreases from the moment of contact between a liquid drop and the substrate, ie. there is a spillage of liquid on the substrate. This phenomenon may affect the accuracy of the experimental results. For a large number of liquids which interact with a surface there can be found a variety of static contact angles, which leads to inaccurate results. For this purpose there is introduced the concept of dynamic contact angle. It is a measure of the diffusion of the liquid in time.

II. Material and Methods

The polyaniline (PANI) material that was researched in this study was synthesized by chemical polymerization. The polymerization is carried out in an aqueous solution of sulfuric acid (1 M aqH₂SO₄), wherein was used ammonium peroxydisulfate (NH₄)₂S₂O₈ (APS) as an oxidizing agent. The synthesis of PANI was conducted at different temperatures, at 0°C and room temperature (20°C). After obtaining the solution PANI H₂SO₄ there followed the production of thin films by using a spin coater (Model P-6708D, Specialty Coating Systems, Indianapolis, IN) whose rotational speed can reach 8000 rev/min [6].

Methods of measuring the contact angle are divided into optical (using a goniometer) and tensiometric (force measurement) [1]. The optical method is also called static, Sessile drop method or the hanging drop method [2]. This is the most widely used method for measuring the contact angle, and was used in this study too. When a drop of liquid comes in contact with a solid flat surface, the drop forms a specific shape. Contact angle is measured between the base plane (contact surface between the liquid and the solid matter) and tangent of the drop profile on the three-phase contact line (solid, liquid and gas).

There are methods of calculating the surface energy and surface tension from the known values of the contact angle, which are based on the use of Young's equation. Among them are the method by Zisman, equation of state, the method by Fowkes, expanded method by Fowkes, method by Owens, Wendt, Rabel and Kaelble (OWRK method), Wu method, Schultz method and acid - basic method by Oss and Good. In our work we used to method by Owens i Wendt to determine the polar and dispersive part of the surface free energy of solid bodies.

Knowing the contact angle we can calculate as well the surface free energy by the Owens i Wendt equation states: $\gamma_L(1 + \cos\theta) = 2\left[\sqrt{\gamma_L^d\gamma_S^d} + \sqrt{\gamma_L^p\gamma_S^p}\right]$, where:

γ_L (mJ/m²) - total adhesion parameter of the reference liquid
 γ_L^d (mJ/m²) - non-polar component of the adhesion parameter of the reference liquid
 γ_L^p (mJ/m²) - polar component of the adhesive parameter of the reference liquid
 γ_s^d (mJ/m²) - non-polar component of the adhesion energy of the test surface
 γ_s^p (mJ/m²) - polar component of the adhesion energy of the test surface
 θ (°) - Contact angle between the reference liquid and the test surface

By solving the system of two equations with two unknowns (two reference liquids) we get the parameters γ_s^d (mJ/m²) and γ_s^p (mJ/m²) whose sum represents the total free energy of the test surface γ_s (mJ/m²).

III. Experimental Results and Discussion

After chemical polymerisation of polyaniline at 2 different temperatures (0°C and 20°C) which is carried in an aqueous solution of sulfuric acid (1 M aqH₂SO₄) with ammonium persulfate (NH₄)₂S₂O₈ (APS) as an oxidizing agent, followed by obtaining thin films PANI-H₂SO₄ with the spin coater (model P-6708D, Specialty Coating Systems, Indianapolis, IN). Obtained were 8 films at different speeds of rotation, after which the films were dried first in the desiccator for a few days, and then in the air [6,7].

For measuring the contact angle we used the method of droplets, where measured was the contact angle between the film and ethylene glycol, and the film and distilled water immediately after liquefaction. Since distilled water has a higher surface tension than ethylene glycol, the contact angle between distilled water and the film is higher than the contact angle between the film and ethylene glycol (Figure 2). The measurement of the contact angle was carried out 10 times for each film.

Based on the mean value of the contact angle we calculated by Fowkes equation the surface free energy of films made at different speeds, namely polar and dispersed free energy. The sum of these two energies gives the total free surface energy (Table 1 and 2).



Figure 2: Photography of "A Droplet" of distilled water and ethylene glycol on the film of PANI-H₂SO₄ which was formed from a solution synthesized at 20°C and at a speed of 6000 rpm

No. of measurement	Rotational speed (rpm)	contact angle - H ₂ O	contact angle - ethylene glycol	γ_s^p [mJ/m ²]	γ_s^d [mJ/m ²]	γ_s [mJ/m ²]
1	600	39.13	11.37	48.55234	10.14972	58.70206
2	700	40.56	11.88	46.32071	10.94956	57.27027
3	800	36.78	13.18	53.03631	8.417213	61.45352
4	1100	39.57	15.13	49.11639	9.524473	58.64086
5	2000	36.15	11.93	53.64102	8.345561	61.98658
6	2500	33.29	11.22	58.00928	7.093111	65.1024
7	4000	34.21	13.68	57.41224	7.042906	64.45515
8	6000	35.63	12.55	54.69789	7.955379	62.65327

Table 1: Results of measuring the contact angle for ethylene glycol and water on thin films of PANI-H₂SO₄. For its preparation the solution was synthesized at 0°C, and the calculation of surface free energy for these films was performed for the angles measured.

No. of measurement	Rotational speed (rpm)	contact angle - H ₂ O	contact angle - ethylene glycol	γ_s^p [mJ/m ²]	γ_s^d [mJ/m ²]	γ_s [mJ/m ²]
1	600	46.28	15.07	37.744193	14.343522	52.087715
2	700	54.64	11.62	23.430458	24.049241	47.479698
3	800	56.15	12.77	21.454532	25.542432	46.996964
4	1100	66.69	18.72	9.3622674	38.451643	47.813910
5	2000	56.01	18.09	23.104312	23.063167	46.167478
6	2500	55.00	16.06	24.006083	22.787000	46.793083
7	4000	62.69	22.50	15.105751	29.465374	44.571125
8	6000	74.77	25.66	3.6203089	48.076884	51.697193

Table 2: Results of measuring the contact angle for ethylene glycol and water on thin films of PANI-H₂SO₄. For its preparation the solution was synthesized at 20°C, and the calculation of surface free energy for these films was performed for the angles measured.

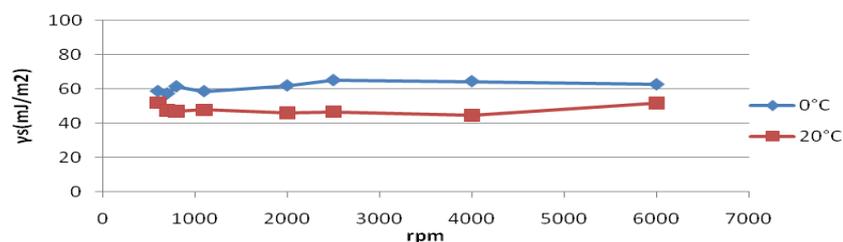


Figure 3: Dependence of the surface free energy on the number of rotations for the films formed from the solutions which were synthesized at 0°C and 20°C.

Figure 3. shows that the dependence of the surface free energy on the number of rotations is almost linear. Also, we see that as the temperature rises free surface energy decreases because increase in temperature also increases the kinetic energy of the particles, they move faster, weaken bonds between molecules, and surface tension and free surface energy decrease.

Also the measurement of contact angle was performed for the samples synthesized at 0°C and at 20°C immediately after liquefaction, after 10 s, 30s and 60s. (Table 3 and 4)

Rotational speed (rpm)	Contact angle - H ₂ O				Contact angle - ethylene glycol			
	t (s)				t (s)			
	0	10	30	60	0	10	30	60
600	57.14	43.27	34.29	31.82	23.03	19.53	16.51	15.25
700	52.63	40.45	35.64	33.82	19.58	17.48	16.00	13.59
800	53.78	40.12	32.83	30.65	26.13	22.44	18.89	17.00
1100	59.75	46.84	43.51	41.31	26.37	25.54	24.55	22.26
2000	59.28	44.96	43.35	41.19	21.60	18.62	18.09	16.46
2500	69.56	55.14	50.38	46.71	20.34	17.40	16.22	15.71
4000	60.46	48.45	43.85	39.39	23.14	21.47	20.58	18.68
6000	76.96	66.27	61.85	58.77	20.47	17.32	16.62	16.06

Table 3: Results of measuring the contact angle in the dependence of time for ethylene glycol and water on thin films of PANI-H₂SO₄ for the preparation of which a solution is synthesized at 0°C.

Rotational speed (rpm)	Contact angle - H ₂ O				Contact angle - ethylene glycol			
	t (s)				t (s)			
	0	10	30	60	0	10	30	60
600	79.52	61.87	58.74	56.15	17.97	13.25	12.93	12.14
700	71.06	58.65	56.86	53.55	16.71	15.93	13.73	12.99
800	43.16	33.20	31.30	29.76	19.50	14.84	13.84	12.66
1100	50.18	37.78	33.43	31.93	26.26	22.74	21.17	20.30
2000	62.69	51.82	45.07	41.18	25.90	24.80	23.75	22.64
2500	76.08	67.70	64.98	61.29	28.15	25.82	25.24	24.67
4000	69.02	59.36	55.29	53.20	29.52	25.84	25.29	24.03
6000	69.65	64.87	63.52	61.28	18.26	17.81	16.90	16.11

Table 4: Results of measuring the contact angle in the dependence of time for ethylene glycol and water on thin films of PANI-H₂SO₄ for the preparation of which a solution is synthesized at 20°C

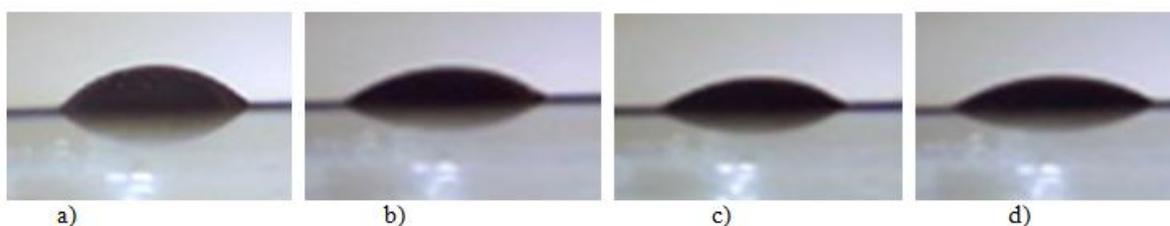


Figure 4: Photography of "A Droplet" of distilled water on the film of PANI-H₂SO₄ which was formed from a solution synthesized at 0°C and at a speed of 700 rpm: a) immediately after liquefaction, b) after 10 s, c) after 30 s, d) after 60 s.

The figure 4 shows one example of reduction of the contact angle depending on the time for the film obtained at 700 rpm. The dependence of the contact angle on the time for ethylene glycol and water on thin films of PANI-H₂SO₄ for the preparation of which the solution was synthesized at 0°C and 20°C, is shown in the figures 5 and 6, respectively. We made measurements of the contact angle for the films obtained at other speeds of rotation.

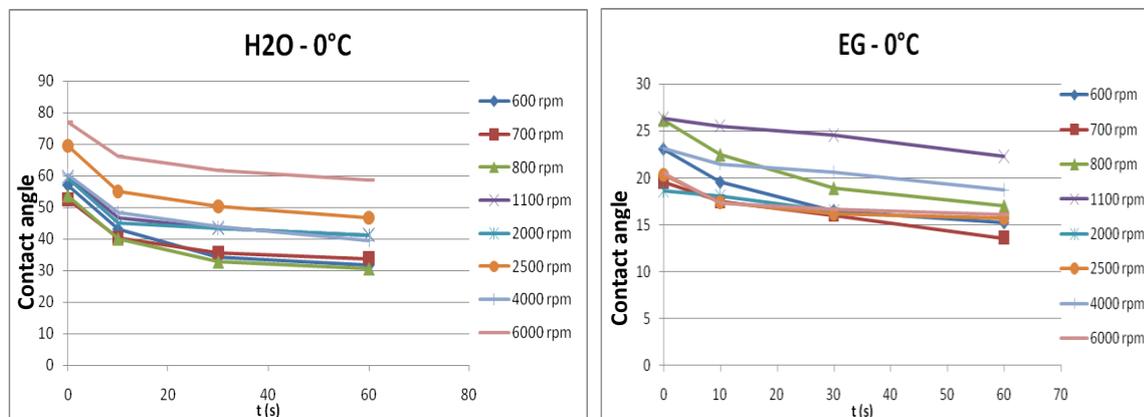


Figure 5: Dependence of the contact angle of the time for ethylene glycol and water on thin films of PANI-H₂SO₄ for the preparation of which a solution is synthesized at 0°C

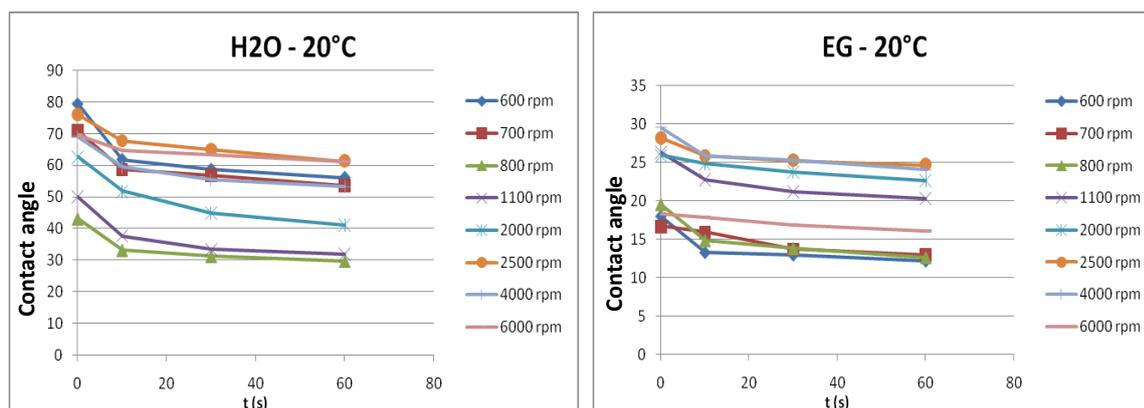


Figure 6: Dependence of the contact angle of the time for ethylene glycol and water on thin films of PANI-H₂SO₄ for the preparation of which a solution is synthesized at 20°C

Experimental data show similar behavior. From all of these measurements it can be seen that the contact angle decreases over time, because as time flows the thin film absorbs more liquid and this results in decrease of the contact angle. This phenomenon is most pronounced in the first 20 seconds.

IV. Conclusion

Based on the experimental results, we can conclude:

- the contact angle between ethylene glycol and the film PANI H₂SO₄ resulting from the solution synthesized at 0°C and at 20°C is smaller than the contact angle between distilled water and the same film as ethylene glycol has a lower surface energy than distilled water and thereby it has greater wettability,
- contact angles, both for the ethylene glycol and the distilled water, for the films formed at various speeds of rotation are approximately equal,
- the surface free energy is approximately equal for films made at different speeds,
- increase in the temperature at which the solution is synthesized for production of the film, leads to a reduction in the surface free energy.
- the contact angle decreases with time flow.

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