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Layer confinement effect on charge migration in polycarbonate/poly(vinylidene fluoride-co-hexafluoropropylene) multilayered films

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Forced assembly microlayer coextrusion was used to produce polycarbonate/poly(vinylidene fluoride-co-hexafluoropropylene) [PC/P(VDF-HFP)] layered films for dielectric capacitor applications. Low field dielectric spectroscopy was systematically carried out on the layered films and controls. A low frequency relaxation was found that shifted to higher frequency and decreased in intensity as the (P(VDF-HFP) layer thickness was reduced. The interfacial Maxwell-Wagner polarization, being layer thickness independent, could not account for this reduced low frequency relaxation behavior as the layer thickness decreased. Charge diffusion models by Sawada and Coelho, however, satisfactorily predicted the observed layer thickness effect, indicating that the migration of impurity ions in the (P(VDF-HFP) layer caused the low frequency relaxation. A new, convenient fitting procedure was developed for the Sawada model yielding an ion concentration and diffusion coefficient of $2 \times 10^{21}$ ions/m$^3$ and $2 \times 10^{-13}$ m$^2$/s, respectively, for films with layer thicknesses of 430 to 50 nm. Thicker layers of 7000 nm had significantly different diffusion parameters, which were attributed to differing crystal orientations in the P(VDF-HFP) layers. These findings show that low ion concentrations, whether from catalyst residue and processing or intentionally added, significantly affect the dielectric properties and can play a vital role in many applications (i.e., LCD displays, solar cells, light-emitting electrochemical cells, capacitors).

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I. INTRODUCTION

Microlayer coextrusion has been used to produce a wide range of layered polymeric structures with enhanced mechanical, optical, transport, and dielectric properties. When the layer thickness is reduced to the micro and nanometer scales, profound property changes often occur. In the field of dielectrics, submicron thick layers of a poly(vinylidene fluoride-co-hexafluoropropylene) copolymer [P(VDF-HFP)] combined with polycarbonate (PC) exhibit enhanced dielectric properties. The enhanced breakdown strength and energy density are often attributed to a barrier effect whereby layers and interfaces impede the propagation of a breakdown channel, which is evidenced by unique treeing patterns around the failure site. In the present work, low-field broadband dielectric spectroscopy (BDS) measurements were carried out and revealed a low frequency relaxation that changed with layer thickness.

Similar dielectric phenomenon at low frequencies and high temperatures (i.e., a sharp increase in the dielectric loss and storage) have been reported. Some researchers have proposed that dc conductivity is responsible. Others attribute the anomalous behavior to ionic conduction, where ionic impurities migrate in response to an applied electric field. In both cases, this effect has important practical implications because polymeric materials are used in a wide range of electronic applications (i.e., electrical insulation, capacitors, liquid crystal displays (LCDs), and semi-conductor materials). In insulating materials, it is desirable to remove and prevent the generation of charge carriers that may cause ionic or dc conduction. In other applications, however, ionic impurities are added to exaggerate and exploit ionic conduction; several examples include double-layer electrochemical capacitors, membranes, light-emitting electrochemical cells, and solar cells. The ions serve to increase the conductivity, create interfacial charge build up, and alter the band-gap distributions.

In order to determine and study the mechanism responsible for the low frequency dielectric relaxation in PC/P(VDF-HFP) layered films, a series of layered films and controls were produced using microlayer coextrusion. The high flexibility of this processing technique enables it to be an ideal technique for studying ion migration phenomenon in polymers. This processing method has the capability of combining 2 or 3 polymers in an ABABABAB or ABCBABCB configuration creating films with 2 to 4096 layers and layer thicknesses ranging from tens of microns down to less than 10 nm on a continuous basis. Because diffusion models predict that decreasing layer thickness reduces the amount of ion motion, thin layers may improve properties for electrical insulation and capacitor applications. Thick layers or those with ionic impurities intentionally added can be tailored with custom diffusion behavior for semi-conductor applications, membranes, and solar cells. In addition, ion migration may play an important role in the high-field dielectric properties such as energy density, breakdown strength, and polarization hysteresis of layered films.
II. BACKGROUND THEORY ON CHARGE MIGRATION IN POLYMERS

The movement of charge carriers in an insulating polymer matrix has been modeled as a one-dimensional (1D) diffusion process [see Fig. 1]. Two analytical treatments have been given in the literature, both of which assume that only one type of ion moves (i.e., either a positive or negative ion). If more than one type of ion moves, then expressions for the loss and storage need to be used for each ion. The final result will be a linear addition of contributions from all types of ions. The first modeling treatment by Sawada et al. results in Eqs. (1) and (2) where \( \varepsilon' \) is the real part and \( \varepsilon'' \) is the imaginary part of the complex permittivity that are derived by simultaneously solving the equations for drift current, diffusion current, and the charge-current continuity. In the remainder of the paper, the model of Sawada et al. will often be referred to as the Sawada model. Drift current is caused by the movement of ions in response to an applied electric field. Diffusion current occurs when ions of the same charge build up at a blocking electrode, and thermal motion and the tendency of like charges to repel each other cause the ions to diffuse away from the blocking electrode. An equilibrium charge density distribution is reached when the diffusion current balances the drift current [see Fig. 1]. The second modeling approach differs from the first one in that Gauss’s law is added to the set of equations to account for the effect of charge build up on the electric field distribution. This approach results in Eqs. (3) and (4). For a given set of input parameters, the addition of Gauss’s law causes the real and imaginary parts of the complex permittivity to decrease slightly while shifting the relaxation peak to a somewhat higher frequency. This effect increases as the thickness and ion concentration increase [see Fig. 2].

\[
\varepsilon' = \left( \frac{n_q^2 D}{\varepsilon_0 k_b T} \right) \left( \frac{1 + 2 e^{\varepsilon_0} \sin(R) - e^{-2R}}{1 + 2 e^{2R} \cos(R) + e^{-2R}} \right) + \varepsilon'_{\text{matrix}},
\]

(1)

\[
\varepsilon'' = \left( \frac{n_q^2 D}{\varepsilon_0 k_b T} \right) \left( \frac{1 + 1 - 2 e^{\varepsilon_0} \sin(R) - e^{-2R}}{R(1 + 2 e^{2R} \cos(R) + e^{-2R})} \right) + \varepsilon''_{\text{matrix}},
\]

(2)

where \( R = d \sqrt{\varepsilon_0/2D} \), \( n \) is initial ion concentration [ions/m\(^3\)], \( q \) is charge of a single-charged ion [1.602 \times 10^{-19} C], \( D \) is ionic diffusion coefficient [m\(^2\)/s], \( \varepsilon_0 \) is permittivity of free space [8.854 \times 10^{-12} F/m], \( \omega \) is angular frequency of the applied voltage [radians/s], \( k_b \) is boltzmann’s constant [J/K], \( T \) is absolute Temperature [K], \( d \) is thickness of P(VDF-HFP) [m], and the subscript “matrix” denotes value of the matrix material, which is P(VDF-HFP).

\[
\varepsilon^* = (\varepsilon_{\text{matrix}}) \left( \frac{1 + io\tau}{io\tau + \tanh(Y/Y)}, \right)
\]

(3)

where \( Y = d \left( \frac{1 + io\tau}{D\tau} \right)^{1/2} \) and

\[
\tau = \left( \frac{\varepsilon_{\text{matrix}} k_b T}{n q^2 D} \right)^* \text{ with } * \text{ denoting a complex permittivity.}
\]

(4)

The real and imaginary parts of the complex permittivity of Coelho’s model were plotted using MATHEMATICA software.

A. Development of fitting algorithm

The diffusion model by Sawada et al., being mathematically simpler while having a similar real and imaginary permittivity as compared to that by Coelho, was used for fitting to the experimental dielectric spectroscopy data. Relatively

FIG. 1. Schematic showing the charge density distribution, \( \rho \), of a one-dimensional (1D) diffusion process in an insulating matrix.

FIG. 2. Comparison of Sawada and Coelho diffusion models in a matrix with \( \varepsilon'_{\text{matrix}} = 11 \), \( \varepsilon''_{\text{matrix}} = 0.5 \), and \( n = 8 \times 10^{19} \) ions/m\(^3\). Parameters used: (a) \( D = 9 \times 10^{-12} \) m\(^2\)/s, \( d = 357 \) nm and (b) \( D = 9 \times 10^{-12} \) m\(^2\)/s, \( d = 3750 \) nm.
The ion concentration fitting equation, Eq. (8), was then derived by using an R value of 2.225 in Eq. (5) and solving to determine the diffusion coefficient and ion concentration for n. The convenience of this fitting technique enables one to determine the diffusion coefficient, film thickness, and frequency, the diffusion coefficient can be determined by using 2.225 for R and the experimentally measured loss peak frequency as shown in Eq. (7).

\[
\varepsilon'' = \left( \frac{n\varepsilon_0 d^2}{2e_0k_b T} \right) \left( \frac{1}{R^2} \right) \left( 1 + \frac{1 - 2e^R\sin(R) - e^{2R}}{R(1 + 2e^R\cos(R) + e^{2R})} \right) + \varepsilon''_{\text{matrix}},
\]

(5)

\[
F(R) = \left( \frac{1}{R^2} \right) \left( 1 + \frac{1 - 2e^R\sin(R) - e^{2R}}{R(1 + 2e^R\cos(R) + e^{2R})} \right),
\]

(6)

\[
D = \frac{n\pi d f_{pk}}{2.225}, \quad \text{where } f_{pk} \text{ is the frequency of the maximum value of the loss.}
\]

(7)

The ion concentration fitting equation, Eq. (8), was then derived by using an R value of 2.225 in Eq. (5) and solving for n. The convenience of this fitting technique enables one to determine the diffusion coefficient and ion concentration by simply knowing the frequency (f_{pk}) and amplitude (\varepsilon''_{pk}) of the peak in dielectric loss.

\[
n = 24.28(e''_{pk} - e''_{\text{matrix}}) \left( \frac{\varepsilon_0 k_b T}{q^2 d^2} \right),
\]

(8)

**B. Use of diffusion equations in a layered film**

Because multilayered films contain both a material where charge diffusion takes place [e.g., P(VDF-HFP)] and an insulating material that blocks the ion motion [e.g., PC], a model was developed to separate the PC and P(VDF-HFP) components of the dielectric spectra. The layered film was assumed to be equivalent to an ideal capacitor with negligible loss (in the PC layer) in series with a lossy capacitor [in the P(VDF-HFP) layer] as shown in Fig. 4. Polycarbonate was chosen to be an ideal capacitor for its low loss behavior (shown in Sec. IV) as well as low diffusion coefficient (i.e., D = 1 \times 10^{-18} \text{ m}^2/\text{s} for evaporated gold or silver\textsuperscript{21}).

The PVDF based layers were proposed to behave as high loss capacitors because the P(VDF-HFP) control was measured to have significant dielectric loss and a diffusion coefficient of 1 \times 10^{-12} \text{ m}^2/\text{s} (shown in Sec. IV). All layers of the same material have the same nominal thickness and all layers are in series. Consequently, individual layers were not included explicitly. AFM measurements of the cross-section indicates that the layer thicknesses may vary as much as 10%. This net affect results in a broadening of the loss peak.

The mathematics associated with the equivalent circuit of Fig. 4 is as follows. The net capacitance was calculated for series capacitors yielding Eq. (9).

\[
\frac{1}{C_m} = \frac{1}{C_{PC}} + \frac{1}{C_{P(VDF-HFP)}}, \quad \text{where } C_m = C_m^* - iC_m' \quad \text{(9)}
\]

with "m" denoting the experimentally measured value.

Capacitance was then converted to permittivity by normalizing on the basis of the sample geometry [see Eq. (10)].

\[
C_m^* = \frac{\varepsilon_m^* \varepsilon_0 A}{(d_{PC} + d_{P(VDF-HFP)})}, \quad \text{(10)}
\]

Next, the film composition of 0.5 was introduced, since the film layers are of equal thickness

\[
\frac{1}{\varepsilon_m^*} = \frac{0.5}{\varepsilon_{PC}^*} + \frac{0.5}{\varepsilon_{P(VDF-HFP)}^*}, \quad \text{(11)}
\]

\[
\frac{1}{\varepsilon_{P(VDF-HFP)}^*} = \frac{2}{\varepsilon_m^*} - \frac{1}{\varepsilon_{PC}^*}. \quad \text{(12)}
\]

Equation (12) was then solved for \varepsilon_{P(VDF-HFP)}^* and separated into its real and imaginary parts (\varepsilon_{P(VDF-HFP)}' and \varepsilon_{P(VDF-HFP)}'') yielding Eqs. (13) and (14).

![Fig. 4. Equivalent circuit of PC/P(VDF-HFP) layered films. Layered film can be modeled as equivalent to an ideal PC capacitor in series with a lossy P(VDF-HFP) capacitor.](image-url)
The diffusion model of Sawada et al. was adapted to fit the data of layered films by first extracting the P(VDF-HFP) component using the 14 μm thick PC control data [see Eqs. (13) and (14)]. These equations assume that any changes in the PC spectra as a function of thickness are negligible. The Sawada diffusion model was then fit to the extracted P(VDF-HFP) layer data using Eqs. (7) and (8) in order to determine the diffusion coefficient and the ion concentration.

### III. EXPERIMENTAL

#### A. Materials and rheology

Two polymers were chosen for this study; one with inherent impurities and the other with highly insulating properties. A P(VDF-HFP) copolymer, Solef® 21508 from Solvay Solexis, was chosen to learn more about its anomalously low loss at low frequency (resistivity of $1 \times 10^{14}$ Ω-cm from manufacturer datasheet). PC, Makrolon® 2205 from Bayer MaterialScience, was selected as the confining layer for its high electrical resistivity, $1 \times 10^{16}$ Ω-cm (from manufacturer datasheet), that acts as a blocking electrode. This layered system was also chosen because of previous measurements showing enhanced breakdown strength and energy density.4,5 In this work, low field dielectric spectroscopy measurements were carried out. All layered films and controls were coextruded with a sacrificial polyethylene (PE) skin layer that surrounded the films in order to improve the film surface smoothness, handleability, and immunity to damage. This skin layer, having only a weak interaction with the materials in the layered film, was peeled off prior to any measurements.

A coextrusion temperature of 250°C was chosen based on the rheological compatibility of the two polymers in the melt. The polymer rheology was characterized by using a melt flow indexer (MFI), Kayeness Galaxy 1, at a shear rate that was similar to extrusion conditions (10 s⁻¹). Prior to processing, the PC pellets were dried in a vacuum oven for 48 h at 80°C. The films listed in Table I were produced for charge migration studies.

#### B. Dielectric spectroscopy

BDS measurements were performed using a Novocontrol unit (0.001 Hz to 100 kHz at 25 to 100°C) under a vacuum of <20 miliTorr. Measurements with a dc bias were carried out with an HP 4284 A RCL meter (20 Hz to 1 MHz) under similar conditions. DC resistivity was measured with a Keithley electrometer model 6517. Circular gold electrodes (1 cm diameter and 25 nm thick) were sputtered onto both sides of a film using a Hummer 6.2 sputter coater. Silver paste was used to ensure good contact with both electrodes.

\[
\varepsilon'_{PVDF-HFP} = \frac{0.25 \varepsilon'_{PC}}{\varepsilon'_{PC} - \varepsilon'_{PC} \varepsilon_m + 0.25 (\varepsilon_m^2 + \varepsilon_m^2)},
\]

\[
\varepsilon''_{PVDF-HFP} = \frac{0.5 \varepsilon''_{PC} \varepsilon_m}{\varepsilon'_{PC} - \varepsilon''_{PC} \varepsilon_m + 0.25 (\varepsilon_m^2 + \varepsilon_m^2)}.
\]

#### C. X-ray diffraction

Wide angle x-ray diffraction (WAXD) patterns were obtained by aligning the incident x-ray beam parallel to the extrusion direction (ED) of the film. The measurements were performed at 45 kV and 0.88 mA using a Confocal Max-Flux® optic with a sealed tube microfocus x-ray source (Rigaku MiroMax-002®), giving a highly focused beam of monochromatic Cu Kα radiation (λ = 0.154 nm). The sample-to-detector distance was 140 mm, and the diffraction was calibrated using a CaF₂ standard. The patterns were collected using an image plate with a 50-μm pixel size with a Fujifilm FLA-7000 scanner.

#### D. Differential scanning calorimetry

The thermal properties (i.e., crystallinity, melting temperature, and crystallization temperature) were characterized on a Perkin-Elmer (Boston, MA) Series 7 differential scanning calorimeter (DSC) at a heating/cooling rate of 10°C min⁻¹.

### IV. RESULTS AND DISCUSSION

#### A. Dielectric spectroscopy of P(VDF-HFP) and PC controls

The low-field dielectric measurements of P(VDF-HFP) (14 and 7 μm thick films) and PC (14 μm thick film) controls were carried out at different temperatures (i.e., 25, 50, and 100°C) and frequencies (0.001 Hz to 10 kHz). The dielectric storage and loss permittivity at 25 and 100°C are shown in Fig. 5. Two relaxation peaks were observed in the ε’’ for the P(VDF-HFP) controls; one at a high frequency (~20 Hz) and one at a low frequency (<0.1 Hz). The high frequency relaxation [see Figs. 5(a) and 5(c)] is commonly observed and reported as the $\gamma_C$ peak in $\gamma$-phase PVDF, which is attributed to dipole wagging along the helical axes.22 Having origins in the molecular scale, the $\gamma_C$ relaxation should not be affected by the film thickness, which was on the order of sub-micrometers and above. Low frequency dielectric relaxations, typical of those shown in Figs. 5(b) and 5(d), are often attributed to dc conduction and/or ion migration.8 From Figs. 5(b) and 5(d), this low frequency peak is significantly affected by layer thickness, shifting to a higher frequency.

### Table I

<table>
<thead>
<tr>
<th>Layer thickness (nm)</th>
<th>D (m²/s)</th>
<th>n (#/m³)</th>
<th>ε’pk (Hz)</th>
<th>ε’pk</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14,000</td>
<td>1.6 × 10⁻¹²</td>
<td>5.3 × 10¹⁹</td>
<td>0.013</td>
</tr>
<tr>
<td>1</td>
<td>7,000</td>
<td>1.2 × 10⁻¹²</td>
<td>1.1 × 10¹⁰</td>
<td>0.004</td>
</tr>
<tr>
<td>2</td>
<td>7,200</td>
<td>2.6 × 10⁻¹²</td>
<td>7.8 × 10⁹</td>
<td>0.08</td>
</tr>
<tr>
<td>32</td>
<td>430</td>
<td>2.3 × 10⁻¹³</td>
<td>1.9 × 10¹¹</td>
<td>2</td>
</tr>
<tr>
<td>32</td>
<td>190</td>
<td>1.1 × 10⁻¹³</td>
<td>3.1 × 10¹¹</td>
<td>5</td>
</tr>
<tr>
<td>128</td>
<td>50</td>
<td>3.2 × 10⁻¹³</td>
<td>1.0 × 10¹¹</td>
<td>200</td>
</tr>
</tbody>
</table>

8 From Figs. 5(b) and 5(d), this low frequency peak is significantly affected by layer thickness, shifting to a higher frequency.
and lower amplitude in the 7 μm film as compared to the 14 μm film. Regarding the PC control, the storage and loss are small in comparison to the P(VDF-HFP) films and are not affected by frequency.

B. Effect of dc bias voltage on dielectric property of P(VDF-HFP) control

In order to further study the behavior of the low frequency relaxation, dielectric spectra of the 14 μm P(VDF-HFP) control were obtained at 100 °C using a standard sinusoidal waveform combined with a dc bias voltage ranging from 0 to 36 V [see Fig. 6(a)]. The results for ε" vs. frequency are shown in Fig. 6(a). The δc peak was observed as well as the shoulder of the ion migration peak. The bias voltage had no significant effect on the δc relaxation. The low frequency peak shoulder, however, decreased significantly as the dc bias was increased, which is in agreement with a charge migration mechanism rather than a Maxwell-Wagner interfacial polarization mechanism. Assuming a charge migration mechanism, the asymmetric voltage profile (i.e., AC and DC) caused the ions to migrate to an interface (either amorphous-crystal interface or the electrode-sample interface), where their hindered movement prevented them from contributing to the low frequency relaxation.

A second bias experiment was conducted on the 14 μm P(VDF-HFP) control as follows. An initial dielectric spectrum was measured at 100 °C. Then, a dc bias of 100 V was applied for 72 h while monitoring the current, which became stable over this period of time. The bias was removed, and a second dielectric spectrum was recorded immediately (total measurement required 15 min). The sample was then allowed to relax for two hours, after which a third and final dielectric spectrum was measured. The results are shown in Fig. 6(a).

FIG. 5. Dielectric storage and loss permittivity as a function of frequency for P(VDF-HFP) (14 and 7 μm film thickness) and PC (14 μm film thickness) controls. (a) Storage permittivity at 25 °C, (b) storage permittivity at 100 °C, (c) loss permittivity at 25 °C, and (d) loss permittivity at 100 °C.

FIG. 6. (a) Effect of a dc bias voltage on the dielectric loss of a P(VDF-HFP) 14 μm control at 100 °C. (b) Loss dielectric spectroscopy as a function of frequency for a 14 μm P(VDF-HFP) control at 100 °C initial measurement (blue circle), after applying a 100 V bias for 72 h (light orange circle), and 2 h after further annealing at 100 °C (green triangle). The dc conductivity contribution to the loss permittivity is plotted as the black line in the plot.
Similar to the results shown in Fig. 6(a), the \( z_c \) and shoulder of the charge migration relaxations are visible [see Fig. 6(b)]. However, in this experiment, the bias was removed just prior to the measurement, and the loss peak was still reduced. Then, after the film was allowed to relax for two hours without bias, the amplitude of the charge migration dielectric loss increased as compared to the measurement immediately after the bias was removed. To determine the role of dc conductivity on the dielectric loss, a measurement was taken and converted to loss using the equation for capacitive impedance,

\[
R = \frac{1}{\omega C_L},
\]

where \( R \) is impedance (dc resistance), \( \omega \) is angular frequency, and \( C_L \) is the loss expressed as units of capacitance. Specifically, the capacitance was calculated as a function of frequency using the measured resistance of \( 3 \times 10^{10} \Omega \) (or conductivity of \( 6 \times 10^{-14} \) S·cm\(^{-1} \)). The capacitance was then converted to loss permittivity by normalizing on the basis of sample geometry. The component of loss permittivity that was attributed to dc resistivity was more than five times smaller than the dielectric loss immediately after the bias was removed. This low dc conductivity indicated that it played a minor role in the low frequency dielectric loss behavior.

Instead, the data support a charge migration mechanism which is described as follows. The proposed charges (i.e., impurity ions in the form of surfactant or catalyst residue) in \( P(VDF-HFP) \) were randomly distributed initially. When an ac voltage profile was applied during the dielectric measurements, the ions moved in the film and contributed to the dielectric loss. Then, a 100 V dc bias caused the ions to drift to the film surface(s) where their movement was restricted. The subsequent dielectric measurement (taken before the ions were allowed to completely relax away from the film surface), therefore, had a lower dielectric loss. After the dc bias was removed and the film was annealed for 2 h, the ions began to relax away from the interface and became available to diffusive motion, which increased the magnitude of the dielectric loss at low frequencies.

C. Effect of layer thickness on the low frequency dielectric relaxation

In order to study the effect of layer thickness (or diffusion distance) on the low frequency dielectric properties, broadband dielectric spectroscopy measurements were carried out on 50/50 (by vol.) PC/P(\( VDF-HFP) \) multilayered films with layer thicknesses ranging from 7000 to 50 nm [see Fig. 7]. In agreement with the diffusion models of Sawada and Coelho, the relaxation peak shifted to higher frequencies and decreased in magnitude with decreasing the layer thickness. When the layer thickness decreased to 50 nm for the 256-layer film, the low frequency relaxation peak was completely suppressed.

To gain more information on the ion diffusion process, the diffusion models were fit to the experimental data by first extracting the \( P(VDF-HFP) \) component [see Eqs. (15) and (16)] from the multilayered film data. A comparison between the original multilayer film data and the extracted 430 nm \( P(VDF-HFP) \) layers is given in Fig. 8. As expected, the extracted data of \( P(VDF-HFP) \) has a much higher loss. The loss peak of the extracted \( P(VDF-HFP) \) data is located at a slightly lower frequency than that for the multilayered film data.

Sawada’s model was then fit to the extracted \( P(VDF-HFP) \) data using the fitting technique derived in the background theory. The results are plotted in Fig. 9. The Sawada model followed the experimental data very well except that the experimental data had a slightly broader peak width at half maximum (PWHM) and a higher intensity at lowest frequencies. We have assumed that the low frequency loss in the vicinity of the low frequency peak is due to a single type of ion. However, the difference between the experimental data and the single ion model can be explained if more than one type of ion participates in the loss. While one could postulate a series of ions, which would result in a better fit, the data do not warrant such a complex analysis. Further, the

FIG. 7. Loss permittivity as a function of frequency for the 50/50 PC/P(\( VDF-HFP) \) multilayered films with different layer thicknesses at 100 °C. As a consequence of the PC blocking electrodes, the magnitude of the layered films is much smaller than the \( P(VDF-HFP) \) control.

FIG. 8. Loss permittivity as a function of frequency for a 32-layer 50/50 PC/P(\( VDF-HFP) \) film with 430 nm layers at 100 °C (green triangle) and the extracted \( P(VDF-HFP) \) component (red diamond).
subsequent increased loss following the relaxation peak may be due to a second much slower ionic relaxation which would be outside of our frequency domain.

The experimental loss peak amplitudes and frequencies along with the calculated diffusion coefficients and ion concentrations using Eqs. (13) and (14) are given in Table I. The values are consistent with those that have been reported for ion diffusion in various materials (e.g., liquid crystal polymers).\(^7,23\) For the layer thicknesses below 430 nm, the fitting parameters are quite comparable—approximately \(2 \times 10^{-13}\) m\(^2\)/s and \(2 \times 10^{21}\) ions/m\(^3\) for the diffusion coefficient and ion concentration, respectively. According to the diffusion theory under ideal experimental conditions, the diffusion parameters are thought to be independent of the layer thickness.\(^7,20\) However, the thick layers had a diffusion coefficient that was one order of magnitude higher and an ion concentration that was one order of magnitude lower than layers with thicknesses of 430 nm and thinner. The variation in these properties has several possible causes. First, interphase material may play an important role; this is the finite volume of material between two layers where mixing and chain entanglement occur.\(^24\) Because the interphase thickness is thought to be independent of the layer thickness, the fraction of interphase increases with decreasing layer thickness. The effects can include increasing/decreasing the effective layer thickness or trapping the ions. Based on measurements of other immiscible multilayered systems, the interphase thickness was estimated to be 7 nm.\(^24\) In a worst case scenario, each of the layer thicknesses were increased or decreased by 14 nm, which will have a larger effect on the films with thinner layers. This, however, was insufficient to account for the observed differences in the calculated properties. Regarding charge trapping, thinner layers with a greater fraction of interfacial material should exhibit a reduced ion concentration as opposed to what was observed. A second possible explanation is the effect of charge buildup on the electric field distribution (Gauss’s law). To check this, the model by Coelho, which takes Gauss’s law into account, was fit to the loss peak in the extracted P(VDF-HFP) layers (within 1% of the peak frequency and amplitude) and found to yield diffusion parameters quite close to Sawada’s model. A third factor is the morphology of P(VDF-HFP), which in reality contains both amorphous and crystalline phases. This can have an effect because crystals are impermeable to ion migration.\(^16\) To investigate this, WAXD [see Fig. 10] and DSC [see Table II] measurements were carried out. Some WAXD data are shown in Fig. 10. The DSC results for the crystallinity, melting temperature, and crystallization temperature are listed in Table II.

It was found that the crystal orientation was significantly affected by layer thickness. Thickness effects in WAXD have also been observed in confined crystallization studies.\(^25\) In the 7 µm control and 2 L PC/P(VDF-HFP) film, the meridional (020) WAXD reflection indicate an on-edge crystal orientation with the crystallographic b-axis perpendicular to the layers (Figs. 10(a) and 10(b)). This was speculated to be attributed to the mechanical stretching during the film take-up process. In the thin 50 nm layers, the (020) reflection was in the equatorial direction, evidencing another on-edge crystal orientation with the b-axes parallel to the layers (Fig. 10(d)). The missing reflection of (100) on the meridian suggested that the crystallite size along [100] might be too small and/or the a-axes tilted from the layers. The 32 L film also had an on-edge orientation; however, the (020)

![Fig. 9. Dielectric loss of extracted P(VDF-HFP) data (blue diamond) as compared to the fitted Sawada model (green circle) at 100°C. (a) 7200 nm P(VDF-HFP) layers from 2 L film and the 7000 nm P(VDF-HFP) control, (b) 430 nm P(VDF-HFP) layers from 32 L film, (c) 190 nm P(VDF-HFP) layers from 32 L film, and (d) 50 nm P(VDF-HFP) layers from 256 L film.](image-url)
### V. CONCLUSIONS

Microlayer coextrusion processing technology was successfully used to produce PC/P(VDF-HFP) layered films and controls with P(VDF-HFP) thicknesses ranging from 14 μm down to 50 nm. Dielectric spectroscopy measurements showed a distinct relaxation peak at a low frequency that shifted to a higher frequency with a lower amplitude as the layer thickness decreased. In addition, the relaxation decreased after the application of a 100 V dc bias for 72 h and then partially recovered after a two hour annealing with no bias. To determine whether the responsible mechanism was dc conductivity or ion migration, conductivity measurements and diffusion modeling were carried out. Because the dc conductivity effect on the loss was much smaller than the ion conduction, the former effect was negligible. The diffusion models by Coelho and Sawada, however, predicted that an ion migration peak increases in frequency and decreases in amplitude with decreasing layer thickness, which is in agreement with the experimental data. In order to gain more information on the diffusion mechanism, the model by Sawada was fit to the experimental data using a newly developed and convenient fitting technique. More specifically, the model was fit to the peak in the experimental dielectric loss using two equations for calculating the diffusion coefficient and ion concentration. For layer thicknesses of 430 nm and below, the amplitude correction in the Sawada model, these differences may be due to uncertainty in the dielectric loss amplitude. More specifically, the calculated ion concentrations (Table I) in the thick layers differed from those in the thin layers. Because ion concentration correlates only with the relaxation amplitude in the Sawada model, these differences may be due to uncertainty in the dielectric loss amplitude. More specifically, the proposed second relaxation at very low frequencies overlaps and increases the measured loss amplitude. This second ion relaxation can be accounted for in films with thicknesses of 430 nm and below. However, the amplitude correction in thick films required measurements outside our frequency domain. Further study is necessary in the future.

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**TABLE II.** The crystallinity, melting temperature, and crystallization temperature of P(VDF-HFP) controls and 50/50 PC/P(VDF-HFP) layered films using DSC.

<table>
<thead>
<tr>
<th>Layer thickness (nm)</th>
<th>Crystallinity (wt. %)</th>
<th>T_m (°C)</th>
<th>T_c (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14 000</td>
<td>25</td>
<td>131</td>
</tr>
<tr>
<td>1</td>
<td>7000</td>
<td>24</td>
<td>131</td>
</tr>
<tr>
<td>2</td>
<td>7200</td>
<td>24</td>
<td>131</td>
</tr>
<tr>
<td>32</td>
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<td>25</td>
<td>131</td>
</tr>
<tr>
<td>32</td>
<td>190</td>
<td>23</td>
<td>131</td>
</tr>
<tr>
<td>256</td>
<td>50</td>
<td>19</td>
<td>131</td>
</tr>
</tbody>
</table>

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Regarding the thermal properties of P(VDF-HFP) layers listed in Table II, the melting and crystallization temperatures were not affected by layer thickness, which indicates that the lamellae thickness was unaffected. The crystallinity was also fairly constant dropping from 25 wt. % in the 14 μm P(VDF-HFP) control to 23 wt. % in 190 nm layers and 19 wt. % in 50 nm layers. Although the lower crystallinity in thin layers should act to increase the diffusion constant, the change in crystallinity was not enough to offset the orientation effect.

The extrusion direction wide angle x-ray diffraction of (a) 7 μm thick P(VDF-HFP) control, (b) 2 L PC/P(VDF-HFP) with 7 μm layers, (c) 32 L PC/P(VDF-HFP) with 430 nm layers, and (d) 256 L PC/P(VDF-HFP) with 50 nm layers. Schematic in (e) shows the crystal orientations found in the layered films and control.

Reflection was observed in both the meridional and equatorial directions, indicating that the above two types of on-edge crystal orientations mixed in the sample; one with the b-axes perpendicular the layers and another with the b-axes parallel to the layers (Fig. 10(c)). Judging from the line widths of the (020) (sharp and strong) and (100) (diffuse and weak) reflections, the crystallite size along the b-axes must be longer than that along the a-axes. As a result, the in-plane cross-sectional area should be larger when the b-axes were parallel to the layers than the situation when the b-axes were perpendicular to the layers. It is known that crystals are impermeable to ions. Therefore, the impedance to ion migration was expected to be higher when the b-axes were parallel to the layers. In other words, the thin layers (≤430 nm) had greater crystal cross-sectional areas that inhibited ion migration and decreased the diffusion coefficient.

The calculated ion concentrations (Table I) in the thick layers differed from those in the thin layers. Because ion concentration correlates only with the relaxation amplitude in the Sawada model, these differences may be due to uncertainty in the dielectric loss amplitude. More specifically, the proposed second relaxation at very low frequencies overlaps and increases the measured loss amplitude. This second ion relaxation can be accounted for in films with thicknesses of 430 nm and below. However, the amplitude correction in thick films required measurements outside our frequency domain. Further study is necessary in the future.
primarily to differing crystal orientations in P(VDF-HFP). In summary, this work provides a convenient and accurate framework for studying ion migration in polymers or other insulating materials, which can be used to improve both current and new applications (e.g., solar cells, light-emitting electrochemical cells, capacitors, and LCD displays).

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