

Uniaxial Prestretch Dependence of Dielectric Permittivity in Polyacrylate Elastomers

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ABSTRACT

Dielectric elastomers function on the basis of a voltage-induced deformation for purposes of energy actuation or generation. This deformation can be mathematically explained by the Maxwell stress, the electrostatic pressure that results from the deposit of opposite electric charges on electrodes that sandwiches a dielectric elastomer film in typical applications. Regardless of the purpose, the dielectric constant, also called the dielectric permittivity, directly influences this deformation process. As such, its characterization for prestrain dependency would be crucial to shaping the performance of a dielectric elastomer.

One of the most promising dielectric elastomer has been the polyacrylate VHB elastomer. This report shall focus on the uniaxial prestrain dependence of VHB 4905 elastomer at room temperature. Results collected from a Novocontrol High Frequency Analyzer showed that the dielectric constant decreases with increasing prestretch and frequency. It is also studied that the initial thickness of the elastomer can affect its permittivity in relaxed and non-relaxed static states.

Several numerical models were applied to describe the dielectric constant of VHB 4905 elastomer. First, the prerequisite to establishing uniaxial prestretch dependency is to account for effect of temperature and frequency. This is done so using the well-known Cole-Cole empirical equation. The parameters fitted were then transferred to a second relation in product form with the Cole-Cole equation multiplying a prestretch polynomial. The inspiration for such a model has arisen from past developments where a temperature prefactor was used. The prestretch polynomial's reference values are set at a relaxed state to correspond with the Cole-Cole temperature model, though it can be modified to any other prestretch state due to numerical similarities in permittivity trends.

1. INTRODUCTION

Dielectric elastomers (DEs) are a class of electroactive polymer materials that can have a functional deformation in response to an applied voltage. Due to their large strains, lightweight, and low-cost DEs have seen growing applications in robotics, mechanical and biomedical engineering. Dielectric elastomer is mostly used as both an actuator and a generator for energy conversion in contemporary applications, though there are other miscellaneous usages such as tactile displays.

The working principles of dielectric elastomer actuators (DEA) is illustrated as follows. Fig. 1 shows the fundamental arrangement of a DEA where a membrane of DE is sandwiched in between two electrodes, typically

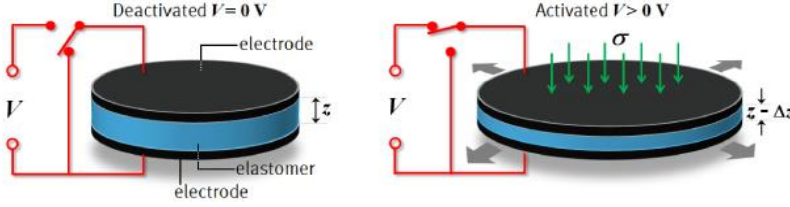


Figure 1: Operation of Dielectric Elastomer Actuator [1]

compliant, which applies a high voltage to induce mechanical deformation. This is made possible by the electric field established so that a compressive stress is generated in the direction of the field.

Quantitatively, this stress is characterized as the Maxwell pressure, σ . It is created by the positive charges deposited on the top surface of the DE film and the negative

charges on the bottom surface of the DE and complies with Eq. (1):

$$\sigma = \epsilon_0 \epsilon_r E^2 \quad (1)$$

where ϵ_r is the relative permittivity of the DE, ϵ_0 is the permittivity of free space, and E is the magnitude of the electric field applied.

From classical electrostatics, the setup in Fig. 1 is recognized as a capacitor. Boundary conditions tells us that $\vec{a}_{n1} \cdot (\vec{D}_1 - \vec{D}_2) = \rho_s$ from which we get the equation $E = \frac{Q}{\epsilon_0 \epsilon_r A} = \frac{V}{d}$ where Q is the charge deposited on each surface, A is the area of the electrode, and d is the thickness of the film. Thus, the Maxwell pressure can be written as

$$\sigma = \epsilon_0 \epsilon_r \left(\frac{V}{d}\right)^2 \quad (2)$$

Assuming the material is isovolumetric, strains in thickness and planar directions can be calculated using Eq. (3) and (4) as below:

$$\gamma_z = -\frac{\sigma}{G} = -\frac{\epsilon_0 \epsilon_r}{G} \left(\frac{V}{d}\right)^2 \quad (3)$$

where γ_z is the strain in the z -direction, and G is relaxation modulus. Additionally we may the strain in the lateral direction, γ_a , with respect to the E -field direction as

$$(1 + \gamma_a)(1 - \gamma_z) = 1 \quad (4)$$

such that $\Delta A = \gamma_a A = (\gamma_x + \gamma_y + \gamma_x \gamma_y) L_x L_y$ where $\gamma_{x,y}$ are Cartesian strains and $L_{x,y}$ are the initial lengths.

The planar strain is the parameter of interest in actuators as voltage is converted to useful deformation. For dielectric elastomer generator (DEG), it is the voltage that we seek to quantify under a release of tension from a pre-stretched and pre-charged state.

Regardless of the mode of operation, dielectric properties affect DE applications. Most noticeably, the dielectric permittivity (or dielectric constant) ϵ_r is a quantity that is directly involved in the process as shown in Eq. (2) and (3). Therefore, the performance of DEs is tied to their dielectric constants, which has been an inspiration for research in the given field.

1.1 Contemporary Research into Dielectric Permittivity

Investigations into DEs were present since the late 1990s. During the years, extensive investigation has been made to the characterization of electromechanical properties in order to determine optimal cycles of operation constrained by modes of failure such as material rupture, electrical breakdown, electromechanical instability, etc. In terms of dielectric properties' research, a popular material to characterize has been the polyacrylate copolymer VHB 4910 produced by the 3M Company in the United States. VHB 4910 has been considered an ideal DE due to its wide accessibility, and preferred dielectric properties.



Figure 2: VHB 4910 Polymer [2]

In general, the dielectric constant can be expressed as a function of temperature, pre-stretch and frequency. The temperature dependence of the VHB polymer has been well researched which will be further discussed in the sections to come. It is the research into pre-strain that has been debated lately with different narratives presented by researchers. The most common pre-stretch tests performed are biaxial in nature; uniaxial pre-strain have also been done though to a lesser extent.

The general trend uncovered relates a decreasing dielectric constant to an increasing frequency. This has been attributed to the decrease in dipole polarization at higher frequencies [3]. In terms of temperature, the dielectric constant is seen to peak at a critical temperature (around 273K for VHB 4910) and then decreased to a relative small value at 373K [3]. Changes are extremely significantly around the glass transition temperature from 233K to 253K. These phenomenon are related to the increase in thermal energy in dipoles and then the subsequent increase thermal random motion that reduces the permittivity as the temperature continues to rise [3]. Numerical models have been established using the Cole-Cole equation that well fits both the temperature and frequency dependence. This model will be later used in junction with a polynomial law first described by T. Vu-Cong et al. [4] to model the prestrain and frequency dependence of dielectric constant at a constant temperature.

1.2 Research Objective

As mentioned above, extensive research is devoted to the classification of properties of VHB 4910 polymer. A similar material that is also widely accessible, VHB 4905 polymer, is however barely mentioned in literature. The 4905 model is identical in composition to 4910 model but half its thickness (0.5mm_{VHB 4905}). Commercially, it is available as a double-sided transparent tape with good adhesive properties but limited number of tests have been done on its behaviour.

In this report, uniaxial prestretch testing is done on VHB 4905 polymer and subsequently compared to similar tests done on VHB 4910. Key reasons for choosing uniaxial prestrains in testing for changes in permittivity is due to the lack of such tests done in VHB 4910 where biaxial testing is more prevalent, and to infer any possible connections between initial sample thickness to the values of permittivity measured.

2. EXPERIMENTAL SETUP AND APPARATUS

2.1 Preparation of Samples

The 3M VHB 4905 samples used in this investigation were commercial adhesive tapes, as shown in Fig. 2. To achieve consistent results, samples were prepared under identical room temperature of 22°C. During the experiment it was found changes in the original stretch area affected the measurements, though not to a significant degree. As a result, all samples tests were initially 30mm x 50mm x 5mm in dimensions which was found to produce optimal results. Static prestretch was done on a universal testing machine (UTM) where the sample was held fixed on the 50mm side with 2 laser-cut rectangular frames that ensures uniform force application.

As with previous experiments [4], it is most desirable to keep the entire process at quasi-equilibrium so to avoid any material instability or anisotropy. Strain rate of the UTM was set at a speed of 1mm/sec with a pre-determined termination strain percentage. Thickness in the given experiment was measured by a micrometre with a precision of 0.1µm.

Table 1. Thickness of Uniaxial Prestrain VHB 4905 Elastomer

Elastomer	Static Uniaxial Prestrain Factor, λ	Measured Thickness (mm)
3M VHB 4905 Polymer	1.00	0.520
	2.00	0.330
	3.00	0.240
	4.00	0.230
	5.00	0.205
	6.00	0.195
	7.00	0.180

Once the elastomer has been prestrained, two additional acrylic frames with attached gold-plated electrodes were applied on to the sample. The acrylic frames serve to minimize the occurrence of air gaps in between the interface of the sample and the electrodes. Additionally, when the frames were initially fabricated, a design element incorporated was its ability to minimize the fringing effect of the electric field near the edges of the electrodes that shall lead to parasitic capacitance [4]. It is also important to consider minimizing the dust falling onto the VHB during preparation as it will interfere with the dielectric measurements which was accounted for in the experimentation. A total of 7 prestretched were tested under such conditions with the results given on Table 1.

2.2 Dielectric Measurement

For each sample, the dielectric spectroscopy was performed using a Novocontrol Alpha-A High Frequency Analyzer. Frequency was set from 0.1Hz to 0.3MHz, covering all usual frequency range of dielectric applications. For each pre-strain 3 different samples were taken to average out the results. The sweeping direction was chosen from high to low, i.e. starting from 0.3 MHz and ending at 0.1Hz, to minimize the effect of dipolar rotation's time-response which may be attributed to Mullin's effect.

3. RESULTS AND DISCUSSION

3.1 Effect of frequency and uniaxial prestrain on VHB 4905 polymer

Permittivity of VHB 4905 elastomer is greatly influenced by both frequency and pre-stretch. Dielectric constant values were almost constant from [0.1 Hz, 1000 Hz] forming a plateau before decreasing at high frequencies (Fig. 3). The contour plot of permittivity versus frequency and prestretch shows that this decrease maintains linearity beyond 10^4 Hz from $\lambda \in [1,4]$. A summarizing trend would be that dielectric constant decreases with increasing frequency in VHB 4905 model.

A similar effect was observed in the material's prestrain strain dependence. Overall, as the uniaxial prestrain increased the permittivity decreased, however, there are deviations from this general trend. A relative large drop in dielectric measurements in transition from 400% to 500% prestrain was recorded. Compared to studies in literature (K. Patra [5]), the VHB 4910 under similar static prestrain did not experience such abrupt change. The most noticeable deviation observed was that of a local maximum attained by the dielectric constant at 100% prestretch before precipitating a monotonic decrease in permittivity.

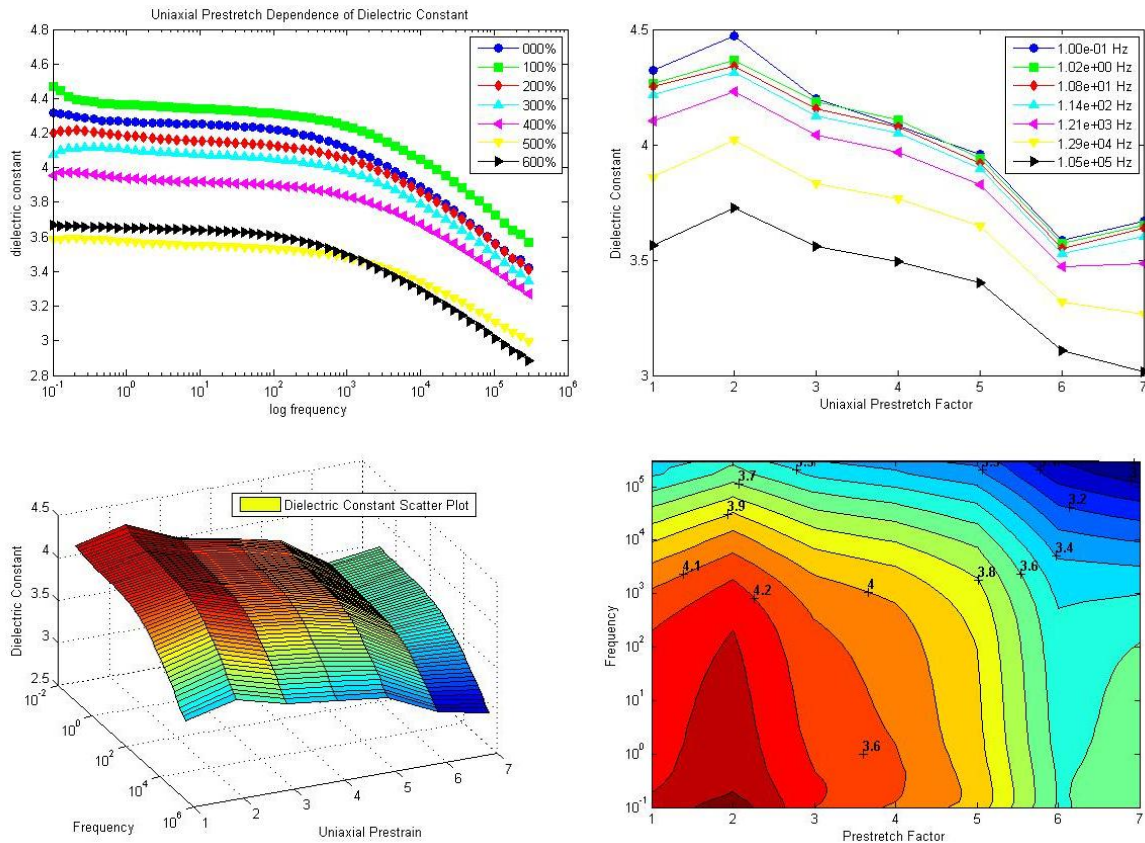


Figure 3. a) Frequency and b) uniaxial prestretch dependence along with c) surface scatter plot and d) contour of dielectric constant at various uniaxial prestretch factors

The existence of such a peak at 100% prestrain ($\lambda = 2$), and the direct difference in permittivity measured in relaxed state between VHB models 4905/10 suggests that dielectric constant is also influenced by initial sample thickness. Investigations done by K. Patra [5] on VHB 4910 model showed that its dielectric constant attained a maximum value at $\lambda = 1$ with $\epsilon'_{VHB\ 4910} \cong 4.7$ at low frequencies while the current results showed that the $\epsilon'_{VHB\ 4905}(\lambda = 1) \cong 4.3$, an approximate 15% decrease. Moreover, the report finds a slight ramp up in VHB 4905's dielectric permittivity at 600% ($\lambda = 7$) prestretch (in fig. 3b) which is not seen in Patra's results.

The two investigations both converged on the fact that there is less polarization at both high frequency and prestretch; implying reduced diffusion of dipoles toward the applied electric force field [5]. Thus it can be said that the two parameters induce similar effects.

3.2 Theoretical connection between prestretch and permittivity

Although there exists no physical model to completely describe the collective behaviour of electroactive polymers, there are underlying theoretical principles that may be part of the rationale in explaining the observed phenomenon in dielectric permittivity. To begin understanding these connections, it is important to consider the dielectric relaxation process in VHB 4905 from its own classification.

Normalized dielectric relaxation can be described from the following integral relation that associates measured permittivity to its limiting value at high frequencies as [6]:

$$\frac{\varepsilon'(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty -\frac{d}{dt} \frac{\langle \bar{\mu}(0) \cdot \bar{\mu}(t) \rangle}{\langle \mu(0)^2 \rangle} \exp(-i\omega t) dt \quad (5)$$

where $\varepsilon'(\omega)$ is the permittivity measured at frequency ω , ε_0 is the permittivity of free space, ε_∞ is the limiting value as $\omega \rightarrow \infty$. $\bar{\mu}(t)$ represents the dipole moment of the polymer chains at time t . According to the Stockmayer terminology, polymers can be grouped into 3 categories, each with a particular microscopic description as given below.

Table 2. Classification of amorphous polymers and their dielectric relaxation process (R Diaz-Calleja [6])

Classification	Type A	Type B	Type C
Characteristics	Structural units of the polymer chain are parallel to the chain contour	Contains polar polymer chains that are rigidly attached to the polymer backbone	Contains polar polymer chains separated from backbone by flexible segments
Stretching Effect	$\bar{\mu} \sim \bar{r}$	$\langle \bar{\mu} \cdot \bar{r} \rangle = 0$	
Dielectric Relaxation Process	Correlation function can be expressed in terms of \bar{r} vector	No correlation between stretching and dipole moment; implying from a dielectric relaxation perspective stretching should not have an effect on permittivity, theoretically.	

Note: \bar{r} represents the end-to-end distance vector of the polymer chain.

Since VHB 4905 model is a type C polymer then we can see that even if stretching was performed, an increase in \bar{r} does not necessarily translate into any significant changes of moment that may influence the measured dielectric constant [6]. But this is contrary to the phenomenon observed where ε' depends on both frequency and prestretch. Despite research efforts made into deepening the relevant theoretical understanding, the exact cause is still unclear. It has been reported in literature that changes in permittivity may be due to two reasons:

- 1) Crystallization of the dielectric elastomer
- 2) Shift in rubber-glass transition temperature

These have been reported by R. D-Calleja and E Riande in their commenting paper regarding influence of stretching on dielectric permittivity [6].

3.3 Accounting for temperature effect in the relaxed state

The first step in establishing a mathematical model for the dielectric constant is to account for temperature dependence of the very quantity in the relaxed state. In the experiment, all samples were kept and tested at 22°C room temperature. Although the temperature remains uniform through all tests, its influence cannot be neglected.

Presently several models exist that can be used to describe the variation of permittivity with respect to temperature. These include the Debye Model, Cole-Cole Equation, HN (Havriliak and Negami) Model, etc. Based on numerical comparison done by Junjie Sheng et al [3], Cole-Cole equation produces the best results for VHB elastomers. The precise reasoning has been that the Cole-Cole empirical formula can account for the distribution for relaxation times, where VHB has possesses at least three relaxation times [3].

Using this model, we can acquire the needed fitting parameters to describe the dielectric behaviour at room temperature. The equation used and the results are shown below.

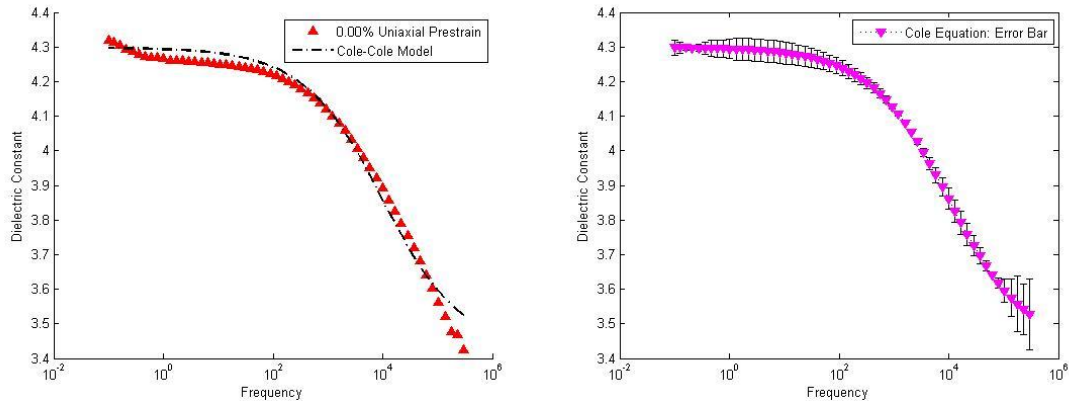


Figure 4. a) Cole-Cole equation and b) error bars of model regression

$$\text{Cole-Cole Model Equation: } \varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (i\omega\tau)^\beta} \Leftrightarrow \varepsilon'(\omega, \tau) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \frac{1 + (\omega\tau)^\beta \cos(\frac{\beta\pi}{2})}{1 + 2(\omega\tau)^\beta \cos(\frac{\beta\pi}{2}) + (\omega\tau)^{2\beta}} \quad (6)$$

Parameter Description: From Eq. (6), ω is the angular frequency of the applied electric field, ε_∞ is the limiting value of the dielectric permittivity at high frequencies, ε_s is the static dielectric constant (plateau value at low frequencies), β is an empirical fitting parameter.

The parameter τ represents the relaxation time and can be expressed as a function of temperature according to Arrhenius law

$$\tau = \tau_0 \exp\left(\frac{E}{RT}\right) \quad (7)$$

where τ_0 is a prefactor, R is the gas constant, T is the absolute temperature, and E is the activation energy of the relaxation process.

Using MATLAB's `fittpe()` module, a non-linear anonymous function was defined to be fitted with the input data. Based on the empirical cumulative distribution sampled, a 95% confidence interval was constructed for each parameter fitted. This procedure was applied to the multivariable surface fitting in the section below. The table summarizes the obtained parameters.

Table 3. Cole-Cole Model Parameter Fitting Results

Coefficient	Mean	95% Confidence Interval
$\alpha = \tau^\beta = \tau_0^\beta \exp\left(\frac{E\beta}{RT}\right)$	0.00346	(0.002416, 0.004505)
β	0.5137	(0.4865, 0.5410)

It is important to take note although β was the only parameter that has to be fitted, $\alpha = \tau^\beta$ was also treated as another fitting coefficient due to uncertain activation energy for VHB 4905 model. Thus actual fitting equation became

$$\varepsilon'(\omega, \tau; \alpha, \beta) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \frac{1 + \alpha\omega^\beta \cos\left(\frac{\beta\pi}{2}\right)}{1 + 2\alpha\omega^\beta \cos\left(\frac{\beta\pi}{2}\right) + (\alpha\omega^\beta)^2} \quad (8)$$

Model Effectiveness: From fig. 4a) and b) the Cole-Cole Model satisfies the data well in terms of errors encountered. In fig. 4b the maximum error until 10^5 Hz was around 2%, representing high effectiveness for the model.

3.4 Mathematical model of joint frequency and uniaxial prestretch dependence at constant temperature

Using the Cole-Cole equation from Eq. (6) as a key foundation, a model to describe the dual dependency of dielectric constant on frequency and uniaxial prestretch would only be complete with the finding of a suitable and separable function relating to the prestretch factor. Fortunately, there already exists such attempts in literature. T. Vu-Cong et al [1] used a temperature prefactor expression multiplied by a direct linear polynomial law in terms of two biaxial prestretch factors to account for prestretch. Taking a modified approach, that original temperature prefactor is now swapped with the much more sophisticated Cole-Cole model to account for temperature and frequency. The simple Debye model was used to account for temperature influence that formed this prefactor in the previous work. This is inadequate because Debye model is more accurate in the high frequency range rather than across the frequency spectrum. It also cannot capture the distribution of relaxation times in VHB as was mentioned already. Materializing this new mathematical model to include the effect of uniaxial prestretch, dielectric constant can now be written in the following form:

$$\varepsilon'(\omega, \lambda, T) = \varepsilon'(\omega, \tau)p(\lambda) \quad (9)$$

$$p(\lambda) = 1 + \sum_{i=1}^n c_i (\lambda - 1)^i \quad (10)$$

where $\varepsilon'(\omega, \tau)$ is permittivity expression from the Cole-Cole model, and $p(\lambda)$ is the prestretch polynomial expressed in terms the final prestretch factor λ .

Parametric Description: Concentrating on the pre-stretch polynomial $p(\lambda)$, using numerical analysis it is found that a quintic expression would yield the smallest error without having a much longer formula. Again using the same procedure as described for the Cole-Cole model fitting, the results are summarized below.

Table 4. Cole-Polynomial Model

Coefficient	Mean	95% Confidence Interval
c_1	+ 0.01631	(+ 0.005915, + 0.026700)
c_2	- 0.002567	(- 0.011600, + 0.006468)
c_3	- 0.003953	(- 0.006386, - 0.001521)
c_4	+ 0.0005351	(+ 0.0003310, + 0.0007391)

Model Effectiveness: The adoption of a product law involving a polynomial to describe the prestretch and a well-established Cole-Cole empirical formula models the dielectric dependency at constant room temperature relatively

well. The error contour shows that the maximum error is typically very small ($< 3.0\%$). The maximum error encountered is 5.05% at room temperature. It can also be noted that the Cole equation is originally designed to fit the data in the relaxed state. Due to identical permittivity trends shown in fig. 3a and 3b, this equation may also be applied at a non-relaxed mode (say $\lambda = \Delta$) then the prestretch polynomial becomes $p(\lambda; \Delta) = 1 + \sum_{i=1}^n c_i(\lambda - \Delta)^i$.

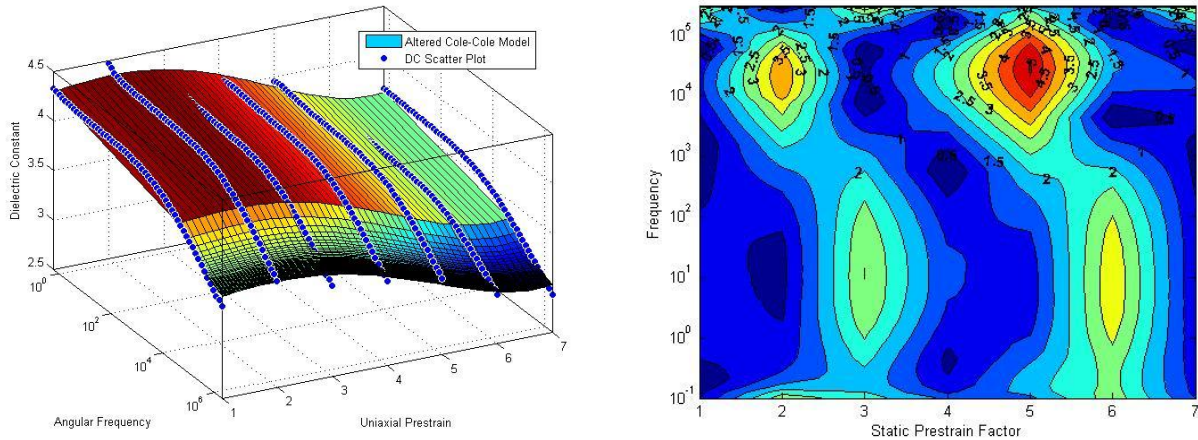


Figure 5. a) Cole-polynomial surface fit and b) associated error contour of dielectric constant model

4. CONCLUSION

During this study, the report investigates the dielectric behaviour of VHB 4905 elastomer, a material that is identical but half the thickness of the most used dielectric elastomer: VHB 4910 polymer. The collected results have suggested although that the two elastomers are chemically similar in composition the reduction in original sample thickness led to a decrease in both the relaxed and prestretched states. This implies that the sample thickness can be an influential factor in controlling a given electro-active polymer film's permittivity. There may be future applications where the sample thickness is manipulated for better dielectric performance. As such it is highly recommended that tests be done with films of different initial thickness to better explore this possibility. The results have also suggested that besides thickness influence, VHB 4910 and 4905 models share similar frequency and uniaxial prestretch dependencies. To better understand the changing nature of the dielectric constant in the face of such factors, the report presents a new mathematical model that may be used to estimate the permittivity at constant temperature. This is achieved by using Cole-Cole empirical model and a polynomial law to describe prestretch.

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