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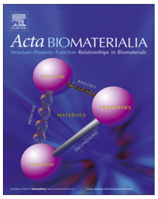

Full length article

Stiffness, strength and adhesion characterization of electrochemically deposited conjugated polymer films

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A B S T R A C T

Conjugated polymers such as poly(3,4-ethylenedioxythiphene) (PEDOT) are of interest for a variety of applications including interfaces between electronic biomedical devices and living tissue. The mechanical properties, strength, and adhesion of these materials to solid substrates are all vital for long-term applications. We have been developing methods to quantify the mechanical properties of conjugated polymer thin films. In this paper, the stiffness, strength and the interfacial shear strength (adhesion) of electrochemically deposited PEDOT and PEDOT-co-1,3,5-tri[2-(3,4-ethylene dioxythienyl)]-benzene (EPh) were studied. The estimated Young's modulus of the PEDOT films was 2.6 ± 1.4 GPa, and the strain to failure was around 2%. The tensile strength was measured to be 56 ± 27 MPa. The effective interfacial shear strength was estimated with a shear-lag model by measuring the crack spacing as a function of film thickness. For PEDOT on gold/palladium-coated hydrocarbon film substrates an interfacial shear strength of 0.7 ± 0.3 MPa was determined. The addition of 5 mole% of a tri-functional EDOT crosslinker (EPh) increased the tensile strength of the films to 283 ± 67 MPa, while the strain to failure remained about the same (2%). The effective interfacial shear strength was increased to 2.4 ± 0.6 MPa.

Statement of significance

This paper describes methods for estimating the ultimate mechanical properties of electrochemically deposited conjugated polymer (here PEDOT and PEDOT copolymers) films. Of particular interest and novelty is our implementation of a cracking test to quantify the shear strength of the PEDOT thin films on these solid substrates. There is considerable interest in these materials as interfaces between biomedical devices and living tissue, however potential mechanisms and modes of failure are areas of continuing concern, and establishing methods to quantify the strengths of these interfaces are therefore of particular current interest. We are confident that these results will be useful to the broader biological materials community and are worthy of broader dissemination.

1. Introduction

Conjugated polymers (CPs) such as poly(3,4-ethylenedioxythiophene) (PEDOT) are both ionic and electronic conductors, and are of particular interest for applications such as organic electronics, biosensors, and biointerfacing materials [1–8]. CP coatings create high surface area, low impedance interfaces between neural tissue and metal electrodes [9]. CP-coated neural electrodes have been shown to be more effective than bare metal electrodes in both short term and long-term animal studies [10,11]. These organic materials can also be chemically modified to realize specific biological functions [12]. However, the internal cracking of CP coatings deposited on metallic electrodes has been observed [13–15]. Failures due to delamination and cracking of PEDOT coated onto stainless steel pad electrodes were also observed in animal tests after extended implantations *in vivo* [11].

1.1. Mechanical properties and failure of CP coatings in neural interface applications

Although the stiffness of spun-cast [16,17] and electrochemically deposited [19,21] PEDOT films have been previously examined, there is little information available about their intrinsic

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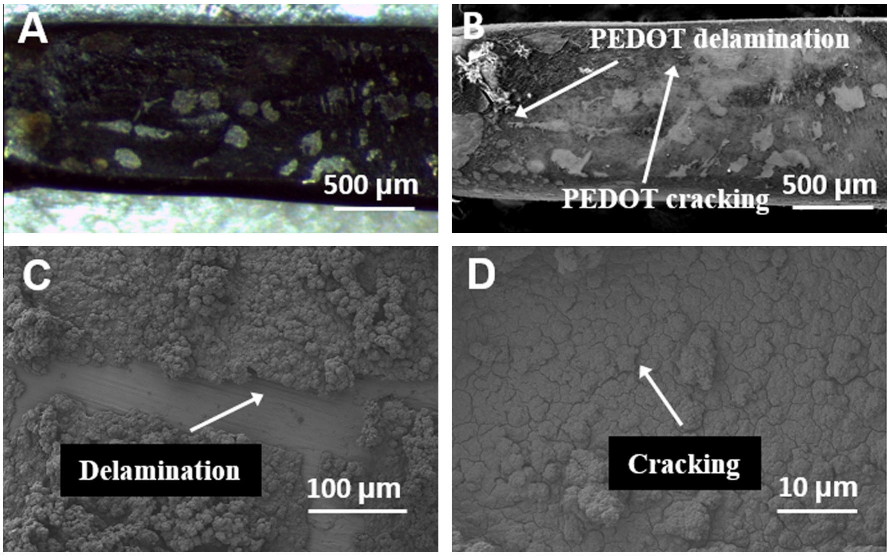

Fig. 1. Failure modes of CP coatings. (A and B) Correlated reflective light optical microscopic and scanning electron microscopic (SEM) images of PEDOT coated neural electrode after 7-month *in vivo* test; (C and D) SEM images of PEDOT coated stainless steel RPNI electrode after 7-month *in vivo* test.

strength and adhesion to solid substrates. There is a therefore a need to design testing platforms and methods to reliably and accurately measure the mechanical properties and estimate the durability of CP coatings. PEDOT failures were observed after 14 days of pulse stimulation [15]. CP coating failures were also discovered just after the ethylene oxide (ETO) sterilization, even before any neural stimulation. In a recent study of a Regenerative Peripheral Nerve Interface (RPNI), PEDOT-coated stainless steel electrodes were examined after 7-months of *in vivo* testing [11] with both optical and scanning electron microscopy (Fig. 1). The PEDOT films showed evidence for both delamination from the metal substrate and internal cracking (Fig. 1). These results show that there is a need to improve both the adhesion of PEDOT to the solid substrates, as well as its intrinsic strength and ductility. It also demonstrates the need for better information about the mechanical properties of these coatings for optimizing the durability of candidate materials for long-term *in vivo* applications.

1.2. Mechanical property characterization methods for CPs

Previously, the mechanical properties of PEDOT:PSS solution cast films have been explored. The Young's modulus of different PEDOT:PSS forms have been reported to be between 0.8 and 2.4 GPa [16,17]. The mechanical properties of electrochemically polymerized PEDOT have rarely been reported, due to the limitations of analytical techniques applicable to such thin films (typically a few microns or less) deposited onto relatively stiff metal electrodes. Commercially available PEDOT (Baytron® P or Clevios™) is an aqueous dispersion of a PEDOT:poly(styrene sulfonate) (PSS) polyelectrolyte complex. In order to get good dispersions, the polymeric dopant PSS is provided in excess (typically at a 2.5:1 to 6:1 weight ratio versus PEDOT) [18]. The doping of electrochemically polymerized PEDOT, on the other hand, is often done with small molecules (such as $LiClO_4$) and at lower effective doping concentrations [19]. The mechanical properties of electrochemically polymerized PEDOT and solution cast chemically polymerized PEDOT (Baytron® P) are thus expected to be different [20].

The experimental difficulty in obtaining large, free-standing electrochemically polymerized PEDOT films makes their mechanical characterization a challenge. Nanoindentation and PeakForce QNM (quantitative nanomechanical property mapping) AFM have both been used to estimate the modulus of electrochemically deposited PEDOT [19,21]. The Young's modulus of PEDOT:$LiClO_4$ was reported to be 1.39 ± 0.79 GPa when measured with QNM AFM mode [19]). However, in this study the reference used to calibrate the tip spring constant was quite soft when compared to the CPs, which may result in an underestimation of the Young's modulus. The fuzzy and porous structure of the PEDOT surface also brings limitations to nanoindentation methods, including irreproducible indentation patterns and large surface noise. Also nanoindentation methods only provide information about the relatively small-strain elastic response (modulus), whereas the tensile strength, strain to failure, and adhesion to the substrate are also of interest, particularly for long-term durability studies.

Here, we describe methods for measuring the elastic modulus and interfacial shear strength of electrochemically deposited CP coatings on gold-coated soft substrates. PEDOT was electrochemically deposited on gold/palladium-coated hydrocarbon film (Parafilm M®). The thin metallic coating was used to create a conductive surface in order to electrochemically deposit the PEDOT from solution. The Young's modulus of Parafilm M® is 30–60 MPa, and the rupture strain is around 400%. During the stretching/tensile tests, the cracking behavior of PEDOT and a chemically crosslinked PEDOT derivative (PEDOT-co-EPH) were observed *in situ* by optical microscopy, providing information about the tensile strength and the interfacial shear strength of PEDOT on the substrate. The cracking phenomena observed in this test are analogous to previous observations of brittle coatings on ductile substrates [22,23,30].

The advantages and disadvantages of the applicable mechanical characterization methods are listed in Table 1. Compared to the normal tensile test and indentation methods, our method provides information about crack propagation, cracking density, and interfacial shear strength. Our methods also avoid potential errors induced by the tip selection and characterization in nanoindentation and QNM AFM methods. By directly observing the crack propagation process, detailed information about the mechanisms of film failure are obtained.

2. Theory

Since the PEDOT coated hydrocarbon film is a laminar composite, the Voigt model was used to estimate the in-plane Young's modulus [24,25]. This model is based on the assumption that the strain of reinforced layers and the matrix are the same: