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Long-term ageing of PEDOT:PSS: wettability Study

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ABSTRACT

Known for its electric properties, poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) has emerged as a good candidate for organic electronics and more recently for bio-applications. Despite its growing use in engineering applications, little is known about the stability in time of its interface properties. Here, we consider the surface ageing of PEDOT:PSS when it is stored in environments with various relative humidity and temperature conditions and as a function of the cross-linking agent's (3-glycidoxypropyltrimethoxysilane) concentration. Our systematic wettability study over 6 months reveals that the PEDOT:PSS interface undergoes significant reorganization and some irreversible changes on these timescales regardless of the concentration of cross-linker added.

1. Introduction

Commercially produced on a large-scale, the poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) is one of the forerunner materials in organic electronic [1]. Known for its high conductivity, ease of processing and electrochemical stability, this conducting polymer is extensively used as a conductor or an electroactive material in various electronic devices such as organic light emitting diodes [2], solar cells [3,4], electrochemical transistors/sensors [5,6] or electrochromic windows [7]. More recently, it has emerged as a good candidate for bio-applications given its biocompatibility, softness and high hole conductivity. Several applications of this material in neural interfaces [8], drug delivery [9], in-vitro diagnostics [10], and tissue engineering [11] are currently being pursued.

The ageing of PEDOT:PSS during processing steps [12,13] or throughout the life of devices can have a huge impact on the evolution of device's performances [14,15]. Until now, the studies on the stability of this polymer have been mostly focused on its physical bulk properties predominantly characterized in air. More recently, the electroactivity and electrical resistance/impedance of the polymer have been studied while it is stored under ambient conditions for 4 months [16], in saline solution for 35–75 days [17–19] or when it is washed several times [20]. Despite the fact that the surface properties, such as the water wettability, play a crucial role in the evolution of those physical properties of the polymer, the ageing of its interface has not been systematically studied over the long-term in air and even less in liquid. Indeed, the wetting properties of PEDOT:PSS has been previously studied only during 10 h of immersion [21]. Those experiments have shown that partial dissolution was occurring during the first hours of immersion which can be detrimental to the integration of the material in devices. In order to enhance the integration and the durability of the polymer in devices, it seems important to know how the surface behaves on a longer timescale when it is preconditioned, stored or used.

In this paper we present a detailed investigation of the long term ageing of the wetting properties of PEDOT:PSS when it is stored in various environments: dry air, ambient atmosphere and DI water at different temperatures. We systematically perform dynamic contact angle measurements over a 6 months period and show that the polymer is highly sensitive to the time, temperature and humidity of the surrounding medium. Moreover, given the growing use of cross-linking agents to stabilize PEDOT:PSS in aqueous environment, we study the impact of adding the silane based cross-linking agent, 3-glycidoxypropyltrimethoxysilane (GOPS) which is used in a large variety of bioelectronics devices [22–24]. The results obtained provide valuable insights into the dynamics of PEDOT:PSS surfaces in air and in water which should be taken into account in the design, fabrication and use of devices incorporating this material.

2. Experimental section

2.1. Preparation of conducting polymer films

As described in our previous paper [21], the conducting polymer studied is the PEDOT:PSS coming from a solution composed by 100 mL of the industrial dispersion Clevios PH 500 (HERAEUS) mixed with 5.25 mL ethylene glycol (Sigma Aldrich) and 250 µL

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dodecylbenzenesulfonic acid (DBSA, Sigma Aldrich). We add those products to enhance the conductivity and the formation of the PEDOT:PSS films, respectively. The substrate is a glass microscope slide from Thermo Scientific coated by evaporation with 3 nm of titanium and 50 nm of gold. The gilded glass substrate is cleaned with acetone and isopropanol. Then a first adhesion layer is deposited by spin-coating at 2500 rpm during 30 s in order to prevent the delamination of the PEDOT:PSS coating. PEDOT:PSS formulation combined with 1 wt% of the polymer cross-linking agent 3-glycidoxypropyltrimethoxysilane (GOPS, Sigma Aldrich) is used as the adhesion promoter. The ratio of GOPS is calculated as function of the mass of the PEDOT:PSS colloidal dispersion. Following the adhesion layer deposition, we bake the samples for 30 s at 110 °C and we deposit a layer of PEDOT:PSS solution by spin-coating (at 550 rpm during 30 s). This solution does not contain GOPS to form pristine PEDOT:PSS films named 0 wt%, or includes different ratio of GOPS (0.1, 0.5, 1 or 1.3 wt%) to form cross-linked PEDOT:PSS films. The samples are baked under atmospheric conditions for 30 s at 110 °C and for 1 h at 140 °C. Finally they are immersed in deionized water under stirring (50 rpm) during 15 h to ensure the short term stability of the interface by removing the excess PSS [21].

Despite the fact that the term 'cross-linked' PEDOT:PSS is used in the literature to describe the polymer stabilized by GOPS, the mechanisms of cross-linking are not well understood given the diversity of the reactions which can occur. Indeed, GOPS has four reactive groups [25]: on one side it presents three methoxysilane moieties and on the other side an epoxide. Methoxysilanes are known to undergo silanization reaction resulting on the formation of silanol groups. Those latter can be covalently bound to hydroxyl groups (OH) by the loss of water molecules. And epoxide can react with nucleophile groups. Finally, given the high density of cycles and groups with the capability to form covalent bonds, the enhancement of the film stability can be due to bonds between PEDOT-GOPS chains and predominantly to bonds between PSS-GOPS and GOPS-GOPS chains [26].

2.2. Contact angle measurement

We use a goniometer (KRÜSS, DSA100, Germany) for all the contact angle measurements at room temperature (19–26 °C) in a cleanroom controlled environment. Advancing and receding angles are determined by the DSA100 software (analysis method: Tangent 2). In order to limit the impact of sample heterogeneity on measurements, we deposit three droplets in different positions on the substrate and calculate the mean of the measured contact angles to establish the values discussed below. The standard deviation includes all error types.

To access the advancing and receding angles by the sessile drop technique, we record sequences where the initial 2 µL droplet is inflated to 8 µL through a thin capillary presenting an external diameter of 155 µm. and is deflated until the droplet's disappearance. We use a 50 µL/min flowrate in both cases. Advancing contact angle (ACA) is measured during inflation just before the liquid–gas interface advanced. The receding contact angle (RCA) is measured during deflation just before the liquid–gas interface receded. We use volumes smaller than 10 µL as, under these conditions, the strength of gravity is smaller than capillary forces leading to a droplet shape mainly determined by surface tension [27].

2.3. Ageing process and characterization

The samples are stored in different environmental conditions. We use three environments: under low pressure (−0.1 MPa) in presence of silica gel (relative humidity RH < 20%), in deionized (DI) water and exposed to the laboratory's atmosphere. Moreover the PEDOT:PSS films stored in DI water are maintained at different temperatures in a fridge at 5 °C, in a sterilizer at 37 °C or in a bath at room temperature. While the cleanroom where the samples are stored and characterized is a controlled environment, we observed variations of the RH and temperature during the 6 months duration of the experiment. The RH oscillated between 28% and 55% and the room temperature between 16 °C and 25 °C.

For the characterization of the samples stored under low pressure, we systematically break the vacuum 30 min before opening the sample-box. Once the samples are out we wait 10 min in air and perform sessile drop measurements. We systematically characterize the films maintained in DI water 10 min after drying them with N_2 air-blower.

2.4. X-ray photoelectron spectra

X-Ray photoelectron spectroscopy (XPS) is used to evaluate surface composition of our polymer films and carried out using an ESCALAB 220 XL spectrometer from Vacuum Generators featuring a monochromatic Al Kα X-ray source (1486.6 eV). The spectra are analyzed with the MultiPeak and XPSPeak 4.1 softwares. We calculate the ratio of PSS to PEDOT and the ratio of cross-linker to PEDOT:PSS in order to determine our films' composition.

To calculate the ratio of PSS, we focus on the relative intensities of S (2p) peaks at 165 eV associated with the sulfur from the PEDOT thiophene ring and the doublet peak at 168–169 eV associated with the sulfur from the sulfonate moiety of PSS [28]. The ratios of PSS to PEDOT correspond to the ratio of the area of the peak assigned to PEDOT and the integral area of the doublet due to PSS.

We define the ratio of cross-linker as the ratio of the silicon which is present only on GOPS molecules over the sulfur which is found both in PEDOT and PSS. The ratio is calculated from the absolute area of the peaks divided by the atomic sensitivity factors specific to each atom. We used 0.283 for the silicon and 0.57 for the sulfur which are the values of atomic sensitivity factors established by Perkin-Elmer Corporation, Physical Electronics Division for X-ray source at 90°.

In order to facilitate the comparison of our different spectra, we normalize the intensity of the peak by the area of peaks (S2p) associated with PEDOT. Examples of spectra are shown in the Supplementary Content (Fig. S1).

2.5. Thickness and roughness measurements

To evaluate the thickness and the roughness of the films, we use an profilometer Bruker DEKTAK XT equipped with a 2 µm-radius tip and we complete our observation by measurement on the atomic force microscope (AFM) Bruker ICON in tapping mode equipped with a triangular cantilever (Model SNL-10 C from Bruker k = 0,24 N/m). The average roughness is calculated on 100 µm profiles measured with the profilometer and on 50 μm^2 AFM scans.

3. Results

3.1. Impact of the humidity and the pressure

First, we compare a pristine sample (0 wt% of GOPS) to a cross-linked one containing 1 wt% of GOPS. We consider these two formulations because they correspond to the concentrations of GOPS commonly seen in literature [24,29–31]. We divide each sample in three parts and store them in different environments. The first one is stored in a plastic sample-box left at room atmosphere, the second one in DI water and the third one under low pressure and low RH. The samples are left in the same room with controlled temperature (21 ± 5 °C) to guarantee they are exposed to the same temperature variations if any. For this experiment, we discuss only the evolution of the ACA. Indeed, the RCA measured by the sessile-drop method are constant and equal to zero for all the samples.

During the first weeks, the storage conditions do not impact drastically the evolution of the wettability of the pristine films (Fig. 1a). Whatever the environments, the polymer films become more hydrophobic. Indeed, during this short period, the initial ACA which is about