Conducting Polymer Actuators: Temperature Effects

by

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ABSTRACT

In order to utilize conducting polymer actuators as a viable engineering solution, it is necessary to produce usable levels of force with a reasonable bandwidth. Polypyrrole actuated at temperatures as high as 100 °C increases stress magnitudes by as much as 4× and stress rates by 5×. The effect is caused by a combination of decreased solution resistance and increased ion diffusion within the polymer. However, these temperatures cause accelerated degradation due to the time-temperature correlation common to viscoelastic polymers. Actuation at these temperatures can decrease cycle life by as much as 20×. Excessive heating without actuation can also result in poor actuator performance. Impedance spectroscopy coupled with electro-mechanical analysis highlighted previous results and also showed an improved frequency response from actuation at high temperatures.

Thesis Supervisor: Ian W. Hunter

Title: Hatsopoulos Professor of Mechanical Engineering
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While being at MIT was an amazing experience, my fondest memories of this place will be on the Boston side of the river. I ended up living where I did strictly by chance, as did all those who would eventually become closest to me. But our group bonded to survive this place and I had the time of my life as a result. I can truly say that the best and worst times of my life have been here. My buddies made the bad times bearable and I wouldn’t have traded the good times for anything. I’ll never forget the best Halloween parties in Boston, the Sigma Bar, or that fact that ‘we’re not going to make it.’ Drew, John, Kevin, Rene, Ricky and our long lost pledge brother Paul: you guys are my family and I look forward to many more ridiculous memories while remembering the old ones. I owe a lot of who I am now to you guys and I will always be grateful to have met you. Boston is not the same without all of you here, but I am proud of what you have accomplished since we were all together.

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I regret that all those I care about can’t be with me always.
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4.34: Magnitudes as a function of frequency of electro-mechanical impedance measurement of polypyrrole in log-log axes .......................73
Polymers are typically considered to be insulators; however, there is a class of polymers that inherently conduct electricity. These conducting polymers are formed from certain aromatic monomers, such as pyrrole or aniline. [1] Examples of conducting polymers are shown in Figure 1.1. These materials feature a conjugated backbone structure that allows the polymer to undergo volumetric changes that can be used to perform useful work. [2,3] Expansion and contraction are typically the result of an ion flux that changes the oxidation state of the polymer. [4] This charge transfer allows these polymers to not only serve as conductors, but also other electrical elements, such as transistors, capacitors, batteries, and sensors. [5] A comparison of the electrical properties of one conducting polymer, polypyrrole, to copper is shown in Table 1.1.

![Figure 1.1: Examples of conducting polymers. Source [5].](image-url)
Table 1.1: Comparison of electrical properties of polypyrrole conducting polymer to copper [6]

<table>
<thead>
<tr>
<th></th>
<th>Polypyrrole (PPY)</th>
<th>Copper</th>
<th>Comparison Copper vs. PPY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg/m$^3$)</td>
<td>1000</td>
<td>8920</td>
<td>8.9 ×</td>
</tr>
<tr>
<td>Current density</td>
<td>&gt;10$^7$</td>
<td>10$^7$</td>
<td>same</td>
</tr>
<tr>
<td>Conductivity (S/m)</td>
<td>4.5×10$^4$</td>
<td>5.8×10$^7$</td>
<td>129 ×</td>
</tr>
<tr>
<td>Capacitance (F/kg)</td>
<td>10$^5$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cost ($/kg)</td>
<td>&lt; 3</td>
<td>10</td>
<td>3.3 ×</td>
</tr>
</tbody>
</table>

The molecular mechanism that drives actuation in each conducting polymer varies and depends on the particular structure. For example, the oxidation and reduction of polypyrrole drives a hinge mechanism to close and open each link of the polymer. The mechanism can be seen in Figure 1.2. In a bulk material sense, ion flow causes a swelling mechanism, resulting in a volume change. This is illustrated in Figure 1.3.

Conducting polymer actuators are of such interest due to low operating voltages, typically 1-2 V, which produce relatively large forces, corresponding to typical stresses of 10 MPa. These actuators demonstrate many of the desirable qualities of shape memory alloys [7], but with the added benefit of better controllability, low cost, and higher efficiencies. Forces from conducting polymers exceed the 350 kN/m$^2$ of mammalian skeletal muscle by an order of magnitude and require virtually no further energy expenditure to hold a load. [2] The power to mass can be as high as 150 W/kg and strain rates of 3 %/s have been observed. [9]
Since actuation is driven by ion movement, the oxidation state of the polymer controls the conformation changes. Thus, an electrochemical cell is required to operate these polymer devices.

Figure 1.2: Molecular mechanism of actuation for polypyrrole conducting polymer [8]

Figure 1.3: Ionic swelling mechanism for polypyrrole conducting polymer [6]
1.1 Electrochemistry

In an electrochemical cell, ion motion completes an electrical circuit. [10] Chemical reactions occur at electrodes submerged in solution, causing the bulk flow of charge in one direction. Ions carry the charge, in the form of electrons, through the solution from one electrode to the other. Electrochemical systems include both reversible and irreversible reactions. Examples of electrochemical cells include batteries and fuel cells. Faraday’s Law relates the amount of charge involved in an electrochemical reaction to the number of moles of the reactant and the number of electrons required for the reaction to occur,

\[ Q = zmF, \]  

where \( Q \) is the charge, \( z \) is the number of electrons, \( m \) is the number of moles of reactant, and \( F \) is Faraday’s constant, 96,500 C/mol.

The solvent, working and counter-electrodes must be properly matched in terms of the chemistry in order to ensure directionality in the flow of charge. In the case of a conducting polymer electrochemical system, the polymer serves as the working electrode and most conductive metals can function as the counter-electrode. The solvent is chosen based on which ions are compatible to bond with the active sites in the molecular mechanism of the polymer. For polypyrrole, two common solvents are tetraethyl-ammonium hexafluorophosphate (TEAPF\(_6\)) dissolved in propylene carbonate (PC) and liquid salts, including 1-butyl, 3-methyl imidizolium hexafluorophosphate. An illustration of a typical polymer electrochemical system is shown in Figure 1.4. The reference electrode is used to convert the charge carriers in the electrodes to the charge carriers in solution. The reaction at the reference electrode must be practically reversible, a reaction is that thermodynamically reversible and occurs at a significant rate. [10] The reaction at the reference electrode must not interfere with the reactions at the other electrodes. The reference electrode also helps to determine the open circuit potential in the cell. One common reference electrode in conducting polymer systems is Ag/AgCl.

The electrochemical cell is driven by an electrical signal, but the rate of reaction is a diffusion-driven process, controlled by the motion of ions in the solution and the
polymer. Once the cell is activated, the ions must first diffuse to the electrodes before a reaction can occur. A buildup of charge on the surface of the electrode accumulates as electrons flow through the cell. There is a tendency for charged species to be attracted to or repelled from the surface of the electrode. This gives rise to a separation of charge, and the layer of solution with different composition from the bulk solution is known as the electrochemical double layer. As a result of the variation of the charge separation with the applied potential, the electrochemical double layer has an apparent capacitance. [10] The charging and discharging of this double-layer capacitance effects the electrical response of the cell in a similar manner to a typical capacitor.

![Figure 1.4: Polymer electrochemical system. Source [11].](image)

1.2 Electrochemical Deposition

Synthesis of conducting polymers can be either strictly chemical or electrochemical in nature. Polypyrrole is typically synthesized electrochemically, where pyrrole monomer in solution is polymerized and deposited onto the working electrode of a cell. The deposition solution used to manufacture polypyrrole used in the following experiments contained 0.05 M pyrrole monomer, 0.05 M TEAPF$_6$, used for the counterions, and 1% water in PC. Thus, polypyrrole is synthesized in a doped state, immediately conductive due to the presence of ions on the polymer backbone. The working electrode
is a glassy carbon crucible and the counter-electrode is typically a copper sheet. The surface area of the counter-electrode should be about twice that of the working electrode to ensure the reaction is only limited by presence of monomer. The depositions normally take place at -40°C to avoid degradation of the monomer, which is both temperature and light sensitive. A current density of 0.5 A/m² was used to power the electrochemical cell, translating to approximately 15 mA of current given the surface area of the working electrode. The depositions last approximately 10 hours. The synthesized conducting polymer is in the form of a film that is peeled from the working electrode and is fully functional directly after deposition. Deposited polypyrrole film is shown on the crucible in Figure 1.5 and free standing in Figure 1.6. Typical depositions produced a film thickness of 20 µm with 0.024 m² of usable polymer.

Figure 1.5: Glassy carbon crucible and deposited polypyrrole conducting polymer. Source [6].

Figure 1.6: Free standing polypyrrole conducting polymer film. Source [6].
1.3 Models of Mechanical Actuation

The conducting polymer electrochemical cell is a system with a coupled electrical and mechanical response, linked by ion diffusion. Thus, two models are necessary to appropriately describe the total response of the system to an electrochemical signal. There has been a significant effort in the modeling of a conducting polymer electrochemical system [11-13], however the models presented in this section are simplified in order to explain trends in later experiments.

1.3.1 Mechanical Model

It is important to note that the mechanical state of the conducting polymer actuator always has both a passive and active component. The passive component is determined in a similar fashion to any other polymeric solid. Most polymers are governed by viscoelasticity, where a mechanical response shares characteristics with both Hookean solids and Newtonian liquids. This analysis, along with the basics of dynamic mechanical analysis, is presented in Section 2. The active portion of the mechanical state of the polymer relates the charge density present in the polymer to a physical deformation by the strain to charge ratio, \( \alpha \), which is assumed to be roughly constant for any given state of the polymer,

\[
\sigma = E \cdot \varepsilon + E \cdot \alpha \cdot \rho, \quad [12] \quad (1.2)
\]

where \( \sigma \) is the stress state, \( E \) is the elastic modulus of the material, \( \varepsilon \) is the strain, or deformation, state, and \( \rho \) is the charge density. It is clear from this model that stress can be generated either from a passive deformation of the material or by an influx of charge. This is an instantaneous stress state and each of these quantities would vary as a function of time throughout the course of an experiment.

\[
\sigma(t) = E(t) \cdot \varepsilon(t) + E(t) \cdot \alpha(t) \cdot \rho(t). \quad (1.3)
\]
In most solids, material properties, such as $E$ and $\alpha$, are typically assumed to be constant over the course of an experiment. There is no indication that the strain to charge ratio varies greatly over the course of testing, however viscoelastic behavior results in a time and rate dependent modulus. The charge density is determined by the electrochemical signal and it is clear how oscillations in an electrical input would result in mechanical oscillation. In most tests, one mechanical output, either stress or strain, is held constant in order to verify the generation of useful work.

1.3.2 Electrical Model

The electrical model determines the charge state of the electrochemical cell. The system must include both the polymer impedance and the solution resistance. The two elements are in series as electrons are carried by ions through the solution to complete the circuit between electrodes. The polymer is not replaced strictly by a resistor in this model due to the ability of the material to retain charge in the form of the double-layer and bulk capacitance. The polymer impedance should then at least contain a single resistor and capacitor in parallel, although more complex models more appropriately describe the electrical response of the system. [11-13] The polymer will be left as an impedance block $Z$ for the purpose of simplifying future analysis. A schematic of the circuit is shown in Figure 1.7. Thus, the current through the polymer block can be related to the charge flux into the material and the subsequent mechanical state is unique.

![Figure 1.7: Schematic of electrical circuit model for a conducting polymer system.](image-url)
1.4 Outline of Thesis

Chapter 2 – Examines the basic principles of dynamic mechanical analysis and its relation to the actuation of conducting polymers.

Chapter 3 – Investigates a parallel actuation scheme for conducting polymers that mimics the bundling of mammalian skeletal muscle.

Chapter 4 – Investigates the effects of temperature on both the passive and active properties of polypyrrole conducting polymer actuators

References


Dynamic mechanical analysis (DMA) is described as applying an oscillating force to a sample and analyzing the material response to that force. Early attempts to do oscillatory experiments to measure the elasticity of a material date back to 1909. DMA relates an applied force to a material deformation. Typically, the input force is reported as a stress, $\sigma$, defined as the applied force divided by the cross-sectional area over which the force is applied. Stress has the units of Pa,

$$\sigma = \frac{F}{A}. \quad (2.1)$$

The deformation is calculated as a strain, which is defined in different ways depending on the application. Two common definitions are the engineering and true strain. The engineering strain is defined as the change in length divided by the original length in the direction of applied force. True strain is the natural logarithm of the engineering strain. Strain is a dimensionless measure of deformation,

$$\varepsilon = \frac{\Delta L}{L_0}, \quad (2.2)$$

$$\varepsilon = \ln \left( \frac{\Delta L}{L_0} \right). \quad [3] \quad (2.3)$$

The strain discussed throughout the course of the following experiments is the engineering strain. The relation between the stress state and strain of a material is defined as the modulus, $E$. If the response is elastic and fully recoverable, the behavior is described as Hookean, where:

$$E = \frac{d\sigma}{d\varepsilon}. \quad (2.4)$$

For Hookean behavior, the modulus is a constant and not rate dependent, resulting in a linear stress-strain curve. One common DMA technique is to apply a sinusoidal dynamic input force over a static force and measure the material response. For a material
that behaves in the perfect elastic regime, the strain will be exactly in phase with the applied stress and the amplitude will be related by the elastic modulus. For other materials that are nonlinear in nature, a phase lag \( \delta \) is present that is rate dependent. The modulus still retains the same relation to stress and strain, but becomes complex and also rate dependent.

### 2.1 Viscoelasticity

Polymers typically portray non-linear stress-strain behavior. The complex modulus is defined as \( E^* \). It is the sum of the real elastic modulus and the imaginary loss modulus. The elastic modulus \( E' \) is associated with the recoverable or stored energy, while the loss modulus \( E'' \) is associated with a damping energy,

\[
E^* = E' + iE''.
\]  
(2.5)

The tan delta, the tangent of the phase lag \( \delta \), is the ratio of the loss to storage moduli and implies a measure of non-linearity,

\[
\tan \delta = \frac{E''}{E'}.
\]  
(2.6)

In Newtonian liquid flow, the typical behavior of liquids, there is no strain in the direction of the applied force. Liquid flow is a shear-driven process, dependent on rate. The stress is then related to the shear strain rate by the viscosity, \( \eta \). The viscosity is a measure of the loss associated with shear strain,

\[
\sigma = \eta \left( \frac{d\gamma}{dt} \right).
\]  
(4)  
(2.7)

A non-linear solid behaves with a complex viscosity \( \eta^* \), which is frequency dependent in the sinusoidal model,

\[
\eta^* = \frac{E^*}{\omega}.
\]  
(2.8)
Almost all polymers are viscoelastic materials, with behavior that combines that of both an elastic Hookean solid and a Newtonian fluid. It could be argued that losses are associated with any sinusoidal stress-strain oscillation in a material. However, for metals and other linear solids, the timescale of such a loss is large enough to be considered insignificant.

Viscoelastic materials exhibit hysteresis in the stress-strain curve due to viscous losses, as there is no pure elastic regime of behavior. These materials experience stress relaxation, a decreasing stress in response to a step function in strain. Creep also occurs, an increasing strain to a constant step in stress. Thus, the complex modulus becomes a function of time. In a dynamic test, the response is frequency dependent, where a time constant $\tau$ determines the response,

$$E(t) = E_0 \exp[-t / \tau], \quad (2.9)$$

$$E(\omega) = i\omega \tau E_0 / (1 + i\omega \tau). \quad (2.10)$$

The state of a viscoelastic polymer is dependent on its entire history, both previous loading and unloading. The effects of creep and stress relaxation are permanent. The material can be considered linear viscoelastic if the response in creep or stress relaxation is mathematically separable from the load [1]. In this case, the response of creep or stress relaxation is an exponential with a time constant depending on an effective modulus and viscosity. The same behavior exists in shear modes. Simple models exist for linear viscoelastic materials that combine Hookean spring and linear dashpot elements in both series and parallel. The Maxwell model places one such spring and dashpot in series. The standard linear solid model places the Maxwell model in parallel with another Hookean spring. The standard linear solid model can be seen in Figure 2.1.
Both models correctly predict the basic dynamic behavior of a linear viscoelastic solid, however, the Maxwell model continues to creep infinitely and eventually stress relaxes completely. The standard linear solid model has limits to creep and stress relaxation due to the second spring in parallel. The creep and stress relaxation responses to step inputs for this model are shown in Figures 2.2 and 2.3. In a standard linear solid the time constant of creep or relaxation is the ratio of viscosity to stiffness in the elements on the same branch,

$$\tau = \frac{\eta}{k_2}.$$ 

The linear viscoelastic regime is only approximately applicable for most elastomeric polymers within 0.02 strain and much of polymer behavior quickly becomes nonlinear. However, the standard linear solid model sufficiently predicts the type of viscoelastic response seen in most experiments. One other important effect of viscoelastic behavior on polymer response is the time-temperature dependence. Viscoelastic properties change as a function of temperature depending on the microstructure of the polymer. There exists an equivalence between high temperatures for short times and low
temperatures for long times. Thus, experiments run at different temperatures correspond to different frequencies of oscillation and a master curve can be developed for a polymer.

![Standard Linear Solid Model - Creep](image1)

Figure 2.2: Creep response of standard linear solid model to step input.

![Standard Linear Solid Model - Stress Relaxation](image2)

Figure 2.3: Stress relaxation response of standard linear solid model to step input.
2.2 Electrochemical-Mechanical Coupling

The previous description of linear viscoelastic effects is purely passive in nature. Conducting polymer actuators are subject to both creep and stress relaxation, and while dynamic mechanical analysis could determine these effects, this technique is more importantly used to investigate the active properties of the material. The electrochemical signal produces a mechanical response in conducting polymer actuation. An unconstrained sample would contract and expand traction-free as ions move between the polymer and solvent. The sample would experience a zero stress volumetric contraction. This sample, however, would not be producing any usable work. Thus, the sample must be constrained in a manner such as to capture mechanical work in the form of either stress or strain. An isometric test is performed at a constant strain, or extension, and measures the stress production of the sample. An isotonic test is performed at a constant stress and measures strain production. Isotonic testing requires a control algorithm to hold the sample at a desired stress. In most cases, a simple Proportional-Integral-Derivative (PID) control scheme provides sufficient resolution for actuation testing. However, many experiments were performed in isometric mode to avoid excess noise and further complexity in testing.

Two modes of electrochemical excitation are used in mechanical testing. Potentiostatic and galvanostatic control both drive the same ionic motion between the working and counter-electrode, but current control is more deterministic in the amount of charge transferred to the polymer. Thus, faster mechanical responses are apparent in current control, but the sample degrades more rapidly since the cell continually raises the potential to achieve a certain level of actuation. Mechanical testing in potentiostatic mode sets the input signal and allows the sample to determine the level of actuation. Also, potential control is better suited in gauging performance in a real-world application that would be battery-powered. In addition, most experiments were performed in potential control to monitor current response as a measure of performance and degradation.
2.3 Dynamic Mechanical Analyzer

A dynamic mechanical analyzer (DMA) was built for the unique test applications of the conducting polymer films. The DMA consisted of a linear motion stage aligned with a load cell to measure force production. The linear motion stage was a unit from New England Affiliated Technologies [5], while a 1 N load cell was used from Futek, model L2357 [6]. The polymer sample was clamped using alligator clips, forming the working electrode. A solvent bath lined with stainless steel counter-electrode was raised around the sample. An Ag/AgCl reference electrode was lowered into the solvent next to the working electrode. The reference electrode with the working electrode determines the open circuit potential in the electrochemical cell. The distance between all electrodes should be minimized to reduce the effects of solution resistance to ion mobility.

The instrument was designed for isometric testing of small samples inside a Cincinnati SubZero MicroClimate Chamber [7], a temperature-controlled chamber. The MicroClimate, which was also used for polymer electrochemical depositions, can be seen in Figure 2.4. The experimental setup is shown in Figures 2.5 and 2.6. The electrochemistry for testing was controlled with a Princeton Applied Research VMP2 multichannel potentiostat [8], shown in Figure 2.7. The data acquisition was performed by a National Instruments DAQPad 6052E [9]. The linear motion stage was controlled by a Compumotor from Parker Hannifin Corporation [10]. The load cell was routed through a 2311 Signal Conditioning Amplifier from Vishay Measurements Group [11].
Figure 2.4: Cincinnati SubZero MicroClimate temperature chamber.

Figure 2.5: Experimental setup, DMA shown with bath and electrodes in MicroClimate.
Figure 2.6: Experimental setup, DMA shown from above.

Figure 2.7: Princeton Applied Research VMP2 Multichannel Potentiostat.

A sample mechanical test is shown in Figure 2.8. The test was performed in isometric mode under potentiostatic control. The potential limits were 0 to 1.0 V to avoid moving more than one species of ion during oxidation and reduction. The charge is the integral of the current, and while this is the cell current, not strictly the current though the
polymer, it is a good approximation of the charge moved during actuation. Also note that the sample achieves an active stress as high as 5.5 MPa during this test. This stress corresponds to a sample 5 mm wide by 20 μm thick producing approximately 0.5 N.

Figure 2.8: Isometric test, polypyrrole showing large active stress as high as 5.5 MPa.
2.3.1 High Temperature Performance

The Futek load cell measures force using an S-beam configuration and might be susceptible to the temperature changes necessary for planned experiments. A test rig was configured holding the load cell in a vertical position and the voltage output was monitored in an unloaded state and for two calibration weights exceeding the forces expected from testing. The amplified output signal from the load cell was allowed to equilibrate at temperature before adding the weights. Once loaded the signal did not vary as a function of time. The results are shown in Figure 2.9. The load cell did not significantly respond to changes in temperature, eliminating the need for corrections for the device at temperature.

![Futek L2357 Load Cell Temperature Calibration](image)

Figure 2.9: Futek L2357 load cell temperature calibration
2.4 Investigation of Poly (3-hexyl thiophene)

As new conducting polymers are synthesized, the mechanical properties must be investigated in search of better actuation. One such new material is poly (3-hexyl thiophene) (P3HT), a conducting polymer that has a conductivity an order of magnitude lower than that typically observed in polypyrrole. This polymer also needs to be doped with ions regularly in order to maintain conductivity, in comparison with polypyrrole which is synthesized in a doped state. Passive testing revealed that the stiffness of the P3HT is also an order of magnitude lower than that of polypyrrole. However, the P3HT has a comparable yield strain to polypyrrole. These results are shown in Figure 5.1.

![Stress vs Strain](image)

Figure 2.10: Passive stress-strain curve for poly (3-hexyl thiophene).

The actuation studies of P3HT show promise, but the active stress produced, approximately 0.25 MPa, is significantly less than that of polypyrrole. One isometric test for P3HT is shown in Figure 5.2. It is also interesting to note that the mechanical
response of P3HT is opposite that of polypyrrole, indicating a flow of the oppositely charged ions during actuation. The current-voltage profile shows a hysteresis consistent with a double-layer capacitance within the polymer. The cyclic voltammogram of a pure resistor, by comparison, would be linear with no hysteresis. This profile is shown in Figure 5.3. This indicates that the polymer is not solely conducting charge, however the capacitance seems minimal with no substantial peaks in the current-voltage profile that would indicate significant charging and discharging of the double-layer. The current-voltage profile demonstrated better capacitance later in the series of tests, indicating that a training period may be required since the polymer in not synthesized in a doped state.

![IsoTest Data](image)

Figure 2.11: Isometric test for poly (3-hexyl thiophene).
This chapter has explained the basic principles of dynamic mechanical analysis and the application to a conducting polymer system. The types of dynamic analysis for a system such as this are unique due to the combination of active properties of the material and the passive viscoelastic effects. Also illustrated in this chapter is the experimental setup used in the following parallel actuation and thermal experiments.
References


Chapter 3  Parallel Actuation

Diffusion time is crucial to the timescale of actuation. The diffusion based time constant is inversely proportional to the diffusion constant and directly proportional to the square of the appropriate length scale, in this case half the thickness of the polymer sample,

\[ \tau_D = \frac{a^2}{4D}. \]  

[1] (3.1)

The diffusion curve as a function of position within the polymer is then parabolic for all times, ignoring edge effects. As such, the thickness of the sample is crucial in determining actuation speed. In order to use polypyrrole conducting polymer actuators as a practical engineering solution the total force production must be on the order of newtons. A single sample thick enough to perform this measure of force would actuate too slowly to be of use in a practical application.

The individual muscle fibers in mammalian skeletal muscle are similarly weak compared to the force production needs. Skeletal muscle has evolved into a bundling scheme where force is proportional to the overall cross-sectional area of the combined fibers. An illustration of skeletal muscle is shown in Figures 3.1 and 3.2. A parallel actuation system for thin film conducting polymers would work in the same way, increasing overall force production while maintaining the faster actuation speed associated with shorter diffusion times.

It is important in any actuation scheme to maintain a factor of 5 when comparing the surface area of the counter-electrode to that of the polymer. This is a result of the fact that charge is distributed into the bulk of the conducting polymer, but acts only as a surface reaction on the counter-electrode. It is also desirable to minimize the distance between each sample and the counter-electrode. The clamping system must accommodate these geometry restrictions and also allow each sample to remain in tension relative to each other, or provide a means to adjust tension of individual samples. Each
sample, even those cut from the same deposition, may experience varying degrees of stress relaxation, depending on the unique electrochemical and physical history.

Figure 3.1: Illustration of mammalian skeletal muscle. Source [2].

Figure 3.2: Illustration of bundling in mammalian skeletal muscle. Source [2].
3.1 Clamp and Bath Design

While clip-style clamps have proven the most effective in the past, this demanded an undesirable separation between the samples and the counter-electrode. A design using a series of flat plates bolted together provided the necessary clamping force, but not the ability to adjust relative tensioning. The chosen clamp design utilized Capstan friction in tightening the samples. The Capstan effect relates the ratio of the tension increase in a cable wrapped around a circular object to the number of turns and coefficient of friction between the cable and the object,

\[ T_o = T_i e^{\mu \theta} \]  \hspace{1cm} [3]  \hspace{1cm} (3.2)

The clamp consisted of a bolt with a slit along approximately half the length. This allowed the polymer film to slip vertically down the bolt, minimizing the distance between samples. As the bolt was tightened to the bath structure, the polymer was wound around the diameter. The polymer wrapped onto itself, increasing the tension beyond predicted by the Capstan effect. The clamp is shown with tightened polymer samples in Figure 3.3. This design also allowed individual tensioning of the samples. The slits were machined using a Charmilles Technologies Robofil 1020SI Wire Electric Discharge Machine (EDM). [4] This is a forceless machining process that uses electric discharge to remove stock. The wire EDM is shown in Figure 3.4.

![Figure 3.3: Bolt-type clamp design for parallel actuator.](image)

In order to minimize the distance between the sample and the counter-electrode, a fin-type counter-electrode was also machined on the wire EDM. Polymer films were loaded between fins vertically maintaining a large surface area of counter-electrode for each sample. The counter-electrode was fit into a rectangular bath that also featured holes to align the fixed set of clamps. A scheme using ten samples was chosen to ensure at least a few samples were in tension and operating concurrently. The bath was printed
on a Viper Laser Stereolithography (SLA) machine. [5] This machine uses laser-hardened resin to print CAD files in 3D. The Viper SLA is shown in Figure 3.5.

Figure 3.4 Charmilles Technologies Wire EDM.

Figure 3.5: Viper Laser Stereolithography machine.
The bath also featured a slider, a solid piece holding one end of each of the samples, which could be temporarily tightened to the bath in order to apply pre-tension before connecting this unit to a force transducer. The samples were individually tightened and balanced to avoid a short circuit between the polymer and counter-electrode. Once connected to the force transducer, the slider was released from the bath and was free to move in the direction of actuation. The bath also featured two pulleys to connect the slider to the force transducer, which was the same Futek load cell used in the construction of the DMA in Section 2.2. The polymer samples shown in the design are 50 mm long and the bath is 75 mm wide. The CAD assembly file is shown in Figure 3.6. An electrical contact was created at the counter-electrode through the bottom of the bath. The wire serving as the working electrode was wrapped around both sets of clamps to ensure consistent voltage along the substantial length of the sample. No reference electrode was used in the electrochemistry of this experiment. The reference lead was connected to the counter-electrode, which does not accurately measure the electrochemistry of the cell, but still allows the flow of charge. The assembled parallel actuator is shown in Figure 3.7. An enhanced view of the polymer samples and counter-electrode is shown in Figure 3.8.

Figure 3.6: CAD assembly file of parallel actuator.
Figure 3.7: Assembled parallel actuator.

Figure 3.8: Assembled polymer samples and counter-electrode in parallel actuator.
3.2 Mechanical Testing of Parallel Scheme

Once loaded with samples, the parallel actuator unit was connected to the Futek load cell and the bath was filled with 0.05 M tetraethylammonium hexafluorophosphate (TEAPF₆) in propylene carbonate. Two tests were performed in order to assess the force production of the unit. A square wave in current usually provides the fastest response in stress. Galvanostatic operation deterministically defines a volume of charge moved in each cycle. This allows greater control over stress production. The results from the modular galvanostatic test are shown in Figure 3.9.

![Modular Galvanostat - Parallel Actuator](image)

**Figure 3.9:** Modular galvanostat testing of parallel actuator.

The maximum force production in this test was 1.0 N, at 0.1 N/s. This stress rate is comparable to performance seen in single sample tests. Cyclic voltammetry (CV) was used to demonstrate maximum force production. The CV was run at 100 mV/s in order to allow the samples ample time to contract completely. The upper limits of the CV were increased incrementally until the sample began to degrade, which occurred approximately at 4.0 V. The results of the CV are shown in Figure 3.10. The maximum force
production in this test was 2.0 N. This corresponds to an active stress of 4.4 MPa, given the total cross-sectional area of the samples. This is also consistent with single sample performance. This device demonstrates that several samples can function in parallel in both rate and magnitude to the capacity of a single sample.

![Cyclic Voltammetry - Parallel Actuator](image)

**Figure 3.10:** Cyclic voltammetry of parallel actuator.

### 3.3 Design Limitations and Future Work

The clamp and counter-electrode design were very successful in this application. The material choice for the bath is not conducive to long term application. The resin material from the SLA is eroded by propylene carbonate and other solvents common to actuation. Ionic liquids would not be as corrosive, but are much more expensive for a large volume application. Teflon would be a better choice for future bath designs.

While the ability to individually adjust the relative tension between samples worked well in the design, the parallel unit was not able to easily adapt to variations in stress relaxation. The slider was frequently not perpendicular to the direction of actuation and several samples became completely slack during actuation testing. This accounts for
the difference in the results from the expected 5.0 N force. The samples, on average, were still operating in the expected range, but not to full capacity. It appears as if a few samples were actuating significantly above average and other samples were not contributing at all.

The design needs a structure that automatically averages tensioning between samples. The samples must be free to move in the direction perpendicular to actuation, without allowing contact with the counter-electrode. One possible design would be a tree structure, where each split between branches is connected with a pin joint. This would equilibrate the tension in the appropriate direction between branches without reducing the actuation potential of any individual sample. Stops could be added that prevent the working electrode and polymer from contacting the counter-electrode. This would allow a greater range of operation and make the device more applicable as an engineering solution.

References
Chapter 4   Temperature Effects

A benefit in actuation speed was observed in polypyrrole trilayer applications at temperatures higher than ambient conditions. In a polypyrrole linear application, this benefit would translate to increased stress rate when tested in isometric mode and increased strain rate in isotonic mode. Such an increase would allow the polymer actuator to reach its target stress or strain for an application in less time, increasing the operating bandwidth of the device.

4.1 Mechanical Testing

Mechanical testing was performed on the dynamic mechanical analyzer in order to measure a variation in actuation rate. The tests were run in isometric mode for this experiment. Isometric testing is a constant length mechanical test that is used to measure an active stress profile. Potential control was used for the electrochemistry of the experiment, opposed to galvanostatic, or current, control. The current determines the amount of charge supplied to the electrochemical cell in the form of ions. The solvent used to supply these ions was 1-butyl, 3-methyl imidizolium hexafluorophosphate, an ionic liquid. Potential control was chosen in order to observe the effect of temperature on the stress rate. The limits of the square wave were chosen to be 0 and 1.0 V. A low potential magnitude was used to maintain typical actuation without damaging the sample throughout the course of the experiment. Using only positive potentials was an attempt to minimize the transfer of both species of ion in the solvent to the polymer sample, resulting in a smoother active stress profile. The electrochemical and mechanical results of one such isometric test taken at room temperature are shown in Figure 4.1. The electrochemical data is also shown in the form of a current-voltage graph in Figure 4.2.

Each sample was brought to a passive stress of 2.0 MPa prior to initiating an isometric test. The open circuit potential between the polymer sample and solvent was approximately 0.3 V against an Ag/AgCl reference electrode. The flow of charge expands and contracts the polymer sample. This results in an active stress profile above the passive starting point. The relation between the direction of charge flow and the
mechanical contraction of the polymer depends on which ions are mobile in the solvent. The magnitude of active stress generation can also vary between solvents.

Each sample was prepared for mechanical testing by performing a sweep in potential between -1.0 and 1.0 V at a rate of 50 mV/s. The sweep was cycled until the current-voltage profile was repeatable. This cyclic-voltammogram (CV) was performed under zero load. One such CV is shown in Figure 4.3.

Figure 4.1: Isometric test at room temperature including both electrochemical and mechanical data.
Figure 4.2: Electrochemical data from isometric testing at room temperature.

Figure 4.3: Cyclic voltammogram performed prior to mechanical testing.
4.1.1 Effect on Actuation

The samples of polypyrrole used in this experiment were all of the same size, approximately 10 mm long, 3 mm wide and 18 μm thick. The same sample was used over the course of any one experiment. Isometric testing was performed in increments of 25 degrees between 25 and 100 °C. The sample was removed from the experimental setup as the temperature of the bath was raised in order to minimize polymer degradation due to decreased cycle life at higher temperature, as shown in Section 4.2. When the bath was brought to temperature, the sample was immersed and allowed to equilibrate before performing mechanical testing. Each test comprised of ten cycles at 0.1 Hz. The first cycle starts at the open circuit potential and is not controlled to 0 V. As such, cycles two through ten were averaged at each temperature and are shown in Figure 4.4.

![Thermal Actuation Test, 0-1.0V Potential Square Wave, 1-17-06](image)

Figure 4.4: Averaged stress production of isometric mechanical testing at various temperatures, solid lines are raising the temperature from 25 °C to 100 °C, dotted lines are cooling from 100 °C back down to 25 °C.
As the temperature was raised from 25 to 100 °C, both the stress rate and overall stress magnitude were increased by temperature. This data is indicated by the solid lines in Figure 4.4. The dotted lines indicate data where the sample is cooled from 100 °C back to 25 °C. At 75 °C, the stress production is repeatable whether heating or cooling, but as the sample is cooled further, degradation appears to occur as no appreciable stress production is observed. The initial slopes of the stress production as a function of temperature are shown from several tests in Figure 4.5. The initial stress rate increases with temperature, however, the sampling in temperature is not high enough to resolve a specific correlation. The samples originated from different depositions, explaining the variation in initial slope at 25 °C. For one test, June 3, premature degradation occurred, while the test on June 8 was the only test performed as a reverse scan, starting at 100 °C, which may explain the high initial stress rate at this temperature as compared to the other tests.

Figure 4.5: Initial slopes of stress production in several isometric tests.
One significant variation between the tests in June and January is the performance of the sample at 50 °C. In the later tests, there is no significant variation between the tests run at 25 °C and 50 °C. All of the tests performed in June heated the polymer sample with the electrolyte bath, as opposed to the January tests where the sample was removed during heating. One test performed in June is shown in Figure 4.6.

![Thermal Actuation Test, 0-1.0V Potential Square Wave, 6-1-05](image)

**Figure 4.6:** Averaged stress production of isometric mechanical testing at various temperatures.

There is also a large degree of stress relaxation apparent in the 100 °C test that was not present in the January tests. Both effects can be attributed to the viscoelastic properties of the polymer. The polymer sample is expected to experience more stress relaxation at high temperatures. However, this effect is not as immediate as the benefit in actuation performance. The samples tested in June spent approximately four hours in heated solvent over the course of the experiment, whereas the samples in January were heated for less than ten minutes. Increased stress relaxation could not occur in this short time scale, as each test ran for approximately two minutes. This is immediately evident in the 100 °C case of the June tests, where the active stress profile declines instead of reaching a steady state of stress production. In Figure 4.4, such stress relaxation is not
evident in the 100 °C case. The viscoelastic effect at 50 °C is more subtle. The actuation performance of 50 °C is approximately the same as the 25 °C case, as evidenced by Figure 4.4. Therefore, the same volume of ions is drawn into the polymer at the same rate in both tests. The model shown in Section 1.3.1 separates the active and passive stress in the material. The passive stress in all tests is equivalent at the starting point of the experiment, however, the starting strain was not consistent. This can be explained by a variation in the viscoelastic modulus. The modulus also is present in the active stress term and an increase in modulus would produce more stress for a given volume of ions. The increase in modulus may have come from heating under tension. In this case, the augmented viscoelastic modulus allowed for improved actuation given the same ion movement. At higher temperatures, the benefit in actuation due to temperature is more apparent, however, the amplified viscoelastic effects can produce undesirable stress relaxation when heated extensively.

It is observed in Figure 4.4 that only the 100 °C case reached steady state at the 0.1 Hz excitation frequency due to the increase in stress rate. In an attempt to allow each test to reach steady state, the frequency of the square wave excitation was reduced to 0.033 Hz, giving the sample 15 seconds to equilibrate at 1.0 V. The results are shown in Figure 4.7 with corresponding exponential fits using a single time constant. The tests successfully reached steady state, however it appears that a single time constant is insufficient in describing the behavior of the active stress profile. Also, these results are consistent with the previous data concerning actuation at 50 °C, as the sample was removed during solvent heating. Figure 4.8 shows the comparison of two exponentials in describing the 100 °C case in this longer test. The exponential using two time constants better simulates actuation behavior. Exponentials of this form were fit to the data and the gains and time constants as a function of temperature are shown in Figures 4.9 and 4.10.
Figure 4.7: Averaged stress production of isometric mechanical testing at various temperatures shown with exponential fits.

Figure 4.8: A comparison of two exponentials in describing 100 °C actuation behavior.
Figure 4.9: Gains from exponential fits of actuation data.

Figure 4.10: Time constants from exponential fits of actuation data.
4.1.2 Basis for Improved Performance

The effect of temperature on conducting polymer actuation involves both an increase in stress magnitude and rate. The magnitude increase can be explained using the electrical model shown in Section 1.3.2, where the frequency dependent impedance of the polymer is in series with a solution resistance. It is shown that the largest effect on the conductivity of polypyrrole is from the dopant ion and temperature does not have a significant effect. [1] Thus, the resistance of the polymer remains roughly constant as a function of temperature. Further, the magnitude of an active stress profile is independent of the double-layer capacitance, as the final magnitude is a steady state condition. The solution resistance, however, is expected to decrease as a function of temperature. This is a result of increased ion mobility in the solution at higher temperatures. Reduced solution resistance in series with a temperature independent polymer impedance would result in increased current at higher temperatures for a given voltage profile. Higher currents translate to a larger charge volume per cycle. Increasing the total charge introduced into the polymer increases the total stress magnitude in a given cycle. Both the steady state and peak currents would increase as a result of decreased solution resistance, which is consistent with data collected during the experiment.

The decreased solution resistance also affects the stress rate of actuation. In this resistance driven model, the double-layer capacitance would remain roughly constant with temperature, since the volume of ions necessary to charge the double-layer does not vary with temperature. This resistive time constant or time necessary to charge the double-layer is given by J. Madden, PhD Thesis, 2000 [2]:

$$\tau_{RC} = R_s C,$$  \hspace{1cm} (4.1)

where R is the solution resistance and C is the double-layer capacitance. In the diffusion driven model, ion mobility within the polymer is increased at higher temperatures, also reducing the time constant of actuation. The time constant associated with diffusion is given by:

$$\tau_D = \frac{a^2}{4 \cdot D},$$  \hspace{1cm} [2]  \hspace{1cm} (4.2)
where $a$ is the characteristic length scale of diffusion, in this case half the thickness of the polymer sample, and $D$ is the diffusive constant that is a linearly increasing function of temperature.

The response of stress rate to an increase in temperature will be a combination of these two effects. The measured time constant from Figure 4.10 is shown with the simulated diffusive and resistive time constants as a function of temperature in Figure 4.11. The curve for the resistance driven model was acquired using a measured solution resistance and a double-layer capacitance calculated from the electrochemistry. It was assumed that the capacitance was constant as a function of temperature. The curve for the diffusion driven model was obtained using the measured polymer thickness and by assuming the slope $dD/dT$. The curves are shown normalized to the initial measured time constant.

Figure 4.11: Measured and simulated time constants of conducting polymer actuation.

This figure implies that the resistance driven model dominates the diffusion driven model at higher temperatures. The combination of these models corresponds to a decrease in the time constant of actuation, increasing stress rate as a function of
temperature. The combined effect of temperature on both solution resistance and ion diffusion within the polymer accounts for the improvements observed in both magnitude and rate of actuation.

4.2 Cycle Life Testing

It is expected that the cycle life of a polymer sample decreases with increased actuation temperature. In order to maintain consistency with previous results, the same experiment using 0 to 1.0 V excitation was performed on samples held at temperature. In the interest of time, the frequency of the cycles was increased to 0.25 Hz. This experiment was also run in isometric mode. The test was run until either the sample stopped actuating altogether or the actuation shifted significantly out of phase with the excitation. The cycle life results in terms of averaged stress magnitude are shown in Figure 4.12. Given the specific excitation, actuation at 25 °C yielded a cycle life of 22 hours, or nearly 20,000 cycles, 50 °C corresponded to 4 hours and 3,600 cycles, and the sample at 75 °C lasted less than 1 hour and 1,000 cycles.

![Cycle Life Testing](image)

Figure 4.12: Cycle life testing results at various temperatures.
It can be seen clearly in Figure 4.13 that the initial cycles at 75 °C produce larger stress magnitudes than the room temperature case. However, the magnitude drops off relatively quickly as compared to actuation at 25 °C. The performance at 50 °C is also consistent with previous results, with no apparent initial benefit in actuation over the 25 °C case. Despite the lack of improvement in actuation, the cycle life at 50 °C is largely affected by the increase in temperature. The stress magnitudes are lower than previous experiments due to the increased frequency of excitation. The cycle life results are important in exploiting the benefit in actuation at higher temperatures for engineering applications if heated samples may only last 5% as long as samples kept at ambient conditions. However, a more careful experimental setup that allows better oxygen control may increase the cycle life at temperature.

Figure 4.13: Initial cycles of cycle life testing at various temperatures.
4.3 Effect on Elastic Modulus

The effect of temperature on the elastic modulus of a polymer depends on the structure of the material. Previous results suggest that the elastic modulus of polypyrrole increases with temperature. Typically, this is indication of crosslinking within the structure. Polymer samples were placed in a Perkin Elmer DMA 7e [3], shown in Figure 4.14, and were simultaneously subjected to an increase in temperature and constant frequency oscillations in stress. The magnitude of the 1 Hz perturbation was 500 MPa dynamic oscillation over 1000 MPa static stress. The sweep in temperature was controlled at a rate of 1 °C/min. The sample dimensions were consistent with previous experiments. Tests were performed both in air and submerged in solvent. It is important to note that these tests are entirely passive in nature with no electrochemical stimulation.

![Perkin Elmer DMA 7e used for passive elastic modulus testing.](image-url)
4.3.1 Typical Polymer Response

Polymers will typically experience a transition in modulus from a glassy phase to a rubbery phase as temperature is increased. [4] The magnitude of the drop in elastic modulus after the transition phase varies among polymers. Poly (3-hexyl thiophene) is a conducting polymer that portrays the typical polymer response in elastic modulus to a shift in temperature. This test was performed in dry air and the results are shown in Figure 4.15. It is evident from the results that Poly (3-hexyl thiophene) does not display the qualities of a crosslinked polymer. The modulus of a crosslinked polymer would remain constant or even increase as a function of temperature after the rubbery transition.

![Modulus vs Temperature](image)

Figure 4.15: Modulus vs. temperature for poly (3-hexyl thiophene).

4.3.2 Passive Mechanical Testing

A similar experiment was performed with polypyrrole, with a larger sweep in temperature. The temperature was also cycled back down to ambient conditions in order
to verify the repeatability of the behavior. The first test performed in dry air showed no repeatability as the elastic modulus increased in both the forward and reverse scans in temperature. The inconsistency was believed to be the result of the evaporation of the remaining solvent left in the polymer after deposition. The experiment was repeated with the sample submerged in 0.05 M TEAPF₆ in propylene carbonate, the solvent used for deposition. The effect of evaporating solvent in dry air appears to artificially increase the measured modulus, but does not account for the inconsistency in repeatability. The results of these tests are shown in Figure 4.16.

![Figure 4.16: Modulus vs. Temperature for polypyrrole in both dry air and solvent.](image)

It is unclear from these results if an irreversible change occurs consistently during the heating process or if the first cycle is dissimilar from any subsequent cycles. The same test was repeated in the propylene carbonate with three identical consecutive sweeps in temperature. The results are shown in Figure 4.17. While the first cycle does behave differently than the subsequent cycles, it appears that the mechanism driving the rise in elastic modulus is consistent throughout the test. The modulus experiences the largest change when subjected to high temperatures. Each cycle causes the modulus to shift upwards, in successively smaller steps. The sample is subjected to constant oscillations in stress and it is unclear if this is affecting the measurement. As the sample
temperature is increased, the magnitude of the strain oscillations decreased and did not recover as the sample was cooled back to ambient conditions. It is not unreasonable to assume that the first cycle produces the most dramatic results considering that the electrochemical deposition occurs at -40 °C. However, polypyrrole does not exhibit the typical response of a non-crosslinked polymer. The transition point of polypyrrole between the glassy and rubbery phases could exist at a lower temperature than ambient conditions.

![Modulus vs Temperature](image)

Figure 4.17: Modulus vs. temperature for polypyrrole in propylene carbonate shown with repeated cycles.

If the behavior at high temperatures is driving the variation in elastic modulus, it is expected the magnitude of the change should fluctuate with the cycled maximum temperature. Several tests were performed for a range of maximum temperatures. The results are shown in Figure 4.18. The magnitude of shift in modulus differs between samples, with the higher temperatures producing the largest rise. It is also important to note that the lower temperature cycles produce a more consistent shift over the course of
the experiment, whereas the higher temperature cycles produce the largest shift in the first cycle. This would imply that the process is gradual and ultimately limited by the structure of the material. The modulus appears to progress towards an equilibrium state, where successive cycles in temperature would produce no further variation in modulus. It is also apparent that the response is not only dependent on the magnitude of the temperature shift, but also the time spent at elevated temperature. It is reasonable to assume that a slow temperature change over the course of the previous high temperature actuation experiments of Section 4.1 could have caused an increase in the elastic modulus of the polymer.

![Modulus vs Temperature](image)

Figure 4.18: Modulus vs. temperature for polypyrrole in propylene carbonate cycled at various temperatures.

While electrochemical deposition occurs in 0.05 M TEAPF₆ in propylene carbonate, the previous actuation experiments were performed in ionic liquid. It is expected that the measured modulus would vary between solvents used for testing, but it is useful to attempt to duplicate this unique behavior in the same solvent used for
improved actuation at high temperatures. The results of the temperature sweep in ionic liquid can be found in Figure 4.19. The magnitude of the variation in modulus is much lower in ionic liquid and most of the overall transition occurs in the first cycle. Also, the curve is more independent of temperature effects exhibiting a lesser slope than the previous response. The difference in ions present in the solvent would produce variations in polymer structure as ions are absorbed over the course of the experiment. The greater noise source in this test can be attributed to the high viscosity of the ionic liquid compared to propylene carbonate.

![Modulus vs Temperature](image)

Figure 4.19: Modulus vs. Temperature of polypyrrole in ionic liquid.

These results are repeatable across depositions suggesting that the structure of polypyrrole prevents the elastic modulus from decreasing with increasing temperature to the extent expected from a typical polymer.
4.4 Effect of Heat-Treating on Actuation

The shift in elastic modulus in the previous experiments would benefit actuation in producing more stress for a given charge density. However, it is unclear if the process of heat-treating prematurely degrades the polymer. A sample was prepared of similar dimensions to previous experiments and subjected to an independent passive modulus scan in ionic liquid prior to any heat-treating. The modulus test is shown in Figure 4.20. This particular sample demonstrates an initial modulus of 0.34 GPa. It is expected that the modulus will vary when measured in different solvents and at different rates.

\[ y = 3.7 \times 10^2 x - 0.45 \]

A cyclic voltammogram and actuation tests were also performed to verify the active properties. The sample showed typical capacitance as it reached steady state in the CV and displayed actuation data consistent with previous experiments at room temperature in both isometric and isotonic modes. The isotonic tests were conducted with the same parameters as the tests performed in isometric mode. The cyclic voltammogram is shown in Figure 4.21 and the actuation data is shown in Figures 4.22
and 4.23. The sample was then subjected to a passive heat-treating similar to the test shown in Figure 4.17. The test was performed in 0.05 M TEAPF$_6$ in PC to reduce the noise in the measurement. The sample was subjected to a single cycle between 25 and 150 °C, swept at 1 °C/min. The duration of the test was 250 minutes, where the polymer sample was above 100 °C for 100 minutes. The response in elastic modulus was similar to previous experiments showing a rise at high temperatures with no recovery when cycled back to ambient conditions.

![Cyclic voltammogram for polypyrrole in ionic liquid.](image)

Figure 4.21: Cyclic voltammogram for polypyrrole in ionic liquid.
Figure 4.22: Isometric test for polypyrrole in ionic liquid.

Figure 4.23: Isotonic test for polypyrrole in ionic liquid.
After performing the heat-treating in the Perkin Elmer DMA, the sample was subjected to the same sequence of tests in order to determine the effects of extensive heating. All tests were performed at room temperature. The increase in elastic modulus to 0.49 GPa was expected and was consistent with previous measurements that showed a larger modulus increase when measured in PC. This result can be seen in Figure 4.24. The cyclic voltammagram showed limited capacitance even after several cycles, suggesting a decreased actuation potential after heat-treating in this manner. The CV is shown in Figure 4.25. Poor actuation was confirmed with the actuation tests shown in Figures 4.26 and 4.27. In isometric mode, the sample shows force production in phase with excitation, but with negligible magnitude. In isotonic mode, the sample does respond electrochemically to the excitation waveform, but with almost no corresponding mechanical output.

![Passive Stress vs. Strain](image)

Figure 4.24: Passive stress vs. strain for polypyrrole in ionic liquid after heat-treating.
Figure 4.25: Cyclic voltammogram for polypyrrole in ionic liquid after heat-treating.

Figure 4.26: Isometric test of polypyrrole in ionic liquid after heat-treating.
In both actuation tests, the electrochemical current response is similar in shape to previous tests, implying the expected flow of charge. However, it is the magnitude of the peak current that is much lower than anticipated, characteristic of a degraded sample. It is also important to note that the conductivity of sample was not significantly affected by the heat-treating process. Extensive heating does appear to cause decreased actuation potential, but it is unclear if the stress oscillations associated with the continuous modulus measurement were important in reducing the actuation potential of the sample.

![Isotonic Test Data](image)

Figure 4.27: Isotonic test of polypyrrole in ionic liquid after heat-treating.

### 4.4.1 Heating Unconstrained Samples

In order to identify the role of heat-treating in actuation performance, several polypyrrole samples from the same deposition were subjected to various durations of time at elevated temperatures. The samples were placed unconstrained in a bath of ionic liquid. Several samples were left untreated and compared with the same battery of passive and active tests to samples that had endured either 5 or 30 minutes at either 50 or 100 °C. The samples were tested at room temperature to investigate if an increase in
modulus could be observed, and improve actuation, or if samples would begin to degrade at higher temperatures and longer exposure times. The results of the experiment are shown in Table 4.1. Each case is the average of six identical samples. For most of the samples the variations in modulus, mean active stress and strain are negligible. The samples did not appear to be affected by exposure to temperature. The exception is the last case, where samples spent 30 minutes at 100 °C. These samples, based on the actuation data, appeared to experience the same degradation apparent in the tests in Section 4.4. In addition, the measured modulus is slightly larger than the other cases, supporting the previous heat-treating experiments. It is also important to note that changes in conductivity were not significant across the samples.

<table>
<thead>
<tr>
<th></th>
<th>Untreated</th>
<th>50 °C 5 minutes</th>
<th>50 °C 30 minutes</th>
<th>100 °C 5 minutes</th>
<th>100 °C 30 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (GPa)</td>
<td>0.60</td>
<td>0.59</td>
<td>0.47</td>
<td>0.61</td>
<td>0.72</td>
</tr>
<tr>
<td>Mean Active Stress (MPa) (Isometric)</td>
<td>2.36</td>
<td>1.96</td>
<td>2.21</td>
<td>2.07</td>
<td>1.00</td>
</tr>
<tr>
<td>Mean Active Strain (Isotonic)</td>
<td>0.0029</td>
<td>0.004</td>
<td>0.004</td>
<td>0.004</td>
<td>0.002</td>
</tr>
<tr>
<td>Strain /charge (m^3/C)</td>
<td>$1.8 \times 10^{-10}$</td>
<td>$2.3 \times 10^{-10}$</td>
<td>$2.5 \times 10^{-10}$</td>
<td>$2.0 \times 10^{-10}$</td>
<td>$1.2 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Table 4.1: Results of pure heating on actuation of polypyrrole.

This data implies that the variation in modulus from the earlier heat-treating experiments was a result of extended exposure to high temperatures. Given the results in Table 4.1, where 30 minutes at 100 °C was enough temperature exposure to cause a noticeable decay in performance, the samples subjected to the previous heat-treating would have experienced enough time at temperature to justify degradation. It is then reasonable to conclude that the stress oscillations in previous heat-treating experiments may have assisted in increasing the measured modulus, but were not the sole cause of poor actuation.
4.5 Electro-Mechanical Impedance Measurements

It was observed in the cycle life testing that the magnitude of the current response in the electrochemical cell decreased slowly throughout the course of the test, even long after the sample was considered inactive. As such, it was impossible to determine the magnitude of stress production simply by monitoring the electrochemistry. This was unexpected, given the magnitude of the current response increased with actuation temperature in previous experiments. Therefore, the cutoff frequency for decreased current response is at a much higher bandwidth than that of actuation. Thus, the current response is not a good indicator of actuator performance. This point will vary with the magnitude of the excitation signal.

The impedance spectroscopy was performed in isometric mode. The input voltage signal was a constant magnitude swept sine. The 500 mV peak-to-peak signal was swept in logarithmic increments from approximately 5 Hz to 0.2 mHz. The sample remained at each frequency for three cycles. The total experiment time was approximately 13 hours, however this amounted to only 84 cycles. Both total cell current and stress production were measured. The block diagram of the experiment is shown in Figure 4.28. The magnitude of the measured stress output was compared to the excitation frequency. This experiment was performed both at 25 and 75 °C. The low excitation voltage and small amount of cycles aided in avoiding the low cycle life at 75 °C.

At higher temperatures, a higher magnitude and rate of stress is expected based on previous experiments. It is also expected that higher temperatures would lead to higher resolvable actuation frequencies. The sample should respond to higher frequency excitation. The sample kept at 75 °C should reach maximum actuation potential at a higher frequency than the sample at room temperature.

![Diagram](image)

Figure 4.28: Block diagram of impedance experiment.
4.5.1 Electrochemical Response

The impedance of the electrochemical cell was measured as a function of excitation frequency. It is important to note that this is the impedance of the entire cell and includes the solution resistance, where as the impedance modeled in Section 1.3.2 was an electrical model of the polymer only. Both the magnitude and the phase of the impedance at both temperatures are shown in Figures 4.29 and 4.30. The magnitude of the impedance is much larger at 25 °C, which is expected due to decreased solution resistance at higher temperatures. This also indicates a higher current peak during actuation at increased temperature consistent with previous results. It is also expected for the phase to shift negative at lower frequencies as the period of excitation becomes the same order of magnitude as the time needed to charge the double-layer. The lack of phase recovery of the sample at 75 °C at the lowest frequencies can best be attributed to increased diffusion at higher temperatures. Thus, the double-layer and bulk capacitance were charged fully at a larger range of frequencies at 75 °C.

4.5.2 Mechanical Response

The measured stress output for each test is shown in Figures 4.31 and 4.32. Each sample had an initial passive stress of 2 MPa. The sample at 25 °C experienced large stress relaxation in the first stages of the test, which was avoided in the 75 °C case by allowing the sample to better equilibrate before initiating the electrochemistry. Regardless, the 25 °C sample remained in tension throughout the course of the test. As expected, the magnitude of the 25 °C case is much lower than the 75 °C case. It is also apparent from these results that the 75 °C case reached maximum actuation much earlier in the test than the room temperature case. The magnitudes as a function of frequency of each peak were collected and shown in Figures 4.33 and 4.34 as both semi-log and log-log scales.
Figure 4.29: Electro-mechanical impedance measurement of polypyrrole at 25 °C.

Figure 4.30: Electro-mechanical impedance measurement of polypyrrole at 75 °C.
Figure 4.31: Stress data from electro-mechanical impedance measurement of polypyrrole at 25 °C.

Figure 4.32: Stress data from electro-mechanical impedance measurement of polypyrrole at 75 °C.
Figure 4.33: Magnitudes as a function of frequency of electro-mechanical impedance measurement of polypyrrole in semi-log axes.

Figure 4.34: Magnitudes as a function of frequency of electro-mechanical impedance measurement of polypyrrole in log-log axes.
It is apparent from these results that the impedance measurement at 75 °C produced both higher stress magnitudes and a larger rate of increase in magnitude as a function of frequency. The 75 °C case also attained a larger band of resolvable frequencies, where the stress data is reasonably in phase with the excitation voltage signal. This is evident in Figure 4.33. Also, the 25 °C case reaches maximum actuation at almost an order of magnitude lower in frequency than the high temperature case. From Figure 4.34, the curve seems to shift diagonally upwards with temperature. The slope of the initial portion of both curves in the log-log plot is approximately -2. This data firmly supports previous actuation experiments at high temperatures.

4.6 Conclusions

Actuation at higher temperatures results in an increase in both stress magnitude and rate as a result of decreased solution resistance and increased ion diffusion within the polymer. However, the cycle life is reduced by a factor as high as twenty when actuating at these temperatures. Excessive heating has caused poor actuation and one indicator of such behavior is an increase in modulus. The mechanism that drives this modulus behavior is still unclear and future work should focus on understanding how the structure relates to the observed gradual variation. This atypical behavior is important in describing the response of the polymer to temperature. The combination of impedance spectroscopy and mechanical testing has proven to be an effective means of determining actuator performance. The test highlights the frequency response in stress magnitude and rate. The electrochemical data from this test also helps to correlate increased capacitance with increased actuation. Studying the coupling between the mechanical response and the electrochemistry reveals that while the current drawn into the cell determines actuator potential, current alone is not a good indicator of actuator performance. The temperature dependence of this curve is clear and this test combines many of the results seen in previous actuation experiments.
References


Chapter 5  Summary and Future Work

In order to better use conducting polymer actuators as a viable engineering solution, the material properties must continue to be investigated and understood. Current applications are limited by an inability to correctly predict actuator behavior in a variety of unconventional circumstances. However, the basic science and applications must be developed concurrently in order to maintain progress. To understand the limitations of the material is necessary to best develop devices that perform outside of the laboratory. For example, conducting polymer actuators are well-suited to biomimetic applications, or devices that mimic a biological system. One such application is the development of a biorobotic pectoral fin mimicking the geometry and performance of the bluegill sunfish. The fin rays are controlled by a series of muscle fibers that attach at the base of the fin. These muscles can create various fin shapes and adjust the stiffness of the rays. Thus, complex fin motions are the result of many actuators working collectively. Conducting polymers share many similarities with the structures developed by nature for this purpose. Among other needs, this application has requirements for stress magnitude and bandwidth of an actuator device. A parallel scheme seems appropriate given the current state of actuator performance, and utilizing the thermal effects could prove advantageous in shrinking the size of the device. Polypyrrole conducting polymer actuated at temperatures as high as 100 °C increases stress magnitudes by as much as 4× and stress rates by 5×. However, these temperatures can quickly reduce actuator potential, decreasing cycle life by as much as 20×. The structure of these polymers is driving these conformation changes and must be further investigated in order to predict actuator performance.

Most of this conducting polymer research focuses on polypyrrole actuators. Polypyrrole is relatively simple to synthesize, its properties are fairly stable, and actuates well under a variety of circumstances. However, it is not exactly clear what causes the advantage of polypyrrole over other conducting polymer actuators. The search for new materials must continue not only to seek out the next greatest actuator, but to better understand the current system. Poly (3-hexyl-thiophene) is not the better of polypyrrole in terms of performance. The stress magnitude and conductivity of the samples
synthesized are both an order of magnitude lower than that of polypyrrole. P3HT also
does not remain in a doped conductive state. However, this does not exclude P3HT from
use in a conducting polymer application or future research. It must be remembered that
polypyrrole is as successful as has been shown largely because of the enormous effort put
forth for its development. A similar effort must be dedicated as new polymers are
designed and synthesized in search of improved actuators.