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

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Abstract

Conjugated polymers such as poly(3,4-ethylenedioxythiophene) (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 study 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.

Keywords

Young's modulus; tensile strength; adhesion; electrochemical polymerization; poly(3,4-ethylenedioxythiophene); crosslinked PEDOT; neural interface materials

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ASSOCIATED CONTENT

Supporting Information. Stress-strain curve of PEDOT coated and gold coated hydrocarbon film (Parafilm M[®]). Statistics of DMT modulus values of PEDOT and 0.5% crosslinked PEDOT obtained from QNM AFM. This material is available free of charge via the Internet at <http://pubs.acs.org>.

DCM is a Co-Founder and Chief Scientific Officer for Biotectix LLC, a University of Michigan spin-off company that is developing conjugated polymers for interfacing electronic biomedical devices with living tissue.

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][2][3][4][5][6][7][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] [14][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 strength and adhesion to solid substrates. There is 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 to 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 LiClO₄) 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:LiClO₄ was reported to be 1.39 ± 0.79 GPa when measured with QNM AFM mode (Baek et al., 2014). 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:

$$\epsilon_c = \frac{\sigma_c}{E_c} = \epsilon_s = \frac{\sigma_s}{E_s} = \epsilon_{f1} = \frac{\sigma_{f1}}{E_{f1}} = \epsilon_{f2} = \frac{\sigma_{f2}}{E_{f2}} = \dots$$

where σ_f , ϵ_f , σ_s , ϵ_s , σ_c , ϵ_c are the stress and strain of the reinforced layers, the substrate and the whole composite, respectively. As the stress is the force per unit area, a force balance gives:

$$\sigma_c = \sigma_s f_s + \sigma_{f1} f_{f1} + \sigma_{f2} f_{f2} + \sigma_{f3} f_{f3} + \dots$$

Hence the Young's modulus of the whole composite can be calculated as:

$$E_c = \frac{\sigma_c}{\epsilon_c} = \frac{\sigma_s f_s + \sigma_{f1} f_{f1} + \sigma_{f2} f_{f2} + \sigma_{f3} f_{f3} + \dots}{\epsilon_c}$$

$$E_c = E_s f_s + E_{f1} f_{f1} + E_{f2} f_{f2} + E_{f3} f_{f3} + \dots$$

where f is the volume fraction of each component, which we assume is equal to the fractional thickness.

According to the Voigt model, we obtain the Young's modulus of the gold coated hydrocarbon film

$$E_{c1} = E_s f_{s1} + E_g f_{g1}$$

and,

$$f_{s1} = \frac{\delta_s}{\delta_s + \delta_g}, f_{g1} = \frac{\delta_g}{\delta_s + \delta_g}$$

The Young's modulus of PEDOT coated hydrocarbon film is,

$$E_{c2} = E_s f_{s2} + E_g f_{g2} + E_p f_{p2}$$

The volume fractions of each layer are given by,

$$f_{s2} = \frac{\delta_s}{\delta_s + \delta_g + \delta_p}, f_{g2} = \frac{\delta_g}{\delta_s + \delta_g + \delta_p}, f_{p2} = \frac{\delta_p}{\delta_s + \delta_g + \delta_p}$$

Hence,

$$E_{c2} = E_s \frac{\delta_s}{\delta_s + \delta_g + \delta_p} + E_g \frac{\delta_g}{\delta_s + \delta_g + \delta_p} + E_p \frac{\delta_p}{\delta_s + \delta_g + \delta_p}$$

$$E_{c2} = E_s \frac{\delta_s}{\delta_s + \delta_g} \frac{\delta_s + \delta_g}{\delta_s + \delta_g + \delta_p} + E_g \frac{\delta_g}{\delta_s + \delta_g} \frac{\delta_s + \delta_g}{\delta_s + \delta_g + \delta_p} + E_p \frac{\delta_p}{\delta_s + \delta_g + \delta_p}$$

$$E_{c2}=E_{c1}(1-f_{p2})+E_p f_{p2}$$

where δ_s , δ_g , δ_p are the thickness of the hydrocarbon substrate (~127 microns), gold/palladium thin layer (~10 nm) and CP coating (~500 nm), respectively.

The stress environment (brittle coating on ductile substrate) of the materials examined in this test is analogous to other hard coatings in tribological applications [26][30]. According to the Agrawal and Raj (A-R) model[27][28], the maximum interfacial shear stress, τ , that can develop at the interface between the PEDOT coating and the substrate is related to the tensile strength of the PEDOT film, σ , by the following equation:

$$\tau=(\pi\delta\sigma)/\hat{\lambda}$$

where $\sigma = E\varepsilon_f$, ε_f is the strain corresponding to the onset of cracking in the coating; and E and δ are the Young's modulus and thickness of the coating, respectively. $\hat{\lambda}$ is the characteristic crack spacing at the stage where the number of transverse cracks becomes saturated with increasing tensile strain. The value of $\hat{\lambda}$ is determined by the interfacial shear stress between the brittle coating and the more ductile substrate. This model has been previously used to evaluate the adhesion strength of several brittle inorganic [22][23] [29] and organic [30] hard coatings on relatively ductile substrates.

3. Materials and methods

3.1 Sample preparation

Soft hydrocarbon films (Parafilm M®, 127 μm thick) were used as the ductile substrate. A gold/palladium (70/30) alloy was sputtered for 4 min on the substrate before the PEDOT deposition. The metal layer was kept as thin as possible so that the films could be electrochemically deposited into uniform films, but the influence of the metal on the overall mechanics could be minimized. The thickness of the gold/palladium ultrathin film was estimated to be only 50 nm by FIB-SEM (Zeiss Auriga™ 60 Crossbeam FIB-SEM) and 35 nm by X-ray Reflectivity (Rigaku Ultima IV XRD) (Fig. S1, S2 and Table S1). We therefore assumed that the loads in this layer were negligible relative to the much thicker PEDOT film (300–700 nm) and the hydrocarbon film substrate (127 μm). The gold/palladium-coated hydrocarbon film was cut into rectangular shapes with a nominal width of 7 mm. PEDOT and crosslinked PEDOT were electrochemically deposited onto the metal-coated hydrocarbon film.

EDOT monomer, LiClO_4 and propylene carbonate (PPC) were used as received from Sigma Aldrich. Eph was synthesized in our lab [31], based on previously published methods [32]. PEDOT and Eph-crosslinked PEDOT were deposited galvanostatically on gold-coated hydrocarbon film (for tensile test) and gold-coated silicon wafers (for QNM AFM test, the gold coating was ~35 nm thick). An electrochemical cell with 1 cm diameter was used for the 9 electrochemical deposition of PEDOT/ LiClO_4 . The gold/palladium coated hydrocarbon film or gold/palladium coated silicon wafer acted as the working electrode and

a platinum wire soldered at the bottom of the cell was the counter electrode. The stock monomer solution contained 0.1 M EDOT and 0.1 M LiClO₄ in propylene carbonate (PPC). The monomer solutions for 0.1%, 0.5%, 1%, 5% crosslinked PEDOT respectively contained an additional 0.0001M, 0.0005M, 0.001M, and 0.005M of Eph in PPC.

A constant current of 10 μ A was provided by a Metrohm Autolab system, corresponding to a current density of 0.14 μ A/mm² (0.014 mA/cm²). Different deposition times of 2000 s, 3000 s, 4000 s, 5000 s, and 6000 s corresponding to the charge densities of 28.6 mC/cm², 42.9 mC/cm², 57.1 mC/cm², 71.4 mC/cm², 85.7 mC/cm² were applied to deposit PEDOT films with a range of thicknesses corresponding to ~300 nm to ~700 nm. The thicknesses of the hydrocarbon film PEDOT and crosslinked PEDOT films were measured by optical microscopy (Nikon) and by scanning electron microscopy (Zeiss Auriga™ 60 Crossbeam FIB-SEM). A current of 10 μ A (current density of 64.3 mC/cm²) was applied to the Eph-crosslinked PEDOT layer deposition, corresponding to a nominal thickness of 500 nm.

3.2 Thin Film Cracking

The PEDOT and Eph-crosslinked PEDOT coated hydrocarbon film tensile specimens were loaded on a Tytron™ 250 mechanical testing apparatus. The specimens were deformed at a strain rate of 0.02 mm/s, corresponding to a nominal strain rate of 0.1/min. The transverse cracking generated in the PEDOT film was recorded during the experiment as a function of sample elongation. These in-situ video observations were acquired using a Nikon stereomicroscope and DinoCapture software. The characteristic crack spacing data was obtained by averaging out the numbers of the cracks counted on 15 separate fields on different samples. All of the tensile tests were conducted at 25°C.

3.3 QNM AFM

The Young's modulus was obtained by PeakForce QNM® (quantitative nanomechanical property mapping) mode with Nanoscope Dimension 3100 software on a Bioscope Catalyst (Bruker Nano/ Veeco) AFM, and was calculated following the Derjaguin, Muller and Toporov (DMT) model [33]. All samples were measured at room temperature in the dry state. A TAP150A probe (with a force constant of ~5 N/m) was used to indent the sample surface to a depth of about 1–2 nm.

3.4 Statistical analysis

Data were analyzed and plotted with Origin 9.1 software. All data points were expressed as the mean $\pm$ standard deviation (SD).

4. Results and discussion

During the early stage of tensile testing, cracks formed in the PEDOT perpendicular to the direction of the applied deformation (Fig 3. A,B,C). As the assembly was stretched further, the PEDOT cracking increased. Eventually, the crack density saturated, reaching a maximum value characteristic of a particular sample (Fig 3. D,E). The characteristic crack spacing $\hat{\lambda}$ was obtained by measuring the total number of PEDOT cracks along the

stretching direction, and dividing this value by the unstretched dimensions of the sample over the field of view.

4.1 Validation of SIMM

To validate the method, PEDOT coatings of several different thicknesses were tested. The crack spacing of each thickness of PEDOT were counted at least 300 times for each sample (Figure 4).

As well as the initial cracking strain, the local strain when the crack density saturated was also measured. This crack saturation strain was around 10% –15% (Table 3.). Each sample was stretched to around 300% strain, which means the cracking was fully saturated during the stretch process. As shown in Fig. 4B, the distributions of the measured PEDOT crack spacings were broader in the thicker PEDOT films. This is consistent with the rougher surface morphology as the deposition times become longer and films become thicker (Fig. 4A). If the value of PEDOT film tensile strength and film adhesion are the same for different film thicknesses, then the thickness of PEDOT film and the characteristic crack spacing should have a linear relationship. We extracted the characteristic crack spacing values and plotted them as a function of film thickness (Fig. 4B). The data indeed show the anticipated linear relationship between the crack spacing and the thickness [27].

The mechanical property values we determined are compiled in Table 2. The Young's modulus of electrochemically deposited PEDOT was 2.6 ± 1.4 GPa, the tensile strength was 56 ± 27 MPa, and the interfacial shear strength was 0.7 ± 0.3 MPa. The values of these properties were found to be essentially independent of the film thickness. Our results are in a similar range with the values of the Young's modulus (2.8 ± 0.5 GPa, at 23% relative humidity), tensile strain ($\sim 2.5\%$, at 23% relative humidity) and the tensile strength (53.2 ± 9.5 MPa, at 23% relative humidity) of pipetted Baytron® P film measured by Lang [17].

Fig. 5B shows the linear relationship between crack spacing and film thickness of the PEDOT. The Young's modulus of films of PEDOT with different thicknesses are shown in Fig. 5A, showing that there was no significant dependence on thickness.

4.2 Characterization of enhanced mechanical properties of crosslinked PEDOT

Given the apparent success of our approach, we then used these same techniques to evaluate the mechanical properties of EPh-crosslinked PEDOT.

As shown in Fig. 6B, the distribution of 0.1% crosslinked PEDOT crack spacing was the most narrow, which is consistent with the smoother surface morphology seen with 0.1% EPh (Fig. 6A). Adding a small amount of EPh crosslinker made the film surface smoother, but above 0.5% the morphology of the film became rougher. The morphology of the films was consistent with the crack spacing distribution, with the smooth films having a more narrow distribution, and the rougher films showing a larger distribution. The mechanical properties of PEDOT and crosslinked PEDOT films extracted from our testing were compiled and are listed in Table 3.

The addition of EPh crosslinker didn't affect either the cracking strain or the crack saturation strain that much. The tensile strength and interfacial shear strength values as a function of EPh composition are shown graphically in Fig. 7. The results show that the Young's modulus, tensile strength and adhesion to the substrate were all significantly improved by adding the EPh crosslinker to the PEDOT. Specifically, the tensile strength of the 5% EPh crosslinked PEDOT increased to around 300 MPa, whereas the non-crosslinked PEDOT had a strength of ~30 MPa. The interfacial shear strength increased from ~0.5 MPa to ~2.5 MPa with the addition of 5% EPh crosslinker.

4.3 Comparison with QNM AFM

To corroborate the Young's modulus of PEDOT and crosslinked PEDOT obtained from our method, we also conducted quantitative nanomechanical (QNM) AFM experiments. This test provided estimates of the modulus distribution across the surface of the film over the region examined. The data are shown in Fig. 8. We found the average QNM modulus of PEDOT and 0.5% crosslinked PEDOT were around 1.6 GPa and 2.2 GPa respectively. It should be noted that the QNM histograms showed reasonably broad distributions that seemed to be slightly assymetric toward the higher modulus direction. The values of the modulus were somewhat smaller than the results obtained (2.6 ± 1.4 GPa and 5.1 ± 2.6 GPa) from our method, but were still in a similar range.

Conclusions

The measurement of the interfacial shear strength of PEDOT films with different thicknesses shows a linear relationship between crack spacing and thickness. The Young's modulus results are similar to those measured with the nanoindentation and QNM AFM mode and the values of solution cast PEDOT:PSS film. The crosslinking of PEDOT with EPh significantly increased the strength, stiffness, and adhesion of the PEDOT films to the underlying substrates. These results support that contention that EPh is a promising component to enhance the durability of PEDOT coating on neural electrodes. As CPs are mainly used as thin films and coatings, quantitative information about their failure strength and adhesion to substrates are essential for estimating their durability in applications, but cannot be readily obtained by previous methods, such as nanoindentation and AFM. Our methods provide a novel and convenient means for evaluating the stiffness, strength, and adhesion of CP films on solid substrates. The observations of crack propagation and delamination also provide direct evidence of the modes of coating failure under mechanical stress.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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

Fig. 2.
(A) Saturated conducting polymer film cracking on hydrocarbon substrate (Parafilm M[®]) with the experiment setup, (B) mechanism of brittle film cracking on ductile substrate.

Figure 3.
In-situ observation of PEDOT cracking behavior.

Fig. 4.
 (A) PEDOT surface morphology with different deposition times: 2000 s (28.6 mC/cm²), 3000 s (42.9 mC/cm²), 4000 s (57.1 mC/cm²), 5000 s (71.4 mC/cm²), and 6000 s (85.7 mC/cm²) (scale bar=3 μ m); (B) Statistics of crack spacing of PEDOT with different thickness.

Fig. 5.
Young's modulus and cracking spacing as a function of average film thickness

Fig. 6.
 (A) The surface morphology of PEDOT and crosslinked PEDOT; (B) Statistics of crack spacing of PEDOT and crosslinked PEDOT.

Fig. 7.
The relationship of tensile strength and interfacial shear strength with EPh crosslinker composition.

Fig. 8.
The DMT modulus of PEDOT and 0.5% crosslinked PEDOT obtained from AFM comparison with the Young's modulus from our method.

(a) poly(3,4-ethylene dioxythiophene)
(PEDOT)

(b) 1,3,5-tri[2-(3,4-ethylene dioxythienyl)]-benzene
(EPh)

Scheme 1.

Chemical structure of (a) PEDOT, (b) EDOT crosslinker- 1,3,5-tri[2-(3,4-ethylene dioxythienyl)]-benzene (EPh)

Table 1

Comparison of different mechanical characterization methods.

	Tensile Test	Nanoindentation	QNM AFM	Thin Film Cracking
Film type	Chemically polymerized	Chemically & electrochemically polymerized	Chemically & electrochemically polymerized	Chemically & electrochemically polymerized
Mechanical properties	Young's modulus, Tensile strength Tensile strain	Modulus	Modulus	Modulus Tensile strength Tensile strain to failure Interfacial shear strength
Limitations	Not applicable for electrochemically polymerized PEDOT	Value dependency on tip's geometry Irreproducible indentation pattern, Large surface noise	Value dependency on tip's spring constant, Value dependency on calibration method, High cost for AFM tip	Requires deposition onto a more ductile substrate

Table 2

Mechanical properties of PEDOT with different thickness

Charge density (mC/cm ²)	Crack spacing (μm)	Film thickness (nm)	Cracking strain (%)	Young's Modulus (GPa)	Tensile Strength (MPa)	Effective Interfacial Shear Strength (MPa)
28.6	73 ± 11	314 ± 24	2.4 ± 0.4	2.4 ± 0.9	51 ± 14	0.7 ± 0.2
42.9	106 ± 15	411 ± 23	1.9 ± 0.2	3.9 ± 1.7	76 ± 28	0.9 ± 0.3
57.1	134 ± 18	461 ± 65	2.2 ± 0.1	2.1 ± 0.8	43 ± 16	0.5 ± 0.2
64.3	126 ± 31	516 ± 43	2.1 ± 0.3	2.6 ± 1.4	56 ± 27	0.7 ± 0.3
71.4	159 ± 31	617 ± 48	2.1 ± 0.4	2.1 ± 0.6	40 ± 7	0.5 ± 0.1
85.7	187 ± 34	714 ± 84	2.3 ± 0.5	2.5 ± 1.6	64 ± 38	0.8 ± 0.5

Table 3

Crosslinked PEDOT surface morphology with different amounts of EPh.

	Crack Spacing (μm)	Thickness (nm)	Cracking Strain (%)	Crack Saturation Strain (%)	Young's Modulus (GPa)	Tensile Strength (MPa)	Effective Interfacial Shear Strength (MPa)
PEDOT	126 $\pm$ 31	516 $\pm$ 43	2.1 $\pm$ 0.3	10.4 $\pm$ 1.4	2.6 $\pm$ 1.4	56 $\pm$ 27	0.7 $\pm$ 0.3
0.1% EPh	129 $\pm$ 24	536 $\pm$ 59	2.0 $\pm$ 0.3	12.5 $\pm$ 2.5	4.4 $\pm$ 2.4	103 $\pm$ 61	1.4 $\pm$ 0.7
0.5% EPh	174 $\pm$ 40	574 $\pm$ 47	2.8 $\pm$ 0.2	11.2 $\pm$ 1.3	5.1 $\pm$ 2.6	147 $\pm$ 92	1.5 $\pm$ 0.8
5% EPh	198 $\pm$ 48	532 $\pm$ 46	2.3 $\pm$ 0.3	14.7 $\pm$ 3.7	12.6 $\pm$ 3.0	283 $\pm$ 67	2.4 $\pm$ 0.6