Interphase/Interface Modification on the Dielectric Properties of Polycarbonate/Poly(vinylidene fluoride-co-hexafluoropropylene) Multilayer Films for High-Energy Density Capacitors

Zheng Zhou, Joel Carr, Matthew Mackey, Kezhen Yin, Donald Schuele, Lei Zhu, Eric Baer

1Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio, 44106-7202
2Department of Physics, Case Western Reserve University, Cleveland, OH, 44106-7202

Correspondence to: E. Baer (E-mail: exb6@case.edu)

Received 31 January 2013; revised 26 March 2013; accepted 26 March 2013; published online 22 April 2013

DOI: 10.1002/polb.23296

ABSTRACT: Unique three-component multilayer films with ATBT-TATBTA configuration were fabricated using forced assembly multilayer coextrusion for novel dielectric systems. The dielectric breakdown strength, displacement–electric field hysteresis, and dielectric spectroscopy of 65-layer polycarbonate (PC)/tie/poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) were investigated with various tie materials. Three different tie materials, poly(methyl methacrylate) (PMMA), styrene-acrylonitrile copolymer with 30% acrylonitrile content (SAN30), and poly(ethylene terephthalate-co-1,4-cyclohexanedimethylene terephthalate) (PETG) were chosen owing to their various degrees of interaction with either P(VDF-HFP) or PC. The 65-layer PC/PMMA/P(VDF-HFP) films exhibited a 25% enhancement in breakdown properties, 50% higher energy density, 40% smaller hysteresis loop areas, and orders of magnitude slower ion migration relative to the 33-layer PC/P(VDF-HFP) control. These property improvements are mainly attributed to the localized interactions at PMMA/P(VDF-HFP) and PMMA/PC interfaces, forming interphase regions. The modified PMMA/P(VDF-HFP) interphase region can effectively hinder the migration of impurity ions in P(VDF-HFP), reducing their mobility within the layer. Additionally, a small fraction of PMMA can lead to slightly increased dielectric constant of the composite films owing to strong interaction between PMMA and P(VDF-HFP). The other two systems with PETG and SAN30 as tie layers exhibited marginal improvements in dielectric properties owing to their weaker interactions with the P(VDF-HFP) layers.

INTRODUCTION

Polymer films, specifically biaxially oriented polypropylene (BOPP), are widely used in film capacitors owing to their high breakdown properties, low-loss characteristics, and low cost.1,2 New and emerging applications for polymer film capacitors, such as hybrid electric vehicles, grid converters, and pulsed power applications, often require large energy densities in addition to high efficiency (low loss) of the device.3–5 These functional requirements have posed new challenges for researchers and engineers to design and develop new materials that can meet these demands. BOPP is not suited to meet these requirements owing to its inherent low dielectric constant and reduced performance at elevated temperatures.6

Our approach to improving the energy density of polymer films used for capacitors is to microlayer a high-breakdown strength insulating polymer (i.e., polycarbonate [PC] and polyethylene terephthalate [PET]) with a high dielectric constant polymer (i.e., polyvinylidene fluoride [PVDF] and its copolymers). Numerous sets of PC/PVDF (homopolymer and various copolymers) films have been successfully produced using this approach that exhibit enhanced breakdown properties and lifetime characteristics as compared to single-component polymer films.7–9 Mimicking commercial BOPP, multilayer films of PET and poly(vinylidene fluoride-co-tetrafluoroethylene) have also been produced and yield further breakdown property enhancements after biaxial orientation.10 The enhanced breakdown properties in these multilayered materials were attributed to a distinct treeing fracture mechanism, which is observed under a divergent electric field. This fracture mechanism is facilitated by the layer interfaces. These layer interfaces act as “barriers” to impede the breakdown propagation through the film thickness. As a result, the multilayer samples were discharged along the layer interfaces, forming tree-like damage zones on the film surface. As the layer interfaces play such a vital role...
in the breakdown properties, there is a large opportunity to potentially improve these properties by manipulating the nature of these layer interfaces. The relative impact of variables such as adhesion, interface roughness, and layer interdiffusion on the resulting dielectric properties in multilayer films is not well understood. All of these variables can be readily manipulated using the forced assembly coextrusion process.

All of the reported multilayer systems for polymer film capacitors consist of only two components in which the layers are arranged in an ABABAB configuration. The flexibility of the microlayer coextrusion process offers the potential for more layer configurations, including the addition of a third polymer component. Multilayer films with an ATBTATBTA (T is the tie layer) and ABCABCABC can also be produced using this versatile process. For this application, the addition of a tie layer in an ATBTA layer configuration, is of considerable interest owing to the potential to specifically modify the layer interface, adhesion, and level of polymer/polymer interdiffusion. Several three-component multilayer systems with various tie layers have been used to investigate the adhesion characteristics between polymers. Adding a tie layer in these multilayer dielectric systems could potentially change the adhesion characteristics and influence the breakdown properties. Also of interest is the area of layer interdiffusion, where localized mixing of the two layers occurs at the layer interface, creating an interphase region, which essentially acts as an entirely new material. By selecting a tie layer polymer with varying miscibilities/interactions with either one or both of the constituent polymers, the amount of interphase can be directly controlled.

In this study, a series of tie layer materials were selected to directly influence the adhesion, interaction, and interphase characteristics of PC and poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) multilayer films. The tie layers include amorphous polymers, such as PMMA, SAN30, and poly(ethylene terephthalate-co-1,4-cyclohexanediyl terephthalate) (PETG). These materials were chosen based on their compatibility with PC and P(VDF-HFP). For the PC layer, PETG is considered miscible, PMMA is partially miscible or compatible, and SAN30 is immiscible. For the P(VDF-HFP) layer, PMMA is miscible with PVDF-based polymers. Pure polyacrylonitrile (PAN) is considered partially miscible; therefore, certain interaction with P(VDF-HFP) is expected for SAN30. PETG is considered immiscible. Based on their thermodynamic interactions, these three tie layers will have a significant impact on the nature of the interphase/interface in PC/tie/P(VDF-HFP) multilayer systems. Their relative impact on the breakdown properties, hysteresis behavior, low-field dielectric spectroscopy, and layer morphology has been evaluated in this study.

### EXPERIMENTAL

#### Materials

PC was obtained from Bayer Material Science (Makrotron 2207). P(VDF-HFP) was provided by Arkema (Kynar 2500). Poly(methyl methacrylate) (PMMA) was obtained from Dow Chemical (Tyril 880). Styrene-co-acrylonitrile copolymer with 30% acrylonitrile content (SAN30) was supplied by the Dow Chemical (Tyril 880). PETG was obtained from Eastman Chemical (Eastar 6763). PC, PMMA, SAN30, and PETG were all dried under vacuum at 80 °C for 12 h prior to melt processing.

Three-component multilayer films with an ATBTATBTA-layered structure were produced using a forced assembly multilayer coextrusion process. The coextrusion temperature for all three systems was 250 °C. This temperature was chosen based on the viscosity matching of each polymer, as determined by melt flow index at a shear rate that is similar to extrusion condition (10 s⁻¹). The various tie layer systems contained a total of 65 layers (Table 1). Samples were produced at various tie layer thicknesses (6–103 nm) by adjusting the relative pump rate of the tie layer extruder. All of the samples had equal volume amount of PC and P(VDF-HFP) and an overall film thickness of 10 μm. For comparison, a 50/50 33-layer PC/P(VDF-HFP) sample without tie layer was also produced with an ABABA-layered structure. All samples were laminated with two sacrificial low-density polyethylene skin layers during coextrusion to protect the film from damage, improve the surface quality, and reduce the defects. All skin layers were removed prior to any subsequent testing.

#### Dielectric Breakdown Strength Measurements

The breakdown field of the multilayered samples was determined using a ramped voltage of 500 V/s using needle/plane electrodes. The positive needle electrodes had a tip radius of 20 μm and the negative plane consisted of a flat

### TABLE 1 PC/tie/P(VDF-HFP) Multilayer Films Under Investigation

<table>
<thead>
<tr>
<th>Multiayer Film Compositions</th>
<th>Number of Layers</th>
<th>Tie Layer Thickness (nm)</th>
<th>PC or P(VDF-HFP) Layer Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/tie/P(VDF-HFP) (vol %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50/0/50</td>
<td>33</td>
<td>–</td>
<td>312</td>
</tr>
<tr>
<td>49/2/49</td>
<td>65</td>
<td>6</td>
<td>306</td>
</tr>
<tr>
<td>48/4/48</td>
<td>65</td>
<td>13</td>
<td>300</td>
</tr>
<tr>
<td>46/8/46</td>
<td>65</td>
<td>25</td>
<td>288</td>
</tr>
<tr>
<td>40/20/40</td>
<td>65</td>
<td>63</td>
<td>250</td>
</tr>
<tr>
<td>33/33/33</td>
<td>65</td>
<td>103</td>
<td>206</td>
</tr>
</tbody>
</table>

#### Chemicals

- **Eastar 6763**: Polyacrylonitrile (PAN) (Handa Manufacturing).
- **Plexiglas V826**: Poly(methyl methacrylate) (PMMA) (Dow Chemical).
- **Kynar 2500**: Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) (Arkema).
- **Plexiglas V826**: Poly(methyl methacrylate) (PMMA) (Dow Chemical).
- **Kynar 2500**: Poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-HFP)) (Arkema).
- **Tyril 880**: Styrene-co-acrylonitrile copolymer (Dow Chemical).
- **Tyril 880**: Styrene-co-acrylonitrile copolymer (Dow Chemical).
- **Tyril 880**: Styrene-co-acrylonitrile copolymer (Dow Chemical).
rectangular piece of aluminum. A Quadtech (Marlborough, MA) Guardian 20-kV HiPot tester was used as the voltage source. All breakdown experiments were carried out in mineral oil to reduce surface and corona discharging. Twenty repetitions were done on each sample. The needle electrodes were replaced for every 10 measurements.

Atomic Force Microscope
The multilayer sample cross-sections were imaged using atomic force microscope (AFM). The samples were first embedded in epoxy, cured overnight, and sectioned at -100 °C using a Leica Microsystems (Buffalo Grove, IL) EM FC6 ultramicrotome. Polished samples were then imaged using AFM operating in the tapping mode. The phase and height images were recorded simultaneously using a Nanoscope IIIa Multimode scanning probe (Digital Instruments, Santa Barbara, CA).

Broadband Dielectric Spectroscopy
Low-field dielectric spectroscopy was carried out under vacuum at 20 and 100 °C, respectively, using a Novocontrol (Hundsangen, Germany) spectrometer with a frequency sweep from 0.01 Hz to 100 kHz. The sample electrodes were prepared by sputtering two 1-cm diameter circular gold electrodes onto each film surface using an Electron Microscopy Sciences (EMS Q300T, Quantum Technologies, Ashford, Kent, England) sputter coater.

Dielectric Hysteresis Measurements
Electric displacement–electric field (D-E) hysteresis measurements were carried out using a Premiere II ferroelectric tester from Radiant Technologies (Albuquerque, NM). All samples were measured using a triangular waveform, with a frequency of 1 Hz. The applied voltage was increased in increments of 50 kV/mm until the samples broke down. An electrostatic sandwich setup was used to conduct the hysteresis measurements. A thick, 100-μm polyimide mask with a 1 cm diameter circular hole was used to determine the area under applied electric field. The electrodes consisted of two 1.2 × 6 cm² strips of 6 μm thick, aluminum-metalized BOPP film. The charge energy density, \( U_c \), discharge energy density, \( U_d \), and loss energy density, \( U_l \), were calculated from the hysteresis curves according to:

\[
\begin{align*}
U_c &= \int_0^{D(T)} E(t)dD(t) \\
U_d &= \int_0^{D(T)} E(t)dD(t) \\
U_l &= U_c - U_d
\end{align*}
\]

where \( T \) is the time taken for the voltage waveform to reach maximum from zero, \( E(t) \) is the applied electric field and \( D(t) \) is the corresponding electric displacement.

RESULTS AND DISCUSSION
Dielectric Properties of PC/PMMA/P(VDF-HFP)
Multilayer Films with Various PMMA Thicknesses
The dielectric breakdown strength was evaluated for PC/PMMA/P(VDF-HFP) system as a function of PMMA layer thickness (Fig. 1). The breakdown strength of 33-layer PC/P(VDF-HFP) film was also included and taken as the film with 0 nm tie layer thickness and shown as the dashed line in Figure 1. By comparing the dashed line with the solid line, it is evident that the incorporation of a PMMA tie layer in between PC and P(VDF-HFP) had a substantial impact on the dielectric breakdown properties. Initially, the breakdown strength of PC/PMMA/P(VDF-HFP) increased with increasing PMMA layer thickness. The maximum breakdown strength of 880 kV/mm appeared at 25 nm nominal PMMA layer thickness and represented a 25% improvement in dielectric breakdown strength relative to the 33-layer PC/P(VDF-HFP). For samples, with PMMA tie layer thickness >25 nm, the dielectric breakdown strength began to level off and then slowly decrease. Considering PMMA was miscible with P(VDF-HFP) and compatible with PC, the dielectric breakdown strength was rather interesting. It is believed that the nature of the interdiffusion between PMMA and both PC and P(VDF-HFP) dictates this effect.

The hysteresis properties were also determined for the 65-layer PC/PMMA/P(VDF-HFP) system in addition to the 33-layer 50/50 PC/P(VDF-HFP) control. Representative unipolar D-E polarization hysteresis curves are shown in Figure 2. By comparing the plot (a) for the 33-layer 50/50 PC/P(VDF-HFP) and the plots (b–f) for 65-layer PC/PMMA/P(VDF-HFP) with various PMMA tie layer thicknesses, it is evident that the 33-layer 50/50 PC/P(VDF-HFP) had the largest loop compared with PC/PMMA/P(VDF-HFP) system at the same
electric field. The addition of a PMMA tie layer (even as little as 6 nm, 2 vol %) reduced the hysteresis D-E loop area dramatically at the same electric field.

To quantify the hysteresis properties, the charge energy density, discharge energy density, and loss energy density were calculated as a function of electric field for all the 65-layer PC/PMMA/P(VDF-HFP) compositions in addition to the 33-layer PC/P(VDF-HFP) control (Fig. 3). The 33-layer PC/P(VDF-HFP) film sample exhibited maximum charge energy density. However, these samples also contained the lowest discharge energy density owing to the large hysteresis loop areas. The 65-layer PC/PMMA/P(VDF-HFP) samples exhibit much larger discharge energy densities owing to the reduced loop areas. In addition, the 65-layer 46/8/46 PC/PMMA/P(VDF-HFP) sample with 25 nm nominal tie layer thickness possessed the highest breakdown field during D-E loop hysteresis measurements, which correlated well with the needle–plane breakdown data shown in Figure 1. To better

**FIGURE 2** Representative unipolar D-E hysteresis loops for 65-layer PC/PMMA/P(VDF-HFP) films with various PMMA layer thicknesses/compositions. In addition, the 50/50 PC/P(VDF-HFP) 33-layer film was also included for comparison. All films had equal amount of PC and P(VDF-HFP) and film thicknesses were maintained at 10 μm.
illustrate the data in Figure 3, the values for maximum discharge energy density and the hysteresis properties at a given field, in this case, 500 kV/mm, were shown as a function of nominal PMMA tie layer thickness (Fig. 4). The maximum discharge energy densities for the 33-layer 50/50 PC/P(VDF-HFP) film and the 65-layer 46/8/46 PC/PMMA/P(VDF-HFP) film were 5.72 and 8.36 J/cc, respectively. In other words, the 65-layer 46/8/46 PC/PMMA/P(VDF-HFP) sample can store nearly 50% more energy than the 33-layer 50/50 PC/P(VDF-HFP) sample at a given area, which is desirable for capacitor applications.

At 500 kV/mm, the discharge energy density for the 33-layer 50/50 PC/P(VDF-HFP) film was 4.75 J/cc, whereas the 65-layer 49/2/49 PC/PMMA/P(VDF-HFP) had a discharge energy density of 5.54 J/cc. The discharge energy density increased slightly with increasing PMMA layer thickness, and then dropped gradually when the PMMA thickness was above 25 nm. It is speculated that there are at least two contradictory reasons that dictate the trend in discharge energy density for the 65-layer PC/PMMA/P(VDF-HFP) system with various PMMA tie layer thicknesses. One reason is that a small fraction amount of PMMA can increase the capacitance...
for storing more electric energy. It was speculated that the slightly increase in dielectric constant was owing to either increased content of $\beta$-crystal in the P(VDF-HFP) layer or loosening up of the dipole in the amorphous part of P(VDF-HFP) facilitated by PMMA chains. The other reason is that incorporation of large fraction of PMMA would decrease the total film dielectric constant of 65-layer PC/PMMA/P(VDF-HFP) based on the series model. The dielectric constant of PMMA, 3.71, is lower than the dielectric constant of the 33-layer 50/50 PC/P(VDF-HFP) control, 4.46. Therefore, combing PMMA with 50/50 PC/P(VDF-HFP) should decrease the dielectric constant of PC/PMMA/P(VDF-HFP).

At 500 kV/mm, the loop area for the 33-layer 50/50 PC/P(VDF-HFP) film was 4.79 J/cc, whereas the 65-layer PC/PMMA/P(VDF-HFP) samples had the loss energy density as low as 2.80 J/cc. This represents an approximate 40% reduction in the hysteresis behavior as compared to the 33-layer samples with no tie layer. The cause of the reduction in loss energy density in these systems was not immediately clear; however, it was speculated that the interface/interphase modification in the PC/PMMA/P(VDF-HFP) system had a significant impact on the hysteresis properties. To help clarify this point, low-field dielectric spectroscopy was used to probe the ion migration characteristics in these materials.

Ion migration in PC/PVDF (and PVDF copolymers) multilayer systems significantly contributes to the resulting hysteresis behavior of the overall films. It was found that by reducing the PVDF layer thickness, this ion motion was inhibited and was effectively probed using low-field dielectric spectroscopy at a wide range of measuring frequencies and temperatures. Following this approach, dielectric spectroscopy was measured at 20 and 100 °C for the various samples. At 20 °C, one broad peak around 50 Hz was observed and attributed to both $\alpha_c$ of P(VDF-HFP) and $\beta$-relaxation of PMMA. A rise in $\tan(\delta)$ was observed at very low frequencies (0.1 Hz or below) for the 33-layer 50/50 PC/P(VDF-HFP) samples (Fig. 5). For the 65-layer PC/PMMA/P(VDF-HFP) samples at 20 °C, no such behavior was observed.

To better probe the ion migration behavior in the 65-layer PC/PMMA/P(VDF-HFP) system, elevated temperatures as high as 100 °C were used to drive the ion migration peak to higher frequency (Fig. 6). The peak $\alpha_c$ was not observed because the peak frequency has drifted above $10^5$ Hz. PMMA and the 33-layer 50/50 PC/P(VDF-HFP) samples were included for comparison. $\beta$-Relaxation peak of PMMA,

![FIGURE 4 Maximum discharge energy density and hysteresis property values at 500 kV/mm as a function of PMMA tie layer thickness for the 65-layer PC/PMMA/P(VDF-HFP) multilayer films.](image)

![FIGURE 5 Dielectric loss tangent of 65-layer PC/PMMA/P(VDF-HFP) films in addition to the 33-layer PC/P(VDF-HFP) as a function of frequency at 20 °C. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 μm.](image)

![FIGURE 6 Dielectric loss tangent of 65-layer PC/PMMA/P(VDF-HFP) films in addition to 33-layer PC/P(VDF-HFP) and PMMA controls as a function of frequency at 100 °C. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 μm.](image)
associated with localized motion of methoxy groups, was observed at 10,000 Hz. The 33-layer 50/50 PC/P(VDF-HFP) film exhibited an ion migration peak centered around 30 Hz which was assigned to the ion migration in the P(VDF-HFP) layers. Incorporation of the PMMA tie material into the system shifted the ion migration peak to lower frequencies. The peak frequency of the ion peak decreased with increasing PMMA layer thicknesses. The reduction in the ion migration peak frequency indicated that the ion migration was suppressed in the 65-layer PC/PMMA/P(VDF-HFP) system, which correlated to the reduction in the hysteresis loop area shown in Figure 3(c). One possibility is that the localized mixing of PMMA and P(VDF-HFP) along the layered interphase created ion trap sites that can tie up these ionic species and significantly decrease the ionic species mobility under electric field. The other possibility is that the PMMA chains intermix with amorphous part of P(VDF-HFP), rigidify the amorphous P(VDF-HFP) chains, make ion movement in the interphase region impossible, and reduce the ion migration distance and mobility.20

Through breakdown strength, D-E hysteresis and low-field dielectric spectroscopy measurements, it was concluded that the 65-layer PC/PMMA/P(VDF-HFP) system exhibited enhanced dielectric breakdown strength, decreased hysteresis loss energy density, and slower ion migration peaks. It was obvious that the improved dielectric properties were attributed to the introduction of the PMMA tie layers. Therefore, the interaction between PMMA and both PC and P(VDF-HFP) was an important structural parameter that might directly influence the resulting dielectric properties. To better visualize these material, AFM was used to quantify the PMMA tie layer thickness and attempt to observe the layer interphase in the 65-layer PC/PMMA/P(VDF-HFP) system with selected PMMA nominal layer thicknesses. Representative AFM images for the 65-layer PC/PMMA/P(VDF-HFP) samples with 25, 63, and 103 nm PMMA tie layers, in addition to the 33-layer 50/50 PC/P(VDF-HFP), are shown in Figure 7(a). In samples with no PMMA tie layers in between PC and P(VDF-HFP), sharp layer interface boundaries were observed. In the sample with 25 nm PMMA tie layers, no distinct PMMA layers were observed and PMMA was completely interdiffused with both PC (lighter layers) and P(VDF-HFP) (darker layers) layers. In addition, a diffuse interface boundary was observed between PC and P(VDF-HFP) layers. In samples with 63 and 103 nm PMMA tie layers, a distinct portion of the PMMA remained with rich interdiffused regions surrounding it. The measured distinct PMMA tie layer thicknesses were much lower than the nominal tie layer thickness. Based on the AFM images, a schematic representation of the layer structure in the 65-layer PC/PMMA/P(VDF-HFP) samples was proposed [Fig. 7(b)]. In these 65-layer PC/PMMA/P(VDF-HFP) samples, the material between the PC and the P(VDF-HFP) layers would consist of a new two-dimensional (2D) interphase material or localized 2D blend of PC/PMMA and P(VDF-HFP)/PMMA.13

As the PMMA is miscible with PVDF-based polymers and only partially miscible with PC, the interphase portion of P(VDF-HFP)/PMMA was expected to be much larger than the PC/PMMA interphase region. No discrete tie layer was observed in the 46/8/46 PC/PMMA/P(VDF-HFP) 65-layer samples, with a nominal PMMA tie layer thickness of 25 nm. Assuming that both PMMA/PC and PMMA/P(VDF-HFP) interphases were symmetrical, the total interphase thickness of PMMA/PC and PMMA/P(VDF-HFP) interphase regions was
twice the nominal PMMA tie layer thickness, 50 nm, after complete interdiffusion. The interphase thickness for PC and PMMA in these multilayered samples based on their interaction parameters and coextrusion conditions was estimated to be around 10 nm.\(^\text{14,25}\) Therefore, the remaining 40 nm of material consisted of an interphase region or blend of P(VDF-HFP) and PMMA. In thicker tie layers, these interphase regions are expected to be similar, and the interphase thickness for miscible PMMA/P(VDF-HFP) system could be around 40 nm.\(^\text{14}\) This is verified in the AFM images where discrete PMMA layers are observed in the samples with a nominal PMMA tie layer thickness of 63 and 103 nm. An accurate measurement of the actual PMMA tie layer thickness in this sample is difficult owing to the diffuse nature of the interphase regions; however, the discrete PMMA tie layers are thinner than the PMMA nominal thickness.

Dielectric Properties of 65-layer PC/tie/P(VDF-HFP) Multilayer Films with Various Tie Materials

The breakdown field was evaluated for the various PC/tie/P(VDF-HFP) multilayer samples as a function of tie layer thickness (Fig. 8). The breakdown properties of the PC/P(VDF-HFP) 33-layer samples were also evaluated and plotted at a tie layer thickness of 0 nm. The average value for this sample was plotted as a dashed line for comparison. Three different tie materials, PMMA, SAN30, and PETG, were chosen owing to their various degrees of interaction with either PC or P(VDF-HFP). From these data, it is evident that the incorporation of a tie layer in between the PC and the P(VDF-HFP) layers had an impact on the resulting dielectric breakdown properties. The nature of the interaction between the tie layer material and both PC and P(VDF-HFP) dictated this effect. For the remaining samples, the films with PETG, and SAN30 tie layers, did exhibit a marginal improvement in the breakdown properties, again with maximums occurring at a tie layer thickness of 25 nm. The ability to incorporate
an additional material in the multilayer dielectric systems and directly influence the breakdown properties is rather interesting from both a scientific and a practical perspective.

It is evident that the tie layer materials in addition to the tie layer thickness are critical parameters for the determination of the resulting breakdown properties. As the tie layers were expected to have different degrees of interaction to the PC and P(VDF-HFP) layers, the nature of the interphase/interface between these materials is an important structural parameter that may directly influence the resulting breakdown properties. AFM was used to quantify the tie layer thickness and attempt to observe the layer interphase/interface in selected PC/tie/P(VDF-HFP)-multilayered samples. Representative AFM images for the PC/tie/P(VDF-HFP) 65-layer samples with 25 and 103 nm PMMA, SAN30, and PETG tie layers are shown in Figures 9 and 10, respectively.

For the samples with nominal tie layer thickness of 25 nm (Fig. 9) the layer interface appeared diffused with no distinct tie layer material being observed for both PMMA and PETG tie layers. As mentioned in the previous section, PMMA layers were fully interdiffused in to both PC (light layers) and P(VDF-HFP) (dark layers). PETG is highly miscible with PC\(^{14}\) and immiscible with P(VDF-HFP): therefore, for the 25-nm PETG tie layers, it was assumed that the PETG was completely interdiffused into the PC layers, with very little material (<5 nm) diffused into the P(VDF-HFP) layers. For the 25-nm SAN30 tie layer sample, the interface appeared sharp with a discrete SAN30 tie layer material being observed between the PC and the P(VDF-HFP). The measured layer thickness of the SAN30 tie layers was around 20–30 nm which matched closely to the nominal tie layer thickness. The AFM images were analyzed using Image J software to obtain a contrast profile, indicating relative gray values across the images. For the PC/PMMA/P(VDF-HFP) system, the profile exhibits the broadest transition between the PC (high gray value) and the P(VDF-HFP) (low gray value) layers. For the PC/PETG/P(VDF-HFP) system, the tie layers are mostly diffused into the PC layers; however, a sharp transition between P(VDF-HFP) and PC was observed owing to poor miscibility between PETG and P(VDF-HFP). For SAN30 system, the SAN30 tie layers (highest gray value) are observed in between PC and P(VDF-HFP) with steep transitions occurring in both PC/SAN30 and P(VDF-HFP)/SAN30 boundaries owing to the lower interaction of SAN30 with both PC and P(VDF-HFP).

In samples with larger 103-nm tie layers (Fig. 10) all of the samples exhibited discrete tie layers from the AFM images, even in the samples with PMMA tie layers. Consistent with AFM images, tie layers were also observed in the gray-value profiles. However, the layer interfaces in the 103-nm PMMA tie layer samples did appear quite diffused into both dark P(VDF-HFP) layers and light PC layers, with measured PMMA tie layer thicknesses that are much lower than 103 nm. For the 103-nm PETG tie layer, the PETG tie layers...
diffused mainly into the PC layers owing to its miscibility with PC. In these samples, the interface between P(VDF-HFP) and PETG was still rather sharp. The discrete PETG tie layer thicknesses are lower than 103 nm. For the 103-nm SAN30 tie layer, the layer interface appeared rather sharp on both PC and P(VDF-HFP) interfaces. In addition, the measured tie layer thicknesses was around 100–130 nm which matched well to the nominal tie layer thickness. An accurate measurement of the actual PMMA and PETG tie layer thickness in this sample was difficult owing to the diffuse nature of the interphase regions; however, the PMMA and PETG tie layers did appear thinner when compared to the SAN30 systems with similar nominal tie layer thicknesses.

The observed structural features in these materials match the expected thermodynamic behavior/interactions described in the "Introduction" Section. The PMMA tie material was expected to diffuse into both the PC and the P(VDF-HFP) layers, causing the layer interphase to appear rather diffuse on both sides. The PETG tie material was expected to diffuse into the PC layers rather than P(VDF-HFP) layers, causing the layer interphase to appear diffused on PC side and sharp on P(VDF-HFP) side. The SAN30 tie material was not miscible with either PC or P(VDF-HFP); therefore, the layer interface is rather sharp on both sides. Theoretical simulation indicates\(^\text{26}\) that a broad interfacial region with gradient dielectric constant distribution along the layer thickness direction could lead to high breakdown strength. The breakdown and dielectric data in addition to the AFM images for PC/tie/P(VDF-HFP) confirm the conclusion. The PMMA tie layers diffuse into both PC and P(VDF-HFP) layers, forming a gradient change in PMMA tie layer composition, and gradient dielectric constant distribution along the layer thickness direction. Therefore, the multilayer samples with PMMA as tie layers exhibited the largest enhancement in breakdown properties among all tie materials tested.

The layer interfaces have been reported to influence the hysteresis properties of PC/PVDF- and PC/P(VDF-HFP)-multilayered films.\(^\text{20,21}\) However, no emphasis has been put to study the effect of the interface/interphase on the resulting properties of these materials. As these various PC/tie/P(VDF-HFP) systems directly varied the interfacial characteristics, these systems were interesting platforms to probe this phenomenon. The composition of 46/8/46 was chosen for 65-layer PC/tie/P(VDF-HFP) films for further study as samples exhibited maximum breakdown strength at this composition. The hysteresis properties were evaluated for the 46/8/46

**FIGURE 11** Representative unipolar D-E polarization hysteresis loops for selected 46/8/46 PC/tie/P(VDF-HFP) 65-layer films. The selected tie layers were PMMA, SAN30, and PETG. In addition, the 50/50 PC/P(VDF-HFP) 33-layer film was also included for comparison. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 \(\mu\text{m}\).
PC/tie/P(VDF-HFP) 65-layer samples in addition to the 50/50 PC/P(VDF-HFP) 33-layer sample. Representative hysteresis curves are shown for the selected systems (Fig. 11). Both the hysteresis loop area and the discharged energy density were calculated as a function of electric field for all of the samples (Fig. 12). Quantifying the loop area verified that including a tie layer in the PC/P(VDF-HFP) samples effectively reduced the observed hysteresis behavior (Table 2). The largest reduction was observed in samples with the PMMA tie layers. Interestingly, all the remaining tie layer systems exhibited a marginally reduced hysteresis behavior. For the discharged energy density, the 65-layer PC/tie/P(VDF-HFP) samples generally possessed larger discharged energy densities at a constant electric field. The best systems contained PMMA possessed approximately 20% higher energy densities. In general, the PMMA tie layer system could also be measured at much higher electric fields, which also resulted in higher energy densities. These results correlated with the previously determined breakdown properties. In addition, these experiments also revealed that the PC/PMMA/P(VDF-HFP) 65-layer system possessed better hysteresis behavior as compared to the other two systems with PETG and SAN30 as tie layers. The cause of the reduction in hysteresis behavior in these systems was not obvious; however, it was evident that modifying the layer interphase/interface in these systems had an impact on the hysteresis properties. To help clarify this point, low-field dielectric spectroscopy for the various systems was used to probe the ion migration characteristics in these systems with various tie materials.

FIGURE 12 (a) Charge energy density, (b) discharge energy density, and (c) loss energy density as a function of field for the various 46/8/46 PC/tie/P(VDF-HFP) 65-layer films in addition to the 50/50 PC/P(VDF-HFP) 33-layer film.
At 20 °C, the dielectric constant and loss tangent of the dielectric constant was measured for the various 65-layer 46/8/46 PC/tie/P(VDF-HFP) systems in addition to the 33-layer 50/50 PC/P(VDF-HFP) control (Fig. 13). One major peak was observed and related to $\alpha_c$ of P(VDF-HFP) around 50 Hz in Figure 13(b). The 65-layer PC/PETG/P(VDF-HFP) and PC/SAN30/P(VDF-HFP) systems in addition to the 33-layer PC/P(VDF-HFP) control exhibited ion migration peak below 1 Hz; however, no ionic peaks were detected in the frequency range tested [Fig. 13(b)]. Another interesting feature was that the PMMA tie layer system had the highest dielectric constant at 20 °C [Fig. 13(a)]. A list of the dielectric constants for PC/tie/P(VDF-HFP) systems at 1 Hz is shown in the first column of Table 3. A frequency of 1 Hz was chosen because it is the one for D-E hysteresis measurements and is well above the ionic relaxation peak. The second and third columns show the calculated dielectric constant and effective dielectric constant of P(VDF-HFP) based on the following equations:

$$\frac{1}{\varepsilon_{\text{calculated}}} = \frac{0.08}{\varepsilon_{\text{tie}}} + \frac{0.46}{\varepsilon_{\text{PC}}} + \frac{0.46}{\varepsilon_{\text{P(VDF-HFP)}}}$$

(4)

$$\frac{0.46}{\varepsilon_{\text{eff,P(VDF-HFP)}}} = \frac{1}{\varepsilon_{\text{Measured}}} - \frac{0.08}{\varepsilon_{\text{tie}}} - \frac{0.46}{\varepsilon_{\text{PC}}}$$

(5)

where $\varepsilon_{\text{calculated}}$, $\varepsilon_{\text{tie}}$, $\varepsilon_{\text{PC}}$, $\varepsilon_{\text{P(VDF-HFP)}}$, and $\varepsilon_{\text{eff,P(VDF-HFP)}}$ are the calculated dielectric constants of 65-layer films, tie materials, PC control, P(VDF-HFP) control, and effective dielectric constant of P(VDF-HFP) layer, respectively. Equations (4) and (5) do not take into consideration the loss part of the dielectric constant. Equation (4) assumes that the intermix of tie material with PC and P(VDF-HFP) does not change the dielectric constants of tie materials, PC and P(VDF-HFP). Equation (5) assumes that the dielectric constants of tie materials and PC in the layered films are the same as in bulk. Dielectric constants of 10 μm PC, P(VDF-HFP), PMMA, SAN30, and PETG films were measured to be 2.81, 11.20, 3.71, 2.90, and 3.40, respectively. The calculated effective dielectric constant was highest for PMMA tie system. One speculation is that PMMA can induce the formation of $\beta$-crystals in P(VDF-HFP), which has higher dielectric constant than $\alpha$-crystals in bulk P(VDF-HFP). The system with SAN30 tie material exhibited intermediate effective dielectric constant of P(VDF-HFP). Pure PAN is considered partially miscible with P(VDF-HFP), and therefore some level of interaction was expected for SAN30 and may result in a similar behavior although to a much smaller degree. For the system with PETG tie material, the effective dielectric constant was very close to the series model owing to very little

**TABLE 2** Maximum Discharge Energy Density and Hysteresis Property Values at 500 kV/mm as a Function of Nominal Tie Layer Thickness for the 65-Layer 46/8/46 PC/tie/P(VDF-HFP) Multilayer Films

<table>
<thead>
<tr>
<th>Tie Material</th>
<th>Maximum Discharge Energy Density (J/cc)</th>
<th>Discharge Energy Density at 500 kV/mm (J/cc)</th>
<th>Loss Energy Density at 500 kV/mm (J/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No tie</td>
<td>5.72</td>
<td>4.75</td>
<td>4.79</td>
</tr>
<tr>
<td>PMMA</td>
<td>8.36</td>
<td>5.62</td>
<td>2.90</td>
</tr>
<tr>
<td>PETG</td>
<td>6.11</td>
<td>5.07</td>
<td>3.79</td>
</tr>
<tr>
<td>SAN30</td>
<td>4.86</td>
<td>4.86</td>
<td>3.85</td>
</tr>
</tbody>
</table>

**FIGURE 13** Measured (a) dielectric constant and (b) dielectric loss tangent of various 46/8/46 PC/tie/P(VDF-HFP) 65-layer films. The 50/50 PC/P(VDF-HFP) 33-layer was also included for comparison. All tests are done at 20 °C.
interaction between PC and P(VDF-HFP). From the effective dielectric constant of P(VDF-HFP) data of the various tie materials, it is concluded that the interaction between the P(VDF-HFP) and the tie material played significant role rather than interaction with PC.

To gain a better understanding on the ion migration behavior in these materials, the low-frequency dielectric spectroscopy was measured for the various 46/8/46 PC/tie/ P(VDF-HFP) 65-layer samples in addition to the 50/50 PC/ P(VDF-HFP) 33-layer sample at a measuring temperature of 100 °C to drive the ion migration peak to higher frequencies (Fig. 14). The data for the 50/50 PC/P(VDF-HFP) sample clearly show a peak centered at 30 Hz which was assigned to the ion migration in the P(VDF-HFP) layers. Addition of a tie layer had a varying effect on this ionic peak. For the PETG and SAN30 tie layers, the ionic peak was centered around 40 and 25 Hz, respectively. All of the changes were minor in these systems with PETG and SAN30 tie materials. However, the samples with PMMA tie layers produced a dramatically different result. The ionic peak in these samples shifted to lower frequencies, which was around 4 Hz. This reduction indicated that the ion migration was suppressed in 65-layer PC/PETG/P(VDF-HFP) which correlates to the reduction in the hysteresis loop area for these 65-layer PC/ PMMA/P(VDF-HFP). One possibility is the localized mixing of PMMA into P(VDF-HFP) in the interphase regions may be tying up these ionic species, making them more immobile under an applied electric field. The other possibility is the PMMA molecules intermix with the amorphous part of P(VDF-HFP), making P(VDF-HFP) chains harder to move, and effectively excluding the ions and reducing the ion mobility.

CONCLUSIONS

The inherent flexibility in the multilayer coextrusion process allows for the production of a wide range of layered structures. Utilizing this flexibility, three-component multilayer films with ATBTATBTA configuration were produced to directly modify the layer interphase/interface between PC and P(VDF-HFP) layers. The tie layer materials were chosen specifically to vary the interaction of these materials. Incorporation of a tie layer between PC and P(VDF-HFP) in multilayers had a significant impact on the dielectric properties of these materials. The 65-layer PC/PETG/P(VDF-HFP) system exhibited enhanced dielectric breakdown strength, decreased hysteresis loss energy density, and slower ion migration behavior. It was determined that the improved dielectric properties were attributed to the high interactivity between PMMA tie layers and both PC and P(VDF-HFP) layers. The other two systems with PETG and SAN30 as tie layers exhibited marginal improvements in dielectric properties because PETG and SAN30 do not highly interact with P(VDF-HFP). Highly interacting tie layers, in this case PMMA, resulted in enhanced breakdown properties, with approximately a 25% enhancement with only 25-nm PMMA layers as compared to the PC/P(VDF-HFP) films without tie layers. The layered structure in these PC/tie/P(VDF-HFP) multilayer samples was evaluated using AFM. Distinct PMMA tie layers were not found in the samples with 25-nm nominal PMMA layer thickness with the layer interface, appearing rather diffuse into both PC and P(VDF-HFP) layers. It was determined that the PMMA tie layers were completely interdiffused into both the PC and the P(VDF-HFP) layers. This interphase region is believed to be responsible for the enhanced

<table>
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<tr>
<th>TABLE 3 Measured and Modeled Dielectric Constants of PC/tie/P(VDF-HFP) 46/8/46-Multilayered Films at 20 °C, and Effective Dielectric Constants of P(VDF-HFP) Calculated from Series Model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Measured Dielectric Constant</strong></td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>50/50 PC/P(VDF-HFP)</td>
</tr>
<tr>
<td>46/8/46 PC/PMMA/P(VDF-HFP)</td>
</tr>
<tr>
<td>46/8/46 PC/SAN30/P(VDF-HFP)</td>
</tr>
<tr>
<td>46/8/46 PC/PMMA/P(VDF-HFP)</td>
</tr>
</tbody>
</table>

Dielectric constants of PC, P(VDF-HFP), PMMA, SAN30, and PETG controls were measured to be 2.81, 11.20, 3.71, 2.90, and 3.40, respectively.
breakdown properties by smoothing dielectric constant distribution along the film thickness direction. The impact of these materials also extended to the hysteresis properties, where the PMMA tie layers reduced the hysteresis loop area and increased the maximum discharged energy density. The reduction in hysteresis properties in these samples was correlated to a reduction in the ion migration peak, which was shifted to lower frequencies as a result of the localized mixing of PMMA and P(VDF-HFP) along the layer boundaries. This interphase region can effectively reduce the ion mobility within the layer by creating ion trapping sites in PMMA/P(VDF-HFP) interphase or reducing the ion migration distance inside P(VDF-HFP). Additionally, a small fraction of PMMA in P(VDF-HFP) can increase the effectively dielectric constant of P(VDF-HFP) significantly. One speculation is that PMMA was miscible with P(VDF-HFP), the PMMA material could act as a lubricating agent which loosens up the dipoles in P(VDF-HFP) layers. Another speculation is that PMMA could induce the formation of \( \beta \)-crystals in P(VDF-HFP), which has higher dielectric constant than \( \alpha \)-crystals in bulk P(VDF-HFP).

**ACKNOWLEDGMENT**

This research was generously supported by the National Science Foundation through the Center for Layered Polymeric Systems (CLiPS) Science and Technology Center Grant DMR-0425914 and the Office of Naval Research Grant N00014-11-0251.

**REFERENCES AND NOTES**