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Tunable polyvinyl chloride (PVC) and thermoplastic polyurethane (TPU)-based soft polymer gel sensors

Justin Neubauer, H Jeremy Cho and Kwang J Kim*

Mechanical Engineering Department, University of Nevada, Las Vegas, NV 89154, United States of America

E-mail: kwang.kim@unlv.edu

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Abstract

Polyvinyl chloride (PVC) gels have recently been found to exhibit mechanoelectrical transduction under mechanical deformation. These mechanoelectrical properties of PVC gels are largely uncharacterized and the underlying transduction mechanisms are currently unknown. These soft electroactive polymers have tunable properties such as modulus and response voltage based on physical dimensions and the amount of plasticizer content within the material making them ideal candidates for complaint sensors. This study aims to investigate PVC gels comprised of various plasticizers to further investigate underlying mechanisms of mechanoelectrical transduction and broaden possible sensing applications. Plasticizers used in this study include dibutyl adipate, dibutyl phthalate, dioctyl phthalate, otherwise known as bis(2-ethylhexyl) phthalate, diisodecyl adipate, and the environmentally friendly biodegradable plasticizer acetyl tributyl citrate (ATBC). ATBC is often used in cosmetics and food packaging applications and is even used as a food additive which may lead to future biocompatibility for these gel sensors. These plasticizers are used to produce PVC gel sensors that are experimentally tested for mechanoelectrical transduction properties and sensing performance. In this study, a Langmuir adsorptive model is fit to the collected mechanoelectrical transduction data. These results are also nondimensionalized and compared to the characteristic dimensionless Langmuir adsorptive model. This simple model agrees very well with the experimental data. Additionally, a study on the mechanoelectrical transduction of an alternative polymer lattice structure, thermoplastic polyurethane (TPU), is discussed. This is a novel electroactive polymer investigated for mechanoelectrical transduction properties. This portion of the study aims to further knowledge of underlying mechanisms of mechanoelectrical transduction as well as show feasibility of additional lattices for soft polymer gel sensors. These TPU gel sensors show strikingly similar mechanoelectrical transduction properties to analogous PVC gels, insinuating that the polymer structure has a limited role in the underlying sensing mechanism and PVC itself is not unique to polymer gel sensing. The TPU-based soft polymer gel sensors however do display some level of mechanoelectrical hysteresis which may be attributed to viscoelastic properties and display a small amount of fatigue possibly due to exudation of liquid plasticizer. This study provides further characterization of mechanoelectrical response for varying plasticizers, provides a theoretical framework for underlying mechanisms, and displays the potential for further polymeric gel sensors.

* Author to whom any correspondence should be addressed.

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Keywords: polyvinyl chloride, thermoplastic polyurethane, polymer, sensors

(Some figures may appear in colour only in the online journal)

1. Introduction

Polyvinyl chloride (PVC) gels are relatively simple materials comprised of PVC and various industrially available plasticizers. Plasticized PVC is used in many applications such as flexible hosing, cable insulation, clothing, and many healthcare products due to its high biocompatibility [1, 2]. PVC gels as a smart material are comprised of a much higher plasticizer content than commercial plasticized PVC products, typically greater than 1:1 PVC to plasticizer ratios by weight. These electroactive polymers have been studied in detail for electromechanical actuation performance [3–6]. There have also been electromechanical studies altering the amounts and types of plasticizers in these polymeric materials to investigate effects on actuation performance [7, 8]. These PVC gel smart materials produce advantageous actuation properties and, due to biocompatibility and dynamic compliance, have been investigated for artificial muscle applications [6, 9–11]. These materials exhibit anodophilic behavior under an applied electric field where the interstitial plasticizer will migrate to a space charge layer. This causes a decrease in modulus in this adsorbed region and a combination of electrostatic and Maxwell stress results in the signature anodophilic actuation. The actuation is described as anodophilic due to the creeping of the gel around the anode. Actuators are typically situated in a stacked configuration of alternating electrode and PVC gel layers to increase overall deformation. In this configuration, these actuators can expect approximately 15% strain. While the actuation performance has been studied in great detail, studies on sensing performance are currently sparse. This study aims to further investigate these mechanoelectrical transduction properties, which are not well understood.

Some preliminary studies show the ability of mechanoelectrical transduction within these gel materials [12–15]. One study contributes this electrical response to piezoelectric-like properties and compares piezoelectric constants of various plasticized PVC films under dynamic cyclical strain applications [12]. However, these materials do result in a steady-state mechanoelectrical response from a constant loading application. An additional study investigated PVC gels under compressive impact loading where a ball was dropped onto gels in an impulse-type loading application which showed the ability of mechanoelectrical transduction with some preliminary investigation of plasticizer dependencies [13]. One study proposed a triboelectric nanogenerator for energy harvesting and tactile sensing, which studies the effects of exposure on the human body on these gel materials [14]. A single study investigating the fundamental mechanoelectrical response of these gels was conducted under compressive loading [15]. This study successfully investigated some basic dependencies such as applied strain rate, plasticizer content, the thickness of the sample, and cross-sectional area. The steady-state mechanoelectrical response seemed to be independent of the applied strain rate in the tested region. Greater plasticizer content resulted in both higher saturated mechanoelectrical response as well as a higher sensitivity in the low force region. The electrical response was not affected by altering the thickness of the sample but was highly dependent on the cross-sectional area. This insinuates that the mechanoelectrical transduction properties of these gel materials are potentially surface-dominated. This previous work begins to uncover major steady-state signal dependencies of PVC gel sensors fabricated with dibutyl adipate (DBA) which this work attempts to extend to other polymer and plasticizer types for further investigation of material and mechanoelectrical transduction properties.

This study aims to expand on the investigation of polymeric gel sensors and analyze other polymers to determine the uniqueness of PVC to these polymer gel materials as well as the role of the polymer lattice in mechanoelectrical transduction. Another polymer gel in this study, thermoplastic polyurethane (TPU), has not been studied for electromechanical or mechanoelectrical properties. These novel electroactive polymer gels observe similar material properties in that there is a polymer lattice with weakly bonded plasticizer to decrease the modulus of the material. This TPU polymer lattice includes long carbon chains similar to that of PVC, stiff aromatic diisocyanates, and urethane linkages. Another key characteristic of TPU is the absence of crosslinking on the lattice structure, comparable to that of PVC. This material was chosen as a gel polymer sensor due to similar chemical makeup and structure, comparable density, comparable solubility properties, and compatibility with plasticizers used in experimentation. A sufficient amount of plasticizer was added to these composite gels to prompt the migration of free interstitial plasticizer under applied mechanical deformation. These polymer materials have not been investigated for electroactive behaviors and provide a foundation for a broad range of polymers to potentially be used in this gel sensing capacity.

The proposed theory of mechanoelectrical transduction in these materials is attributed to adsorptive-like surface phenomena. This theory aims to provide a fundamental foundation for polymeric gel sensors. Adsorption theories attempt to explain the phenomena of dispersed fluids migrating to a solid interface due to changes in chemical potential or concentration [16, 17]. The Brunauer–Emmett–Teller (BET) adsorption model is an adsorption model that can be used to describe liquid adsorption onto a solid surface in multiple layers [18]. This model can be simplified to a monolayer, which is also known as Langmuir adsorption. Langmuir adsorption assumes a single layer of adsorbate onto the solid interface, does not account for the surface roughness of the interfacial layer, and does not consider the interactions between the adsorbed species [19, 20]. The Langmuir adsorption model is commonly used to model

Table 1. List of variables.

Variable	Description
n	Number of adsorptive layers
Θ	Fractional occupancy of adsorptive sites
V_{resp}	Voltage response
c	Concentration of bulk species
K_S	Equilibrium constant of surface layer
K_L	Equilibrium constant of subsequent layers
S_E	Proportionality constant containing electrical packing surface properties

liquid adsorption to a solid interface due to its straightforward nature and ability to predict liquid adsorption performance over a wide range of adsorption phenomena [20, 21]. This relatively simple model has also been used to describe the migration of polar fluid molecules to form polarized interfacial layers [21]. A list and description of varibles used in Langmuir and BET adsorption models is given in table 1. Traditionally the BET model has been used to describe multilayer adsorption of strictly gaseous states onto a solid but has been modified to describe liquid adsorption onto a solid interface as described in equation (1) [22]

$$\Theta = \frac{K_S c\left[1-(n+1)(K_L c)^n+n(K_L c)^{n+1}\right]}{(1-K_L c)\left[1+\left(\frac{K_S}{K_L}-1\right)K_L c-\left(\frac{K_S}{K_L}\right)(K_L c)^{n+1}\right]} \quad (1)$$

where Θ is the dimensionless fractional occupancy of adsorptive sites, and K_S and K_L are the equilibrium constants of the surface and subsequent layers respectively. These equilibrium constants are derived from equating the rate of adsorption and desorption on the respective layers. As the concentration of fluid is increased, this equilibrium constant will increase meaning the rate of adsorption will increase causing saturation at a faster rate. The saturation will occur once all adsorbent sites are occupied, or when the fractional occupancy of adsorbent sites equals one. The number of possible adsorptive layers is the constant n. If n is unbounded, physically meaning there is no maximum of adsorptive layers, the equation reduces to equation (2)

$$\Theta = \frac{K_S c}{(1-K_L c)(1-K_L c+K_S c)} \quad . \quad (2)$$

When n is constrained to a single layer, meaning strictly modeling monolayer adsorption, the modified BET model is simplified to the Langmuir adsorption model and is seen in equation (3)

$$\Theta = \frac{K_S c}{1+K_S c} \quad . \quad (3)$$

This describes the adsorption of a single adsorptive species onto a solid interface, quantified by the fractional occupancy of adsorptive sites, in terms of the bulk species concentration. This equation can also be modified to model competitive adsorption when more than one adsorptive species is present. Another important characteristic of the Langmuir adsorption model is its universality when plotted nondimensionally. When the nondimensional concentration, $K_S c$, is plotted in semi-log space with the adsorption fraction, Θ, all Langmuir isotherms, regardless of equilibrium constant, converge onto the same curve. This curve takes a classic S-shape and has a 'halfway point'. The 'halfway point' occurs when the concentration is equal to the reciprocal of the equilibrium constant, and one-half of the total adsorptive sites are occupied [23].

The surface reactions at a liquid–solid interface may also be influential in PVC gel sensing. Surface interactions, specifically in dipolar fluids, may cause an electric potential. This electric potential may stem from van der Waals, hydrogen bonding, and/or other weak electrostatic interactions. Plasticizers are dipolar fluids that may polarize due to these weak electrostatic interactions at the surface. These fluids have been shown to migrate interstitially through the PVC lattice when under applied electric fields and display mobility of plasticizer within the material [4, 24].

In this study, we aim to investigate the sensing performance of differing plasticizers in PVC gels. The stress–strain relationship and mechanoelectrical transduction properties of each plasticizer type in PVC gels are also explored. The electrical responses of these gels are compared to the Langmuir adsorptive model to potentially explain the underlying mechanism of mechanoelectrical transduction in these materials. The electrical response is currently deemed to be directly proportional to the concentration of dipolar plasticizer near the surface of the electrode. This may be a result of both polarization and/or intermolecular interactions due to electrostatic effects. The collected mechanoelectrical transduction data is nondimensionalized and compared to the Langmuir adsorption curve showing the classic S-shape with the 'halfway point', where the concentration is equal to the reciprocal of the equilibrium constant. Additionally, various plasticizer weight ratios are explored to determine the effect on mechanoelectrical response. Additional work is completed on the viscoelastic hysteresis and fatigue of these soft polymeric gel sensors. Scanning electron microscopy (SEM) imaging was also completed to optically illustrate this adsorptive theory as the underlying mechanism of mechanoelectrical transduction and to additionally show migration characteristics of interstitial plasticizer through the porous polymer lattice.

2. Methodology

Fabrication of these polymer gel materials is comprised of a casting process. The process begins with a liquid solution of tetrahydrofuran (THF) in which PVC powder (molecular weight (M_W) = 80 000 g mol^{-1}) and the respective type and amount of plasticizer is added. TPU (M_W = 85 000 g mol^{-1}) is also soluble in THF, so the solution process is similar to that of PVC when creating TPU gel sensors. In this study, we investigate five separate plasticizers at a P4 ratio, meaning the gel contains a 1:4 PVC to plasticizer ratio by weight. The five plasticizers used in this study are DBA (M_W = 258.38 g mol^{-1}), dibutyl phthalate (DBP, M_W = 278.34 g mol^{-1}), dioctyl phthalate otherwise known as bis(2-ethylhexyl) phthalate (DOP or DEHP, M_W = 390.56 g mol^{-1}), diisodecyl adipate (M_W = 426.67 g mol^{-1}), and the environmentally friendly biodegradable plasticizer acetyl tributyl citrate

Table 2. Fabricated PVC gel samples showing composite weight ratios and naming convention.

Name	P3	P4	P5	P6
PVC: plasticizer ratio	1:3	1:4	1:5	1:6

(ATBC, $M_W = 402.48$ g mol^{-1}). ATBC is also investigated under varying plasticizer weight ratios including P3, P4, P5, and P6 samples as shown in table 2. These plasticizer weight ratios are investigated to show the general trends of soft polymer gel sensors for varying plasticizer weight ratios. Once the contents of the solution are added, the solution is stirred for 4 h. This solution is then briefly placed in the vacuum to remove any trapped gasses introduced during the stirring process. Once the solution is taken out of the vacuum, it is poured into a casting dish. The casting dish is left undisturbed for four days to allow the solvent to evaporate from the solution. The finished sample in the casting dish is then cut using a punch to obtain the experimental samples, which reduces any edge effects incurred during the casting process. The samples used in these experiments were 12 mm in diameter. This process is illustrated in figure 1.

The experimental setup consists of a modified 3D printer for force applications and mechanical deformation. This device provides very fine applications of mechanical deformation and is lowered onto the gel samples in stepped increments of less than 10 μm. This force application mechanism has an integrated load cell (Transducer Technologies GS0-250) with associated copper electrodes. Another advantage of this modified system is the interchangeable load cell to alter the load range of interest. The sample is placed on the lower electrode, and the plunger with the upper electrode attached is incrementally lowered onto the gel sample to apply stepped compressive loading. This mechanism is shown in figure 2 with a magnified region showing the testing area for gel samples.

Raw data is collected using a Keithley DAQ6510 data acquisition and multimeter unit, which is measuring both the load from the integrated load cell and the electrical response of the PVC gel sample by measuring the voltage differential across the electrodes. A sample data set that demonstrates a complete compressive loading cycle can be seen in figure 3. A single exponential time-decaying function is fit to both the load and electrical voltage response data using a nonlinear least-squares regression for all stepped loading applications (equation (4)):

$$y = a\mathrm{e}^{-bt} + c. \tag{4}$$

The exponentially decaying load is equivalent to modeling the material as a standard linear solid (SLS) viscoelastic material model. The stress relaxation that occurs in these materials due to a step in strain can be described from a first order generalized Maxwell model, resulting in the single exponential decay observed in the SLS model [25]. The response is more phenomenalistic but assumes that the electrical response is directly related to the applied load. An example of steady-state estimations for a single load application is seen in the magnified plot in figure 3 for compressive loading applications to a PVC ATBC P5 sample. In this example, the estimated steady-state response is 8.41 mV and the estimated steady-state load is 61.52 g. The 95% confidence interval for the steady-state response is between 8.17 mV and 8.65 mV while the 95% confidence interval for the steady-state load is between 59.59 g and 63.44 g. This data point has the largest confidence interval range among all steady-state estimations in response (0.48 mV) and load (3.85 g).

A dynamic mechanical analyzer (Perkin Elmer Pyris Diamond DMA) was also used to construct a stress–strain relationship for each of the gel samples. The effects of the differing types of plasticizers on the material modulus might differ across tested P4 samples. This was done to isolate the effect of plasticizer type on the material properties of gel samples. Additionally, the weight ratio of these samples may be equal across all tested P4 samples, but the molecular weight of each of these plasticizers differs. This potentially relates to different amounts of free interstitial plasticizer and volumetric differences in plasticizer migration.

Using equation (3), the Langmuir adsorption curve was multiplied by a proportionality constant, S_E, to relate the fractional occupancy of adsorptive sites, Θ, to the mechanoelectrical response, V_{resp}, as seen in equation (5)

$$V_{resp} = S_E\Theta. \tag{5}$$

This assumes the mechanoelectrical response is directly proportional to the surface concentration of adsorbed species. The proportionality constant is a single fitting parameter, S_E, which incorporates effects such as the dipolar strength, molecular packing parameter of the fluid plasticizer, and surface area of the sample in contact with the electrode. In essence, this constant relates the fractional occupancy of adsorptive sites to the electrical potential and is an unknown parameter that is fit using experimental data. Another assumption of this model includes how the applied pressure directly relates to a change in strain, which can be found from the stress–strain relationship in the experimental region. Furthermore, knowing the high compressibility of polymeric chains, such as the ones observed in PVC, and the very low to complete incompressibility of fluid plasticizer, this change in strain may closely relate to a direct change in bulk concentration in this tested region. This model assumes the applied strain directly correlates to a change in bulk concentration of plasticizer content.

The first mechanoelectrical transduction test in this study aims to assess the performance of PVC gel sensors with the five varying plasticizer types. The gels were fabricated with approximately the same thickness (1 mm) and experimentally tested for mechanoelectrical properties. The steady-state response and load were calculated using equation (4). These steady-state results were then fit using the Langmuir curve expressed in terms of the response voltage (equation (6)) with S_E and K_S as fitting parameters via a nonlinear least-squares regression

$$V_{resp} = S_E\frac{K_S c}{1 + K_S c}. \tag{6}$$

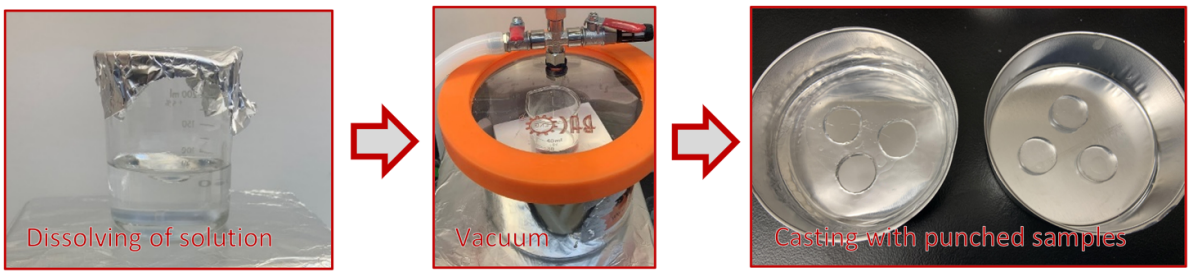

Figure 1. Fabrication of PVC gel samples with various plasticizer content including stirring of dissolved polymer and plasticizer solution (left), vacuum to remove trapped gasses (middle), and pouring into casting dish with completed punched samples (right).

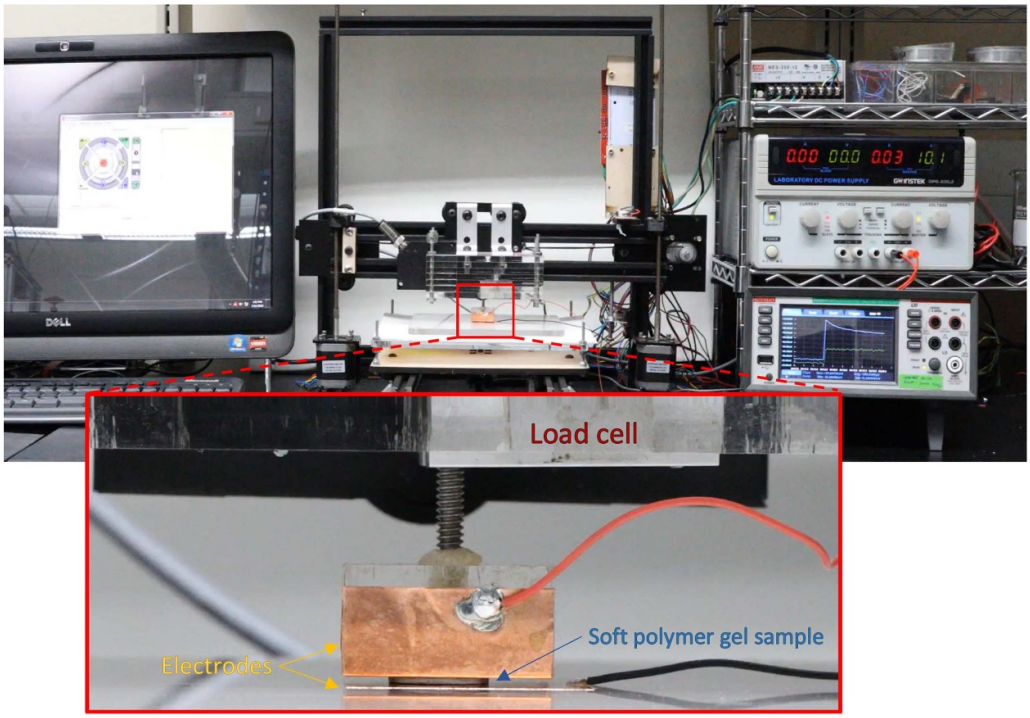

Figure 2. Experimental setup for mechanoelectrical testing of soft polymer gel samples in compression including magnified testing region with integrated load cell, plunger, electrode locations, and soft polymer gel sample.

This shows the characteristic curve for each plasticizer type in PVC gel sensors for steady-state voltage generated from a constant load. The data obtained in this test is then nondimensionalized by dividing V_{resp} by S_E to compare to the Langmuir adsorption curve (equation (3)) and to determine the goodness of fit across many plasticizer types. The next test aims to observe the performance of PVC gels with varying plasticizer amounts. The same equation is used to fit the mechanoelectrical transduction data obtained from samples with varying amounts of ATBC plasticizer. This data is also nondimensionalized and compared to the Langmuir adsorption curve to show agreeableness irrespective of the amount or type of plasticizer. TPU gel sensors are also tested with similar ATBC plasticizer content and compared to PVC gel sensors.

To obtain images from the SEM (Hitachi TM3030), an *in situ* compression stage (200N Deben Tensile Stage) was used to observe the polymer gel sensors under varying compressive strains. The Hitachi TM3030 SEM was used for imaging the adsorptive-like phenomena that is seen in these gel materials under compressive loading. The compression stage was incrementally closed to apply greater compressive loads. The SEM is also equipped with the Quantax 70 energy dispersive x-ray spectrometer, which allows for imaging the distribution and composition of individual elements. The material being imaged is made strictly of PVC (C_2H_3Cl) and ATBC ($C_{20}H_{34}O_8$). The composition of the PVC can be shown through the distribution of chlorine, and the composition of the ATBC can be shown through the distribution of oxygen. This imaging method has an inherent voltage application to the material being imaged, which may alter the gel material itself. This imaging method is strictly used to show the migration abilities in the gel during variable compressive load applications.

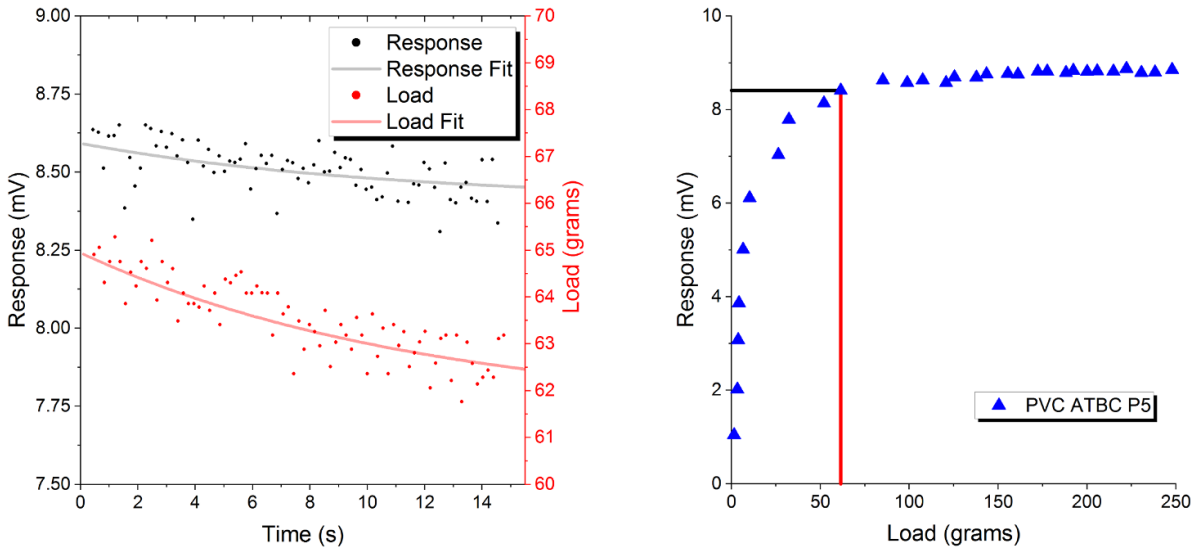

Figure 3. Raw data from mechanoelectrical transduction experimentation including transient response and load with fitting of decaying exponential function (left) for steady-state estimation of response and load in a PVC ATBC P5 sample (right).

3. Results and discussion

The stress–strain relationship was investigated for varying plasticizer types across P4 samples using a DMA, the results can be seen in figure 4. These results show that even though the samples were created using the same weight ratio despite the plasticizer having different molecular weights, the stress–strain relationship of each of the PVC gel samples had similar results. Another interesting characteristic is the pseudo-linear stress–strain plot in this small region of interest. The experimentally tested region for mechanoelectrical transduction includes applied stresses up to 22 000 Pa.

The mechanoelectrical transduction (or sensing performance) of these PVC gel samples was recorded in figure 5. DBP outperforms the other tested plasticizers in this region with the largest overall mechanoelectrical response. DBA, which has advantageous actuation properties, is chemically very similar to DBP and performs similarly. These two plasticizers are the most similar of all tested plasticizers. DBP and DBA have similar volumetric properties on a molecular level (266.9 ml mol^{-1} compared to 273.4 ml mol^{-1}), but DBP has a slightly larger dipole moment (2.83 D compared to 2.49 D). This potentially explains the similar yet slightly larger amplitude in the mechanoelectrical response of DBP. The molecular packing at the electrode interface may be similar, but the dipole moment may affect the mechanoelectrical response, which would support the theory of a polarized surface layer near the electrode. If this potentially small polarized surface layer has a slightly larger dipole moment, then the response amplitude would be slightly larger. DOP performs on the other end of the spectrum. DOP is a very common plasticizer but does not perform nearly as well as the other tested plasticizers in the tested region. DOP has a much higher molecular volume at 394.5 ml mol^{-1} and a dipole moment of 2.89 D. There may also be intermolecular interactions in the polarizing surface layer that affect the overall mechanoelectrical response. ATBC has the lowest rate of saturation and may saturate at a higher electrical response at higher force applications. The Langmuir adsorption fit curve with proportionality constant shows a slightly higher saturation voltage for ATBC compared to DBA. This lower rate of saturation may be advantageous in a certain region of force applications. This provides a tunable gel sensor to provide optimal sensing response for an expected range of mechanical deformation.

The nondimensionalized results can be seen in figure 6. These results show that all plasticizers follow this Langmuir adsorption model curve when plotted in semi-log space, displaying both the classic S-shape and intersecting the ‘halfway point’. This implies that adsorptive-like phenomena are the underlying mechanism for mechanoelectrical transduction in PVC gels independent of plasticizer type. There may be additional interactions causing mechanoelectrical transduction within these polymeric gel sensors, but the phenomena may be predicted with a relatively simple model.

Samples with varying amounts of ATBC were also investigated for mechanoelectrical response in PVC and TPU soft polymer gel sensors. The stress–strain relationship is shown for both PVC and TPU-based polymer gels in figure 7. This testing region shows a very linear compressive modulus for lower weight ratio plasticizers, similar to other P4 samples tested. At larger plasticizer weight ratios, the modulus becomes more nonlinear. TPU gels have a higher compressive modulus compared to PVC gel materials of similar plasticizer weight ratios but show the same correlation of decreasing modulus with increasing amounts of plasticizer.

It has been shown that larger weight ratios of plasticizer result in larger mechanoelectrical response as well as higher

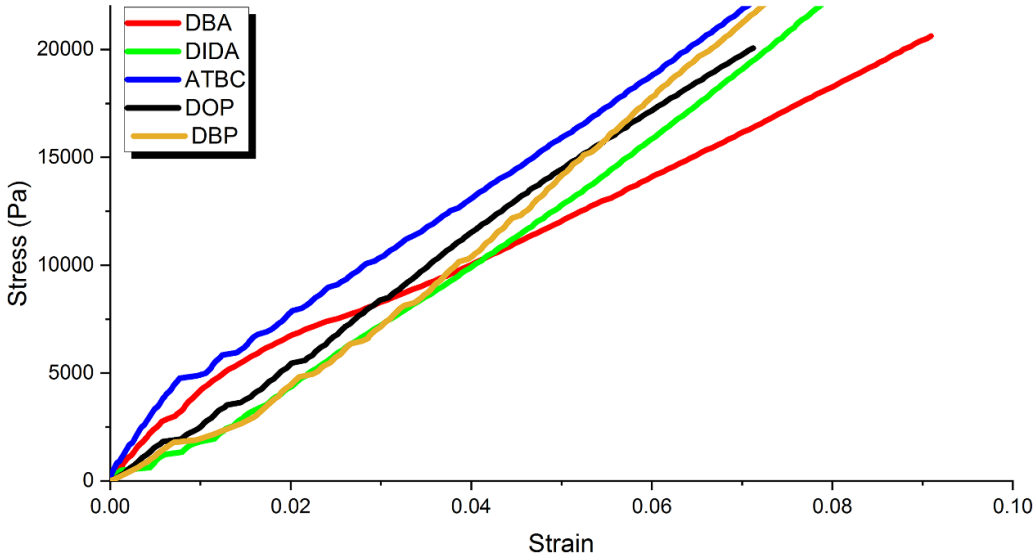

Figure 4. Stress–strain relationship constructed from DMA results for PVC gel samples made from all plasticizers of interest.

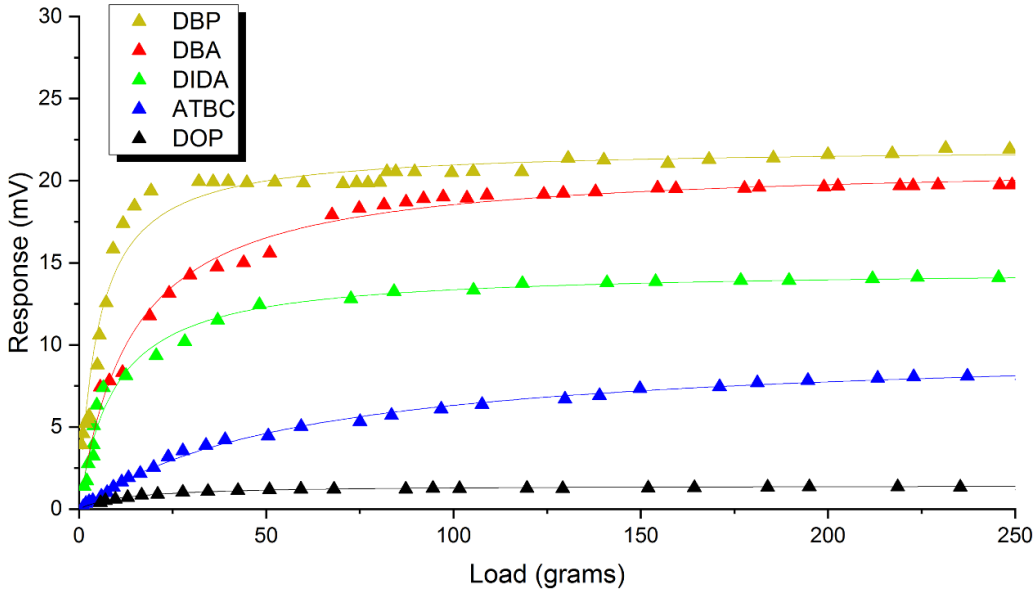

Figure 5. Steady-state mechanoelectrical transduction results for PVC gel samples with varying types of plasticizers.

sensitivity in the low force region, which is seen in this experiment as well, this experiment however extends the force application region to further understand this phenomenon. The results from this study can be seen in figure 8. Once the gel reaches a certain level of plasticizer, in this case P4 and above, the gels saturate at a similar voltage output. This is potentially due to the complete occupancy of adsorptive sites at the electrode interface which is also dependent on the molecular packing parameter at this interface. The molecular packing parameter may determine how many adsorptive sites are available at the interface, but once all sites are occupied the voltage will completely saturate. This parameter is interwoven with molecular volume and morphology. This potentially occurs when the monolayer of polarized molecules at the electrode interface is completely occupied. With insufficient plasticizer, the adsorptive sites may not be completely occupied due to inadequate amounts of interstitial plasticizer, and in turn the sensor will not reach saturation voltage. There may be additional layers being formed beyond the single adsorptive layer at the interface that provides little to no more generated voltage due to this adsorptive mechanism. Once the amount of plasticizer required for saturation voltage is satisfied, in this case approximately P4 weight ratio, adding additional plasticizer results in an increased rate of saturation. This could be due to the mechanical deformation causing a larger change in bulk concentration compared to lower plasticizer weight ratio

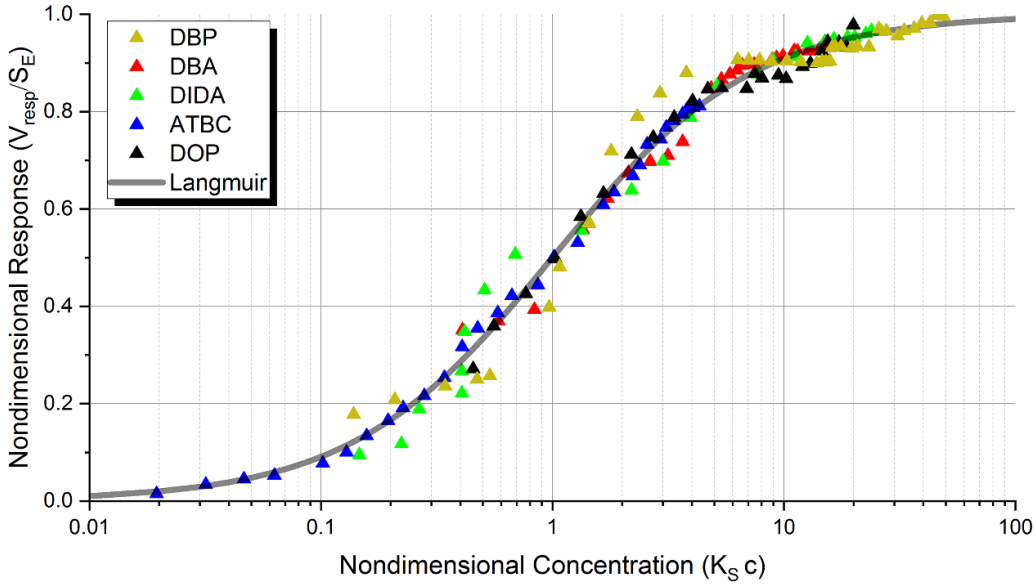

Figure 6. Nondimensionalized mechanoelectrical testing data from samples with various types of plasticizers with comparison to Langmuir adsorption curve (equation (3)).

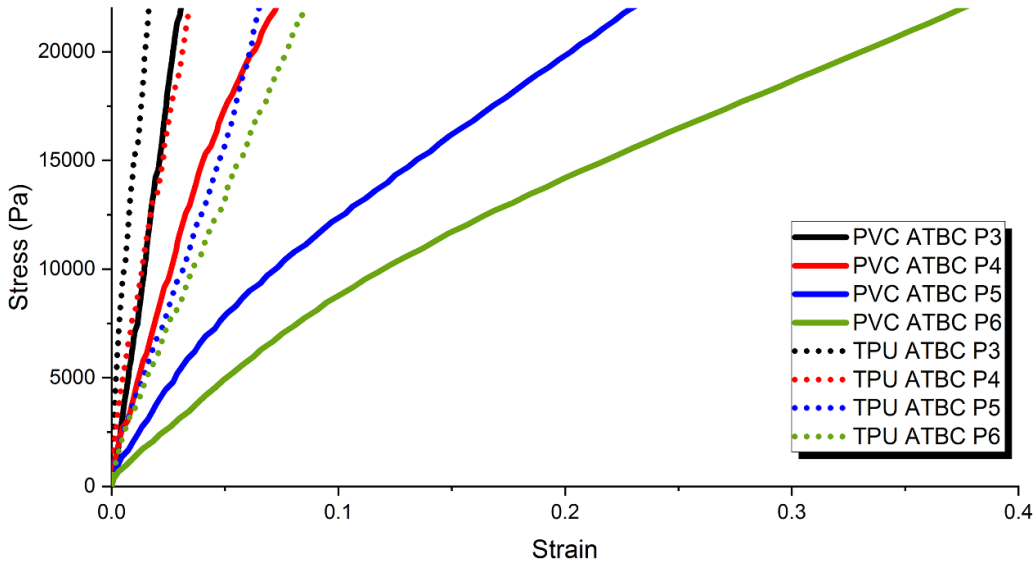

Figure 7. Stress–strain relationship for both PVC and TPU-based polymer gel sensors with varying amounts of ATBC plasticizer.

samples. This is also explained by the Langmuir adsorption-based model.

These results were nondimensionalized as well to show the agreeableness with the nondimensional Langmuir adsorption curve, which can be seen in figure 9. The equilibrium constant, K_S, was derived from each individual Langmuir adsorption fit from figure 8. Once the material reaches sufficient plasticizer to saturate at the maximum voltage response, the nondimensional nature shifts the curve to the right as the plasticizer weight ratio increases. This is due to the increasing saturation rate of mechanoelectrical response as seen in P4 samples and above.

These results for PVC-based polymer gel sensors of varying amounts of ATBC plasticizer were compared to TPU-based polymer gel sensors. The TPU gel sensors had a lower voltage output compared to PVC gel sensors when observing the response against the applied load. This behavior is observed in figure 10. The generated voltage was then compared against the mechanical strain and is shown in figure 11. This shows a very good correlation with the PVC samples when comparing similar plasticizer weight ratios. This also supports the Langmuir adsorption model as a change in strain may directly correlate to a change in bulk concentration of plasticizer. The amount of adsorbed species is directly related

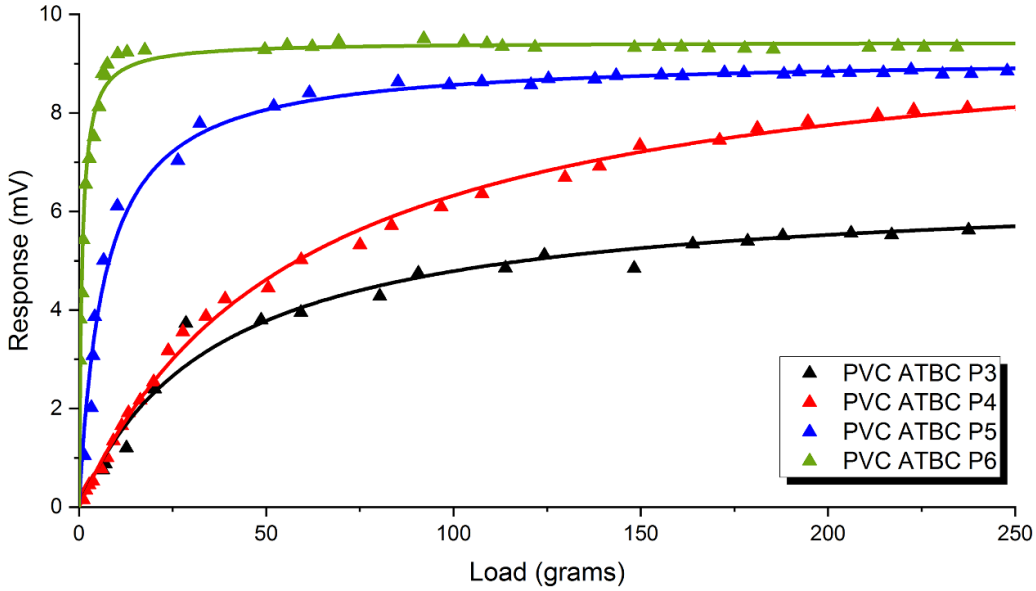

Figure 8. Results from mechanoelectrical testing of samples with various amounts of ATBC.

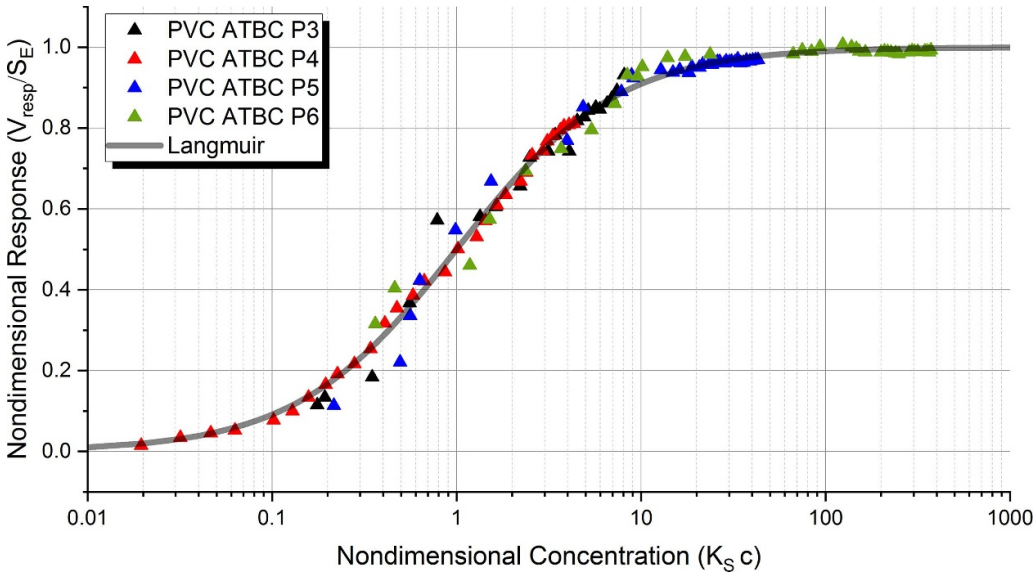

Figure 9. Nondimensionalized mechanoelectrical testing data from samples with various amounts of ATBC with comparison to Langmuir adsorption curve.

to the bulk concentration according to this model. As a result, the non-uniqueness of PVC as a candidate for soft polymer gel sensors is apparent. Given the similarity in mechanoelectrical transduction behavior between PVC and TPU gel sensors, it is apparent that materials other than PVC can be used for soft polymer gel sensors. This foundational study shows the potential for many other polymers to be used in this sensing capacity. This also indicates that the polymer lattice structure itself provides a limited role in the underlying mechanism of mechanoelectrical transduction, demonstrating little to no impact other than altering the modulus of the material. In essence, the mechanical and electrical properties may be decoupled to a degree supporting the adsorptive-like theoretical basis for these materials. In summation, table 3 displays the approximate sensing range in terms of applied stress, sensitivity, and saturation voltage of the PVC and TPU-based soft polymeric gel sensors used in experimentation. The compressive sensing range is given in Pa to show the variation of mechanical properties across differing polymer structures and in terms of strain to show similarities in this regard. This sensing range was determined to be equivalent to 80% of the saturated output voltage in order to easily quantify this range. When above this range, the signal becomes difficult to discern between additional compressive strain applications. The sensitivity is presented in units of mV per Pa which represents the electrical response to a change in compressive stress. This sensitivity is nonlinear throughout the compressive loading application as observed in experimentation, and higher

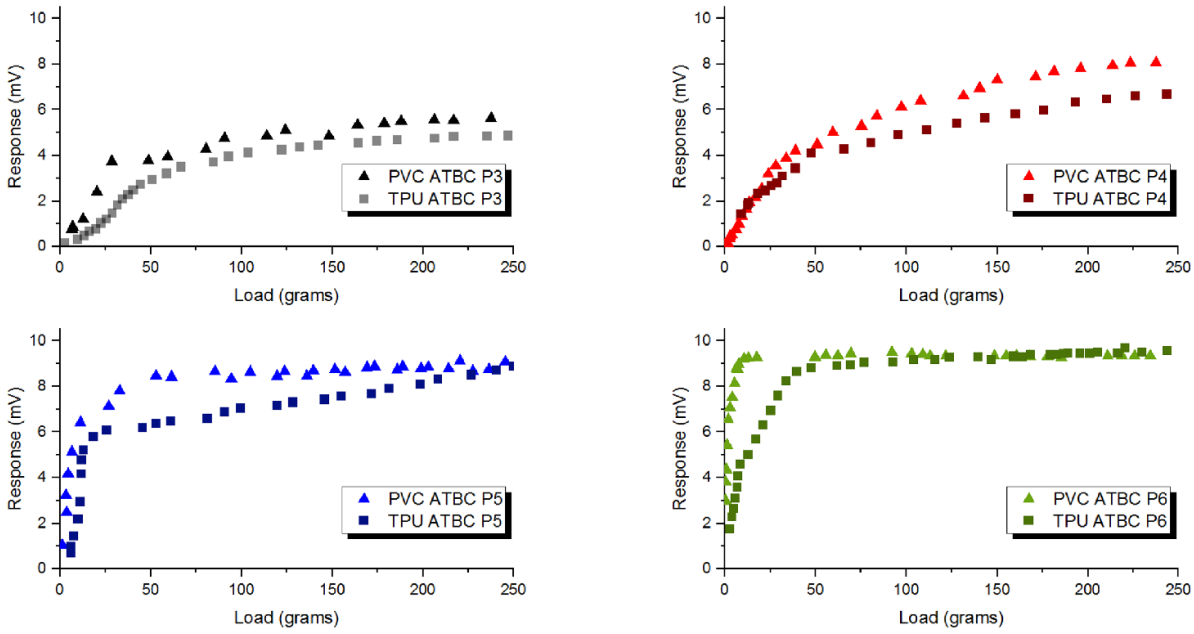

Figure 10. Response plotted against applied compressive force for PVC and TPU-based polymer gel sensors for P3 (top left), P4 (top right), P5 (bottom left), and P6 (bottom right).

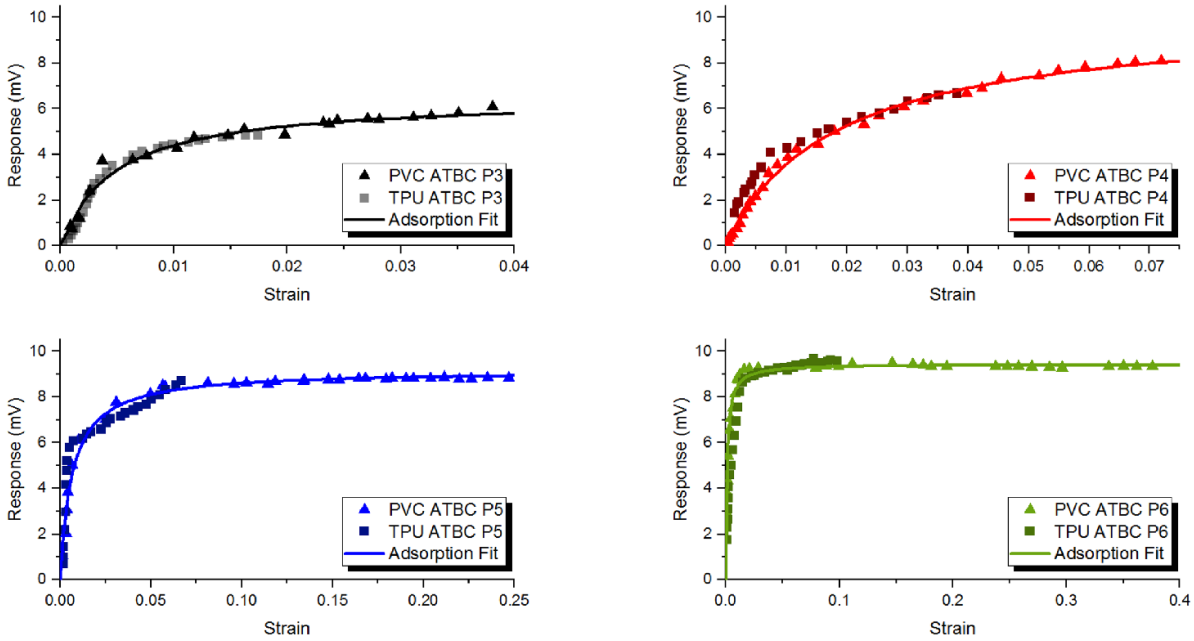

Figure 11. Response plotted against applied compressive strain for PVC and TPU-based polymer gel sensors for P3 (top left), P4 (top right), P5 (bottom left), and P6 (bottom right).

sensitivities are observed under lower loading inputs. This sensitivity was quantified by calculating the average sensitivity across the useable sensing range. Lastly saturation voltage is presented in terms of mV per cross-sectional area. The sensors used in experimentation were 12 mm in diameter, or roughly 113 mm^2. This table reinforces similar saturation voltages across PVC and TPU gel samples of analogous plasticizer content as well as the increase in mechanical modulus in TPU-based soft polymeric gel sensors.

Investigation of the hysteresis and fatigue effects of these sensors was also completed. Additional dynamic mechanical analysis with compressive loading and unloading shows a level of fatigue and hysteresis in both PVC and TPU-based soft polymer gel sensors as seen in figure 12 where n denotes the number of applied loading cycles. The PVC samples seem to have less hysteresis during unloading as well as less observed fatigue at 100 cycles. The TPU gel sensors show higher levels of hysteresis as well as an increase in compressive modulus at

Table 3. Characteristics of PVC and TPU-based polymeric gel sensors.

Polymer	Plasticizer	Weight ratio	Sensing range (Pa)	Sensitivity (mV Pa^{-1})	Saturation voltage (mV mm^{-2})
PVC	DBP	P4	0–1822	0.00966	0.195
	DBA	P4	0–4895	0.00345	0.187
	DIDA	P4	0–3298	0.00354	0.129
	DOP	P4	0–4426	0.00026	0.013
	ATBC	P3	0–21 088	0.00027	0.063
	ATBC	P4	0–20 220	0.00040	0.087
	ATBC	P5	0–2300	0.00318	0.081
	ATBC	P6	0–347	0.02176	0.084
TPU	ATBC	P3	0–22 000+	0.00022	0.060
	ATBC	P4	0–22 000+	0.00030	0.088
	ATBC	P5	0–8643	0.00102	0.078
	ATBC	P6	0–2177	0.00446	0.089

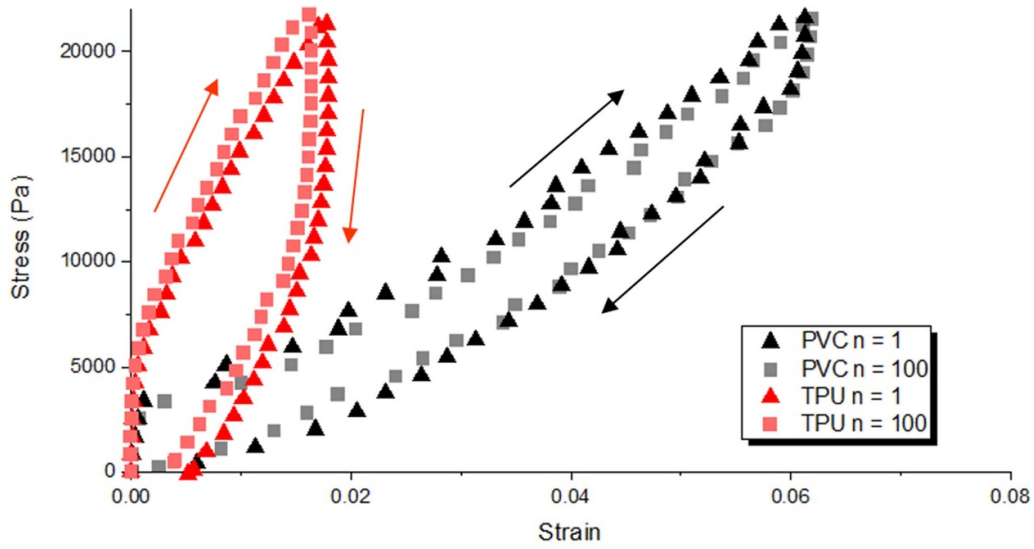

Figure 12. Stress–strain relationship constructed from DMA results for PVC and TPU gel samples made from ATBC plasticizer at a P4 ratio showing hysteresis and fatigue effects.

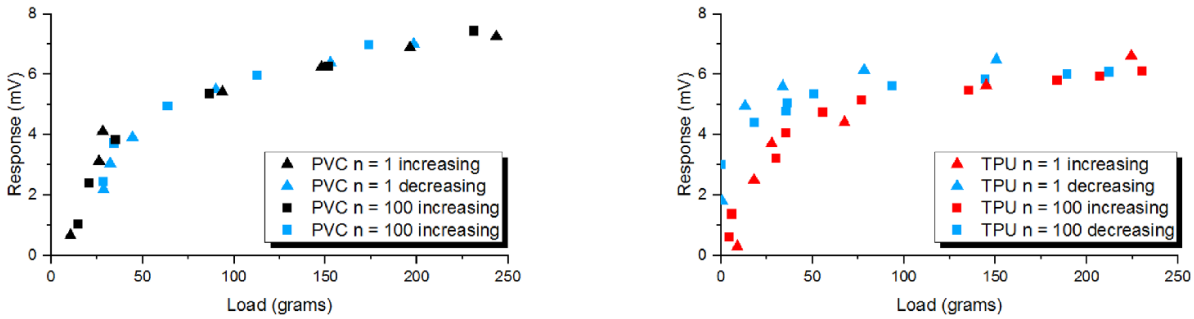

Figure 13. Mechanoelectrical transduction results for PVC and TPU gel samples made from ATBC plasticizer at a P4 ratio showing hysteresis and fatigue effects.

the 100-cycle mark. This may be related to the level of exudation of plasticizer from the polymer lattice. As the polymer exudes plasticizer from the lattice structure, less free plasticizer exists within the material potentially causing an increase in compressive modulus. The effects of this viscoelastic hysteresis and fatigue behavior on the sensing performance is shown in figure 13. The fatigue effects are negligible under the 100-cycle loading application in both PVC and TPU-based soft polymer gel sensors. This is also confirmed by the stress–strain relation observed in figure 12. PVC-based soft polymer gel sensors seem to exhibit very little hysteresis effects throughout compressive loading applications. TPU however

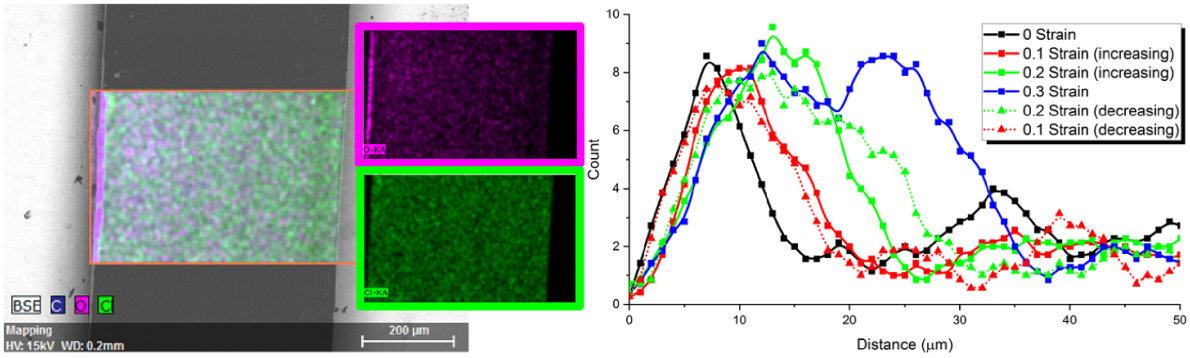

Figure 14. SEM imaging from P4 ATBC sample with increasing amounts of compressive loading from left to right.

does show some noticeable signs of mechanoelectrical hysteresis, particularly when unloading from high levels of compression and is most noticeable under low levels of compression. No noticeable degradation of either polymeric gel sensor is observed in 100 complete compressive loading cycles.

SEM imaging was completed at varying amounts of compression using an *in situ* compression stage. Using the SEM energy dispersive x-ray spectrometer (XRD), the distribution of individual elemental components was also imaged. Using a line scan, the individual elemental components were counted through the thickness during compression as seen in figure 14. It is clear to see the migration of oxygen, which is only found in the plasticizer, as the compressive load is increased. The chlorine, only found in the PVC, is uniformly distributed throughout the compressive loading. This shows the ability of the plasticizer to migrate through the polymer lattice during compression. This compressibility is seen in the polymer lattice during compression as well, which may lead to the change in bulk concentration of plasticizer content. There are inherent flaws with this imaging technique, as the voltage applied during imaging affects the material itself. It should be noted that these images are to strictly show the ability of the plasticizer to migrate during compressive loading applications. Also seen in figure 14, this material shows very little hysteresis in terms of the thickness of the interfacial layer when undergoing compressive loading and returning to the original mechanical state. This is also supported by experimental work seen in figure 13 where very little hysteresis is observed in PVC-based soft polymer gel sensors for a complete compressive loading cycle.

4. Conclusion

PVC and TPU gels were experimentally tested for mechanoelectrical transduction properties. The comparison to Langmuir adsorption curves, specifically when observing the response per strain, shows promising results and alludes to adsorption-like underlying mechanisms of sensing properties. Under this strain comparison, TPU and PVC gels performed very similarly when analyzing analogous plasticizer weight ratios. This suggests that PVC is not unique in enabling gel sensing behavior. Other polymers, such as TPU, undergo the same underlying mechanoelectrical transduction mechanisms, but with differing mechanical properties. Strain inputs were calculated using a stress–strain relation derived from DMA testing for each plasticizer and weight ratio sensor. Nondimensional response plots also show convergence with the Langmuir adsorption isotherm across multiple plasticizers and plasticizer weight ratios. This shows the ability to accurately model and potentially predict the performance of soft polymer gel sensors using the relatively simple Langmuir adsorption model. When comparing similar plasticizers DBP gels had a slightly increased amplitude when compared to DBA gels in the tested region, which may be due to slightly increased dipole moment (2.83 D compared to 2.49 D). Hysteresis and fatigue effects were observed for PVC and TPU-based polymer gel sensors showing some level of hysteresis in TPU-based sensors and negligible degradation over 100 loading cycles. The SEM imaging also shows the porosity of the sensor structure and the ability of plasticizer migration through the porous polymer lattice.

Data availability statement

The data generated and/or analyzed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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Author contributions

J N fabricated all testing samples. J N and K J K designed and performed experiments. J N, J C, and K J K analyzed data. J N, J C, and K J K prepared all figures. The manuscript was prepared by J N and K J K with help from J C All authors reviewed the manuscript.

ORCID iD

Kwang J Kim https://orcid.org/0000-0003-2134-4964

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