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Effect of surfactants on surface tension of PEDOT:PSS aqueous solution

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Abstract. This article examines the effect of surfactant content on the surface tension of a PEDOT:PSS solution to determine the possibility of coating substrates with different values of critical surface tension. One of the disadvantages of applying PEDOT:PSS coatings from an aqueous solution (e.g. spin-coating) is that water has a relatively high surface tension, which leads to poor wettability of substrates with a low critical surface tension.

Keywords: PEDOT:PSS, surface tension, conductive polymer, surfactants, Triton X-100

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Влияние поверхностно-активных веществ на поверхностное натяжение водного раствора PEDOT:PSS

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Аннотация. В данной статье исследуется влияние содержания ПАВ на поверхностное натяжение раствора PEDOT:PSS для определения возможности нанесения покрытий на поверхности подложек с разными значениями критического поверхностного натяжения. Одним из недостатков нанесения покрытий PEDOT:PSS из водного раствора (например, центрифугированием) является то, что вода обладает относительно высоким поверхностным натяжением, что приводит к плохой смачиваемости подложек с низким критическим поверхностным натяжением.

Ключевые слова: PEDOT:PSS, поверхностное натяжение, электропроводящие полимеры, поверхностно-активные вещества, Triton X-100

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Introduction

Polymer solutions have a slightly lower surface tension than water [1], but it is not enough for complete wetting, e.g. polyethylene terephthalate (PET). Surfactants are traditionally used for effectively reducing surface tension. However, the high content of surfactants has a negative impact on the electrophysical properties of PEDOT:PSS [2]. To determine the surface tension of a liquid at which complete wetting of a specific substrate occurs (critical surface tension), one can use the Zisman plots at zero contact angle [3]. By measuring the surface tension of PEDOT:PSS solutions, the required surfactant concentration can be determined to achieve the desired solution surface tension and complete wetting of the substrate. This will avoid excessive addition of surfactants, as well as significantly reduce the waste of material when determining the appropriate concentration. There are numerous studies where PEDOT:PSS is deposited onto silicon surfaces from aqueous solutions without the addition of surfactants. Our observations indicate that when applying the PEDOT:PSS film from the original solution using spin-coating, a dewetting effect occurs. Over time, the solution begins to gather from the liquid film into separate droplets, accompanied by a gradual decrease in the coating thickness over most of the sample and a significant increase in thickness at the droplet locations.

Materials and Methods

Contact angles (θ) were determined using a photographic method based on the width and height of the drop. For drops with volumes up to 1 μL, the influence of gravity on the drop shape can be neglected, allowing us to consider the drop as a segment of a sphere [4]. When determining the values of contact angles, the consideration of evaporation, drop spreading, and absorption of water vapor from the environment was achieved by extrapolating the kinetic curve onto the time axis. Linear extrapolation was performed using the least squares (MLS) method. The obtained contact angle value can be considered to correspond to the equilibrium contact angle [4]. The measurements were taken at a fixed humidity (33–34% R.H.) and close to room temperature (22–23 °C). Humidity control was maintained using a saturated solution of calcium chloride, as detailed in the method presented in this paper[5].To determine the surface tension, two test substrates made of PET and paraffin were utilized. Deionized water (γ_{lv} = 72.8 mJ/m^2), glycerol (γ_{lv} = 63.4 mJ/m^2) and dimethyl sulfoxide(γ_{lv} = 44 mJ/m^2) were employed to assess the surface energy of the substrates. The study employed 3.4% PEDOT:PSS (produced by Sigma Aldrich) with a PEDOT:PSS ratio of 1:2.5. Different volumetric fractions of Triton X-100 (produced by Sigma Aldrich) were added to the aqueous PEDOT:PSS solution, while maintaining a constant volumetric fraction of the original PEDOT:PSS solution (95%).The surface tension (γ_{lv}), particularly its polar (γ_{lv}^p) and dispersive (γ_{lv}^d) components, was determined using formulas derived from the Owens-Wendt [6] method:

$$\gamma_{lv} = 1/\left(A^2 + B^2\right), \tag{1}$$

$$B = \begin{vmatrix} \left(\dfrac{1+\cos\theta}{2}\right)_1 & \sqrt{\left(\gamma_{sv}^p\right)_1} \\ \left(\dfrac{1+\cos\theta}{2}\right)_2 & \sqrt{\left(\gamma_{sv}^p\right)_2} \end{vmatrix}^2 \Bigg/ \begin{vmatrix} \sqrt{\left(\gamma_{sv}^d\right)_1} & \sqrt{\left(\gamma_{sv}^p\right)_1} \\ \sqrt{\left(\gamma_{sv}^d\right)_2} & \sqrt{\left(\gamma_{sv}^p\right)_2} \end{vmatrix}^2 = \sqrt{\gamma_{lv}^d} \Big/ \gamma_{lv}, \tag{2}$$

$$A = \left| \begin{matrix} \left(\frac{1+\cos\theta}{2}\right)_1 & \sqrt{\left(\gamma_{sv}^d\right)_1} \\ \left(\frac{1+\cos\theta}{2}\right)_2 & \sqrt{\left(\gamma_{sv}^d\right)_2} \end{matrix} \right|^2 \Bigg/ \left| \begin{matrix} \sqrt{\left(\gamma_{sv}^p\right)_1} & \sqrt{\left(\gamma_{sv}^d\right)_1} \\ \sqrt{\left(\gamma_{sv}^p\right)_2} & \sqrt{\left(\gamma_{sv}^d\right)_2} \end{matrix} \right|^2 = \sqrt{\gamma_{lv}^p} \Big/ \gamma_{lv}, \qquad (3)$$

where γ_{sv} is the surface energy of the substrate (subscript 1 denotes the first substrate, 2 denotes the second). The surface energy values and their dispersive and polar components for the substrates were also determined under the same conditions using formulas derived from the same method.

Results and Discussion

As a result, Zisman plots (Fig. 1) were obtained along with the critical surface tension (γ_c) values for paraffin (γ_c = 16.12 mJ/m^2) and PET (γ_c = 47.86 mJ/m^2). These low values allowed for the experimental determination of the contact angles of the PEDOT:PSS solution. The values of the surface tension of the PEDOT:PSS solution at different volume fractions of Triton X-100 have been determined (Table).

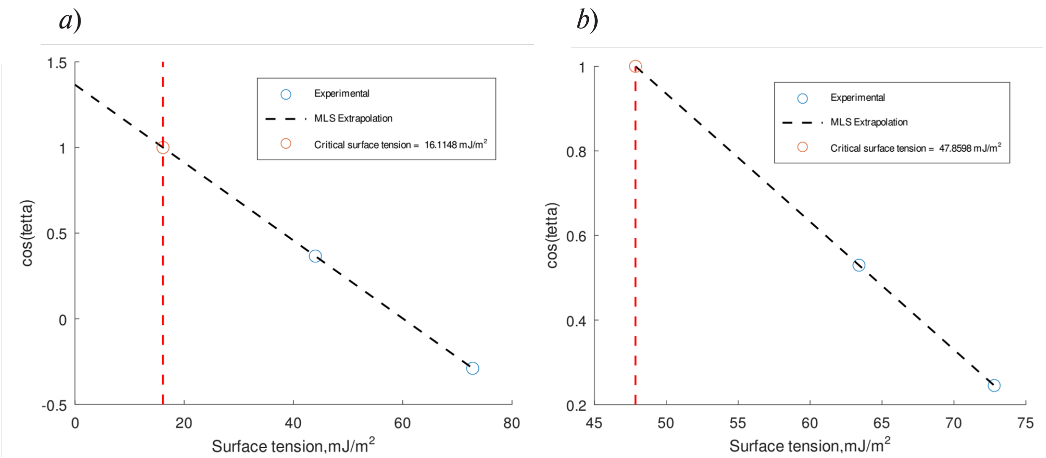

Fig. 1. Zisman plots for paraffin (*a*) and PET (*b*)

Table

Dependence of the surface tension of the PEDOT:PSS with Triton X-100

Triton X-100, vol.%	Surface tension, mJ/m^2		
	γ_{lv}	γ_{lv}^p	γ_{lv}^d
0	64.01±1.55	45.42±0.97	18.59±0.58
0.005	59.81±0.58	49.10±0.32	10.71±0.26
0.010	54.99±0.58	34.66±0.39	20.33±0.20
0.050	57.20±0.45	52.02±0.24	5.9±0.21
0.100	53.19±0.24	49.95±0.12	3.24±0.12

The surface tension of a PEDOT:PSS solution, like other polymer solutions, nonlinearly depends on the surfactant content, which is confirmed in the work [1].

It is shown that the addition of even 0.1 vol.% Triton X-100 reduces the surface tension of the PEDOT:PSS solution by 20%. The obtained values are far from the critical surface tension of silicon γ_c = 34.7 ±7.1 mJ/m^2 [7].

Conclusion

The critical surface tension for paraffin and PET was determined. The surface tension of the aqueous PEDOT:PSS solution (3.4%, 1:2.5) was found to be too high for complete wetting of silicon and various other substrates. It is highly probable that the addition of surfactant concentrations sufficient for complete wetting of silicon would lead to a significant deterioration of its electrical conductivity [2].

Due to the dewetting effect, the thickness of the film deposited by spin-coating is likely to be dependent on the time elapsed before sample baking, significantly hindering the precise control of film thickness, a crucial parameter of thin film.

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