

# Thermo-Mechanical Characterization of Polypyrrole Compliance using Stochastic System Identification.

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**Abstract**—Conducting polymers such as polypyrrole are studied as novel biologically inspired actuators. Their capacity to generate stresses of up to 5 MPa, strains of up to 10% at low voltages (2 V) make them ideal candidates to be used as artificial muscle materials. It has been shown that the modulus of polypyrrole can change when the material is electrochemically excited. In this paper we develop a technique that uses a stochastic stress input that can be used to measure the compliance frequency response (between  $10^{-2}$  Hz and 100 Hz) of polypyrrole in-situ. We validate the compliance calculated from the stochastic stress input by comparing it with the compliance calculated from a single sinusoidal stress input. We also measure the compliance as a function of temperature using both techniques and show that the stochastic compliance follows the same trends as the compliance calculated from single sinusoidal stress input.

## I. INTRODUCTION

Conducting polymers have shown promising applications in many varied applications such as biologically inspired actuators, sensors, pumps etc. To gauge their use as a potential muscle-like material their electrical, electrochemical and mechanical properties have been extensively studied. Actuators developed from conducting polymer such as polypyrrole are electrochemically activated and have been shown to be able to generate active stresses as large as 5 MPa, strains as high as 5-10% and operate at low voltages (1-2 V) [1]. However, it is desirable to optimize the performance of these materials and in particular the total strain and strain-rates that they can generate. Optimizing these parameters will be critical in its further development as an actuator. During actuation, charge is injected into the polymer that causes a volumetric expansion. This volumetric expansion accounts for a large portion of the overall strain generated; however there are some other underlying mechanisms that can also influence polymer actuator behavior. For example, the compliance of the polymer can change as ions diffuse in to and out of the polymer [2]-[7]. Since this is a diffusion dominated process increasing the temperature can lead to higher actuation rates [7]-[10]. If the

polymer is held in tension then the changing compliance can also contribute to the overall strain. The changing compliance can then be considered as another way to increase the overall strain that can be generated by the polymer. However, the effect of the changing modulus on actuation in these situations is not well understood. There are a large number of factors such as plastization by the counter ions, solvent swelling, excitation frequency, which can influence the compliance yet only a few have been explored [2], [11]. There are also a number of discrepancies in the literature that describe the changing compliance of polypyrrole as it is actuated [2]. The in-situ measurement of the compliance during actuation is difficult since there is no simple, fast and efficient way to make this measurement as charge is injected into the polymer. In prior work, we [11] have demonstrated a technique that used a stochastic stress input that can be applied to measure the dynamic compliance of polypyrrole as a function of the charge injected into the material as well as a function of frequency. The stochastic stress input is a high frequency input that is superimposed on a low frequency voltage input. The low frequency component of the strain generated can be removed and the high frequency strain is used to calculate the compliance. The stochastic signal can then be used to decouple competing effects and then it can be used as a powerful tool to study coupled phenomenon. In this work, we further validate the same stochastic system identification technique by comparing it to the compliance calculated at individual frequencies using a sinusoidal stress input. We also apply this technique to determine the thermo-mechanical properties of the compliance of polypyrrole as a function of temperature and frequency.

## II. MATERIALS AND METHODS

### A. Sample Preparation

Pyrrrole (Aldrich 99%) was vacuum distilled before use. Polypyrrole was electrodeposited on a glassy carbon substrate at  $-40^{\circ}\text{C}$  at a constant current density of  $1.0 \text{ A/m}^2$ . The deposition solution used was 0.05 M pyrrole in 0.05 M tetraethyl ammonium hexafluorophosphate ( $\text{TEAPF}_6$ ) in propylene carbonate. The resulting polypyrrole films were peeled from the surface of the electrode and cut in  $2 \text{ mm} \times 10 \text{ mm}$  strips. The thickness of the films were between 10-15  $\mu\text{m}$  and they were tested using a custom built electrochemical dynamic mechanical analyzer (EDMA) developed in [7].

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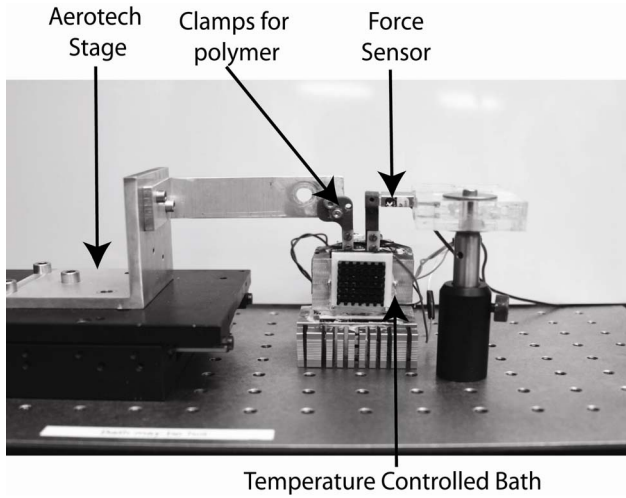


Fig. 1. Electrochemical Dynamic Mechanical Analyzer. Show: Polymer clamping mechanism, temperature control bath with Peltiers effect temperature controllers, Aerotech stage and Futek force sensor.

### B. Experimental Setup

The EDMA (Fig. 1) allows us to clamp the polymer in tension while applying an electrochemical stimulus using a three electrode cell. The temperature of the electrochemical bath is also controlled using a set of stacked Peltier effect thermoelectric temperature controllers (TE Technology). A platinum RTD temperature sensor is immersed in the bath to measure the temperature of the polymer. The temperature is controlled using a PID controller implemented in Visual Basic, the same software also controls the Aerotech stage, the force sensor and a potentiostat. The linear stage (Aerotech, ALS 130) was used to generate a stochastic stress input and the corresponding stochastic strain was measured using an encoder on the stage. The stress input consisted of a stochastic signal having a shaped power spectrum and Gaussian probability density function with mean amplitude of 8 MPa, a standard deviation of 0.5 MPa and a bandwidth of 30 Hz. Linear stochastic system identification techniques [11] [12] were used to estimate the parameters of the compliance impulse response function and the compliance frequency response function of polypyrrole.

$$R_{xx}h_{xy} = R_{xy}, \quad \begin{bmatrix} R_{xx}(0) & R_{xx}(1) & \cdots & R_{xx}(n) \\ R_{xx}(1) & R_{xx}(0) & \ddots & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ R_{xx}(n) & \cdots & \cdots & R_{xx}(0) \end{bmatrix} \begin{bmatrix} h_{xy}(0) \\ h_{xy}(1) \\ \vdots \\ h_{xy}(n) \end{bmatrix} = \begin{bmatrix} R_{xy}(0) \\ R_{xy}(1) \\ \vdots \\ R_{xy}(n) \end{bmatrix} \quad (1)$$

To find the impulse response 40 point auto and cross correlation function estimates were made of the stress and strain and were used to fill the elements of (1), where  $R_{xx}$  is a Toeplitz matrix of the  $n+1$  autocorrelation function values,  $R_{xy}$  is the  $n+1$  cross correlation function estimates and  $h_{xy}$  is the  $n+1$  samples of the impulse response function to be determined. We solve for  $h_{xy}$  using a Toeplitz matrix inversion technique implemented in MATLAB. The dynamic compliance frequency response function may then

be determined from the Fourier transform of  $h_{xy}$  and is normally referred to as the transfer function with magnitude and phase. The magnitude represents the absolute value of the complex compliance of the polymer. This function was calculated using the `tffestimate` function available in Matlab. The coherence squared function [11] can be used to measure the degree to which the system may be represented by a linear dynamic model. It is determined using (2), where  $S_{xy}(j\omega)$ ,  $S_{xx}(j\omega)$  and  $S_{yy}(j\omega)$  are the average cross, stress and strain power spectral densities respectively. If there is any sensor noise or non-linearities present within the system the coherence squared will be less than one.

$$coh^2(j\omega) = \frac{|S_{xy}(j\omega)|^2}{|S_{xx}(j\omega)||S_{yy}(j\omega)|} \quad 0 \leq coh^2(j\omega) \leq 1 \quad (2)$$

### C. Mechanical Testing

An initial test was conducted to measure the compliance using the stochastic stress input. The data were used to calculate the compliance impulse response using the stochastic stress input described in the above section. The data were sampled at 1000 Hz. The compliance was also calculated by applying a sinusoidal stress waveform at single frequencies of 0.1 Hz, 1 Hz, 10 Hz, 20 Hz, 50 Hz and 100 Hz and measuring the corresponding strain. The compliance was then calculated as the ratio of the strain amplitude with respect to the stress amplitude.

### D. Thermo-Mechanical Testing

The polypyrrole strip was immersed in neat 1-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF<sub>6</sub>). The temperature was increased in steps from 27 °C to 85 °C and then cooled to 27 °C. The dynamic compliance was calculated using the stochastic input at different temperatures. The compliance at 1 Hz and 10 Hz was also calculated using a sinusoidal signal in order to compare it to dynamic compliance from the stochastic signal.

## III. RESULTS AND DISCUSSION

### A. Mechanical Testing

Fig. 2 shows the frequency response of polypyrrole compliance between  $2 \times 10^{-2}$  Hz and 500 Hz. The black curve was calculated using the `tffestimate` function in Matlab which was given the stochastic stress input and the corresponding high frequency strain. The grey circles represent the compliance calculated using the sinusoidal stress input at the single frequencies. The compliance calculated in both ways shows the same trend with a constant offset of 20%. This is due to the averaging that is done in the Matlab function `tffestimate`. The compliance calculated by both techniques corresponds very well to each other and also follow the same trends when one goes to frequencies of up to 100 Hz. The coherence squared (Fig. 3) is close to 1 between  $10^{-2}$  Hz and 100 Hz, which implies that the compliance is dynamically linear within that frequency range. Beyond 100 Hz there are

significant noise and/or non-linearity's that degrade the linear dynamic system identification procedure. There are also known mechanical past 200Hz that also degrade the quality of the identification procedure at higher frequencies. The noise comes primarily from the sensors and instrumentation used to characterize the polymer and not from the polymer itself. However, the polymer is rarely mechanically excited at speeds or frequencies that exceed 100 Hz so it is not necessary to measure the compliance at those frequencies.

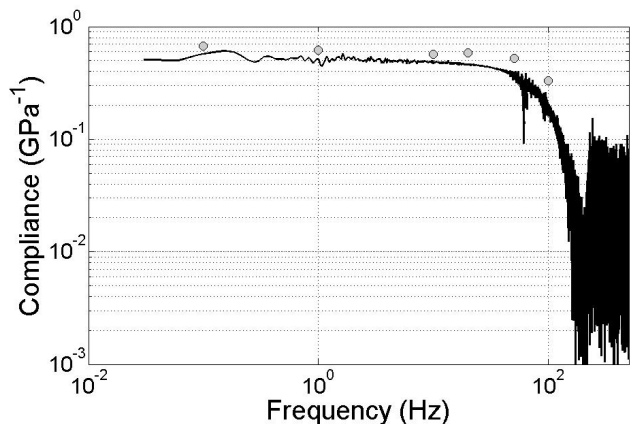


Fig. 2. Compliance of polypyrrole as a function of frequency. The solid line represents the compliance frequency response calculated using the stochastic data and the grey dots represent the compliance calculated using the single sinusoidal inputs.

The coherence squared is lower at frequencies less than 1 Hz because the test lengths are around 100 s. If longer tests are conducted the coherence squared estimates at lower frequencies approach one. The frequency sweep data matches up well with the results of the stochastic input. This shows that the stochastic tests can represent the compliance over a wide range of frequencies and can be used as a powerful technique by which to calculate the compliance.

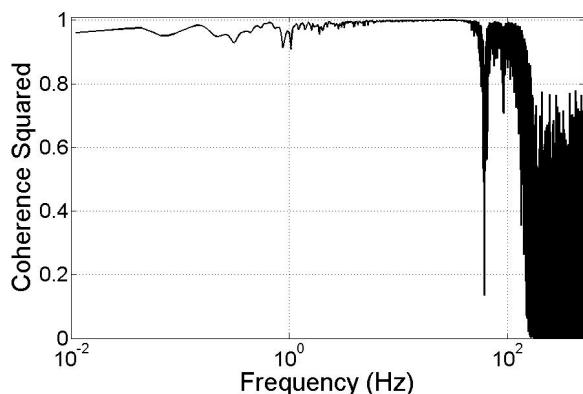
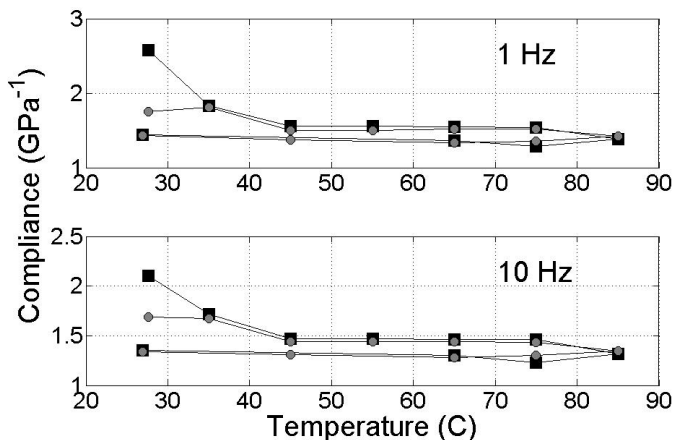


Fig. 3. The coherence squared estimate of the compliance response. The coherence squared estimate indicates that the response is dynamically linear between  $10^{-2}$  Hz and 100 Hz.

### B. Thermo-Mechanical Testing

The compliance of polypyrrole was measured at multiple temperatures using both a stochastic stress input as well as a single sinusoidal input at 1 Hz and 10 Hz. Fig. 4 shows the data collected using both techniques at 1 Hz and 10 Hz as the temperature is increased to 85 °C and brought back down



to 27 °C.

Fig. 4. Compliance measured at 1 Hz using both stochastic and sinusoidal techniques. The black squares represent the data collected using the stochastic input and the grey circles represent the sinusoidal input.

The temperature sweep shows that compliance slowly decreases as the temperature is increased. The data collected from the stochastic input represents more frequencies than those shown in Fig. 4, which shows only a small portion of the response. This shows that the stochastic technique can again capture the compliance data as well as capture the trends in the changing compliance. Also note that the compliance in Fig. 4 is different from the low frequency compliance in Fig. 2 because the sample used to collect the data in Fig. 2 was stored in air for much longer after deposition, which can significantly reduce the compliance as the polymer dries up.

### IV. CONCLUSIONS AND FUTURE DIRECTIONS

We have demonstrated that the stochastic technique can be used to characterize the frequency spectrum of the compliance of polypyrrole. This technique is promising since it can be used in situ during the actuation cycle to calculate the compliance. We will be applying this technique to study the effect of multiple solvents and ionic environments on the compliance of conducting polymers. This can also be applied as a general visco-elastic material characterization tool to characterize the frequency dependence of the compliance.

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