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The Effect of Ion Delivery on Polypyrrole Strain and Strain Rate under Elevated Temperature

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ABSTRACT

Conducting polymers can act as actuators when an electrochemical stimulus causes the materials to undergo volumetric changes. Ion flux into the polymer causes volumetric expansion and ion outflow causes contraction. Polypyrrole is an attractive actuator material due to its ability to generate up to 30 MPa active stress and 10% to 26% maximum strain with voltage supply lower than 2 V. The polymer's mechanical performance depends upon the solvent used and the dominating ion species. In this study, we used 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) to characterize the effect of temperature increase on ion flow and how it contributes to strain and maximum strain rate of polypyrrole. In this solvent, the cation BMIM⁺ diffuses in and out of the polymer under applied voltage to cause strain changes. For approximately each increment of 10°C from 27°C to 83°C, isotonic tests were done with +/-0.8 V square pulses, using a custom built device that is capable of performing temperature controlled dynamic mechanical analyses and electrochemistry simultaneously. Results showed that, independent of voltage polarity, from 27 to 83°C the strain increased from 0.4% to 2.0%. Both the maximum charge and strain rate rates increased with temperature, and were higher at positive voltage than at negative voltage throughout the same temperature range. Positive voltage caused the maximum strain rate to increase exponentially from 0.1 %/s to 0.67 %/s, while negative voltage caused it to increase more linearly from 0.06 %/s to 0.23 %/s. The results suggest that the increase in strain resulted from the charge delivered to the polymer in higher quantities at higher temperature. Furthermore, BMIM⁺ ions are expelled faster than those being attracted in to the polymer, perhaps due to the ions preferentially remaining in the bulk solution. As the temperature increased, the ionic mobility increased and as a result, BMIM⁺ ions are expelled back into the solvent even faster.

INTRODUCTION

Conducting polymers are electrically conductive and can be used as actuators to carry out mechanical work. Some conducting polymer materials include polyacetylene, polyaniline, and polypyrrole. Polypyrrole performs biomimetic actuation at voltages lower than 2 V, and can reach up to 30 MPa active stress and 10% to 26% maximum strains [1-3]. Under electrochemical stimulus the polymer expands as ions flow in and contracts as ions leave. Volumetric change of the polymer depends upon the size of the active species, polymer volumetric capacity, the applied voltage, ionic mobility, and

stiffness.

Applications of polypyrrole may be used over a wide range of temperatures, which can be an important factor to affect actuation performance [4]. Our previous work involving temperature-dependent isometric tests showed an increase in peak stress from 0.2 MPa at 27°C to 7 MPa at 75°C following an exponential trend, and past 75°C the peak stress started to reach a plateau [5]. A similar trend in maximum charge per volume was also observed. We concluded that although stiffness decreased, charge effect largely determined how peak stress changed with increasing temperature (Equation 1) [5]:

$$\sigma = E(\varepsilon_T - \alpha\rho) \quad (1)$$

σ is stress, E is stiffness, ε_T is total strain, α is a strain to charge coefficient, and ρ is the charge per unit polymer volume.

Isometric tests at temperatures above 65°C became difficult because thermal expansion caused the polymer to buckle. Therefore, the true peak stress at high temperatures might have been larger than what we measured. To resolve the buckling problem and further investigate strain change with temperature, this work includes isotonic actuation of polypyrrole between 27°C and 83°C. In addition, since little work has been done to demonstrate how actuation performance can be affected by ionic flow into versus out of polymer under gradually increasing temperature, here we also compare the actuation performance at both positive and negative voltages.

METHODS

The polypyrrole film was electrochemically synthesized using deposition solution composed of 300 mL propylene carbonate, 50 mM tetra-ethylammonium hexafluorophosphate, 1% (v/v) water, and 50 mM distilled pyrrole monomer. The deposition solution was nitrogen saturated. A glassy carbon crucible served as the working electrode while a copper foil was the counter and the reference electrode. The deposition was set up with constant current density of 1 A/m² under -40°C for 12 hours, which resulted in a 40 μ m thick polypyrrole film [5].

Samples were cut from the polypyrrole film and held in between two gold-coated clamps for isotonic actuation tests. The sample between the clamps was measured to be 8.6 mm in length and 2 mm in width on average. Actuation was conducted using a custom-built electrochemical dynamic mechanical analyzer (EDMA) that simultaneously performed electrochemistry and mechanical testing [6]. And an integrated temperature controlled solvent bath was used for heating up the electrolyte 1-Butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF₆) [5]. BMIM-PF₆ was used because only one ion type, the BMIM⁺ ions diffuse through the polymer to cause polymer actuation and this salt has boiling point of above 340°C [7-8]. For approximately every increment of 10°C from 27°C to 83°C, the polymer was applied with +/-0.8 V square electrical pulses at 0.05 Hz for 20 cycles. For each isotonic test, the polymer was held at a constant stress of 1.5 MPa.

For 27°C, 35°C, 45°C, 55°C, 65°C, 75°C, and 83°C, the charge was obtained by integrating the current generated in the polymer. The first five cycles of strain were

eliminated because electrochemical activity in the polymer took some time to equilibrate. Hence for data analysis only the last 15 cycles of strain were averaged. The amplitude was the peak strain and the steepest slope per second was the maximum strain rate. Furthermore, in order to investigate the effect of positive and negative voltages, maximum strain rates of each sample were determined separately for each temperature. The maximum charge per polymer volume was also obtained by averaging the last 15 cycles of the charge curve, with the polymer volume being the measured dimensions $8.6 \times 2 \times 0.04 \text{ mm}^3$. Peak strain, maximum strain rate, and maximum charge per volume were plotted as functions of temperature.

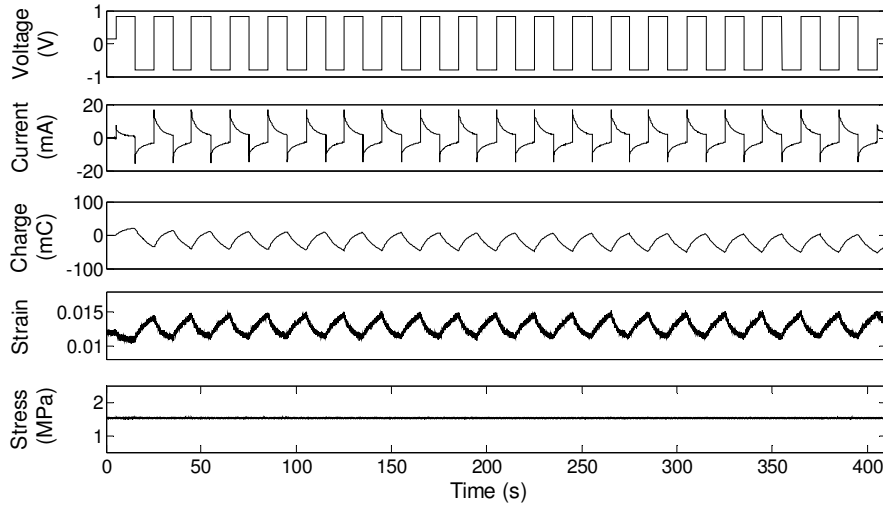


Figure 1. Isotonic results at 27°C that shows voltage, current, charge, strain, and stress versus time. Twenty cycles of square pulses of $\pm 0.8 \text{ V}$ were applied to the polymer.

RESULTS

As $+0.8 \text{ V}$ was applied to the polymer, the BMIM^+ ions were expelled from the sample causing the strain to decrease. As -0.8 V was applied, the BMIM^+ ions were attracted to the polymer. The ion influx caused strain to increase. Figure 1 shows the isotonic results obtained at 27°C. Isotonic results at other temperatures had the same trends in current, charge, and strain.

At $+0.8 \text{ V}$ the averaged strain increased with temperature by 4.8 times, from 0.35% at 27°C to 2.03% at 83°C. At -0.8 V the peak strain increased with temperature by 4.9 times, from 0.34% at 27°C to 2.02% at 83°C (Figure 2, Figure 3). The averaged strain amplitudes at both positive and negative voltages at all temperatures were approximately the same and increased with temperature in an exponential trend (Figure 3).

Similar to peak stress, the maximum strain rate also increased with temperature but with different trends (Figure 4). At $+0.8 \text{ V}$ the maximum strain rate increased exponentially by 5.7 times, from 0.1 %/s at 27°C to 0.67 %/s at 83°C. At -0.8 V the maximum strain rate increased by 3.1 times, from 0.06 %/s at 27°C to 0.23 %/s at 83°C. Past 75°C the maximum strain rate at -0.8 V started to level off. For all temperatures the

maximum strain rate at +0.8 V was higher than that at -0.8 V, and the difference increased with temperature. At 27°C the maximum strain rate at +0.8 V was 0.044 %/s higher than at -0.8 V, and at 83°C the difference increased to 0.44 %/s (Figure 4).

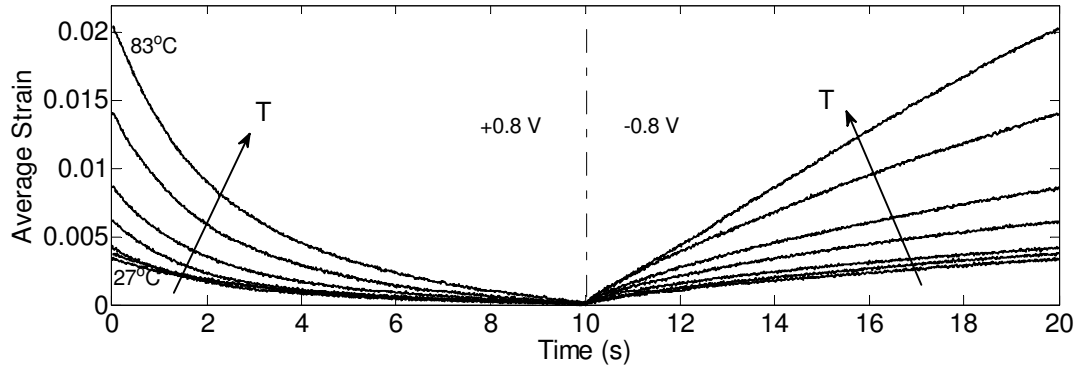


Figure 2. Averaged strain at 27°C, 35°C, 45°C, 55°C, 65°C, 75°C, and 83°C. As the temperature increased the average strain increased. The strain decreased at +0.8 V due to the BMIM⁺ ions leaving the polymer and the strain increased at -0.8 V due to the BMIM⁺ ions entering the polymer.

Similar to maximum strain rate, maximum charge per polymer volume was higher at +0.8 V than at -0.8 V for all temperatures (Figure 5). At 27°C the maximum charge per volume at +0.8 V was 4.5 MC/m³ higher than at -0.8 V, and at 83°C the difference was 11.8 MC/m³. At +0.8 V the maximum charge per volume increased with temperature by 2.4 times, from 11.2 MC/m³ to 38.5 MC/m³. And at -0.8 V it increased by 2.9 times, from 6.8 MC/m³ to 26.7 MC/m³ (Figure 5).

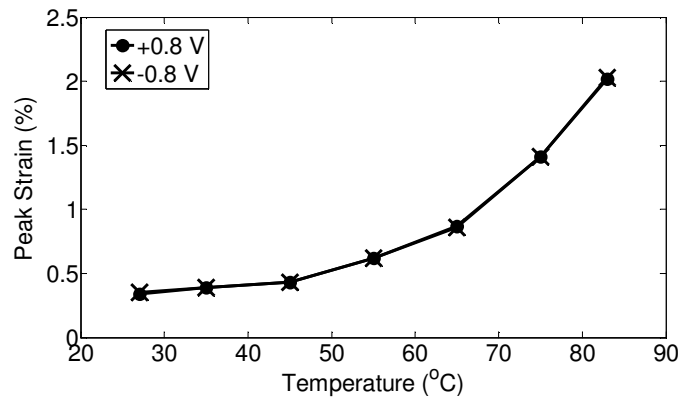


Figure 3. Peak strain at all temperatures at both +0.8 V and -0.8 V were on top of each other. As the temperature increased, peak strain increased by 4.9 times exponentially.

DISCUSSION

Conducting polymers can be used as actuator materials and polypyrrole is one that has attractive mechanical properties. This work demonstrates how elevating temperature

increases actuation strain and strain rate, and how voltage polarity affects actuation performance. According to the results, from 27°C to 83°C the peak strain exponentially increased by 4.9 times independent of the voltage applied to the polymer. At +0.8 V the maximum strain rate was higher than at -0.8 V at all temperatures, and increased much faster with temperature. Similarly, at +0.8 V the maximum charge per volume was also higher than at -0.8 V at all temperature, and increased with temperature faster.

The increases in maximum charge per volume with temperature suggest that heating caused higher ionic mobility, and also allowed more ions to flow in and out of the polymer within the same time frame. Therefore, at high temperatures when the polymer held more ions, the strain was higher than at lower temperatures. And at high temperatures when the ions moved faster in and out of the polymer, the actuation strain rate was higher than at lower temperatures. The exponential temperature-dependent behavior of the polymer can be further explained quantitatively using the charging and the diffusion time constants. The charging time constant is proportional to the solution resistance while the diffusion time constant is inversely proportional to the diffusivity. Both constants were shown previously to decrease with increasing temperature, meaning that the solution resistance decreased and the diffusivity increased [6].

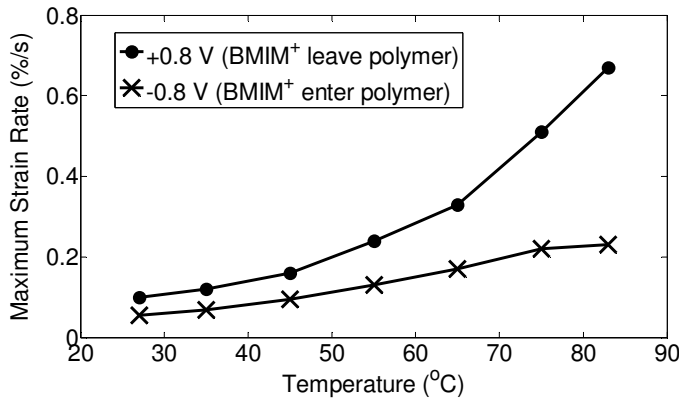


Figure 4.

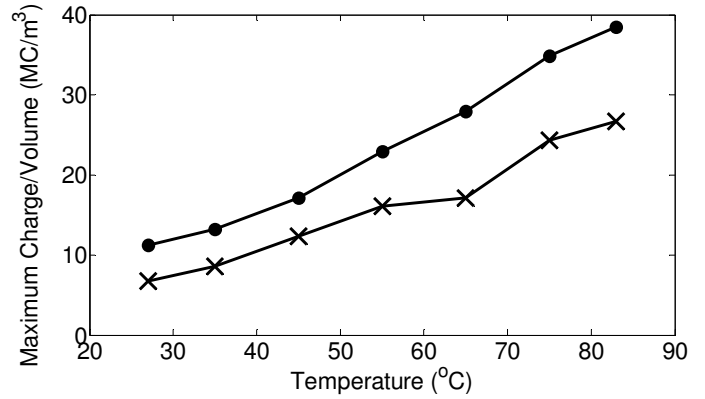


Figure 5.

Figure 4 and 5. Both maximum strain rate and charge per volume at +0.8 V and -0.8 V increased with temperature. For all temperatures, at +0.8 V both had higher values than that at -0.8 V. Figure 4 shows that maximum strain rate at +0.8 V increased much faster with temperature than at -0.8 V.

Based on Figure 4 and Figure 5, both maximum strain rate and maximum charge per volume had greater values at +0.8 V than at -0.8 V. Since the active ion species was BMIM⁺, the results suggest that at +0.8 V the ions preferentially left the polymer to stay in ionic liquid. As the temperature increased, i.e. as the ionic mobility increased, at +0.8 V the BMIM⁺ ions left the polymer even faster than entering the polymer. This explains why the difference in maximum strain rate and maximum charge per volume between +0.8 V and -0.8 V increased with temperature.

CONCLUSIONS

This study showed that with increasing temperature peak strain exponentially increased, and that maximum strain rate increased much faster when ions were diffusing out rather than into the polymer. We did not demonstrate coupling of stiffness and charge effect under increasing temperature because our previous work showed that charge effect more dominantly determined actuation performance [5]. Compared with our previous isometric results, both peak stress and strain exponentially increased with temperature up to about 65°C. The stress trend past 65°C was not conclusive because isometric tests resulted in polymer buckling past this temperature. Moreover, the previous isometric results showed a charge to volume ratio plateau past 75°C, but the isotonic results did not have a plateau. Such discrepancy perhaps results in different thicknesses of the samples and possible variations in deposition process. The average thickness of the polymer for isotonic tests was twice as thick as the film used for previous isometric studies. It is speculated that a thicker film has relatively larger charge capacity and thus allows ion diffusion in higher quantities when temperature was increased while a thinner sample can saturate faster. Future investigation is needed to verify the effect of polymer film thickness.

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