Comparisons of the Mechanical Behaviors of Poly (3, 4-ethylenedioxythiophene) (PEDOT) and ITO on Flexible Substrates

Khalid Alzoubi, Gihoon Choi, Mohammad M. Hamasha, Atif S Alkhazali, John DeFranco, Susan Lu, Bahgat Sammakia, and Charles Westgate.

Abstract—Indium Tin Oxide (ITO) has been widely used as a Transparent Conductive Oxide (TCO) layer in the photovoltaic solar technology because of its excellent electrical and optical properties. However, ITO is brittle, and its conductivity decreases significantly as the ITO films are exposed to stretching or bending strains especially in flexible/foldable solar cell applications. The cracks in ITO appear at very low strains which might cause failure in the conductive layer because of the combination of a very thin film of brittle ceramic material applied to a polymer substrate. Poly (3, 4-ethylenedioxythiophene), abbreviated PEDOT, is of increasing interest as a competitive candidate to ITO. PEDOT has found its way in many applications such as transparent electrode materials and transparent conductive layers in photovoltaic solar cells. In this work, the mechanical behavior of PEDOT was studied under high cycle bending fatigue in which the effects of bending diameter and bending frequency were considered and compared to ITO. High magnification optical images were used to study cracking in the PEDOT as well as the ITO layers. In flexible solar cells, the web will be exposed to folding/bending many times during manufacturing and installation. Therefore, the thin film substrate structure will be exposed to cyclic loading-cyclic tensile and compressive strains. Therefore, this work was designed to mechanically fatigue the structure and study its behavior. It was found that bending diameters as well as material (PEDOT or ITO) have a great influence on the electrical conductivity of the thin films.

Index Terms—Bending fatigue, flexible solar cells, Indium Tin Oxide, flexible electronics, poly (3, 4-ethylenedioxythiophene), and conductive organic materials.

I. INTRODUCTION

Indium Tin Oxide (ITO) has been widely used as a transparent conductive oxide in solar cell structures because of its superior electrical and optical properties. The deposition of ITO on glass substrates requires high temperatures to obtain low sheet resistance and high transparency, which is not suitable for flexible electronics applications. When electronic systems are fabricated on flexible platforms, ITO thin films will not withstand even small strains. Therefore, research is ongoing to identify alternatives that can withstand greater mechanical and thermal strains without degradation in their electrical and optical properties. Organic conductive materials have been investigated, although the electrical and optical properties of organic conductive materials are not as attractive as those for ITO. Organics have excellent mechanical properties and low processing temperatures. PEDOT is among the leading candidates. The chemical structure of PEDOT is shown in Fig. 1.

![Chemical structure of Poly (3, 4-ethylenedioxythiophene)](image)

The mechanics of ITO on flexible substrates is of great interest to many researchers [2, 3, 6, & 7] and comparisons to PEDOT will be useful.

Conductive failure is expressed in terms of crack onset strain (COS), defined as a 10% increase in the electrical resistance, which represents a transition stage in which crack growth becomes unstable (i.e. the change in the electrical resistance with respect to the original resistance; $\Delta R/R_o = 10\%$, where $\Delta R$ is the difference between the current resistance value and the original resistance $R_o$).

For ITO on polymeric substrates the crack density and so normalized resistance change is higher for thicker ITO films [3].

Tensile tests conducted on ITO layers uniformly coated on a polymer substrate showed cracks initiating at defects or impurities and, as the strain increased, the cracks propagated, joined together, and formed larger cracks. Eventually they became unstable and extended across the whole sample. It was also found that at a strain of approximately 3%, the electrical resistance of ITO thin films increased dramatically. Optical micrographs showed that cracks were first observed at a strain of about 2.3%, and then the number of cracks increased up to 2.6% strain, a transverse cracking and tertiary cracks appeared at 6% and 10%, respectively, however, PEDOT films were still...
conductive up to 60% strain compared to 3% for ITO, [5 and 6]. Cracking in the conductive layer is the most common failure for very thin films on flexible substrates [5-10, 12]. Other types of failures such as slipping or delamination can also take place.

Designs of experiment (DOE) principles have been used in many engineering and scientific studies; experimentation is a core step in product realization activities. It plays a major role in process development and improvement to obtain robust designs [11 and 13]. DOE techniques have also been used to conduct a parameter optimization studies in the flexible electronics area [15-17]. In this work, (DOE) methods were used to study the factors affecting the high cycle bending fatigue of PEDOT and ITO thin films on flexible substrates.

II. EXPERIMENTS

The test vehicles used in this study consist of a commercially available PEDOT and ITO coated on a 127μm-thick polyethylene terephthalate (PET) substrate. Eight samples were prepared by splicing a sheet into strips of very small width-to-length ratio. High cycle bending fatigue tester shown in figure 1 was used to conduct the experiments. The electrical resistance of each thin film was measured after a specified number of bending cycles and compared to the initial resistance before starting the test. The relative percent change in the electrical resistance ($\Delta R/R_o$)*100% is plotted against the number of cycles during the test, where $R_o$ is the initial resistance of the film before testing. The electrical resistance was measured while the sample is in a flat position, when the sample is upward bent, the thin film will have tensile stresses and the substrate will experience compressive stresses, the situation will reverse in the downward bending. Cracks open in the upward bending and close in the downward bending. The reference position is when the sample is flat. Consistent electrical resistance measurement was made relative to the original resistance-percent change in electrical resistance—after a selected number of bending cycles.

A. High Cycle Bending Fatigue

The electrical resistance was measured using a two-point probe. In each experiment, the electrical resistance was monitored at various time intervals during the test. A comparison was conducted between ITO and PEDOT thin films as shown in Figure 3. The experiments were conducted at a temperature of 23°C, a relative humidity of 30%, and a bending diameter of 200 mil at a bending frequency of 60 cycles/minute. It was found that the percent change in electrical resistance for ITO was greater than that for PEDOT because of the brittle nature of ITO thin films. Although bending frequency is usually considered as a significant factor in the bending fatigue test, it had a negligible effect in this experiment as shown in Figure 4.
The effect of bending diameter on the bending fatigue was investigated; two different bending diameters were selected, 200 mil and 350 mil. The experiments were conducted at a temperature of 23°C, a relative humidity of 30%, and a bending frequency of about 60 cycles/minutes. The percent increase in electrical resistance was significantly greater when using smaller mandrel diameters and a greater influence on the bending fatigue life of PEDOT on flexible substrates, shown in Figure 7. Tighter mandrels produce greater stresses in the thin film and cause the great increase in electrical resistance and then the early failure.

A set of experiments were conducted to compare the number of failed samples of PEDOT and ITO over time during the bending fatigue experiments, the sample were considered failed if the percent change in electrical resistance is greater than or equal to 10%. The results are shown in Figure 8. It is seen that all the ITO samples failed after 10 cycles according to the criteria considered. However, eight samples of PEDOT failed after the first 10 cycles, five after 20 cycles, one after 30 cycles, one after 40 cycles, and the last sample failed after 50 cycles as shown in Figure 7. Figures 8 and 9 show optical images for cracks extending across the ITO and PEDOT samples respectively, the experiments were conducted at a temperature of 23°C, a relative humidity of 30%, and bending frequency of 60 cycles/min, the cracks were extending along the sample perpendicular to axis of the bending mandrel, cracks usually start as invisible microcracks initiating from voids or impurity particles. Then, these microcracks join together to form larger cracks and so on. The crack density was higher at the center area across the width of the sample and then cracks propagated in the direction perpendicular to the axis of mandrel, the cracks in the PEDOT and ITO have the same pattern, they are between 300 and 400 µm in length after about 2000 bending cycles. The distribution of the cracks is not uniform since cracks form from defects or imperfections.
DOE tools were used to study the effect of four factors on the high cycle bending fatigue life of very thin films on PET substrates. The parameters investigated were: Material (ITO and PEDOT), bending diameter (200 mil and 350 mil), and bending frequency (60 cycles/min and 30 cycles/min). Two levels were selected for each factor, as shown in Table 1. The percent change in electrical resistance at certain number of cycles was selected to represent the response for the DOE analysis. Initial results showed a great influence of bending diameter and material type. The experimental matrix is shown in Table 2, the response is the % change in electrical resistance after 2000 bending cycles. The Analysis of Variance table is shown in Table 3.

Table 1: Factors and levels

<table>
<thead>
<tr>
<th>Factors</th>
<th>Levels</th>
<th>Level 1</th>
<th>Level 2</th>
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<tr>
<td>Material</td>
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<td>ITO/PET</td>
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<tr>
<td>Bending Frequency (cycles/min)</td>
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<td>30</td>
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<tr>
<td>Bending Diameter (mil)</td>
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Table 2: Analysis of Variance (ANOVA) table

<table>
<thead>
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<th>Run</th>
<th>Bending Diameter (mil)</th>
<th>Material</th>
<th>Frequency (Cycles/min)</th>
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<tr>
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<tr>
<td>3</td>
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<td>ITO</td>
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</tr>
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<td>ITO</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>350</td>
<td>PEDOT</td>
<td>60</td>
</tr>
<tr>
<td>6</td>
<td>200</td>
<td>ITO</td>
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</tr>
<tr>
<td>7</td>
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<tr>
<td>8</td>
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Table 2: ANOVA table

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<th>Source</th>
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<th>Adj SS</th>
<th>Adj MS</th>
<th>F</th>
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<td>0.563</td>
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<td>33488928</td>
<td>218.23</td>
<td>0.043</td>
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<tr>
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<td>3960</td>
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<td>0.899</td>
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<tr>
<td>Material*Frequency</td>
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<td>153458</td>
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<td>Total</td>
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</table>

S = 391.737  \ R-Sq = 99.90\%  \ R-Sq(adj) = 99.32\%
Single replicate full factorial experiments were conducted. From the P-values of the Analysis of Variance (ANOVA) table; it is clearly noted that two of the considered factors were significant (i.e. bending diameter and material). The significant interactions were also listed in the ANOVA table as shown in Table 2, where

**BD**: Bending diameter,
**W**: Sample width,
**F**: Bending frequency.

ANOVA table shows different statistical values, such as

- **DF**: Degree of freedom,
- **Seq SS**: Sequential sum of squares,
- **Adj SS**: Adjusted sum of squares,
- **Adj Ms**: Adjusted mean squares,
- **F**: F statistic,
- **P**: Significance measure, if P<0.05, then the considered factor is significant.

Figure 10 shows the main effect plots for the response; it can be seen that bending diameter and material are the most significant effects on the response. The percentage change in electrical resistance is higher for ITO than PEDOT. The percent change in electrical resistance is also higher for the samples tested at tighter mandrels at certain number of bending cycles. Frequency has a little effect on the response. However, since it has interactions with other factors, its influence on resistance change depends on the levels of the other factors. The two factor interaction plots are shown in Figure 11; there is a great interaction between the bending diameter and material.

Figure 12 shows a 3D surface plot for the interactions between bending diameter and bending frequency, bending diameter and material (ITO or PEDOT), and material and frequency. For example in Figure 6(b), in the case of PEDOT, the transition from tight mandrel (200mil) to larger mandrels (350mil) has little effect on the percent change in electrical resistance. However, in the case of ITO, a dramatic decrease in the conductivity took place when the sample was bent around a tighter mandrel.
analysis of variance has revealed that the main effects of material and bending diameter have the greatest influence on the response: percent change in electrical resistance. The resistance change was higher for ITO and when using tighter mandrels. Although bending frequency have little influence on the electrical resistance change, their interactions with the other factors have a great influence too. The response of some factors highly depends on the level (high or low) of other factors and this is a very important note to consider in the parameter optimization during the design and manufacturing processes.

**REFERENCES**


Khalid Alzoubi received the B.S. and M.S. degrees in Mechanical Engineering from Jordan University of Science and Technology (JUST), Jordan in 2002 and 2005 respectively. He also received his Ph.D. in Industrial and Systems Engineering with a specialization in electronics manufacturing from the State University of New York at Binghamton in 2010. He is currently a Postdoctoral Research Associate with the Center of Autonomous Solar Power (CASP) at Binghamton University. His current research interest is studying the reliability of photovoltaic solar cells and systems.

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