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Research Article

Vapor phase polymerization of PEDOT on silicone rubber as flexible large strain sensor

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Abstract: This paper presents a flexible large strain sensor made from ethylenedioxythiophene deposited on silicone rubber (Ecoflex® 00-30) via vacuum assisted vapor phase polymerization (VPP) process. EDOT was used due to its stability when exposed to the atmosphere. VPP is a very simple process requiring only a vacuum bell jar and a vacuum pump. Ferrite chloride ($FeCl_3$) dissolved in tethrahydrofuran was used as the oxidant to make the resulting poly(3,4-ethylenedioxythiophene) (PEDOT) conductive. THF was used because it swells Ecoflex® for better infusion of oxidant and PEDOT adherence. The sensor performs reliably up to 80% strain with a gauge factor of ~2.4 and small hysteresis.

Keywords: flexible large strain gauge; poly(3,4-ethylenedioxythiophene); vapor phase polymerization

1. Introduction

Progress in the development of artificial muscles has seen rapid growth [1]. These artificial muscles are typically light weight and flexible. However, there is a need for lightweight and also flexible sensors to complement these artificial muscles. For example in a hand exoskeleton, even with the use of artificial muscles to reduce the weight and increase the wearability, many still rely on the use of traditional sensors, which are typically rigid, bulky or even heavier than the artificial muscle itself.

The use of conducting polymers as flexible large strain sensors has gained significant interest. There are many reports on the use of such sensors in various applications including measurement of

parachute canopy [2], textile-based wearable sensors [3], measurement of finger forces [4], tactile sensors [5] and pressure sensors [6]. Flexible large strain (FLS) sensors have significant benefits when compared to traditional sensors, which are bulky and rigid in form. The advantages of FLS sensors include larger range of strain, lower weight, lower profile (less bulky) and ability to be fabricated conformal to different surfaces, collectively allowing FLS to be easily integrated with biologically-inspired mechanisms.

In prior work [7], we have presented a FLS sensor using polypyrrole (PPY) on natural rubber. However, there are some disadvantages with this sensor. The disadvantages are limited strain (~20%), degradation of PPY over time making the sensor unstable, and low gage factor (~1.86). This preliminary work aims to address the problem in [7] by using poly(3,4-ethylenedioxythiophene) (PEDOT) on Ecoflex® silicone rubber. PEDOT has been one of the most successful conducting polymers due to its high conductivity and high stability in the oxidized state [8]. Vapor-phase polymerization (VPP) of PEDOT is a promising technology in various applications to provide a thin, uniform, and highly-conductive PEDOT coating [9–12]. VPP possesses the advantage of allowing the mass-production of FLS sensors, combined with a very low cost deposition set-up. This manuscript presents our first demonstration of the use of VPP of PEDOT on silicone rubber as a FLS sensor and process optimization work is an on-going concern.

2. Materials and Method

2.1. Fabrication Procedures

In general 3 steps were taken in the fabrication of the FLS sensor as summarized below:

STEP 1: Fabrication of the Ecoflex® strip

Ecoflex® is an addition curing silicone rubber supplied as two solutions (the silicone base and the curing agent). The base and curing agent were mixed with a volume ratio of 1: 1 and stirred slowly to ensure there were no trapped bubbles. The mixture was then poured into a Teflon mold and held under vacuum in a bell jar for approximately 4 hours at room temperature to cure. A mold was used to make the Ecoflex® strip with dimensions of 55 mm × 10 mm × 2 mm. After the Ecoflex® strip was cured at room temperature; it was placed in an oven at 80 °C for 2 hours and then 1 hour at 100 °C to stabilize the cured silicone.

STEP 2: Soaking with $FeCl_3$ as oxidant

A stretching rig was used to stretch and hold the Ecoflex® strip to 60% strain. While the strip was kept at 60% strain, oxygen plasma treatment (Diener ATTO) was carried out to activate the surface of the strip to improve the wetting by the $FeCl_3$ solution. The strip was then immersed in a solution of 0.5 mol/L $FeCl_3$ [13] in tethrahydrofuran (THF) for 2 hours. After removing the strip from the $FeCl_3$ solution it was allowed to dry overnight. The soaking was carried out in a closed container to limit the exposure of THF to air.

STEP 3: Vapor phase polymerization

A container with 2 mL of a solution of 0.2 mol/L EDOT (3,4 ethylenedioxythiophene) in THF was placed next to the Ecoflex® strip (still held in the stretched/elongated state using the stretching rig) in a vacuum chamber. The vacuum chamber was evacuated prior to closing the vacuum pump valve and allowing the VPP to proceed overnight. On removal from the vacuum chamber, the FLS sensor is complete. Finally the electrical resistance of the FLS sensor was measured with a Keithley

2602 source measure unit (SMU).

2.2. Ecoflex® Preparation

Ecoflex® 00-30 was used in this work and has a tensile strength of 1.4 MPa and 900% elongation at break (per ASTM D-412) [14]. The large elongation capability makes it suitable as a large strain flexible stretch sensor.

After Ecoflex® has been cured and stabilized; it needs to be treated so that the surface is hydrophilic to increase the wetting of the oxidant solution and ensure proper coating of PEDOT. This can be achieved by oxygen plasma treating the Ecoflex® strip. However, using only oxygen plasma requires a substantial plasma exposure time to achieve hydrophobicity and could degrade the Ecoflex® itself. Stretching to elongate the Ecoflex® strip during the oxygen plasma decreased the treatment time required to make the surface hydrophilic. Table 1 shows the time required for oxygen plasma using a Diener ATTO oxygen plasma system at 150W power to surface treat the Ecoflex® strip with or without pre-strain.

Table 1. The contact angle of the Ecoflex® surface with and without stretching after oxygen plasma treatment at 150 W for different plasma exposure time.

No stretching		**Stretched to elongate by 60%**	
Time (s)	Contact angle	Time (s)	Contact angle
180	50.9	30	33.7
240	38.4	60	9.4
300	28.2	90	0.6
360	28.2	120	0
600	15.5		
780	7.3		
900	0		

From Table 1, with a strain to elongate the strip by 60%, oxygen plasma at 150 W will cause the Ecoflex® surface to be completely hydrophilic after 120 s. If the Ecoflex® was not hydrophilic, the PEDOT film on the strip deposited via VPP process would not adhere well.

2.3. Oxidant Solution

An oxidant is required to initiate polymerization of EDOT and form a conductive PEDOT film. Here, a $FeCl_3$ solution acting as the oxidant was prepared by dissolving $FeCl_3 \cdot 6H_2O$ into a solvent. The miscibility of the solvent with the Ecoflex® silicone rubber is important. To improve miscibility, solvents such as THF, benzene and chloroform are suitable as they can slightly swell the silicone rubber and allow $FeCl_3$ infusion. The solvent used in this work was tethrahydrofuran (THF). However, care must be taken when using THF due to its tendency to form highly-explosive peroxides on prolonged exposure in air. The concentration of $FeCl_3$ in THF solution was 0.5 mol/L. The infusion of $FeCl_3$ into Ecoflex® is important as it ensures that the PEDOT film is uniformly conductive. By continuing to hold the Ecoflex® strip in the stretched state (60% strain) during

soaking in $FeCl_3$, oxidant infusion was improved.

2.4. Vapor Phase Polymerization of Ethylenedioxythiophene

In this work PEDOT was fabricated using EDOT monomer purchased from Sigma-Aldrich. PEDOT film was produced from EDOT through the VPP process. VPP differs to a conventional solution based polymerization in that the monomer is introduced in its vapor phase. A high degree of control is available in this technique due to the sequential exposure of the substrate's surface to the oxidant followed by the EDOT vapor. The exposure of the oxidant layer to EDOT monomer vapor focuses the polymerization to occur only on the area where the oxidant layer has been deposited making the resulting PEDOT conductive.

Figure 1. The set-up used for vacuum assisted vapor phase polymerization with EDOT:THF solution.

EDOT monomer in its vapor form can be generated through many processes. Heat is commonly used to evaporate the EDOT monomer solution and obtain EDOT vapor. Exposure to a gas flow such as nitrogen gas on an EDOT solution can also produce EDOT vapor by forcing volatile EDOT molecules to be released from the solution [15]. The introduction of the EDOT vapor into the polymerization reaction can be done by placing both the oxidant coated substrate and the EDOT monomer solution into a polymerization chamber. Alternatively, the EDOT vapor can be produced or stored in a separate chamber and a pressure difference used to drive the flow of EDOT vapor into the polymerization chamber [16]. However, the boiling point of EDOT is 193°C. The use of an elevated temperature to produce EDOT vapor may generate thermal stress on the substrate when all components are contained in a single chamber. This severely limits the types of substrate that can be used as the thermal stress may damage the substrate and interfere with the polymerization process. Generating EDOT vapor using a gas flow can be inefficient and costly as it requires a constant gas flow to maintain the supply of EDOT vapor during the polymerization process. An alternative approach is available through a vacuum assisted VPP. This technique utilizes a low pressure to decrease the boiling point of the EDOT solution such that the EDOT solution can evaporate at room temperature. This avoids exerting thermal stresses on the substrate and is a low cost method of

generating the EDOT vapor. Vacuum assisted VPP requires only a simple set up as the components for the EDOT thin film deposition are contained within a single vacuum chamber which also acts as the polymerization chamber. Figure 1 shows the vacuum assisted VPP set-up used in this work.

EDOT monomer was mixed into THF to create a mixture of 0.2 mol/L. The vapor pressure of THF at 20 °C is ~19.1 kPa [17] and EDOT is ~0.04 kPa [18]. The vapor pressure of the EDOT monomer in THF can be approximated using Raoult's law as in equation (1).

$$P = P_A X_A + P_B X_B + \ldots \quad (1)$$

where,

P is the total vapor pressure of the solution,
P_A is the vapor pressure of component A,
X_A is the mole fraction of component A,
P_B is the vapor pressure of component B,
X_B is the mole fraction of component B,

Using this equation, the vapor pressure of EDOT monomer solution is approximately 18.8 kPa. Hence, after pumping down and achieving equilibrium, the pressure in the chamber will be 18.8 kPa, and EDOT will evaporate from the solution onto the Ecoflex® strip surface. During VPP, the Ecoflex® strip remains in the stretched/extended state to ensure EDOT vapor reacts with the oxidant ($FeCl_3$). Deposition in the stretched state also reduces cracking of the PEDOT film on the Ecoflex® strip, due to the formation of a bellows-like structure as discussed in Section 4.

2.5. Electrical Testing

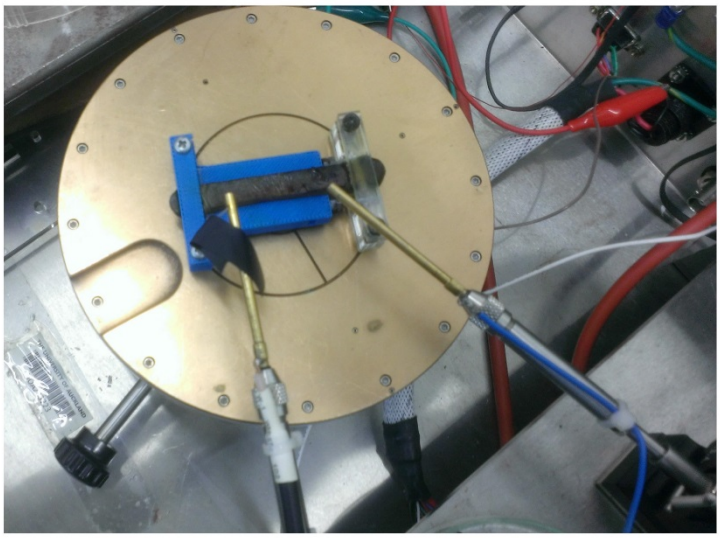


Figure 2. A FLS sensor being probed to measure its resistance with a SMU.

Figure 2 shows the resistance of a FLS sensor being measured using the SMU while the sensor is in its relaxed (unstretched) state. Two electrical tests were conducted. The first test was to determine the current-voltage (*I-V*) characteristic of the FLS sensor. The SMU was swept from +1V

to –1V. The second test involved measuring the resistance of the FLS sensor at a fixed bias voltage of +1 V as the FLS sensor was stretched to extend the strip to different strain levels.

3. Results

The FLS sensor in the relaxed state was probed at the two ends and the SMU was programmed to sweep the voltage from −1V to +1V while recording the current passing through the sensor. Figure 3 shows an *I-V* plot of a FLS sensor in the relaxed state. The slope of the plot is the conductance of the FLS sensor. In this case, the resistance of the PEDOT film coated on the Ecoflex® strip was 500 kΩ. When the FLS sensor is stretched, the resistance will increase. The increase in the sensor length increases the electrical resistance and this can be used to determine the amount of strain. Hence, the PEDOT film behaves as a piezoresistive material since the resistance changes with mechanical strain.

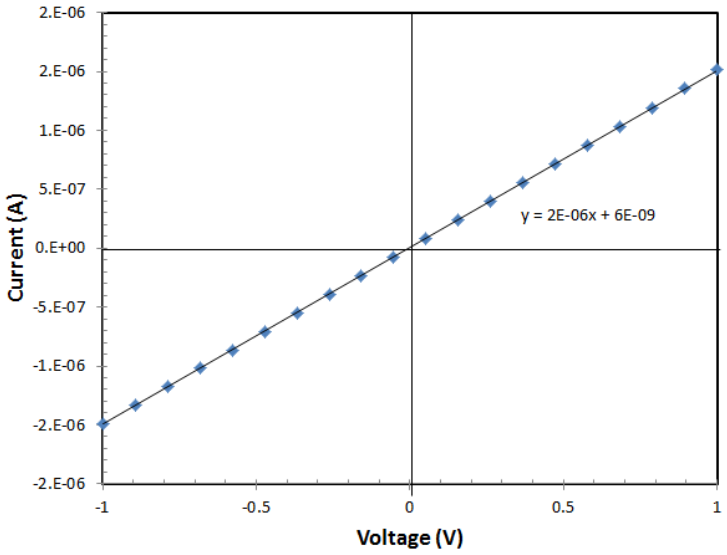


Figure 3. The *I-V* plot of a FLS sensor at relaxed state (unstretched).

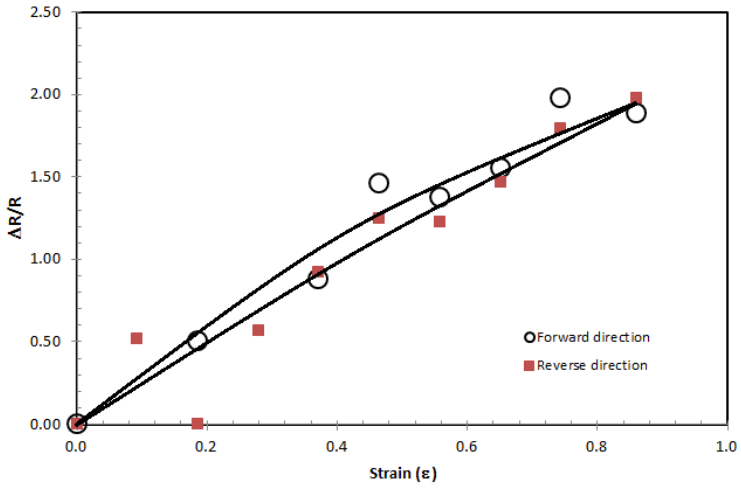


Figure 4. The change in resistance versus strain of a FLS sensor.

The resistance was then measured (*V/I*) at different strain levels (0% to 100%). It was noticed that the resistance increased very significantly after approximately 90% strain, which believed to be caused by the complete breaking of the PEDOT film. This occurs because the PEDOT film on Ecoflex® is not sufficiently elastic to handle strains over 90%. Hence, the amount of mechanical strain was capped to 85% ($\varepsilon = 0.85$). Figure 4 shows the change in resistance ($\Delta R/R_0$) versus strain (ε) when the strain is increased from 0 to 0.85 (0–85%) and then returned back to 0.

The gage factor of the FLS sensor can be calculated using equation (2).

$$\Delta R / R_o = GF \times \varepsilon \tag{2}$$

where

ΔR is the change in resistance caused by strain,
R_o is resistance of the undeformed gauge,
GF is the gage factor
ε is the strain

The gradient of the straight line in Figure 4 is the gage factor and was calculated to be ~ 2.4. A common fault in large strain sensors is hysteresis, where the value of sensor resistance measured when strain is reduced differs from the resistance at the same strain measured while strain is increased. From Figure 4, where the change in resistance in both the forward and reverse strain directions are observed to be quite similar, the hysteresis of our sensor can be assumed to be small. However, there were some instances where fabricated FLS sensors did not behave properly as shown in Figure 5. The FLS sensor characteristic in this instance was not linear and exhibited large hysteresis. The reasons for this deviation will be discussed in Section 4.

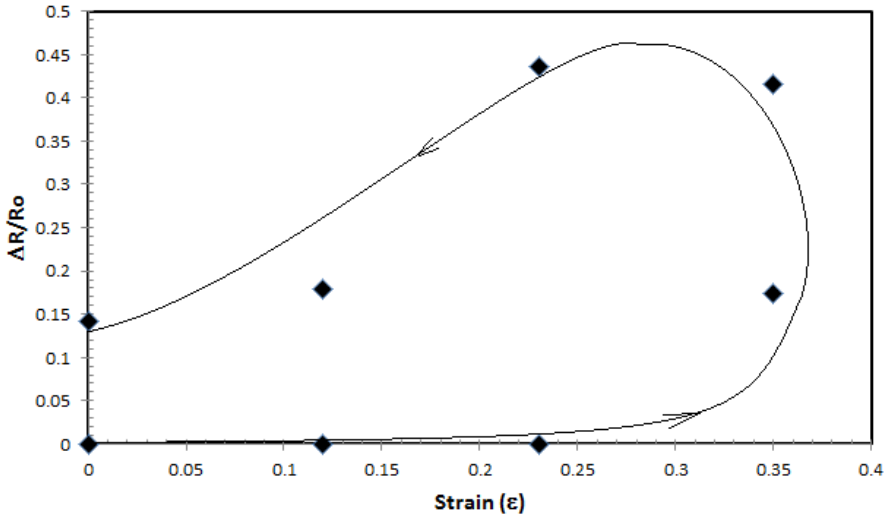


Figure 5. FLS exhibiting large hysteresis and non-linear behavior.

4. Discussion

The preliminary work presented here has demonstrated the use of vacuum-assisted VPP to coat

Ecoflex® silicone rubber with PEDOT film and create a flexible large strain sensor. The sensor has small hysteresis and a gage factor of ~2.4. This is a drastic improvement on our previous FLS sensor [6] using PPY on latex, which yielded a gage factor of 1.86 and was only able to operate up to 20% strain with significant hysteresis. In this work THF was used as the solvent for $FeCl_3$ and also for the EDOT monomer, in an attempt to improve miscibility, however, care has to be taken when using THF to limit its exposure to oxygen. THF is a cyclic ether, which is highly polar due to the presence the oxygen atom and should be used in an inert environment.

Our process of performing VPP of PEDOT while the Ecoflex® strip is held in the stretched/elongated state is important as the PEDOT film itself has limited stretchability [19]. In this work, the Ecoflex® strip was pre-stretched by 60% and this has allowed the completed FLS sensor to be operated with up to 85% strain. When the FLS sensor is used to a strain level below the pre-stretched strain of 60% during fabrication, the PEDOT film will be folded, analogous to the bellows of an accordion at a microscopic level as shown in Figure 6. In Figure 6, the bellows-like structure is clearly visible.

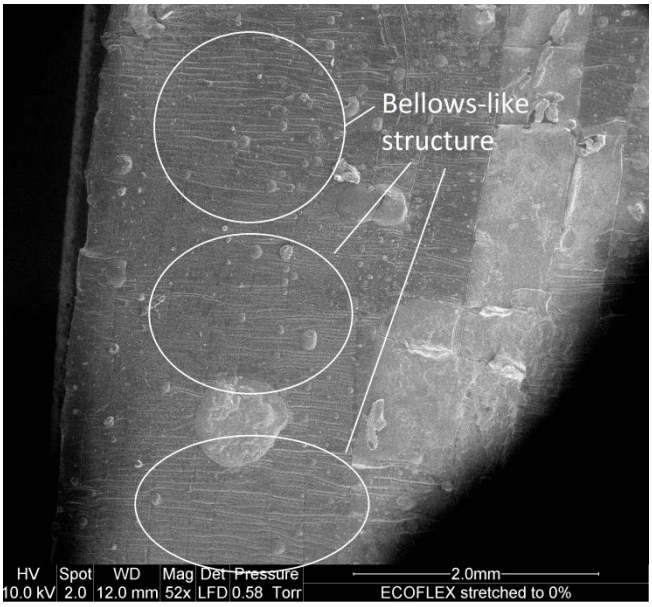


Figure 6. The FLS sensor in the completely relaxed state (no strain).

When the FLS sensor is operated beyond 60% strain, the folded PEDOT film will be stretched, and the electrical resistance will increase further. In the case of an extremely large strain, the PEDOT film will tear as it is insufficiently stretchable. Figure 7 shows the FLS sensor when stretched to 100%. It is clear from this image that the PEDOT film is torn.

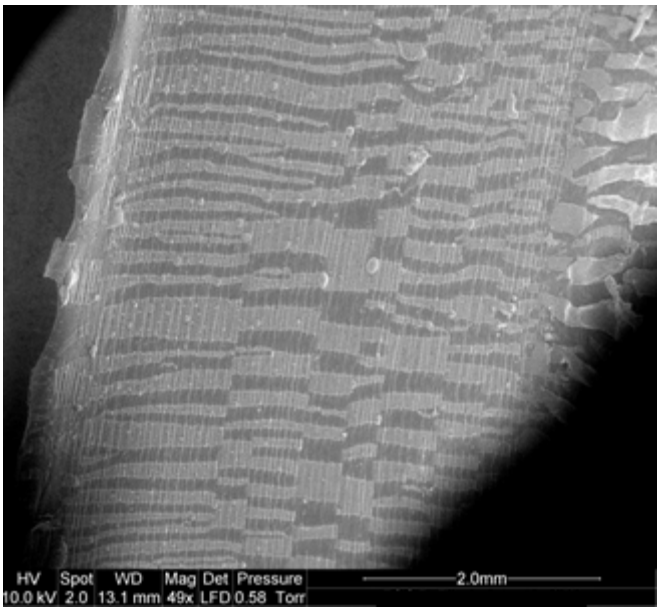
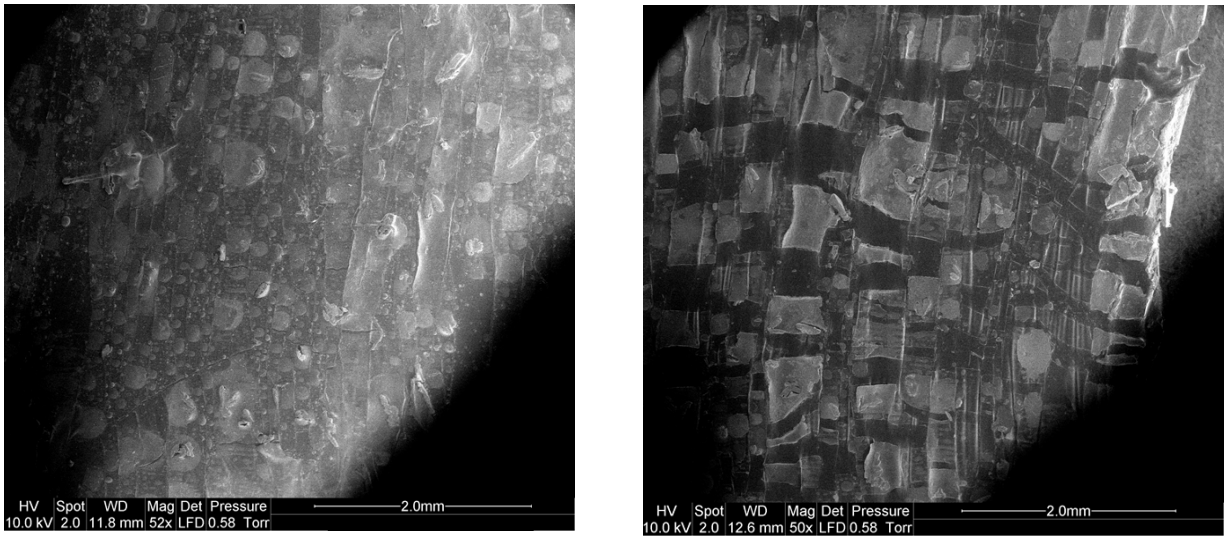


Figure 7. The FLS sensor strained to 100%.

As was discussed in Section 3, there were some occasions when the fabricated FLS sensor did not behave linearly and had large hysteresis (as was shown in Figure 5). The correctly fabricated FLS sensor has bellows-like structure (as shown in Figure 6), and low hysteresis as shown in Figure 4. In contrast, it was observed that the samples without bellows-like structure (as shown in Figure 8), had non-linear behavior and large hysteresis as shown in Figure 5. It is therefore hypothesized that, without the bellows-like structure, as the Ecoflex® is stretched, the PEDOT film might not be stretched accordingly due to slip or cracking and hence exhibit non-linear behavior with large hysteresis.



(a) (b)

Figure 8. (a) Without the bellows-like structure, the PEDOT film on the Ecoflex® strip (b) started to crack when it was elongated by only 30%.

The process using THF significantly weakened the Ecoflex® strip, affecting the stress versus strain characteristic as shown in Figure 9. However, with the elastic property of the FLS sensor weakened, the sensor can stretch with greater ease and lower stress. The low elastic resistance of the THF-weakened Ecoflex® is desirable in many real life applications.

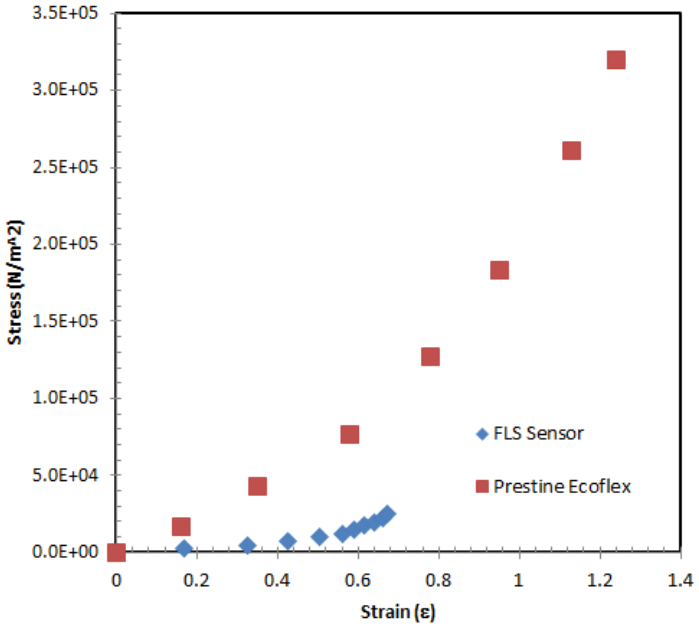


Figure 9. Stress versus strain plots of the FLS sensor and pristine Ecoflex®.

5. Conclusion

Vacuum assisted VPP offers a simple and low-cost method to effectively deposit PEDOT on Ecoflex® as a flexible large strain sensor. Here, we have demonstrated the use of VPP to create a PEDOT film on Ecoflex® to create a flexible large strain sensor capable of operating up to 85% strain with a gage factor of 2.4 and low hysteresis.

Conflict of Interest

There is no conflict of interest related to this document.

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