POLYMER MULTILAYER FILMS FOR OPTICAL AND DIELECTRIC APPLICATIONS

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Polymer Multilayer Films for Optical and Dielectric Applications

Abstract

by

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Chapter 1: Performance of new polymer nanolayer GRIN system with a high temperature polymer, OKP4HT, was evaluated. A combination of extruded nanolayered GRIN film systems, comprised of a total of five different materials, were combined to produce optical laminates with a high refractive index range, 1.445 – 1.630. The optical performance of a series of varied magnitude GRIN lenses was evaluated. Refractive index distribution and surface profile of the GRIN lenses match the expected designed value. Increasing the lens refractive index range resulted in decreased spherical aberrations following analytical optical predictions. An analytical approach was reported to correlate the polymer material UST to the onset of polymer material loss modulus as measured by DMTA. Thermo-optical interferometry measurements of irreversible lens deformation confirmed the lenses upper service temperature (UST) as 125°C for the OKP4HT/PC system as compared to 75°C for an PMM/SAN17 systems.

Chapter 2: Inspired by the soft, deformable human eye lens, a synthetic polymer GRIN lens with an adaptive geometry and focal power has been demonstrated via extrusion and thermoforming of nanolayered elastomeric polymer films. Polymer nanolayered films comprised of two thermoplastic polyurethanes with a refractive index difference of 0.05
were co-extruded via forced assembly technique. The set of thirty nanolayered polymer films exhibited transmission near 90% with each film varying in refractive index by 0.0017 as a result of the nanolayering arrangement. An adaptive GRIN lens was fabricated from a laminated stack of the variable refractive index films with a 0.05 spherical gradient refractive index distribution and mechanically deformability based on mechanical compression of the lens. Variation in the optical properties, 20% variation in focal length and reduced spherical aberration, of the deformable GRIN lens were measured and simulated by placido-cone topography and ANSYS methods. The demonstration of a solid state, dynamic focal length, GRIN lens with improved aberration correction was discussed in contact of potential future implantable devices.

Chapter 3: Enhanced dielectric properties were achieved through interface/interphase modulation and biaxial orientation for the poly(ethylene terephthalate)/poly(methyl methacrylate)/poly(vinylidene fluoride-co-hexafluoropropylene) [PET/PMMA/P(VDF-HFP)] three-component multilayer films. Because PMMA is miscible with P(VDF-HFP) and compatible with PET, the interfacial adhesion between PET and P(VDF-HFP) layers was greatly improved. Biaxial stretching of the as-extruded multilayer films induced formation of highly oriented fibrillar crystals in both P(VDF-HFP) and PET. There were several effects resulted from biaxial orientation. First, the parallel orientation of PVDF crystals reduced the dielectric loss from the αc relaxation in α crystals. Second, biaxial stretching constrained the amorphous phase in P(VDF-HFP) and thus the migrational loss from impurity ions was reduced. Third, biaxial stretching induced a significant amount of rigid amorphous phase in PET, further enhancing the breakdown strength of multilayer films. Due to the synergistic effects of improved interfacial adhesion and biaxial
orientation, the PET/PMMA/P(VDF-HFP) 65-layer films with 8 vol.% PMMA exhibited the optimal dielectric properties with an energy density of 17.4 J/cm$^3$ at breakdown and the lowest dielectric loss. These three-component multilayer films are promising for future high energy density film capacitor applications.

Chapter 4: Advanced film capacitors require polymers with high thermal stability, high breakdown strength, and low loss for high temperature dielectric applications. In order to fulfill such requirements, two polymer multilayer film systems were coextruded via a forced assembly technique. High glass transition (Tg) polycarbonate (HTPC) and polysulfone (PSF) were layered with poly(vinylidene fluoride) (PVDF), respectively. The PSF/PVDF system was more thermally stable than HTPC/PVDF system. For dielectric properties at high temperatures the PSF/PVDF system exhibited higher breakdown strength and lower hysteresis compared with HTPC/PVDF system. These results demonstrated that PSF/PVDF was a superior system to HTPC/PVDF for high temperature dielectric capacitors.
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CHAPTER 1

Evaluation of High Temperature Polymers in Nanolayered Films and Gradient Refractive Index (GRIN) Lenses

1.1 Introduction

Optical grade polymers have been widely used in many optical products and applications, including charge-coupled device (CCD) cameras [1], prisms [2], laser collimation [3], sensors [4], medical disposal optics [5], and optical fibers [6]. Polymer materials have advantages as compared with traditional inorganic glasses which include lower material density, better impact resistance, and ease of mass producibility/lower cost. Polymer materials are generally between one half and one fifth of the densities of comparable inorganic glass. The cost of injection/compression molding and polishing of precision polymer optical devices is cheaper and less time-consuming than that of grinding and polishing glass devices, which offers higher volume production capabilities that are fast, repeatable, and lower cost. Polymers materials also possess higher impact properties and avoid fracture/chipping much better than glass that leads to optical lens durability in high vibration or impact optics for military applications like goggles, vehicle optics, and heads-up displays [1, 7].

However, current optical grade polymers materials have certain drawbacks which limit their application as compared to inorganic glasses. Polymer optical devices have lower environmental exposure conditions, i.e. temperature/humidity/radiation, as compared with inorganic glass. Another disadvantage of polymer optical devices is attributed to its relatively lower refractive index/optical power associated with polymer [8]. To overcome
these drawbacks, an emerging polyester (OKP4HT, Osaka Gas Chemical Co., Ltd) has been developed with a glass transition temperature of 142°C and refractive index of 1.63. This material also has extremely low birefringence and is highly transmissive in the visible and SWIR wavelengths.

Availability of a high refractive index, high temperature resistant optical polymer material like OKP4HT enables potential advances in specialty polymer optics enabling performance and plastic lens inclusion into environments and optical systems were environmental conditions require material survivability above 100°C. Incorporation of the OKP4HT material into nanolayered polymer GRIN lenses is an approach that would benefit from the higher material refractive index and operation temperatures. An alternative way to improve the performance of polymer optical devices is based on advanced processing methodology. Polymeric GRIN lenses, fabricated through a process of nanolayer coextrusion and film lamination [17], have demonstrated high optical performance and lightweight designs through utilization of a variety of axial, radial, and spherical GRIN profiles, large refractive index differences, and lens apertures [17, 18].

The polymeric, nanolayered, GRIN optic fabrication process has demonstrated a high degree of flexibility by fabricating optics over a wide range of sizes, powers, and geometries to demonstrate performance and weight savings advantages of GRIN. A small diameter, 6 mm, biconvex, bio-inspired, aspheric GRIN lens based on the human eye geometry and refractive index distribution was fabricated using a nanolayer coextrusion technique with poly(methyl methacrylate) (PMMA) and a styrene-acrylonitrile copolymer with 17 wt% acrylonitrile (SAN 17). The refractive index difference of this GRIN lens is 0.05 [19]. The focusing property of this GRIN lens has exceeded that of the PMMA lens.
To demonstrate the advantage of a nanolayer polymer GRIN lens against a conventional inorganic glass lens, a 20 mm diameter plano-convex GRIN lens of PMMA/SAN17 was designed and constructed to compare with a bi-convex BK7 lens with similar f/# [20]. The GRIN lens has better focusing properties against the BK7 lens, which were characterized using spot size measurement against a USAF test chart image. Additionally, the GRIN lens achieved similar f# and better focusing properties with a significant weight reduction. The weight of the PMMA/SAN17 GRIN lens was only one quarter of the BK7 glass lens, because the density of PMMA/SAN17 (1.2 g/cm$^3$) is lower than the density of BK7 (2.5g/cm$^3$). Another benefit of nanolayer polymer GRIN lenses is to extend the possibility and flexibility of lens design. Spherical ball lenses, which are attractive because of their low f/# and wide field of view, need large GRIN distribution to reduce or eliminate aberrations [18]. Limitations of current GRIN lens fabrication techniques are on refractive index range and refractive index distribution control. Using nanolayer coextrusion techniques, a spherical ball lens with refractive index range of 0.08 was produced. This technique showed flexibility to control inside refractive index distribution and the GRIN ball lens provided better focusing properties.

The purpose of this work is to evaluate the performance of high temperature polymer, OKP4HT, processed with nanolayer coextrusion for optical applications. Polymer nanolayered films with OKP4HT were extruded using nanolayer coextrusion techniques. The refractive index and light transmission of the films were confirmed. One of the motivations to develop nanolayer GRIN systems was to achieve better optical performance due to its high refractive index. A series of plano-convex lenses were produced with varied magnitudes of gradient refractive index distributions, ranging from 0 to 0.185, through
incorporation of OKP4HT/Polycarbonate (PC) with PMMA/SAN17 nanolayers. The effect of OKP4HT inclusion into nanolayered, polymeric GRIN lenses was evaluated through measurements of the lens optical power and interferometric surface measurements to GRIN lens geometry as a function of cyclic exposure to hot/cold temperature environments. Thermal hysteresis measurements were used to recommend the upper service temperature, i.e. high temperature exposure limit, of a polycarbonate (PC)/OKP4HT GRIN lens and a PMMA/SAN17 GRIN lens. The effect of temperature on the OKP4HT polymer material was also correlated with thermal mechanical properties of polymer nanolayer films.

1.2 Experiments

High temperature polyester was supplied by Fiber Optics (OKP4HT). Polycarbonate was supplied by The Dow Chemical Company (PC, Calibre 201-15). Styrene–acrylonitrile copolymer was provided by Bayer Cooperation (SAN17, Lustran Sparkle) with 17% weight percent of acrylonitrile in the copolymer [21]. Poly(methyl methacrylate) was provided by Arkema (PMMA, Plexiglas V920). Poly(vinylidene fluoride-co-trifluoroethylene) was provided by Solvay Plastics (PVDF-HFP, Solef 21508). All resins were used “as-received” without further purification or modification. A PVDF-blend (PVDFb) was produced by extrusion blending PMMA with PVDF-HFP (1:1 v/v) at 230°C using a Haake 18 mm twin screw extruder. The optical and thermal properties of these materials are listed in Table 1.1.

Polymer nanolayered films were processed via a forced assembly film coextrusion processing technique at Case Western Reserve University [22]. The setup of this continuous processing unit to produce nanolayered films was illustrated in Figure 1.1. In
forced assembly coextrusion, two polymer materials, A and B, were extruded via two single-screw extruders at a matched viscosity extrusion temperature followed with conveyance into the layering dies by two melt metering pumps. The metering pumps were used to ensure a desired volumetric ratio of polymer A and polymer B during melt processing. After the metering pumps, polymer melts A and B were combined in a custom designed three-layer coextrusion feedblock to form a three layer A/B/A structure. The three layer polymer melt then flowed through a series of layer multiplier dies. In each of the multipliers, the number of layers in the polymer melt stream is doubled by a cutting, splitting, restacking process. For example, polymer melts with an A/BA structure were split horizontally into two A/B/A melt flows, compressed in the vertical direction, and restacked and spread horizontally to form an A/B/A/B/A five layer structure after the first layer multiplier die. Additional layer multiplying dies placed in series will continue to sequentially cut, stack, and spread the polymer melt stream resulting in a final polymer melt that can be comprised of $2^{(n+1)}+1$ number of layers where $n$ is the number of layer multiplying dies in series. A sacrificial skin layer of low density polyethylene (LDPE), which was later be removed prior to characterization or lens processing, was used to protect the films from dust as well as to minimize surface roughness during film coextrusion. Ultimately, the layered polymer melt was spread in a 350 mm wide film die and cast onto a heated, chrome polished rotating roll to a target thickness of 50 microns.

Utilizing this technique, polymer nanolayered films with 4097 layers were produced in four different systems including OKP4HT/PC, PC/SAN17, SAN 17/PMMA, and PMMA/PVDF-blend. The final film thickness (without sacrificial skin layer) of all systems was 50 µm. By targeting this film thickness with 4097 layers, the individual layer thickness
of nanolayered film was below a quarter wave of visible light that results in a novel optical nanolayered film property of high optical transparency and volumetric composition controlled refractive index. The volume ratio of polymer A and polymer B in each system was maintained during processing by previously described melt metering pumps and varied in 2% steps, so the respective volume ratio of PMMA/SAN17 were started from 100/0, 98/2 through 50/50 and ended with 0/100. Theoretically, the refractive index of polymer nanolayered films followed a volumetric compositional additive model and the volume compositions of each polymer system were selected to achieve a refractive index step size around 0.002.

The refractive index of the nanolayered films was measured using a 2010 Metricon prism-coupler equipped with a 633nm laser. The measurement was carried out at room temperature. Polymer nanolayered film was push onto a prism with known refractive index under pressure. The laser beam passed through the prism and was normally totally reflected at the interface between the prism and the polymer film onto a detector. By rotating the laser beam, a critical angle was found as the reflected intensity of the laser beam dropped. The refractive index of polymer film can be calculated using critical angle based on Snell’s law [23]:

\[ n_{prism}\sin\theta_{prism} = n_{film}\sin\theta_{film} \] (1)

Where \( n \) is refractive index and \( \theta \) is the angle. \( \theta_{prism} \) is at critical angle, \( \theta_{film} \) equaled 90° and refractive index of the film can be calculated.

Light transmission of the polymer nanolayered films were measured using an Ocean Optics SD 2000 fiber optic spectrometer. The spectrums were collect with wavelengths from 400 to 1000 nm.
Polymer GRIN lenses were fabricated using the following procedure. A series of polymer nanolayered films were stacked and consolidated into a GRIN sheet. The refractive index distribution of the GRIN sheet can be controlled by selecting films with appropriate refractive index. One hundred polymer films with a controlled refractive index distribution were formed into a 5 mm stack. This film stack was then further consolidated to a GRIN sheet by compression molding. The thickness of the final GRIN sheet was 4 mm. Once the GRIN sheet was formed, a GRIN lens preform was fabricated using a compression molder with a concave (R=20.7 mm) and a convex (R=18.1 mm) spherical glass mold. A plano-convex GRIN lens was then fabricated by polishing the concave surface of the GRIN shell preform.

Attenuated total reflectance/Fourier transform infrared (ATR-FTIR, Nexus 870, Thermo Nicolet) microspectroscopy was used to characterize relative polymer composition at each point of the lenses and then used to calculate and confirm refractive index distribution. The microscope was equipped with a germanium crystal and an attenuated-total-reflectance slide-on attachment. The resolution of the spectra was 2 cm\(^{-1}\) (32 scans). The spectra were collected at 500 μm intervals along the diameter on the plano-surface of the lens. The sample area for each spectrum was 75μm x 75μm.

A two-pin-hole method was used with the following procedure to characterize focal length vs. aperture of the GRIN lens [18]. Collimated laser (633nm) was transmitted through a series of two-pin-holes with a varying distance (d₁) from 0.5 mm to 16 mm. After passing through the pinholes, normally collimated laser beams were then focused through the GRIN lens and were projected on a screen. The focal length (f) as a function of lens aperture
was calculated from $d_1$, $d_2$ and the distance from the lens to the screen ($l$) using equation (2):

$$f = \frac{ld_1}{d_1+d_2}$$

Optical form and figure of the GRIN lenses was characterized by surface interferometry at 633 nm using a Zygo Verifire Interferometer. Surface geometry was measured for all lenses with the optics resting unconstrained in a custom fabricated counter-bored optics holder that served as a resting ledge for surface measurements in the vertical interferometer. All measurements were conducted in a climate controlled environment kept at 22°C.

Dynamic mechanical thermal analysis (DMTA) was carried out using a DMA Q800 (TA Instruments) operating in a tensile mode. PMMA/SAN17 films were measured from 20°C to 130°C and PC/OKP4HT films were measured from 20°C to 170°C. Heating rate of DMTA test was 3°C/min and frequency was 1 Hz.

1.3 Results and discussion

**Optical properties of polymer nanolayered films**

The first step to fabricate a GRIN lens with the OKP4HT material involved characterizing optical properties of coextruded polymer nanolayered films to verify the composite film refractive index for building the GRIN distribution. The refractive index (R.I.) of the nanolayered films was measured using a prism coupling technique at room temperature with a laser wavelength of 633 nm. The R.I. of nanolayered films with a systematically varied the polymer composition against a compositional additive model [18] is described in Equation (3).
\[ n = n_1 \phi_1 + n_2 \phi_2 \]  

Where \( n \) is the total refractive index of the film. \( n_1 \) and \( n_2 \) are refractive indices of polymers and \( \phi_1 \) and \( \phi_2 \) are volume compositions of polymers. The refractive indices of OKP4HT (R.I. =1.63) /PC (R.I. =1.58), PC/SAN17 (R.I. =1.57), SAN 17/PMMA (R.I. =1.49), and PMMA/PVDF-blend (R.I. =1.445) films were plotted in Figure 1.2. As predicted for all the nanolayered film systems, the refractive indices of the films increased with increasing ratio of high refractive index components. Therefore, the refractive index range of the system was extended by introducing a high refractive index polymer (OKP4HT, R.I.=1.63).

In addition to the refractive index, light transmission is a key optical property for nanolayered films utilized to constructing optics. The light transmission spectra of PC/OKP4HT, PC/SAN17, PMMA/SAN17 and PMMA/PVDF-b (50/50, v/v) was measured with UV/Vis spectrometer and plotted in Figure 1.3 from 400nm to 1000nm. For all nanolayered films, the film thickness was held constant at 50 \( \mu \)m at 4097 layers that result in an individual layer thickness at approximately 12 nm which is below the quarter wavelength. At this layer thickness, there was no light scattering at layer interfaces and the nanolayered films exhibited uncorrected, i.e. no correction for film-air surface losses, light transmission of about 90\% irrespective of volumetric composition [24].

**Optical performance of high temperature GRIN lens**

Nanolayered films with an appropriate refractive index and light transmission were selected, physically stacked, and thermoformed against a pair of concave and convex
spherical molds under vacuum and heat to produce a laminated GRIN preforms with a linear refractive index distribution through the thickness direction following processes previously described [17]. The laminated GRIN preform was polished on the concave surface to a plano-surface. The final geometry of the GRIN preform and GRIN lens were shown in Figure 1.4. The designed refractive index distribution could be achieved by choosing and stacking polymer nanolayered films with appropriate refractive indices. The refractive index distribution of the GRIN lens along the radius direction is described by Equation (4) [25].

$$n(r) = n_{max} - (n_{max} - n_{min}) \times \frac{\sqrt{r^2 + R_1^2} - R_0}{R_2 - R_1}$$  \hspace{1cm} (4)

Where $n_{max}$ and $n_{min}$ are the maximum and minimum refractive indices of the GRIN sheet/lens; $R_2$ and $R_1$ are the radii of the GRIN lens preform, which are 20.7 mm and 18.1 mm respectively; and $r$ is the distance from the center of the lens to the measured point along the radius direction on the flat side of the lens. To characterize the refractive index profile of the GRIN lens, the composition of the polymer pairs along the radius direction was measured by ATR-FTIR microspectroscopy. The polymer composition at a certain point was determined from normalized peak intensity for OKP4HT at 1721 cm$^{-1}$, PC at 1772 cm$^{-1}$, SAN17 at 698 cm$^{-1}$, PMMA at 1727 cm$^{-1}$, and PVDF-HFP at 876 cm$^{-1}$ [25]. The refractive index of the measured point was calculated from the composition of the polymers. The predicted and ATR-FTIR-measured refractive index distributions of a GRIN lens with a $\Delta n=0.185$, were plotted in Figure 1.5. The refractive index distribution of the GRIN lens matched the expected design profile.
In order to characterize the optical performance of a high temperature GRIN lens with extended Δn range, a series of GRIN lenses with a Δn up to 0.185 were produced (Table 1.2). An OKP4HT homogeneous lens was also fabricated with the same geometry as the control lens. The GRIN lens focal length is attributed by a combination of optical power contributions, curvature, and internal optic refractive index distribution. The power contribution of lens curvature can be calculated from lens maker’s equation, Equation (5).

\[
\frac{1}{f} = (n - 1)\left[\frac{1}{R_1} - \frac{1}{R_2} + \frac{(n-1)d}{nR_1R_2}\right]
\]  

(5)

Where \(f\) is the focal length of the lens, and \(n\) is the refractive index of the lens material. \(R_1\) and \(R_2\) are radii of curvature of the lens, and \(d\) is the thickness of the lens. Additionally, the contribution of the refractive index distribution can be obtained analytically from the focusing power of a GRIN medium with a parabolic refractive index gradient as discussed in a previous work [6]. After combining the effects of the curvature and refractive index distribution, the focal length (\(f\)) dependence on position of the lens (\(r\)) of the GRIN lens can be described by the following equation, Equation (6):

\[
\frac{1}{f} = \frac{2(n_{\text{max}} - n_{\text{min}})}{R_2^2 - R_1^2}\left(\sqrt{R_2^2 - r^2} - R_1\right) + \left(\sqrt{R_2^2 - r^2} + \frac{R}{\tan(\arcsin(\frac{r \cdot n_{\text{min}}}{R_2 \cdot n_{\text{air}}} - \arcsin(r/R_2)) - R_2}\right)^{-1}
\]  

(6)

Where \(n_{\text{max}}\) and \(n_{\text{min}}\) are the maximum and minimum refractive indices and \(n_{\text{air}}\) is the refractive index of air. \(R_1\) and \(R_2\) are radii of the GRIN lens perform, and \(r\) is the half lens aperture. For the OKP4HT control lens, \(n_{\text{max}}\) is equal to \(n_{\text{min}}\). Therefore, the focal length equation of the OKP4HT control lens can be simplified [18] to Equation (7):
\[
\frac{1}{f} = \left(\sqrt{R^2 - r^2} + \frac{R}{\tan(\arcsin(r/n_{\text{air}}^2 \cdot \arcsin(R) - \arcsin(R^2)) - R_2)^{-1}}\right)
\]

Spherical aberration can be defined as the focal length difference between the center and the edge of the lens. To characterize the spherical aberration correction of a series of GRIN lenses ($\Delta n=0.05$, $\Delta n=0.14$, and $\Delta n=0.185$) and an OKP4HT lens, the focal length as a function of aperture of lens ($r$) is measured against this analytical prediction using the two-pin-hole method [25]. The focal length vs. aperture results for the GRIN lens and OKP4HT homogenous lenses were plotted in Figure 1.6. As expected due to the larger optical path length, a homogeneous lens focal length at small aperture was larger than on the edges. A series of increasing $\Delta n$ of the GRIN optics resulted in a dramatically smaller difference in the focal length between the small and large apertures. The GRIN lens with $\Delta n=0.185$ even exhibited over correction, that resulted in a reversing of the spherical aberration. This demonstrates the ability to design a GRIN lenses with an ability to correct spherical aberrations. Therefore, an optical imaging system with better optical power can be designed and produced by achieving a high $\Delta n$ GRIN system with a high temperature polymer (OKPH4T). Additionally, the optical system can be lighter and less complex with a higher $\Delta n$ GRIN system.

**Temperature survival performance**

High temperature polymer, OKP4HT, can not only increase refractive index range of the GRIN system, but also improve the temperature survival performance. In order to investigate the effect of a high temperature polymer, OKP4HT, on the temperature survival performance of the GRIN system, two polymer GRIN lens systems were fabricated using PMMA/SAN17 and PC/OKP4HT, with the parameters listed in Table 1.3. The 3D surface
topography of an initial GRIN lens was measured using a Zygo interferometer equipped with a diode laser (λ=633 nm). The as molded convex surface of the OKP4HT/PC GRIN lens was measured interferometrically, Figure 1.7, as a reference prior to the thermal treatment. In this image, the red regions corresponded to a measured radius larger (+ deviation) than the designed value (20.7 mm) and the blue regions corresponded to a measured radius less (- deviation) than the designed value. The maximum positive deviation is 0.83 waves or 529 nm (0.83x633 nm), while the maximum negative deviation is 468.42 nm. The deviation along the lines drawn in Figure 1.7a are plotted in Figure 1.7b, and across all the points the deviation was always within 1 wave (<633 nm). The 3D deviation profile of the GRIN lens is shown in Figure 1.7c, and demonstrates that the measured 3D profile matched that of the designed value. The shape of a second PMMA/SAN17 GRIN lens was also measured and found to follow the designed value.

Polymeric GRIN lens upper service temperature (UST) and thermal hysteresis effects on PMMA/SAN17 GRIN lenses were characterized using the following procedure, Figure 1.8. A PMMA/SAN17 GRIN lens was heated in an oven at 30°C for 30 minutes and then cooled down to room temperature over a 4 hour period to ensure internal optic temperature equilibrium prior to interferometric measurements. The convex surface of the lens was measured using Zygo interferometer. The measured shape after heating was compared with original shape of the lens measured at room temperature (25°C). After this, the lens was again heated in the oven at 5°C higher temperatures (35°C) and all the previous steps will be repeated to determine if permanent optic shape changes resulted. Thermal exposures to increasingly higher temperatures were repeated following the previously described
procedure up to the glass transition temperature of the highest nanolayered film polymer material.

The ultimate degree of GRIN optic convex surface radius change was determined by through a comparison of the maximum radius deviation from the initial, room temperature, value. The radius deviation of the PMMA/SAN17 GRIN lens was plotted in Figure 1.9a. The positive and negative deviations of the PMMA/SAN17 GRIN lens were approximately 0.5 waves after heating from room temperature up to 75°C. These values doubled at 80°C and increased dramatically at 85°C. The 2D deviation profile (Figure 1.9a insert) of the PMMA/SAN17 GRIN lens also changed significantly when the temperature reached 80°C. These data suggested that the shape/optical properties of the lens will not be significantly changed by heating with temperature up to 75°C. Therefore, the UST of PMMA/SAN17 system was designated to be 75°C.

Motivated by the need for an optical system with a higher upper service temperature (UST) than that of the PMMA/SAN17 system, a second polymer nanolayered system, PC/OKP4HT, was developed. The UST of the PC/OKP4HT GRIN lens was determined using the same method as discussed previously. The interferometric figure of the PC/OKP4HT GRIN lens was plotted in Figure 1.9b. The positive deviation of the PC/OKPH4T GRIN lens increased from 0.5 waves to 2 waves and the negative deviation increased from 0.5 waves to 1 wave at 130°C, while the 2D radius deviation profile (Figure 1.9b insert) showed similar changes. Therefore, the UST of OKP4HT/PC system was assigned at 125°C which is 50°C higher than PMMA/SAN17 system.

The relation of the UST to the Tgs of homogeneous polymer materials as well as 50/50 nanolayered films was characterized using DMTA. For the PMMA/SAN17 system, Tg of
PMMA and SAN17 were 99°C and 104°C which were determined by loss modulus peak of each polymer (Table 1.4). 4097 layer PMMA/SAN17 film (50/50 v/v) had a single \( T_g \) at 102°C, which represents agreement to a compositional dependent average \( T_g \) of the two homogeneous materials. The \( T_g \) of OKP4HT/PC system followed the similar trend. 4097 layer of PC/OKP4HT film (50/50 v/v) had a \( T_g \) of 145°C, which was approximately the average \( T_g \) of PC (147°C) and OKP4HT (142°C). Based on previous research [26], when two compatible polymers were layered against each other, an “interphase region” was created. The \( T_g \) shifted closer together with decreasing layer thickness. When the individual layer thickness was less than the interphase thickness of the two materials, a single \( T_g \) was exhibited for compatible polymer nanolayered films with thousands of layers. The merged \( T_g \) can be predicted by the volume ratio of the two polymers based on the following equation (8):

\[
T_{g,i} = V_A T_{g,A} + V_B T_{g,B}
\]  

(8)

Where \( T_{g,i} \) is the glass transition temperature of the nanolayered films, \( T_{g,A} \) and \( T_{g,B} \) are the glass transition temperatures of the two materials, and \( V_A \) and \( V_B \) are the mass ratio of the two materials. The glass transition temperatures of PMMA/SAN17 and PC/OKP4HT films (50/50 v/v) followed the prediction based on this equation. The modulus and loss modulus of PMMA/SAN17 and PC/OKP4HT film (50/50 v/v) vs. temperature were measured (Figure 1.10) to correlate UST to glass transition temperature of polymer nanolayered films. Based on the temperature survival performance study, the shape of PMMA/SAN17 lens began to change at 80°C which was corresponded to the onset of the loss modulus peak of the PMMA/SAN17 (50/50 v/v) films. The OKP4HT/PC GRIN lens exhibited a similar trend. There is greater chain mobility and the system becomes more susceptible to creep.
after the temperature is higher than the onset of the loss modulus peak, which accounts for the measured deformation of the lenses upon heating. By introducing a high temperature polymer system (PC/OKP4HT), polymer chain mobility changed to higher temperature with an increased $T_g$ compared with PMMA/SAN17 system. The upper service temperature of GRIN lens with polymer nanolayered materials was extended 50°C through developing a higher temperature polymer nanolayered system with OKP4HT.

1.4 Conclusions

A high temperature polymer, OKP4HT was involved in developing new polymer nanolayered GRIN systems. Nanolayered films for new polymer GRIN system were coextruded with five different polymers including OKP4HT, PC, SAN17, PMMA, and PVDF-b. The refractive index of the films followed a compositional additive model and increase with increasing ratio of high refractive index polymer. The new polymer nanolayered GRIN system exhibited a higher refractive range of 0.185 without sacrificing light transmission of individual films. A series of GRIN lenses with $\Delta n$ from 0 to 0.185 were produced in order to study the optical performance. Refractive index distribution of polymer GRIN lens was confirmed by calculation from composition of the polymers at each position of the lens. The refractive index distribution was found to match the expected designed profile. The GRIN lens with higher $\Delta n$ value exhibited better spherical aberration correction based on focal length vs. aperture measurement. The GRIN lens with $\Delta n=0.185$ even showed an over correction. Therefore, a polymer GRIN system with high refractive index range will provide better optical power and more flexibility for optical system design and manufacture, which potentially may also decrease the weight and complexity of the optical system. The polymer GRIN system involved OKP4HT can not only increase $\Delta n$ of
the system but also enhance temperature survival performance of the polymer GRIN system. UST of PMMA/SAN17 system and PC/OKP4HT system was determined by thermal cycle of the lens followed with interferometric measurement of shape change vs. temperature. The UST of OKP4HT/PC system was determined to by 125oC, 50oC higher than PMM/SAN17 system, which means the polymer GRIN system will have a better temperature survival performance by involving high temperature polymer, OKP4HT. The temperature survival performance of polymer nanolayered system correlated with the onset of the material loss modulus as measured by material thermal-mechanical testing. Even in a nanolayered state, composite polymer nanolayered films exhibited a single film Tg that followed an volumetric average of the film constituent polymer materials. Optical polymer material systems, even fabricated from thousands of nanolayers, appear to follow an UST predictable by its onset of loss modulus peak.

1.5 References


Table 1.1 Materials for high Δn GRIN lens

<table>
<thead>
<tr>
<th>Material</th>
<th>Commercial Name</th>
<th>R.I. @633nm</th>
<th>T_g (°C)</th>
<th>Melting Point (°C)</th>
<th>Films Extrusion Temperature (°C)</th>
</tr>
</thead>
</table>

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<table>
<thead>
<tr>
<th>Material</th>
<th>Brand</th>
<th>n₀</th>
<th>T₀</th>
<th>ΔT</th>
<th>℃</th>
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</thead>
<tbody>
<tr>
<td>OKP4HT</td>
<td>OKP4HT (Fiber Optics)</td>
<td>1.63</td>
<td>142</td>
<td>-</td>
<td>250</td>
</tr>
<tr>
<td>PC</td>
<td>Calibre 201-15 (Styron)</td>
<td>1.58</td>
<td>147</td>
<td>-</td>
<td>250</td>
</tr>
<tr>
<td>SAN17</td>
<td>Lustron (Ineos)</td>
<td>1.57</td>
<td>104</td>
<td>-</td>
<td>230</td>
</tr>
<tr>
<td>PMMA</td>
<td>Plexiglas V920 (Arkema)</td>
<td>1.49</td>
<td>99</td>
<td>-</td>
<td>230</td>
</tr>
<tr>
<td>PVDF-HFP</td>
<td>Solef 21508 (Solvay)</td>
<td>1.40</td>
<td>-29</td>
<td>135</td>
<td>230</td>
</tr>
</tbody>
</table>
Figure 1.1 Multilayer coextrusion is able to produce nanolayer films with individual layer thickness below a quarter of the wavelength of visible light.
Figure 1.2 Refractive index of nanolayered films
Figure 1.3 Light transmissions of nanolayered films
Table 1.2 Parameters of plano-convex high $\Delta n$ GRIN Lens

<table>
<thead>
<tr>
<th></th>
<th>Materials</th>
<th>R. I.</th>
<th>R (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OKP4HT Control</td>
<td>OKP4HT</td>
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<td>20.7</td>
</tr>
<tr>
<td>$\Delta n=0.05$</td>
<td>OKP4HT, PC</td>
<td>1.63-1.58</td>
<td>20.7</td>
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<tr>
<td>$\Delta n=0.14$</td>
<td>OKP4HT, PC, PMMA, SAN17</td>
<td>1.63-1.49</td>
<td>20.7</td>
</tr>
<tr>
<td>$\Delta n=0.185$</td>
<td>OKP4HT, PC, PMMA, SAN17, PVDF-HFP</td>
<td>1.63-1.445</td>
<td>20.7</td>
</tr>
</tbody>
</table>
Figure 1.4 Design size (a, b) and images (c, d) of GRIN lens preform and GRIN lens after polishing
Figure 1.5 Refractive index distribution of $\Delta n=0.185$ plano-convex GRIN lens
Figure 1.6 Spherical aberration correction of lens with varying GRIN lens Δn.
Table 1.3 Parameters of PC/OKP4HT and PMMA/SAN17 GRIN lens

<table>
<thead>
<tr>
<th>System</th>
<th>Materials</th>
<th>R. I.</th>
<th>R (mm)</th>
</tr>
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<tr>
<td>#1</td>
<td>OKP4HT, PC</td>
<td>1.63-1.58</td>
<td>20.7</td>
</tr>
<tr>
<td>#2</td>
<td>PMMA, SAN17</td>
<td>1.57-1.49</td>
<td>20.7</td>
</tr>
</tbody>
</table>
Figure 1.7 Optical figure of GRIN lens fits well with designed value.
Figure 1.8 Protocol to determine upper service temperature (UST)

1. Heated @T for 30 min
2. Cool down @ room temp. 4 hrs
3. Measure shape w/ Zygo
4. Compare w/ original shape
5. Increase 5°C for heating T
Figure 1.9 Shape change vs. temperature of a) PMMA/SAN17 GRIN lens, b) OKP4HT/PC GRIN lens.
Table 1.4 Glass Transition Temperature of GRIN Films

<table>
<thead>
<tr>
<th>Comp.</th>
<th>$T_g$ (°C)</th>
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<tbody>
<tr>
<td>PMMA</td>
<td>99</td>
</tr>
<tr>
<td>PMMA/SAN17 50/50</td>
<td>102</td>
</tr>
<tr>
<td>SAN17</td>
<td>104</td>
</tr>
<tr>
<td>OKP4HT</td>
<td>142</td>
</tr>
<tr>
<td>OKP4HT/PC 50/50</td>
<td>145</td>
</tr>
<tr>
<td>PC</td>
<td>147</td>
</tr>
</tbody>
</table>
Figure 1.10. DMA of a) PMMA/SAN17 system, b) PC/OKP4HT system.
CHAPTER 2

Bio-inspired Adaptive Gradient Refractive Index (GRIN) Lens

2.1 Introduction

The demand for adaptive lenses with high quality focusing capabilities and compact volume has challenged scientists and engineers to innovate advanced material systems and optical designs. Traditional adaptive lenses rely on a combination of constant-focus lenses, which requires translational displacement of the relative position of one or more glass lenses to tune the focal length [1]. Corrective lenses are also required to rectify aberrations and improve focusing ability. Therefore, high quality adaptive lenses are always heavy, bulky, complex and expensive. In contrast, the human eye lens is a much more compact system that can easily manipulate its focal length by changing the shape of the lens, i.e. shortening or lengthening the lens surface curvature, using variable reversible deformable tension from contraction of the ciliary musculature [2]. Additionally, a gradient refractive index (GRIN) distribution is found in the internal volume of the human eye lens, stemming from variation of an internal protein concentration, system to enhance the lens optical power and correct for optical aberration [3]. Inspired by the functionality of the deformable human eye lens, forced-assembly co-extrusion at Case Western Reserve University represents a technological breakthrough capable of fabricate synthetic polymer nanomaterials for construction of spherical GRIN lenses [4] with large refractive range ($\Delta n$), desired refractive profile and large lens aperture. Utilizing this technique, a plastic GRIN lens with similar refractive index range and surface geometry as found in a human eye lens [5] has been fabricated through a film extrusion, lamination, thermal forming and
finishing procedure. Using poly(methyl methacrylate) (PMMA) and a styrene-acrylonitrile copolymer, this GRIN lens provided a refractive index range of 0.05 and exhibited superior focusing properties compared to a homogeneous PMMA lens.

This rigid plastic human eye lens previously reported by Case Western demonstrated technical possibility for GRIN lens fabrication with advanced focusing property, however, material and processing breakthrough are still demanded for focal length tuning. Although there are several documented alternative approaches to produce adaptive lenses in the literature that include solutions pumped liquid lenses, stimulus driven including pressure [6], temperature [7], electrical field [8], and magnetic field [9] actuation, limitations on lens size or lifetime/hysteresis have prevented adaptation in widespread device use. An approach to achieve a variable refractive index gradient was also achieved through ion diffusion (CaCl$_2$) between two injected microfluidic channels [10-11], however, the potential of leakage, gravitation, electrical insulation, and high voltage requirements (>100 V) render it non-applicable to biological systems and applications. An alternative solution based on a solid-state elastomer polymer materials, which more closely resemble the reversibly, mechanically deformable structure of the human eye lens. These adaptive elastomer lenses exhibit several advantages over adaptive liquid lenses. Sealing and evaporation is of no concern for elastomer lens that eliminates two potential modes of failure. Additionally, elastomer lenses exhibit better tolerance to temperature and gravity. Owing to these advantages, adaptive elastomer lenses has been fabricated using polydimethylsiloxane (PDMS) [12]. The modulus of the lens can be controlled with the crosslinking agent. The shape and focal length of PDMS lenses can be manipulated using mechanical compression, thermal expansion, and electric field. Elastomer provides a
feasible solution to adaptive lens, however, no report was found on elastomer GRIN lens fabrication.

This paper seeks to introduce an innovative method that allows for the fabrication of elastomer adaptive GRIN lens with improved optical focal properties utilizing the forced-assembly co-extrusion technique. Nanolayered polymer films have been co-extruded with two thermoplastic polyurethanes (TPU) with a refractive index difference (Δn) of 0.05. Efficient light transmission and the refractive index of the films have been confirmed. Plano-convex adaptive GRIN lenses have been fabricated and compared to identically shaped homogeneous lenses for comparison of optical performance. The curvature of the adaptive GRIN lenses was manipulated via mechanical compression with a comparison of the simulated and experimentally measured adaptive lens shape change.

2.2 Adaptive GRIN lens fabrication

Materials

Two soft thermoplastic polyurethanes (TPU) selected for deformable GRIN lens fabrication were Carbothane (PC-3595A, Lubrizol Advanced Materials) with a refractive index of 1.49 and Texin (RXT90A, Covestro LLC) with a refractive index of 1.54 (Table 2.1). Carbothane is claimed to be suitable for long term implantation and Texin meets the FDA1680 and FDA 2600 requirements. Both of the TPUs exhibited hardness of 90-95A and transparency above 90% at 633nm. The Ultimate Elongation (%) of Carbothane and Texin are 400% and 520%, respectively. All the polymer resins were dried at 60°C under vacuum for 48 hours before processing.

Polymer Nanolayer Films
A series of Carbothane/Texin films with specific refractive index were extruded via nanolayer coextrusion technique which was described in previous literature [13]. The final film thickness was 50µm. In order to achieve transparency above 90%, 4097 alternating layers Carbothane/Texin films were produced with individual layer thickness below the quarter wavelength of visible light. At this condition, the individual layers will not exhibit interfacial light scattering resulting in a higher bulk layered film light transmission [14]. To confirm this theory, light transmission of Carbothane/Texin film was measured at 633nm using an UV/Vis Spectrometer (Ocean Optics SD 2000) and the results were plotted in Figure 2.1a. Light transmissions of Carbothane/Texin films were above 90% (no correction for film-air surface Fresnal losses from the index mismatch).

The refractive index of Carbothane/Texin nanolayered films followed a volumetric compositional additive model [15] which is described in Equation (1).

\[ n = n_1 \phi_1 + n_2 \phi_2 \]  

(1)

Where \( n \) is the refractive index of Carbothane/Texin film. \( n_1 \) and \( n_2 \) are refractive indices of Carbothane and Texin and \( \phi_1 \) and \( \phi_2 \) are volume compositions of Carbothane and Texin. Based on this equation, refractive index could be manipulated by varying volume ratio of Carbothane and Texin. The volume ratio of Carbothane and Texin in each nanolayer film was varied in 3.3% steps during the extrusion process. Therefore, the volume ratio of Carbothane/Texin films were started from 100/0, 96.7/3.3 through 50/50 and ended with 0/100 that resulted in a 0.0017 refractive index step between each composition, theoretically. The refractive index of Carbothane/Texin nanolayer films was confirmed using Metricon prism coupler equipped with a 633nm laser at room temperature and the
result was plotted in Figure 2.1b. The refractive index of Carbothane is 1.49 and the refractive index of Texin is 1.54. As predicted by equation 1, the refractive indices of Carbothane/Texin films increased at 0.0017 steps with increasing Texin ratio. The refractive index range of the system was 0.05.

Adaptive GRIN Lens

Adaptive GRIN lens with linear refractive distribution was fabricated based on the following procedure. A series of polymer nanolayered films with desired refractive index were selected and stacked to achieve designed refractive index distribution. Subsequently, the GRIN film stack was consolidated between two glass plates with a spacer to control the final thickness of the GRIIN sheet. A GRIN sheet (Figure 2.2a) was compression molded at 130°C under 5000 lbs. force. The final thickness of GRIN sheet with linear refractive index distribution was 2.8 mm with 10-20% thickness reduction from GRIN stack. A GRIN lens preform was produced by compression molding the GRIN sheet between a concave (R=21.07) and a convex (R=18.2) spherical glass mold. The plano-convex (Figure 2.2b) was fabricated by polishing the concave side of GRIN preform.

Curvature of adaptive GRIN lens was measured using placido-cone topography and the result is shown in Figure 2.3. The back dots are measured surface profile and the black line a calculated value based on the radius and diameter of the lens. Based on topography measurement, the adaptive GRIN lens exhibits designed curvature.

2.3 Results and Discussion

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Spherical aberration correction

Major advantage on focusing property of GRIN lens is based on spherical aberration correction compared to homogeneous lens. Spherical aberration is defined that incident lights at different parts of the lens are focused to different point. Generally, focal length at the edge of a spherical lens is shorter compared to focal length at the center of the spherical lens. In order to correct spherical aberration, optical designers fabricate aspheric lens or combine several corrected lenses together, which make the optical system complex and difficult to process. GRIN lens is an alternative solution to correct spherical aberration with internal refractive index gradient. Two homogenous lenses with the same geometry were fabricated with Carbothane and Texin respectively to compare focusing properties to adaptive Carbothane/Texin GRIN lens. Based on previous publication [16] focal length \( f \) vs position \( r \) of GRIN lens can be predicted using the following equation:

\[
\frac{1}{f} = \frac{2(n_{\text{max}} - n_{\text{min}})}{R_2^2 - R_1^2} \left( \sqrt{R_2^2 - r^2} - R_1 \right) \\
+ \left( \sqrt{R_2^2 - r^2} + \frac{R}{\tan(\arcsin(\frac{r \cdot n_{\text{min}}}{R_2 \cdot n_{\text{air}}} - \arcsin(\frac{r}{R_2})))} - R_2 \right)^{-1}
\]  

(2)

where \( n_{\text{max}} \) and \( n_{\text{min}} \) are maximum and minimum refractive indices of the GRIN sheet, \( R_2 \) and \( R_1 \) are radii of concave and convex mold for GRIN lens fabrication. When equation 3 is applied to homogenous lens, \( n_{\text{max}} \) and \( n_{\text{min}} \) are equal and equation 2 can be simplified to the following equation:

\[
\frac{1}{f} = \left( \sqrt{R_2^2 - r^2} + \frac{R}{\tan(\arcsin(\frac{r \cdot n_{\text{min}}}{R_2 \cdot n_{\text{air}}} - \arcsin(\frac{r}{R_2})))} - R_2 \right)^{-1}
\]

(3)
Spherical aberration corrections of homogenous and GRIN lens were carried out using a two-pin-hole method. A series parallel laser beams with varying distance ($2r$) was created using a collimated laser transmitting through steel plates with two-pin-holes. The distance of these two-pin-holes varies from 1mm to 18mm. The parallel laser beams were focused through the GRIN lens or homogenous lens and project on a screen. The focal length ($f$) as a function of position ($r$) is calculated from distance of laser spot on the screen ($d$) and the distance between the lens and the screen ($l$) using equation (2):

$$f = \frac{2r \times l}{2r + d}$$  \hspace{1cm} (4)

Using this method, focal length of Carbothane/Texin GRIN lens and two homogenous lenses were characterized and focal length difference [$\Delta L=f(r)-f(0)$] at different position ($r$) are plotted in Figure 2.4. The dots in Figure 2.4 are experiment results and the lines are predicted value based on equation 2 and 3. The dash line is an aberration free GRIN lens ($\Delta n=0.12$) with the same dimension. According to Figure 2.4, experiment results are close to theoretical value which indicates that the fabrication of GRIN lens fits designed parameters. For homogenous lenses, focal length difference increases when incident light moves further from the center (increasing $r$). On the other words, spherical aberration is larger on the edge of the lens than spherical aberration close to the center of the lens. Compared to homogenous lens, GRIN lens provides smaller focal length difference between the center and the edge of the lens. Therefore, GRIN lens exhibits exceeding optical properties compared to homogenous lens.

**Curvature deformation**
Shape and focal length change of human eye lens is achieved via biaxial tension of muscles which is hard to replicate. Instead, the deformation of adaptive GRIN lens was achieved by applying compression stress on lens surface with a tuning ring (Figure 2.5a). Compression will result in a redistribution of materials and a pseudo-biaxial expansion in the radial center of the optic similar to the human eye state. The lens compression rate was controlled by a threaded compression cylinder with a known thread pitch. The metal mold was marked around its circumference to quantitatively record the squeezing compression distance as a function of device rotation x thread pitch. The displacement of the tuning ring on the surface of the lens resulted in shape change, leading to a reduction of radius as shown in the Figure 2.5b.

The deformation behavior of the Carbothane/Texin lens was also simulated by FEA using ANSYS Mechanical at a 100% magnification. SOLID187 element was selected to mesh the compression ring, the lens, and the lens holder. The mesh was set fine for the lens and coarse for the compression ring for an accurate and efficient solution. Contact surface pairs were created for the compression ring/lens and the lens/holder pairs. Only tangential movements were allowed between these surfaces. CONTACT material model was defined for these contact pairs to have the friction coefficient of 0.1.

A second material model, the linear elastic isotropic model, was defined for the aluminum compression ring and lens holder. The Young’s modulus and Poisson’s ratio were set as 70 GPa and 0.33, respectively. Mooney-Rivlin (M-R) model was utilized to simulate the mechanical behavior of the elastic material, where the strain energy density was defined as:

\[ W = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) \]  \hspace{1cm} (1)
$C_{10}$ and $C_{01}$ are two empirically determined material constants, and $I_1$ and $I_2$ are first and the second invariant of the unimodular component of the left Cauchy–Green deformation tensor determined by Equation 2:

$$\begin{align*}
I_1 &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\
I_2 &= \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \\
I_3 &= \lambda_1^2 \lambda_2^2 \lambda_3^2
\end{align*}$$

(2)

In this equation, $\lambda$ is the stretch ratio, and is defined as $\lambda = \varepsilon + 1$, where $\varepsilon$ is the strain in the corresponding direction. Assuming the elastomer is incompressible, the value invariant $I_3$ is 1.

The loads were defined for the compression device and the lens holder as the boundaries for the lens. Nodes affiliated with the lens holder were fixed in all directions. The nodes belonging to the compression device have a displacement of 0.1, 0.2, 0.3, and 0.4 mm in the $-z$ direction. The solution was performed in the “Large displacement static” mode, and was controlled by time increment. The incremental step size for compression was varied between 0.0001 and 0.1 having an end time of 1. Auto-acceleration was allowed. The convergence criteria were defined as 0.01 with the minimum reference number of 0.1.

The Carbothane/Texin lens material is considered a rubber-like thermoplastic elastomer that is nearly incompressible. Under uniaxial tension conditions, the engineering stress of the Mooney-Rivlin model can be expressed as Eq. 3:

$$\sigma = (2C_1 + \frac{2C_2}{\lambda})(\lambda - \frac{1}{\lambda^2})$$

(3)
Where the two invariants $C_1 = C_{10}$, and $C_2 = C_{01}$ as defined in the material model (Eq. 1). Successful fitting was achieved below strain of 0.5 using the M-R model as shown in Figure 2.6(a). The fitting was based on minimizing the sum of the squares of the offsets, and the invariants $C_{10}$ and $C_{01}$ were determined as -0.789 and 3.14, respectively.

To confirm that these two parameters are physically meaningful, Eq. 3 was transformed based on the relationship of $\lambda = \varepsilon + 1$ using Taylor expansions for $|\varepsilon| < 1$. The obtained stress-strain relationship for this M-R model is:

$$\sigma = 6(C_{10} + C_{01})\varepsilon - 6(C_{10} + 2C_{01})\varepsilon^2$$

(6)

In the linear regime of the stress-strain curve, the elastic modulus of the material can be expressed as $E = 6(C_{10} + C_{01}) \approx 14.1 \, MPa$, which falls in the acceptable region for the Carbothane and Texin elastomeric materials.

The total mechanical strain intensity of the elements was examined to confirm that the strains for the lens are within the range of the input material stress-strain curve for valid results. As shown in Figure 2.6 (b), the maximum mechanical strain intensity for the center part (3 mm zone) of the lens is 0.18, where the experimental stress-strain data has satisfactory fitting with the M-R model.

After compression to 0.4 mm in the -z direction, the lens surface profile in the 3 mm zone, as shown in Figure 2.7 (a), becomes more convex, which resembles a parabolic curve with its center having a spherical shape and the edges becoming linear. The simulated lens shape curve overlaps well with the experimental data, particularly in the lens center region, which is responsible for the majority of lens functions. Due to the increasing extent of compression, the lens deformation is increased associated with decreasing radius of
curvature as shown in Figure 2.7 (b). The curvatures obtained from the experimental and simulation data are in good agreement at each level of compression. With squeezing distance of 0.4mm, the estimated contact area between tuning ring and GRIN lens is 11.7 cm$^2$. Taken the modulus of 14.4MPa (from equation 6) into account, the estimated force is 1318N.

**Focalization and actuation**

Focal length actuation was manipulated via shape deformation with measurements were carried out using two-pin-hole method with a constant laser beam distance of 5 mm (Figure 2.8) using a previously reported procedure [12]. The original focal length of Carbothane/Texin GRIN lens was 38.4mm and the focal length decreases with increasing squeezing distance, which follows the same trend with curvature deformation. The minimum focal lens was 30.4 with a squeezing distance of 0.4mm. Compared to the original focal length (38.4mm), this represents a 20% reduction on focal length. The human eye lens [17] exhibits similar spherical GRIN distribution with a $\Delta n=0.05$ magnitude, however, with a lower refractive index (1.37-1.42) compared with Carbothane/Texin GRIN lens ($\Delta n=0.05$ 1.48-1.53). The difference in the material optical refractive index, aqueous vs. air environment, and geometry of the human eye lens – it is constructed as a bi-convex asphere (anterior and posterior) with curvature of 10.2mm and -6mm respectively and the diameter is 9mm, prohibit a direct comparison of the optical tuning and focal parameters to the nanolayered elastomeric lens. In contrast, the Carbothane/Texin GRIN lens is a plano-convex lens with curvature of 21.07 mm and diameter of 20 mm. The larger dimension of Carbothane/Texin GRIN lens was chosen to enable more accurate, i.e. less sensitive, focal length change with compression measurements. The aim of
nanolayered GRIN lens construction was to demonstrate that forced assembly technique provides a great potential to mimic adaptive biology optical system with advanced properties with eventual redesign of future generations of deformable GRIN optics with smaller diameters and steeper aspheric curvatures. Several issues need to be considered for future lens design and fabrication. From lens fabrication point of view, adaptive lens with smaller radius allows greater focal length change, however, suffers from more severe spherical aberration. GRIN systems with higher refractive index range are demanded for advanced focusing properties. From a material selection point of view, the refractive index of the material can be manipulated by tuning the function groups. Generally, refractive index can be decreased by adding fluorinated group and can be increased by adding benzene ring. The refractive index of the material can be predicted via the following equation [18]:

\[ n = \frac{\sum_i R_{v,i}}{M} \]  \hspace{1cm} (5)

Where \( n \) is refractive index and \( M \) is molecular weight. \( R_{v,i} \) is refractive index contribution to the molar refraction which can be found in literature. Investigation and development of elastomeric fluorinated synthetic polymers for nanolayered film processing, and subsequent deformable GRIN lens fabrication, are of interest for next generations devices and demonstrator systems.

In order to characterize zoom-in properties of adaptive GRIN lens, image of Case logo (Figure 2.9) was taken by a CCD camera through adaptive GRIN lens with deformable shape. The Case logo was printed on a Mylar film and external light source was applied.
The magnification between original shape and deformed shape (squeezing distance=0.4mm) differs by a factor of 1.25.

2.4 Conclusions

In this paper, a novel method to fabricated adaptive GRIN lens has been demonstrated. Carbothane/Texin (Δ=0.05) nanolayered films were co-extruded via forced assembly technique. The nanolayered films exhibited desired refractive index manipulated by volume composition of two component and high light transmission (90%) for optical application. Adaptive GRIN lens was fabricated with shape profile close to designed value and exhibited exceeding focusing property compared to homogeneous lens. The shape deformation was achieved by mechanical squeezing with curvature decreased form 21 mm to 16mm. The shape deformation results were comparable with simulation value. The focal length showed a 20% reduction with a magnification difference of 1.25.

This work demonstrates the potential to fabricate adaptive GRIN lens singlet with advanced focusing properties. Compared to traditional method, forced assembly technique for adaptive GRIN lens fabrication exhibited the following advantages. From material point of view, the elastomer eliminates the potential leakage and environment influence of liquid lens. Electric insulation and voltage requirements are of no concern with mechanical squeezing as focal length tuning method. From optical point of view, this is a superior way to fabricate GRIN lens compared to other GRIN technologies including interface-gel polymerization; ion-exchange; plasmonics; and chemical vapor deposition. Polymer GRIN lens fabricated via forced assembly technique exhibits large refractive index range (Δn), desired refractive index profile control, and large lens aperture sizes. In summary, forced
assembly technique provide a novel methodology to produce adaptive GRIN lens with compact volume and superior focusing capability. With the development of FDA approved elastomer, this technique shows a great potential for implant human eye lens fabrication.

2.5 References


18. Krevelen DKV, and Nijenhuis KT. Properties of polymers: their correlation with chemical structure; their numerical estimation and prediction from additive group contributions. Elsevier; 2009 Mar 19.
Table 2.1. Materials for Deformable GRIN Lens Fabrication

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Material</th>
<th>R. I. (@ 633 nm)</th>
<th>Transparency (@ 633 nm)</th>
<th>Ultimate Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbothane</td>
<td>Thermoplastic Polyurethane</td>
<td>1.49</td>
<td>(90 ± 3)%</td>
<td>400</td>
</tr>
<tr>
<td>PC-3595A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Texin</td>
<td>Thermoplastic Polyurethane</td>
<td>1.54</td>
<td>(91 ± 1)%</td>
<td>520</td>
</tr>
<tr>
<td>RXT 90A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2.1 a) Light transmissions of nanolayered films of soft GRIN system, b) refractive index of nanolayered films for soft GRIN lens.
Figure 2.2 a) Carbothane/Texin GRIN sheet, b) Carbothane/Texin GRIN lens
Figure 2.3 Curvature of Carbothane/Texin GRIN lens is close to designed value
Figure 2.4 Spherical aberration correction of soft GRIN lens is better than Carbothane control lens
Figure 2.5 a) lens tuning apparatus, b) procedure of tuning of lens curvature
Figure 2.6 a) Experimental and simulated stress-strain curves for the elastomer material. The simulation was performed using Mooney-Rivlin model, b) total mechanical strain intensity simulation data for the lenses with compression distances of 0.4mm.
Figure 2.7 a) Curvature change of Carbothane/Texin GRIN lens before and after squeezing, b) curvature change as a function of squeezing distance.
Figure 2.8 Focal length change of Carbothane/Texin GRIN lens vs. squeezing.
Figure 2.9 Image acquired by adaptive GRIN lens with original shape (left) and 0.4mm squeezing (right).
CHAPTER 3

Effects of Interphase Modification and Biaxial Orientation on Dielectric Properties of Poly(ethylene terephthalate)/Poly(vinylidene fluoride-co-hexafluoropropylene) Multilayer Films

3.1 Introduction

Polymer film capacitors have been widely used in microelectronic devices and electric power systems, including power electronics in electric and hybrid electric vehicles, grid inverters/converters, and pulsed power devices, because of their high voltage rating, high ripple current, stable capacitance, ultralow loss, and self-clearing properties [1-2]. These emerging applications require advanced capacitors with higher energy storage, lower volume, lighter weight, and excellent reliability at high temperatures. Researchers are seeking new materials and/or new processing techniques to fulfill these requirements [3-5].

Polymer film capacitors, however, possess their own drawbacks. Compared with ceramic capacitors, dielectric constants of polymers are low, typically around 2~4, and thus the energy density ($U_e$) is low, because $U_e$ is proportional to the relative permittivity ($\varepsilon_r$) and the square of the applied electric field ($E$); $U_e = 0.5\varepsilon_r\varepsilon_0E^2$ ($\varepsilon_0$ is the vacuum permittivity).

In recent years, research has been focused on increasing the dielectric constant of polymers while maintaining low dielectric losses [3-4]. Among many proposed strategies, utilization of dipolar polarization in poly(vinylidene fluoride) (PVDF)-based polymers has drawn considerable attention [3, 6-7]. However, there are numerous limitations for PVDF-based polymers. For instance, PVDF homopolymers and associated random copolymers such as...
P(VDF-HFP) and P(VDF-CTFE) (HFP is hexafluoropropylene and CTFE is chlorotrifluoroethylene) are not suitable for film capacitor applications due to their large ferroelectric hysteresis loss [6]. To overcome this shortcoming, relaxor ferroelectric polymers such as P(VDF-TrFE-CFE) and P(VDF-TrFE-CTFE) terpolymers (TrFE is trifluoroethylene and CFE is 1,1-chlorofluoroethylene) have been developed. While relaxor ferroelectric polymers exhibit narrow hysteresis due to the formation of nanosized ferroelectric domains (i.e., nanodomains) via the crystal pinning effect [3, 7], their low Curie transition temperatures ($T_C$) (around room temperature) and relatively low melting temperatures (ca. 120 °C) limit their use in most high temperature applications. Another approach to improve dielectric performance is to graft PVDF-based copolymers with linear dielectric side chains to yield increased dielectric constants and linear dielectric loops [8-12]. However, these graft copolymers are difficult to scale up due to the large amount of copper catalyst used in the graft copolymerization. In addition, when in direct contact with the positive high voltage, PVDF-based polymers undergo electrochemical reactions, emitting HF and corroding metal electrodes [13-14].

To mitigate the above mentioned problems for PVDF-based polymers, our approach is to microlayer a high breakdown and low loss linear dielectric polymer with a high permittivity PVDF-based polymer using the forced assembly technique at Case Western Reserve University [15]. This is a highly flexible technology, which is able to melt-coextrude two or more polymers into a single films (e.g., 10 μm thick) having up to thousands of layers (each layer about 20 nm - a few μm thick). The linear dielectric polymer can be polycarbonate (PC), polysulfone (PSF), and poly(ethylene terephthalate) (PET), as long as they have appropriate interfacial adhesion with PVDF-based polymers. For these unique
multilayer films, a number of dielectric disadvantages from PVDF-based polymers can be suppressed and certain dielectric advantages are enhanced due to the effects of nanoconfinement and permittivity contrast in the system. First, ferroelectric switching is effectively prohibited for PVDF and its derivatives in multilayer films [16]. Because of the large permittivity contrast in PVDF-based multilayer films ($\varepsilon_r^{PVDF} \sim 12$ and $\varepsilon_r$ for PC, PSF, and PET is around 2.8-3.5), the high permittivity PVDF layers have a low nominal electric field, whereas the low permittivity linear dielectric layers bear a high nominal electric field [17-18]. As a result, the low electric field (possibly below the coercive field, $E_C$) in the PVDF layers will not be able to switch the ferroelectric domains in PVDF crystals, but can still rotate the dipoles in the amorphous phase. Consequently, ferroelectric switching of crystalline PVDF is effectively offset to very high operational fields in multilayer films having large permittivity contrast.

Second, migrational loss from impurity ions in the PVDF-based copolymers can be reduced in sub-micron layers and completely suppressed when the PVDF layer thickness decreases to ca. 50-100 nm [16, 19]. For example, the dissipation factor tanδ at 75 °C and 0.01 Hz decreased by about 20 times for the 32-layer PC/PVDF 50/50 (vol./vol.) films with a nominal PVDF layer thickness of 380 nm, as compared to single layer 12 µm thick PVDF control films. This is attributed to the nanoconfinement effect on ionic transport in the nano-layers of PVDF. Namely, impurity ions could not move much in nanometer thick layers.

Third, PVDF-based multilayer films at various volume compositions exhibit enhanced dielectric breakdown strength as compared to simple polymer blends and the weighted average model [20]. The enhanced breakdown strength property is unique and could be
attributed to the interfacial polarization at the interfaces between PVDF and the linear
dielectric polymer such as PC and PSF [21]. Due to large contrasts in both permittivity
and bulk conductivity (e.g., $\sigma_{PC} = 10^{-16}$ S/m and $\sigma_{PVDF} = 10^{-13}$ S/m), space charges
(including electrons/holes and impurity ions) will accumulate at the PC/PVDF interfaces
with PC serving as charge-blocking layers. These charged PVDF/PC interfaces therefore
behave as effective traps for hot electrons injected from the metal electrodes, impeding
their propagation through the dielectric film before the onset of electrical breakdown.
Consequently, multilayer films exhibit enhanced breakdown strengths. This so-called
barrier effect is truly remarkable, given that the effective field in the charge blocking layers
can be up to twice that of the breakdown strength of monolithic films of the polymer itself.

Despite the benefits of interfacial polarization, interfacial adhesion is a potential problem
for multilayer films when the two polymers are immiscible. For example, layer
delamination was observed near the ‘through-film’ breakdown pinholes in PC/P(VDF-HFP)
50/50 32-layer films following electrical breakdown [22-23]. To mitigate this problem, a
poly(methyl methacrylate) (PMMA) tie layer is introduced between PC and P(VDF-HFP)
layers, because PMMA is partially miscible with PC and completely miscible with P(VDF-
HFP). Due to the enhanced interfacial adhesion, the PC/PMMA/P(VDF-HFP) three-
component system exhibited about 25% improvement in breakdown strength, as well as
40% decrease in hysteresis loss in electric displacement-electric field (D-E) loops [24].

Biaxial stretching is an effective way to fabricate uniform thin films with dramatically
enhanced dielectric performance [25-26]. In a preliminary study, biaxial stretching was
performed for the PET/P(VDF-TFE) (TFE is tetrafluoroethylene) multilayer films [27].
Enhanced breakdown strength and high discharge energy density (ca. 16 J/cm$^3$) were
obtained with a relatively low dielectric loss. In this work, we combined biaxial stretching and PMMA tie layers into the PET/PMMA/P(VDF-HFP) three-component system to further enhance the dielectric properties of multilayer films. The goal is to investigate the structure/property relationship for the PET/PMMA/P(VDF-HFP) multilayer films as a function of interphase/interface modification.

3.2 Experimental Section

Materials.

PET resin was supplied by Eastman Chemical Co. (Eastar™ 6763). P(VDF-HFP) resin was obtained from Solvay Solexis (Solef® 21508) with 15 wt.% of HFP comonomer. PMMA resin was supplied by Arkema (Plexiglas® V826). PET and PMMA resins were dried under vacuum at 80 °C for two days prior to multilayer coextrusion.

Fabrication and Biaxial Orientation of Multilayer Films.

Three-component multilayer films of PET/PMMA/P(VDF-HFP) were melt coextruded via a forced assembly technique using three single-screw extruders, each of which was equipped with a melt pump (see Figure 3.1a) [15]. The melt pumps were used to control feeding speeds and thus the volume ratio of three polymers. After melt pumps, three polymer melts converged in a customer-designed five-layer feedblock having an A/T/B/T/A structure (T is the tie layer). The five-layer polymer melt then passed through a series of multilayers. In each multilayer, the number of layers was doubled by a sequential splitting, spreading, and re-stacking process. Finally, two sacrificial skin layers of low density polyethylene (LDPE) were laminated onto both surfaces of the multilayer film before extrusion from the exit die. The coextrusion temperature was selected at 260 °C,
which was determined by viscosity compatibility of the three polymer melts using a melt-flow indexer (Kayeness Galaxy 1) at the same shear rate as the extrusion condition, i.e., 10 s\(^{-1}\). PET/PMMA/P(VDF-HFP) 65-layer films were coextruded, and the compositions of the films are listed in Table 3.1. Compositions of PET and P(VDF-HFP) were kept equivalent, and the PMMA composition varied from 0 vol.% to 20 vol.%. Two film thicknesses were extruded, 10 µm for the “as-extruded” films and 200 µm for the films earmarked for biaxial orientation. LDPE skin layers were peeled off using Scotch tape before any morphological and electrical characterization.

Biaxial stretching of the PET/PMMA/P(VDF-HFP) multilayer films was carried out using a Brückner Karo IV laboratory stretcher (Figure 3.1b) [27]. Briefly, the 200 µm thick PET/PMMA/P(VDF-HFP) multilayer films were cut into 85 mm \(\times\) 85 mm squares. A black ink grid pattern (6.5 mm \(\times\) 6.5 mm) was marked on the film before biaxial stretching to monitor the stretching uniformity. The film was stretched at 105 °C with a simultaneous drawing ratio of 4.5\(\times\)4.5. The stretching rate was 100% s\(^{-1}\). After stretching, no further annealing at elevated temperatures was performed. PET/PMMA/P(VDF-HFP) multilayer films with different PMMA compositions were successfully and uniformly stretched in this way.

**Measurements and Instrumentation.**

Breakdown strength measurements were carried out using a needle-plane electrode geometry [20]. The positive electrode was the needle having a tip of 40 µm diameter, and the negative electrode was a rectangular aluminum plate (30 mm \(\times\) 100 mm). A Quadtech Guardian 20 kV HiPot tester was used to provide a pulsed voltage with a duration of 200
ms. The applied field was increased stepwise by 50 MV/m until electrical breakdown occurred. The tests were carried out at room temperature with sixteen repetitions for each sample. Both electrodes and films were immersed in a mineral oil bath to avoid corona discharging in air. The needle electrode was replaced for every fresh film. A NI AT-MIO-16E-1 data acquisition card (National Instruments) was used to record the applied voltages.

A Radiant Technology Premiere II ferroelectric tester was used to measure D-E loops of the multilayer films at a frequency of 10 Hz using a sinusoidal wave function. Gold electrodes (20 nm thick) were sputter-coated on both sides of the film with a diameter of 2.5 mm. The maximum electric field was increased stepwise at increment of 50 MV/m until breakdown of the film. The discharged energy density ($U_{\text{dis}}$) and the hysteresis loss ($U_{\text{loss}}$) could be calculated based on the D-E loop using the following equations:

$$U_{\text{dis}} = \int_{D(T/4)}^{D(T/2)} E(t) dD(t)$$  \hspace{1cm} (1)$$

$$U_{\text{loss}} = \int_{0}^{D(T/4)} E(t) dD(t) - \int_{D(T/4)}^{D(T/2)} E(t) dD(t)$$  \hspace{1cm} (2)$$

where $T$ is the period of the applied sinusoidal field, $E$ the electric field, and $D$ the electric displacement at different times.

Broadband dielectric spectroscopy (BDS) was measured using a Novocontrol Concept 80 dielectric spectrometer. The film samples were coated with 20 nm thick gold electrodes on both sides ($d = 10$ mm). Real and imaginary relative permittivities ($\varepsilon_r'$ and $\varepsilon_r''$) were measured as a function of temperature from -100 to 110 °C at a constant frequency of 10 Hz. Frequency-scans were carried out from $10^{-2}$ to $10^5$ Hz at constant temperatures of 20 and 100 °C, respectively.
To observe the layer structure and the interphase in the PET/PMMA/P(VDF-HFP) multilayer films, samples were embedded in standard epoxy, which was cured at room temperature overnight. A flat and smooth cross-section of the embedded film was obtained by microtome-polishing at -120 °C using a Leica Microsystem EM FC6 ultramicrotome. Layer continuity and uniformity of the films were characterized using atomic force microscopy (AFM). Phase and height images of the cross-sections were recorded using a Nanoscope Ila Multimode scanning probe (Digital Instruments). AFM was operated using the tapping mode at room temperature.

Dynamic mechanical properties of the PET/PMMA/P(VDF-HFP) multilayer films were characterized using a TA DMA Q800 dynamic mechanical analysis (DMA, TA Instruments). The DMA tests were carried out in a tensile mode from -70 to 140 °C at a heating rate of 3 °C/min. The testing frequency was 1 Hz.

Thermal properties of the PET/PMMA/PVDF-HFP multilayer films were measured using Perkin-Elmer Pyris differential scanning calorimeter (DSC). The instrument was calibrated with indium and tin standards. The heating rate was 10°C/min and the sample weight was ca. 5 mg.

Fourier transform infrared (FTIR) spectroscopy was carried out using a Nexus 870 FTIR ESP (Thermo Nicolet). Spectra were collected in transmission mode at a resolution of 2 cm\(^{-1}\) with 32 scans.

Crystal orientation in the PET/PMMA/P(VDF-HFP) multilayer films were characterized using two-dimensional (2D) wide-angle X-ray diffraction (WAXD). The incident X-ray beam was directed in two ways: 1) parallel to the extrusion direction (ED) and 2) normal
to the film (ND). A Rigaku MicroMax 002+ diffractometer was operated at 45 kV and 0.88 mA. Confocal Max-Flux optics were used to generate a highly focused monochromatic Cu Kα radiation (wavelength of 0.1542 nm) with a sealed tube microfocus X-ray source. CaF₂ was used for calibration of the diffraction angle, and the sample-to-detector distance was 140 mm. 2D WAXD patterns were recorded on a Fuji film imaging plate and scanned using a Fujifilm FLA-7000 scanner at a resolution of 50 μm/pixel.

3.3 Results and Discussion

Dielectric Breakdown Strength Study

Dielectric breakdown strength measurements were carried out using a divergent field (needle-plane) geometry. Compared with plane-plane breakdown measurement geometries, the needle-plane geometry typically yields similar trends, although the absolute breakdown values appear to be higher due to the much smaller test area of the needle tip. In this study, the average breakdown strength was employed. Figure 3.2 shows the breakdown strengths of as-extruded and biaxially stretched PET/PMMA/P(VDF-HFP) films as a function of the volumetric composition of the PMMA tie layer. The breakdown strength of the as-extruded PET/P(VDF-HFP) 33-layer film (i.e., without the PMMA tie layer) was around 750 MV/m. The breakdown strengths of the films containing PMMA tie layers increased with increasing PMMA content. The maximum breakdown strength reached 903 MV/m for the film with 8 vol.% PMMA. Further increasing the PMMA content to 20 vol.%, the breakdown strength decreased to 840 MV/m as compared to the maximum value; however, it was still higher than that of the PET/P(VDF-HFP) control film. After biaxial stretching to a 4.5×4.5 stretch ratio, the breakdown strengths of the PET/PMMA/P(VDF-HFP) films increased about 10% at all compositions. The maximum
breakdown strength of 996 MV/m was again found for the PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA. Note that the PET layers were completely amorphous for the as-extruded films whereas they were semicrystalline with highly oriented crystallites after stretching, and this will be discussed later.

**Discharged Energy Density**

Enhanced breakdown strength for the PET/PMMA/P(VDF-HFP) films implies that these films should achieve enhanced energy density, as the energy density scales to $E^2$ for linear dielectrics. Figure 3.3a shows the $U_{\text{dis}}$ as a function of poling electric field for the as-extruded PET/P(VDF-HFP) film and the biaxially oriented PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA. Indeed, compared to the as-extruded PET/P(VDF-HFP) film, the biaxially oriented film had a much higher $U_{\text{dis}}$ because of its enhanced breakdown strength. Intriguingly, even at the same poling electric field, the biaxially oriented PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA also exhibited a higher $U_{\text{dis}}$ than the as-extruded PET/P(VDF-HFP) film. Figure 3.3 shows the comparison of maximum $U_{\text{dis}}$ for the as-extruded and the biaxially oriented PET/PMMA/P(VDF-HFP) films with various PMMA compositions. For as-extruded films, the maximum $U_{\text{dis}}$ for the PET/P(VDF-HFP) was 7 J/cm³ (note that the maximum field of 500 MV/m in the D-E loop study is lower than that in the breakdown study, because the electrode area increased to 4.91 mm²). After introducing the PMMA tie layers, the maximum $U_{\text{dis}}$ generally increased with a peak value (9.6 J/cm³) at 8 vol.% PMMA. For the biaxially oriented films, the maximum $U_{\text{dis}}$ increased about 70-80% at all PMMA compositions compared to those of as-extruded films. In particular, the biaxially oriented PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA...
tie layer exhibited a maximum $U_{\text{dis}}$ of 17.4 J/cm$^3$, a 150% improvement as compared to the as-extruded PET/P(VDF-HFP) film mainly due to the higher breakdown strength.

**Hysteresis Loop Loss.**

To find out why the biaxially oriented PET/PMMA/P(VDF-HFP) films exhibited a higher $U_{\text{dis}}$ than the as-extruded films at the same poling electric field (see Figure 3.3a), bipolar D-E loops were measured for both films. The first half loops for the as-extruded PET/P(VDF-HFP) film and the biaxially oriented PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA are shown in Figure 3.4a. The biaxially oriented PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA had a slimmer D-E loop than the as-extruded PET/P(VDF-HFP) film, although its maximum $D$ at 400 MV/m was slightly lower.

To obtain quantitative result, the hysteresis loop areas ($U_{\text{loss}}$) at 400 MV/m for both as-extruded and biaxially oriented films are shown in Figure 3.4b. At 400 MV/m, the $U_{\text{loss}}$ for the as-extruded PET/P(VDF-HFP) was ca. 1.0 J/cm$^3$, whereas it was 0.88 J/cm$^3$ for the as-extruded PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA. After biaxial orientation, the $U_{\text{loss}}$ for all PMMA compositions further decreased. For example, the minimum value appeared for the film with 8 vol.% PMMA, i.e., 0.74 J/cm$^3$, which was 26% lower than that of the as-extruded PET/P(VDF-HFP) film. It was the reduced loop loss that increased the discharged energy density for the biaxially oriented film.

The above results demonstrate that introduction of interface/interphase modification and biaxial orientation significantly enhances high-field dielectric properties, including dielectric breakdown strength, maximum energy density, and reduced hysteresis loss. Below, the structure-property relationship will be described to explain these observations.

**Interdiffusion Model and Layer Structures Studied by AFM**
It is known that PMMA is miscible with PVDF (and its copolymers) and immiscible with PET [29]. During the multilayer melt extrusion process, there must be some interdiffusion between PMMA and P(VDF-HFP) layers. In this study, an interdiffusion model for miscible polymer pairs [30] is utilized to describe the interdiffusion between PMMA and P(VDF-HFP). The composition profile can be calculated from the Fick’s law for a non-steady state diffusion:

\[
\frac{\partial W_i}{\partial t} = D_0 \frac{\partial^2 W_i}{\partial x^2}
\]  

(3)

where \(W_i\) is the weight fraction of polymer \(i\), \(t\) the diffusion time, \(x\) the position, and \(D_0\) the mutual diffusion coefficient. To analyze the interdiffusion process in the molten PET/PMMA/P(VDF-HFP), the following assumptions are made. 1) Since PMMA and PET are immiscible and PMMA and P(VDF-HFP) are miscible, interdiffusion between PET and PMMA is neglected. PMMA is only considered to diffuse into P(VDF-HFP). 2) The diffusion rates of P(VDF-HFP) into PMMA on both sides are equal. 3) There is a sharp interface between PMMA and P(VDF-HFP) at the initial condition. 4) The composition gradient is zero at boundaries of inter-diffusing polymers. Based on these assumptions, Eqn. (3) has the following solution [30]:

\[
W_1(x, t) = \frac{L_1}{L_1 + 0.5L_2} + \sum_{n=1}^{\infty} \frac{2}{n\pi} \sin \left( \frac{n\pi L_1}{L_1 + 0.5L_2} \right) \cos \left( \frac{2n\pi x}{L_1 + 0.5L_2} \right) \exp \left[ \frac{-4n^2\pi^2D_0t}{(L_1 + 0.5L_2)^2} \right]
\]  

(4)

where \(L_1\) and \(L_2\) are layer thicknesses for PMMA and P(VDF-HFP) in the multiplier and can be calculated based on the width of the multiplier channel (25.4 mm) and the number of layers (i.e., 65). \(D_0\) is the mutual diffusion coefficient of PMMA and P(VDF-HFP) at the extrusion temperature (260 °C). Please refer to the Supporting Information for determination of \(D_0\). Figure 3.5 shows the calculated weight fraction of PMMA at different interdiffusion times for the PET/PMMA/P(VDF-HFP) film with 20 vol.% PMMA. At the
initial condition ($t = 0$ s), the boundary between PMMA and P(VDF-HFP) is sharp. As the interdiffusion time increased, the boundary between PMMA and P(VDF-HFP) became increasingly diffused. For our multilayer coextrusion process, the interdiffusion time could be as long as 6 min. This calculation of concentration profiles due to interdiffusion can be extended to the extruded multilayer films, and the final profiles will be used to compare to the AFM imaging results in Figure 3.6 below.

The layer structure and interdiffusion in PET/PMMA/P(VDF-HFP) multilayer films were investigated by AFM. Figures 3.6a-c show AFM phase images of as-extruded (200 µm) PET/PMMA/P(VDF-HFP) films with 0, 8, and 20 vol.% PMMA, respectively. For the PET/P(VDF-HFP) film (i.e., 0 vol.% PMMA), boundaries between PET and P(VDF-HFP) were sharp. After introducing 8 vol.% PMMA, a diffused interphase was observed between PET and P(VDF-HFP). This interphase region comprised a graded mixture of PMMA and P(VDF-HFP), with PMMA dominating the overall volumetric composition on the side of the interface with PET and P(VDF-HFP) dominating the volumetric composition into the bulk of the P(VDF-HFP) layer. In this instance, PMMA completely diffused through the interphase and no discrete PMMA layer was observed. However, when the PMMA composition increased to 20 vol.%, distinct PMMA layers could be identified, suggesting that the length scale of the diffusion was less than the expected nominal thickness of the PMMA layer if no diffusion occurred. Normalized gray values could be obtained from these AFM phase images, and are shown in Figures 3.6d-f. Using the interdiffusion model [30] for PMMA and P(VDF-HFP), calculated interphase profiles are shown in Figures 3.6g-i. Reasonable agreement was found between the calculated interphase profiles and the experimental AFM imaging results, indicating that
interdiffusion happened largely as predicted for PMMA and P(VDF-HFP) layers. At 8 vol.% PMMA, all PMMA diffused into the P(VDF-HFP) layer, forming a finite interphase (Figures 3.6e and h). At 20 vol.% PMMA, not all PMMA formed the interphase and a neat PMMA layer could be identified (Figures 3.6f and i).

As reported in a previous publication [22-23], electrical breakdown of multilayer films was always accompanied by layer delamination near the breakdown sites, which could be ascribed to the relatively poor adhesion between PC and P(VDF-HFP). For PET/P(VDF-HFP) 33-layer films, a similar situation was assumed. After introducing PMMA as the tie layers, the interfacial adhesion between PET and P(VDF-HFP) was modified and possibly improved. As a result, the breakdown strength of the PET/PMMA/P(VDF-HFP) multilayer films was improved by the interface/interphase modulation. This interphase modulation was recently suggested by theoretical simulation to improve dielectric breakdown strength for multilayer films [18].

Typically, when two compatible polymers are extruded using our forced assembly technique, an “interphase” region is generated with highly localized inter-mixing. This was reported for polycarbonate (PC) and poly(styrene-co-acrylonitrile) (SAN) multilayer films in a previous publication [31]. When individual layer thicknesses approaches the size of the polymer chains, an intermediate glass transition temperature (T_g) is observed between the two T_g's for neat PC and SAN. This intermediate T_g can be attributed to a finite interphase of mixed PC and SAN generated during multilayer coextrusion. The PET/PMMA/P(VDF-HFP) films studied herein behave similarly, and the PMMA/P(VDF-HFP) interphase is confirmed by DMA (Figure 3.7). As shown in Figure 3.7a, below the T_g of PET (~ 75 °C) the storage modulus, E', of the films increased upon introduction of
PMMA tie layers, since the modulus of PMMA was higher than those of amorphous PET and P(VDF-HFP). The $T_g$ for P(VDF-HFP) in all the multilayer films was not obvious in the $E'$ plot, but became clear ($\sim 35 ^\circ C$) in the tan$\delta$ plot in Figure 3.7b. For the PET/P(VDF-HFP) 33-layer film (i.e., 0 vol.% PMMA), an obvious broad transition was observed ($\sim 20 \sim 0 ^\circ C$) between the $T_g$s of P(VDF-HFP) and PET. It could be ascribed to the $\beta$ transition of amorphous PET, as reported before [32]. This peak became less obvious for the PET/PMMA/P(VDF-HFP) films with 8 and 20 vol.% PMMA tie layers, because it merged with an additional transition around 40 °C, which could be attributed to the $T_g$ of the interphase of mixed PMMA and P(VDF-HFP). This result is consistent with the previous report and will also be confirmed by the BDS study described later.

The layer integrity and crystalline morphology of the PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA after biaxial orientation were characterized using AFM, as shown in Figure 3.8b, where the final film thickness decreased from the original 200 μm (Figure 3.8a) to 10 μm. Continuous PET (brighter) and P(VDF-HFP) (darker) layers were observed, demonstrating good layer integrity after 4.5×4.5 biaxial stretching. However, the interphase became less obvious because of the formation of strain-induced granular or fibrillar crystalline morphology in both PET and P(VDF-HFP) layers (Figure 3.8b). The thermal behavior of the PET/PMMA/P(VDF-HFP) multilayer films before and after biaxial orientation was studied by DSC. For the as-extruded 200 μm film in Figure 3.8c, the $T_g$, the cold-crystallization temperature ($T_c$), and the melting temperature ($T_m$) were observed at 77, 140, and 242 °C, respectively. The $T_m$ for the PVDF crystals in P(VDF-HFP) overlapped with the cold-crystallization of PET with a peak at 129 °C. In the as-extruded 200 μm film, the PET was entirely amorphous as confirmed by WAXD results. After
biaxial orientation, the cold-crystallization of PET was absent because it had already crystallized from stretching at 105 °C. From Figure 3.8c, the $T_g$ and $T_m$ of PET were observed at 93 and 242 °C, respectively. The $T_m$ for P(VDF-HFP) was 132 °C.

**WAXD Study on Crystalline Morphology**

Crystal orientation of PET and P(VDF-HFP) in the as-extruded and biaxially oriented films was investigated by 2D WAXD. The X-ray beam was directed parallel to the extrusion direction, ED, and 2D WAXD patterns are shown in Figure 3.9. For the as-extruded PET/P(VDF-HFP) film (Figure 3.9a), PVDF crystals exhibited isotropic (110)$_\alpha$, (020)$_\alpha$, and weak and broad (120/021/111)$_\alpha$ reflection rings, indicating that the PVDF crystal orientation in P(VDF-HFP) was random. No detectable reflection was observed for PET crystals, indicating PET was completely amorphous. For the PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA, a similar situation with random orientation of P[VDF-HFP] crystals was observed (Figure 3.9b). However, when the PMMA content was increased to 20 vol.%, the PVDF crystallinity significantly decreased, presumably due to the intermixing of PMMA and P(VDF-HFP) (Figure 3.9e).

It has been reported that crystalline morphology of PVDF-based copolymers and PET could be manipulated by mechanical stretching, either uniaxially or biaxially [14, 26, 33]. Stretching below the $T_m$ of PVDF-based polymers resulted in fibrillar crystals aligned in the stretching direction [27]. The structure of PET was determined by the stretching temperature. For example, stretching amorphous PET films below the $T_g$ resulted in densified glass and crystallization of PET was largely prevented, a process known as “cold draw” [34]. When amorphous PET films were stretched above the $T_g$, fibrillar crystals were obtained as a result of strain-induced crystallization [26-27]. In this study, the
stretching temperature of 105 °C is above the T_g of PET and below the T_m of P(VDF-HFP). Consequently, fibrillar crystals were obtained in both the PVDF and PET layers after biaxial stretching (see Figure 3.8b) [27]. Figure 3.9d shows the 2D WAXD pattern for biaxially oriented PET/P(VDF-HFP) 33-layer film. The (100)_α and (110)_α PVDF reflections were oriented on the vertical direction and the (020)_α reflection was in the horizontal direction. Deduced from this crystal orientation [19], the PVDF crystalline morphology is shown in Figure 9h. Namely, the PVDF crystallites were edge-on with their b-axes oriented parallel to the layers. After biaxial stretching, the (010)_PET reflection was observed in the vertical direction, indicating strain-induced crystallization with oriented crystals. For the PET/PMMA/P(VDF-HFP) films with 8 and 20 vol.% PMMA, similar situations were observed. Note that the film with 20 vol.% PMMA exhibited a much lower crystallinity.

In addition to modification of crystal orientation as a result of biaxial orientation, crystal polymorphism in P(VDF-HFP) can be changed by both interphase modulation and biaxial orientation. Although WAXD is sensitive to crystal orientation, it cannot be used to accurately identify different crystalline forms of PVDF. FTIR is sensitive to the conformation changes in different crystalline forms of PVDF. Figure 3.10a shows FTIR spectra of the as-extruded PET/P(VDF-HFP) 33-layer film and biaxially oriented PET/PMMA/P(VDF-HFP) 65-layer film with 8 vol.% PMMA. Base on a previous report [35], the absorbance peak at 766 cm⁻¹ is attributed to the α form PVDF crystal and the absorbance peak at 840 cm⁻¹ is from the β form PVDF crystal. The relative fraction of the β PVDF crystal, F(β), can be calculated using the following equation [36]:

\[ F(\beta) = \frac{A_\beta}{(K_\beta/K_\alpha)A_\alpha + A_\beta} \]  

(5)
where \( A_\alpha \) and \( A_\beta \) are absorbance peak intensity and \( K_\alpha \) and \( K_\beta \) are the absorption coefficients of \( \alpha \) and \( \beta \) form PVDF crystals, respectively. Here, \( K_\beta/K_\alpha \) is about 1.3 [36]. Based on this equation, the \( \beta \) PVDF content in all as-extruded and biaxially oriented films can be estimated, and results are shown in Figure 3.10b. The \( \beta \) PVDF content was 13% (note that this is not crystallinity, but the percentage among \( \alpha \) and \( \beta \) crystals) in the as-extruded PET/PVDF-HFP film. As the PMMA content in the as-extruded films increased and PMMA inter-diffused into P(VDF-HFP), the \( \beta \) PVDF relative content increased to a plateau of ca. 55% for the films with > 8 vol.% PMMA. The \( \beta \) PVDF content was further increased by biaxial orientation, and a maximum value was around 67% for the biaxially oriented PET/PMMA/P(VDF-HFP) films with > 8 vol.% PMMA. Since \( \beta \) PVDF crystals did not have the \( \alpha_c \) relaxation, we expect that the PET/PMMA/P(VDF-HFP) films with a high \( \beta \) content should exhibit a lower dielectric loss than the PET/P(VDF-HFP) films with a high \( \alpha \) content.

**Broadband Dielectric Spectroscopy Study**

BDS studies were carried out to investigate various dielectric loss mechanisms and to confirm the lower dielectric loss in biaxially oriented PET/PMMA/P(VDF-HFP) multilayer films. Figure 3.11a shows the dissipation factor as a function of frequency for various films at 20 °C. For the as-extruded PET/P(VDF-HFP) film, the \( \alpha_a \) relaxation for the amorphous PVDF was observed at frequencies above \( 10^5 \) Hz [37]. The PVDF \( \alpha_c \) relaxation peak was centered at 50 Hz [37], and its intensity slightly decreased after biaxial orientation. This was due to the orientation effect because the \( \alpha_c \) relaxation occurs along the chain axes in the \( \alpha \) crystals. When the chains were perfectly oriented parallel to the
layers, the $\alpha_c$ relaxation should disappear. After adding 8 vol.% PMMA, this $\alpha_c$ relaxation peak became fairly weak due to a high $\beta$ phase content (ca. 55%) induced by PMMA. After biaxial orientation, the $\alpha_c$ relaxation around 10-50 Hz was absent. Again, this could be attributed to the synergistic effects from both the high $\beta$ content and parallel crystal orientation with respect to the layers. We consider that it was the absence of the $\alpha_c$ relaxation in biaxially oriented PET/PMMA/P(VDF-HFP) films that reduced the hysteresis loss as shown in Figure 3.4.

In addition to the $\alpha_c$ contribution, ion migration is another source for dielectric losses. Around room temperature, the impurity ion mobility usually is not high enough to be seen for PVDF and its copolymers [14]. It is therefore necessary to magnify the ion migrational loss at elevated temperatures. Figure 3.11b shows the frequency-scan dissipation factor results for various films at 100 °C. First, as-extruded PET/PMMA/P(VDF-HFP) films with 0 and 8 vol.% PMMA exhibit a $\tan\delta$ peak at around 200-300 Hz, which could be attributed to the migrational loss of fast ions in P(VDF-HFP) [16, 19, 24]. Below 0.1 Hz, another upturn was observed for both as-extruded films, and these could be attributed to the migrational loss from slow ions in P(VDF-HFP). After biaxial stretching, this ion migrational loss peak for the PET/P(VDF-HFP) 33-layer film shifted from 300 Hz to 0.02 Hz, suggesting that crystal orientation in P(VDF-HFP) decreased the mobility of impurity ions, particularly fast ions. For the PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA, the ion migrational peak shifted to an even lower frequency below $10^{-3}$ Hz, suggesting that less polar PMMA in the interphase further decreased the mobility of impurity ions. It was likely that the migrational loss from impurity ions was further reduced for the biaxially
oriented film as a synergistic result of crystal orientation and intermixing of the less polar PMMA with P(VDF-HFP).

Effects of interface/interphase modification and biaxial orientation were further studied for as-extruded and biaxially oriented films using temperature-scan dielectric spectroscopy. BDS results of $\varepsilon_r'$ and $\varepsilon_r''$ for as-extruded PET/PMMA/P(VDF-HFP) multilayer films with 0, 8, and 20 vol.% PMMA are shown in Figures 3.12a,b. For the as-extruded PET/P(VDF-HFP) film, the $\varepsilon_r'$ exhibited two obvious step increases at -36 and 84 °C, corresponding to the $T_g$s of P(VDF-HFP) and PET, respectively. After introducing 8 and 20 vol.% PMMA tie layers, an additional step increase was seen at 42-44 °C, which could be attributed to the $T_g$ of the PMMA/P(VDF-HFP) interphase. This is consistent with the DMA result in Figure 7b. Above this temperature, the $\varepsilon_r'$ for the PET/PMMA/P(VDF-HFP) films appeared to be higher than that for the PET/P(VDF-HFP) 33-layer film; the higher the PMMA content, the higher the $\varepsilon_r'$. This was attributed to the higher permittivity of molten PMMA in the devitrified interphase than the neat PET at 50-70 °C.

In Figure 3.12b for the $\varepsilon_r''$ results, more transitions were identified in addition to the $T_g$s for P(VDF-HFP), interphase, and PET. For the PET/P(VDF-HFP) film, a broad weak transition was observed at 8 °C. This was attributed to the $\alpha_c$ transition for $\alpha$ PVDF crystals in P(VDF-HFP). After adding 8 vol.% PMMA as tie layers, the intensity of the $\alpha_{c, PVDF}$ relaxation peak decreased due to the formation of more $\beta$ PVDF crystals, as previously confirmed via WAXD studies. For the PET/PMMA/P(VDF-HFP) film with 20 vol.% PMMA, the relaxation peak around 8 °C slightly increased compared to the PET/P(VDF-HFP) film. This could be attributed to the $\beta$ transition (around 10-25 °C) for pure PMMA layers between the PET and interphase layers. The $T_g$ peaks of PET were observed around
80-85 °C. With increasing PMMA content, the T_g of PET slightly decreases, indicating certain compatibility between PMMA and PET.

The effect of biaxial orientation is demonstrated in the temperature-scan BDS results in Figures 12c,d. Compared with the as-extruded PET/P(VDF-HFP) film, the α_c,PVDF was not present for the biaxially oriented PET/P(VDF-HFP) film because of the parallel orientation of the PVDF crystals with respect to the layers (see Figure 3.9). After adding 8 and 20 vol.% PMMA tie layers, the T_g of the interphases slightly increased to 50 °C. The weak and broad PMMA β transition was observed for the 20 vol.% PMMA film, indicating the existence of neat PMMA layers between the interphase and PET. Meanwhile, the T_g of biaxially oriented PET in all films slightly increased, probably due to the formation of a rigid amorphous phase [38]. For example, the onset of T_g,PET was ca. 70 °C without biaxial stretching (Figure 3.12b), and it increased to about 80 °C for biaxially stretched films (Figure 3.12d). Note that the higher T_g for PET in the biaxially oriented films than in the as-extruded films was also observed in the DSC results in Figure 3.8. Beyond 85 °C, film-shrinking of the biaxially stretched films was observed, as evidenced by a decrease in ε_r′ in Figure 3.12c. We speculate that the formation of significant amount of rigid amorphous PET might be an important reason for enhanced electric breakdown strength for biaxially oriented PET/PMMA/P(VDF-HFP) multilayer films. Future studies will address this point.

3.4 Conclusions

Structure-property relationships in PET/PMMA/P(VDF-HFP) multilayer films have been studied in this work. PET/PMMA/P(VDF-HFP) multilayer films with good layer integrity were extruded with different PMMA compositions ranging from 0 to 20 vol.%. The interfaces between PET and P(VDF-HFP) layers were modified by the inclusion of PMMA
tie layers that are miscible with P(VDF-HFP) and compatible with PET. The as-extruded multilayer films were then biaxially stretched at 105 °C to orient fibrillar crystals in both PET and P(VDF-HFP) layers. Comparing the biaxially oriented PET/PMMA/P(VDF-HFP) film having 8 vol.% PMMA with the as-extrude PET/P(VDF-HFP) film, several loss mechanisms were minimized. First, interdiffusion of PMMA into P(VDF-HFP) resulted in a higher content of β PVDF crystals (ca. 55%). Second, biaxial stretching further increased the β crystal content to 67%. Third, parallel crystal orientation with respect to the layers impedes dipole flipping along the chain axes, resulting in a negligible α_c relaxation. As a result of the above structural changes in P(VDF-HFP), the α_c loss from the α PVDF crystals was greatly minimized. In addition, migrational loss from impurity ions could also be reduced as a result of interdiffusion of PMMA into P(VDF-HFP) and biaxial orientation, especially at elevated temperatures. Due to biaxial stretching, oriented fibrillar PET crystals constrained the amorphous chains, forming the rigid amorphous fraction with a higher T_g, and further enhanced the dielectric breakdown strength. As a result of these structural changes arising from PMMA inclusion at the interfaces/interphases and biaxial stretching, the dielectric properties were dramatically improved. For example, the biaxial oriented PET/PMMA/P(VDF-HFP) film with 8 vol.% PMMA exhibited 33% improvement in dielectric breakdown strength and 150% enhancement in discharge energy density at breakdown, as compared to the as-extruded PET/P(VDF-HFP) films. Knowledge obtained from this study will help in designing better multilayer films for electric energy storage applications.

3.5 References


Figure 3.1 Schematics of (A) three-component multilayer film coextrusion process via the forced assembly technique and (B) biaxial orientation of multilayer films using a Brückner Karo IV laboratory stretcher (film structure is not drawn to scale).

Table 3.1 List of PET/PMMA/P(VDF-HFP) Multilayer Films (ca. 10 μm thick)

<table>
<thead>
<tr>
<th>Compositions (vol.%)</th>
<th>Number of layers</th>
<th>PMMA layer thickness (nm)</th>
<th>PET and P(VDF-HFP) thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/0/50</td>
<td>33</td>
<td>0</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>
</tbody>
</table>
Figure 3.2 Dielectric breakdown strength (needle-plane geometry) as a function of PMMA tie layer composition for as-extruded PET/P(VDF-HFP) 33-layer films and biaxially oriented PET/PMMA/P(VDF-HFP) 65-layer films.
Figure 3.3 (A) Discharged energy density ($U_{\text{dis}}$) as a function of poling electric field for the as-extruded PET/P(VDF-HFP) 33-layer film (black triangles) and the biaxially stretched PET/PMMA/P(VDF-HFP) 65-layer film with 8 vol.% PMMA (red squares). (B) Maximum $U_{\text{dis}}$ as a function of PMMA composition for the as-extruded and biaxially oriented PET/PMMA/P(VDF-HFP) 65-layer films.
Figure 3.4 (A) The first half bipolar D-E loops for the as-extruded PET/P(VDF-HFP) film and the biaxially oriented PET/PMMA/P(VDF-HFP) 65-layer film with 8 vol.% PMMA. The poling frequency is 10 Hz with a sinusoidal wave function. (B) Hysteresis loop area at 400 MV/m as a function of PMMA volume fraction for as-extruded and biaxially oriented films with different contents of the PMMA tie layers.
Figure 3.5 Calculated PMMA weight fraction profile due to interdiffusion between PMMA and P(VDF-HFP) at different contact times. The calculation is based on the width of the multiplier channel (25.4 mm) with PC 10.16 mm, PMMA 5.08 mm, and P(VDF-HFP) 10.16 mm.
Figure 3.6 AFM phase images for PET/PMMA/P(VDF-HFP) multilayer films with (A) 0 vol.%, (B) 8 vol.%, and (C) 20 vol.% PMMA tie layers. The images are 20 μm × 20 μm. (D) – (F) show experimentally measured gray values from the corresponding AFM images.
in (A) – (C). (G) – (I) show the calculated gray values for the films with 0, 8, and 20 vol.% PMMA tie layers.

Figure 3.7 Dynamic mechanical analysis (DMA) results showing (A) storage modulus (E’) and dissipation factor, tanδ, as a function of temperature for the as-extruded PET/PMMA/P(VDF-HFP) multilayer films (10 μm) with 0, 8, and 20 vol.% PMMA tie layers.
Figure 3.8  AFM phase images of (A) the as-extruded PET/PMMA/P(VDF-HFP) 65-layer film (200 μm) with 8 vol.% PMMA and (B) the corresponding biaxially oriented film (10 μm).  (C) DSC first heating curves for the as-extruded and biaxially oriented
PET/PMMA/P(VDF-HFP) 65-layer films with 8 vol.% PMMA. The heating rate is 10 °C/min.

Figure 3.9 2D WAXD patterns for as-extruded (A, C, E) and biaxially oriented (B, D, F) PET/PMMA/P(VDF-HFP) multilayer films with (A,B) 0 vol.%, (C, D) 8 vol.%, and (E, F) 20 vol.% PMMA tie layers. (G) The X-ray beam is directed along the extrusion direction (ED). (H) Schematic of PVDF crystalline morphology confined between PET layers after biaxial orientation. Note that the film with 0 vol.% PMMA is the PET/P(VDF-HFP) 33-layer film.
Figure 3.10 (A) FTIR spectra for the as-extruded PET/P(VDF-HFP) 33-layer film and the biaxially oriented PET/PMMA/P(VDF-HFP) 65-layer film with 8 vol.% PMMA. (B) Calculated $\beta$ PVDF crystal content of PMMA for as-extruded and biaxially oriented PET/PMMA/P(VDF-HFP) multilayer films.
Figure 3.11 Dissipation factor, tan\(\delta\), as a function of frequency at (A) 20 °C and (B) 100 °C for as-extruded and biaxially oriented PET/PMMA/P(VDF-HFP) multilayer films with 0 and 8 vol.% PMMA tie layers, respectively.
Figure 3.12 Temperature-scan BDS results for PET/PMMA/P(VDF-HFP) multilayer films with 0, 8, and 20 vol.% PMMA: (A) $\varepsilon_r'$ and (B) $\varepsilon_r''$ for as-extruded films, and (C) $\varepsilon_r'$ and (D) $\varepsilon_r''$ for biaxially oriented films. The test frequency is 10 Hz.
CHAPTER 4

Polymer Multilayer Films for High Temperature Capacitor Application

4.1 Introduction

The demand for renewable energy to replace fossil fuels and reduction of carbon emission footprint has challenged scientists and engineering to innovate advanced technology for energy harvest and energy storage [1-2]. Automobile industry, which is considered to be the largest consumption area of fossil fuels, relies on electric capacitors for energy storage and generation. These capacitors require high energy storage, low volume and high operational temperature. Polymer film capacitors have been selected and widely used in the area due to their high breakdown strength, low dielectric loss, and high resistance. Additional advantages of polymer film capacitors include their low processing cost, low weight, and self-healing capability [3]. Current state-of-art polymer film capacitors use biaxial oriented polypropylene (BOPP) based on its high breakdown strength (700 MV/m), low dissipation factors (tanδ~0.0002), and low material cost. BOPP, however, suffers from
low energy density (5~6 J/cm$^3$) and low operational temperature (<85 °C). These disadvantages require larger capacitor size with external cooling unit in automobiles which dramatically increases complexity of power system design and generates extra cost. Therefore, advanced material systems as well as innovative processing techniques are still demanded to improve the energy density and operational temperature.

The low energy density of BOPP is attributed to its low dielectric constant ($\varepsilon_r=2.2$) since energy density ($U$) is proportional to dielectric constant ($\varepsilon_r$) and square of applied electric field ($E$). From material point of view, polymer with high dielectric constant is desired to enhance energy density of polymer film capacitor. Poly(vinylidene fluoride) (PVDF) and its copolymers provide a promising solution due to their high dielectric constant ($\varepsilon_r>10$) [4]. These materials, however, possess high hysteresis, which limits their applications. In order to overcome such drawback, a tremendous work has been developed to decrease hysteresis of PVDF-based polymers including PVDF copolymer synthesis and chemically grafting PVDF-based copolymers [5-7]. These works could solve the problem on the lab scale to prove the principle; however, they are not feasible and cost-effective for large scale manufacture and commercialization.

Our approach is to produce multilayer films with high dielectric constant PVDF-based polymer with high breakdown, low dielectric loss polymers. Utilizing forced assembly technique at Case Western Reserve University [8], polycarbonate (PC) and P(VDF-co-hexafluoropropylene) [P(VDF-HFP)] multilayer films were coextruded with up to 256 layers [9]. These multilayer films possessed enhanced breakdown strength and high energy density (around 13 J/cm$^3$). The dielectric constant difference between PC ($\varepsilon_r=3$) and PVDF-HFP ($\varepsilon_r=12$) generates Maxwell-Wagner interfacial polarization. This interfacial
polarization leads to charge accumulation, which traps space charges and improves breakdown strength. The multilayer structure also exhibited reduced hysteresis by “confinement effect”. The hysteresis of multilayer films decreased with increasing number of layers with identical overall film thickness and material composition [10]. As individual layer thickness decreased to nanoscale with increasing layer number, ion migration in PVDF layer was decreased due to nanoconfinement, which resulted in hysteresis reduction. Therefore, PC/P(VDF-HFP) multilayer film system exhibited enhanced breakdown strength, superior energy density, and reduced hysteresis compared with BOPP film capacitors, however, this system also suffers from low operational temperature since glass transition temperature of PC is only 145 °C and the melting point of P(VDF-HFP) is 133 °C. Forced assembly technique exhibited a promising technology breakthrough for high energy density capacitor application, which was not limited to the PC/P(VDF-HFP) system only. This technique can be applied to nearly all thermoplastic materials, which provides a variety of material candidates to fulfill operational temperature requirements.

The purpose of this work is to develop polymer multilayer system for high temperature capacitor application utilizing the forced assembly technique. High temperature polymers are selected for multilayer coextrusion including high Tg polycarbonate (HTPC, Tg=165 °C), polysulfone (PSF, Tg=185 °C), and poly(vinylidene fluoride) homopolymer (PVDF, Tm=171°C). Two polymer multilayer film systems (HTPC/PVDF and PSF/PVDF) were developed. Thermal stability of these two systems was tested via dynamic mechanical analysis and layer structure was characterized by atomic force microscopy. Dielectric breakdown strength, hysteresis and dielectric spectroscopy of these two systems were also compared as a function of temperature. Hysteresis of PSF/PVDF was further investigated
via confined crystallization. Effect of crystal orientation of PVDF was manipulated by melt-recrystallizing PVDF crystal under confinement of PSF and hysteresis measurements of as-extruded and melt-recrystallized PSF/PVDF film were carried out at high temperature. This paper provides a potential solution for high energy storage capacitor with high operational temperature for automobile industry.

4.2 Experimental

Materials

HTPC (Apec 1745, Covestro) and PSF (Udel 3703, Solvay) were chosen due to their good insulation and high breakdown strength at high temperature. PVDF homopolymer (Solef 6010, Solvay) was selected as high dielectric constant material. HTPC and PSF resins were dried at 80 °C for 24 h to remove moisture before processing. PVDF resin was used as received. Two polymer multilayer systems were selected with their properties listed in Table. 4.1. HTPC/PVDF and PSF/PVDF multilayer films with 33 alternating layers were co-extruded via forced assembly technique. Extrusion temperature was selected at 280 °C for HTPC/PVDF system and at 290 °C for PSF/PVDF system based on viscosity compatibility, which was determined through melt-flow indexer (MFI, Kayeness Galaxy 1) at a shear rate of 10 s⁻¹. Two low-density polyethylene (LDPE 5004i, Dow Chemical) skin layers were laminated on both sides of the multilayer films to protect from damage and surface defects. The sacrificial skin layers were removed prior to structure and property characterization. The film thickness was 12 µm without skin layer and the compositions of HTPC/PVDF and PSF/PVDF were 50/50 by volume.

Atomic Force Microscopy (AFM)
Layer integrity of multilayer films was characterized using AFM. Prior to imaging, multilayer films were embedded in epoxy and cured at room temperature for 24 h. Subsequently, the multilayer films were polished perpendicular to the film direction at -120 °C using an EM FC6 ultra-microtome (Leica microsystem Buffalo Grove, IL). Phase images of film cross-section were characterized under tapping-mode of AFM. The AFM images were recorded at room temperature by a Nanoscope IIIa Mutilmode Scanning Probe (Digital Instruments, Santa Barbara, CA).

**Dynamic Mechanical Analysis**

Dynamic mechanical analysis (DMA, Q800, TA instruments) was used to measure thermal stability of HTPC/PVDF and PSF/PVDF system. The measurement was carried out from -80 °C to 200 °C at a heating rate of 3°C/min. A tensile mode was selected for the characterization with a constant frequency of 1 Hz.

**Dielectric Breakdown Strength Measurement**

Dielectric breakdown strength of multilayer film was measured vs. temperature. Two copper cylinders (diameter = 6 mm) were used as positive and negative electrode. The setup was merged in mineral oil bath to eliminate corona breakdown. A ramped voltage was applied on the multilayer films at 500 V/s using a Quadtech Gradrian 20 kV HiPot tester (Marlborough, MA). Multilayer films were dried at 60 °C under vacuum for 24 h to remove moisture.

**Hysteresis Loop Measurement**

Electric displacement-electric field (D-E) loop measurement was carried out in a mineral oil bath from room temperature to 200 °C. Electron Microscopy Sciences sputter coater
(Quantum Technologies, Ashford, Kent, England) was used to coat gold electrode (thickness = 10 nm and diameter = 2.5 mm) on both sides of multilayer films. Constant electric field of 200 MV/m was applied on the sample using a Radiant Technologies Premiere II ferroelectric tester. The hysteresis of multilayer film (U(t)) was calculated based on the following equation:

\[
U_t = \int_{D(0)}^{D(T)} E(t) dD(t) - \int_{D(T)}^{D(2T)} E(t) dD(t)
\]

where D(t) is the electric displacement and E(t) is the applied electric field. T is the time for the electric field charge/discharge process.

**Broadband Dielectric Spectroscopy**

Broadband dielectric spectroscopy of multilayer film was measured using a Novocontrol (Hundsangen, German) dielectric spectrometer. The measurement was carried out under vacuum under a frequency sweep from 0.01 to 10^5 Hz. Electron Microscopy Sciences sputter coater (Quantum Technologies, Ashford, Kent, England) was used to coat gold electrode (thickness = 10 nm and diameter = 2.5 mm) on both sides of multilayer films.

**Isothermal Crystallization of PVDF**

Isothermal crystallization experiment of the PSF/PVDF multilayer film was carried out through a two-step procedure. First, PSF/PVDF multilayer film was merged in mineral oil at 180 °C for 10 min to melt PVDF, while PSF remained rigid at this temperature. Subsequently, the film was transferred into another oil bath at 135 °C to recrystallize PVDF for 30 min. These temperatures were selected based on thermal properties of PSF and PVDF characterized by a differential scanning calorimeter (DSC, Q2000, TA instruments) at a heating/cooling rate of 10 °C/min.
Wide-Angle X-Ray Scattering

Crystal orientation of as-extruded and recrystallized PVDF films were characterized using wide angle X-ray scattering (WAXS). X-ray patterns were obtained by aligning the incident beam parallel to the extrusion direction (ED) of the film. A highly focused X-ray beam of monochromatic Cu Kα radiation (λ = 0.15418 nm) was generated by a Rigaku (Woodlands, TX) MicroMax-002 instrument operating at 45 kV and 0.88 mA. The diffraction angle was calibrated by a CaF2 standard and the sample-to-detector distance was 140 mm. The X-ray pattern was collected with an imaging plate (pixel size = 50 µm).

4.3 Results & Discussion

Multilayer Layer Structure and Thermal Stability

Multilayer structure is the essential characteristic to achieve high energy density high temperature capacitors. Although conventional capacitors (BOPP and Mylar) possess relatively high breakdown strength, the energy density is not sufficient due to their low dielectric constant and the operational temperature is below 100 °C. Multilayer film capacitor is a technology breakthrough [9], which could overcome such drawbacks by combination of a high energy density, high dielectric constant material with a high temperature, high insulating material. PSF/PVDF and HTPC/PVDF multilayer films with 33 alternating layers were extruded via forced assembly technique with film thickness around 12 µm. Layer integrities of both systems were characterized using AFM. AFM Phase images of film cross-section are shown in Figure 4.1 Based on AFM images,
PSF/PVDF (Figure. 4.1a) and HTPC/PVDF (Figure. 4.1b) exhibited uniform layer structure and the individual layer thickness is around 350 nm. The AFM images confirmed that as-extruded PSF/PVDF and HTPC/PVDF films possess desired layer structure.

In order to extend operational temperature of polymer multilayer films capacitors, high temperature polymers including HTPC, PSF, and PVDF were selected based on their high glass transition/melting temperature. DMA was used to determine thermal stability of HTPC/PVDF and PSF/PVDF multilayer films. DMA spectra of both systems are shown in Figure 4.2 In Figure 4.2a, storage modulus is plotted vs. temperature. For HTPC/PVDF films (dark line in Figure 4.2a), the first modulus drop at around -40 °C was related to glass transition temperature of PVDF amorphous phase. The second modulus drop at around 170 °C corresponded to glass transition temperature of HTPC (165 °C) and melting temperature of PVDF crystal (171 °C). PSF/PVDF film (red line in Figure 4.2a) exhibited similar T_g of PVDF at -40°C. The modulus PSF/PVDF system decreased at higher temperature (183 °C) compared to HTPC/PVDF system due to higher T_g of PSF (185 °C). Tanδ of both system followed similar trend. The tanδ peak for HTPC/PVDF was at 175 °C while PSF/PVDF exhibited a tanδ peak at 190 °C. Therefore, PSF/PVDF system possesses a higher operational temperature compared to HTPC/PVDF system.

**Dielectric Properties of HTPC/PVDF and PSF/PVDF Systems**

Dielectric breakdown strength is vitally important for high energy density capacitors since the energy density (W) is proportional to square of applied electric field (E) and dielectric constant (\(\varepsilon_r\)), given as \(W=0.5\varepsilon_0\varepsilon_rE^2\). Dielectric breakdown strengths of HTPC/PVDF and PSF/PVDF films were measured as a function of temperature and the results are plotted in Figure 4.3. For the temperature below 150 °C, HTPC/PVDF and PSF/PVDF multilayer
films possessed similar breakdown strength. As the temperature increased above 150 °C, PSF/PVDF system exhibited a significant enhancement on breakdown strength. Based on our previous work, the enhanced breakdown strength of multilayer film is attributed to the multilayer structure with dielectric contrast. The charge migration is inhibited by the insulating layer, HTPC or PSF. Moreover, the two-component multilayer system comprised of a high dielectric constant polymer and highly insulating, low dielectric constant material leads to charge build-up at layer interface (Maxwell-Wagner interfacial polarization) [11]. The charge build-up at the layer interface acts as effective traps to prevent injected electrons from penetrating through the film. Therefore, dielectric breakdown of multilayer films can be described as an electro-mechanical process. Multilayer film capacitor will breakdown when the interfacial charge accumulation overcomes the mechanical strength of charge blocking layer [12]. According to this mechanism, the breakdown strength declines as a function of temperature is attributed to the modulus drop and resistivity decrease. When the temperature is close to the \( T_g \) of HTPC \( (T_g = 165 \, ^\circ \text{C}) \), the mobility of polymer chain increases dramatically. Therefore, the reduction of modulus and insulation on HTPC layer cause the breakdown strength decrease and this mechanism explains the superior breakdown strength of PSF/PVDF system above 150 °C. Additionally, PSF/PVDF system provided higher operational temperature compared with HTPC/PVDF system. HTPC/PVDF multilayer films shrank above 170 °C while PSF/PVDF system could hold its shape until 190 °C.

Dielectric hysteresis of HTPC/PVDF and PSF/PVDF multilayer films were measured from room temperature to 190 °C and the results are shown in Figure 4.4. Hysteresis loop of both systems are compared at 170 °C in Figure 4.4a. Based on this plot, PSF/PVDF system
(red loop) exhibited a slimmer loop compared with HTPC/PVDF system (dark loop) indicating that hysteresis of PSF/PVDF system was lower compared with HTPC/PVDF system. The integrated hysteresis loop areas of both systems at every temperature are plotted in Figure 4.4b. According to this plot, hysteresis of both system were similar at low temperature, however, as the temperature increased above 150 °C, PSF/PVDF system possessed lower hysteresis compared with HTPC/PVDF system. Based on our previous publication, reduction of dielectric hysteresis in multilayer films is generated via nanoconfinement [10]. The ion migration is confined in each PVDF layer (350 nm) by adjacent insulating layers, HTPC or PSF. These insulating layers prevent charge penetration through layers and reduce hysteresis. Therefore, this insulation effect is attenuated with elevated temperature since polymer chain mobility is accelerated with increasing temperature. This also explains the slimmer hysteresis loop of PSF/PVDF system compared with HTPC/PVDF system when the temperature is approaching the T_g of HTPC.

Ion migration of both systems can be confirmed using broadband dielectric spectroscopy and the results are shown in Figure 4.5. In this figure, tanδ of both systems are plotted as a function of frequency at 170 °C. The hysteresis of both systems exhibited the largest difference at this temperature. Based on our previous publications, hysteresis of multilayer film is correlated with ion migration measured [10]. According to Figure 4.5, ion migration peak for HTPC/PVDF system was at 300 Hz at 170 °C. When the HTPC was substituted by PSF, ion migration peak was moved to lower frequency (100 Hz) at the same temperature, indicating that ion migration was slowed down by PSF compared with HTPC. Ion migration data is a solid support for the hysteresis measurement. PSF/PVDF system
exhibited reduced hysteresis compared with HTPC/PVDF system because the ion migration in PSF/PVDF system was retarded, which leads to lower conduction loss.

**Reduced Hysteresis by Confined Crystallization**

Hysteresis of PSF/PVDF system can be further reduced by introducing confined crystallization to manipulate crystal orientation. In our previous work [13], confined crystallization is an effective method to control crystal orientation and influence transport properties. Gas permeability of poly(ethylene oxide) (PEO) was reduced by two orders of magnitude by achieving highly oriented, high aspect ratio single lamellae via confined crystallization. Since crystalline phase was considered to be impermeable compared to amorphous phase, gas molecular could only pass through the amorphous phase of the layer between highly oriented, high aspect ratio single lamellae which resulted in dramatic reduction on permeability. This idea could also be applied to manipulate hysteresis of multilayer films. In order to achieved oriented crystal, the confined layer need to be melted and recrystallized between confining layer at nanoscale. The thermal properties and detail procedure are shown in Figure 4.6. Based on DSC thermogram (Figure 4.6a) the melting temperature and crystallization temperature of PVDF were at 171 °C and 135 °C, respectively, and the $T_g$ of PSF was at 185 °C. Melt-recrystallization procedure is explained in Figure 4.6b. PSF/PVDF film was constrained with aluminum mask to maintain the original dimension. The constrained film was first merged in one oil bath at 180 °C for 10 min to melt the PVDF crystal. At this temperature, PSF was still rigid to hold the shape of the films. This was an extra advantage of PSF/PVDF system compared with HTPC/PVDF system. Due to the relatively low glass transition temperature of HTPC (165 °C) which is lower than melting temperature of PVDF (171 °C), multilayer structure will be destroyed.
when the temperature is higher than the melting of PVDF and glass transition temperature of HTPC. After PVDF crystal was totally melted, PSF/PVDF film was transported rapidly into another oil bath at 135 °C and annealed for 30 min. Finally, recrystallized PSF/PVDF film was cooled down to room temperature for characterization.

In order to confirm orientation generated by confined crystallization, wide angle X-ray scattering was used to characterize as-extruded and melt-recrystallized PSF/PVDF films (Figure 4.7). According to X-ray pattern on the film extrusion direction, as-extruded PSF/PVDF film exhibited little orientation, which was generated by the film take-off process with a chill-roll (20 RPM). After melt-recrystallization, four sharp (110) reflections were observed in X-ray pattern indicating the formation of on-edge lamellae with c-axil parallel to the film direction. Further proof of on-edge lamellae was confirmed with sharp (100) reflection appeared at the meridian. After PCVDF was melted, the film was annealed at the crystallization temperature of PVDF (135 °C) and confined within each layers (350 nm) between adjacent rigid PSF layers. The on-edge oriented crystal was achieved due to confinement effect.

The confined crystallization effect on hysteresis was characterized by D-E loop at 125 °C and 150 °C (Figure 4.8). According to hysteresis measurement, melt-recrystallized PSF/PVDF film exhibited slimmer loop compared with as-extruded PSF/PVDF film indicating that confined crystallization could further reduce hysteresis of multilayer system. The mechanism of this phenomenon is comparable with crystal orientation effect on gas permeability. The oriented crystal provides a “barrier effect” to ions so that ions mobility is constrained by well oriented, high aspect ratio crystal. Therefore, confined crystallization exhibits reduced hysteresis by achieving oriented PVDF crystal.
This confined crystallization effect on hysteresis was also confirmed via broadband dielectric spectroscopy. The tanδ data of PSF/PVDF films at 125 °C and 150 °C are plotted at Figure 4.9a and Figure 4.9b respectively. At 125 °C, the tanδ peak at $10^4$ Hz was attributed to $\alpha_c$ crystal of PVDF and tanδ peak at around 1 Hz was correlated to ion migration in PVDF layer. According to Figure 4.9a, melt-recrystallized PSF/PVDF film exhibited lower ion migration compared with as-extruded film since the ion migration peak was shifted to the lower frequency and the peak intensity was also decreased. At 150 °C, tanδ peak (20 Hz) intensity was also decreased by melt-recrystallization which indicated that PVDF crystal exhibited barrier effect to hinder ion migration and decrease hysteresis.

4.4 Conclusion

High temperature multilayer film capacitor systems were developed with high $T_g$ polycarbonate (HTPC), polysulfone (PSF) and poly (vinylidene fluoride) (PVDF). HTPC/PVDF and PSF/PVDF multilayer films with 33 alternating layers were coextruded via forced assembly technique with excellent layer uniformity. PSF/PVDF multilayer system possessed higher working temperature compared with HTPC/PVDF system since glass transition temperature of PSF is 20 °C higher than $T_g$ of HTPC. For high temperature capacitor applications, PSF/PVDF system exhibited enhanced breakdown strength compared with HTPC/PVDF system since polymer chain mobility of PSF is lower than HTPC which resulted in better electric insulation. PSF/PVDF system also provides reduced hysteresis compared with HTPC/PVDF system because ion migration in PSF/PVDF is lower than HTPC/PVDF system. Hysteresis of PSF/PVDF was further decreased by confined crystallization. After melt-crystallization, on-edge crystal orientation of PVDF was achieved under confinement of PSF layer. The on-edge PVDF crystal exhibited a
“barrier effect” which decreased charge mobility and leaded to hysteresis reduction. This work demonstrated that PSF/PVDF was a promising system for high temperature capacitor application.

4.5 References


| Table 4.1. Material Properties of Multilayer Systems |
|-----------------------------------------|------|------|-----|
| Material     | T_g (°C) | T_m (°C) | ε_r |
| System #1     |       |         |     |
| PCHT          | 165   | -       | 3.0 |
| PVDF          | -40   | 172     | 13.0|
| System #2     |       |         |     |
| PSF           | 185   | -       | 3.02|
| PVDF          | -40   | 172     | 13.0|
Figure 4.1 AFM phase images of a) PSF/PVDF and b) HTPC/PVDF multilayer films.
Figure 4.2 Thermal stability of PSF/PVDF and PCHT/PVDF films: a) storage modulus vs. temperature, b) Tanδ vs. temperature.
Figure 4.3 Breakdown strength vs. temperature of PSF/PVDF and PCHT/PVDF films
Figure 4.4 a) Hysteresis loop of PSF/PVDF and PCHT/PVDF at 170°C, b) hysteresis loop area of PSF/PVDF and PCHT/PVDF at various temperatures.
Figure 4.5 Broadband dielectric spectroscopy of PSF/PVDF and PCHT/PVDF at 170°C
Figure 4.6  a) DSC of PSF/PVDF multilayer films, b) thermal treatment procedure to achieve on-edge and in-plan crystal.
Figure 4.7 Wide angle X-ray diffraction of PSF/PVDF multilayer films: a) as-extruded films, b) annealed at 135°C for 0.5hr.
Figure 4.8 Hysteresis loop of PSF/PVDF multilayer films: a) as-extruded films, b) annealed at 135°C for 0.5hr.
Figure 4.9 Broadband dielectric spectroscopy of PSF/PVDF multilayer films: a) as-extruded films, b) annealed at 135oC for 0.5hr.
Appendix

Fluorinated poly(arylene ether ketone)s for high temperature dielectrics

A. 1 Introduction

Today's electronics are involved in many vital functions of everyday life and capacitors serve key roles in these devices [1-4]. Because of miniaturization and increased energy consumption in such applications, new dielectric materials must be developed with higher energy density while maintaining low loss of that energy [1-4]. Considerable research has been devoted to polymeric dielectric materials due to their ease of manufacturing, high breakdown strength, low loss, and self-clearing capabilities [1, 5-6]. Biaxially oriented polypropylene is widely regarded as the current state-of-the-art material and it is well known that many of its properties originate from the biaxial orientation process [7-10]. However, the use of biaxially oriented polypropylene is limited due to its poor performance above ~85°C and low energy density [8-9, 11].

A processing technique under investigation to increase dielectric film performance has been termed forced assembly microlayer coextrusion [12-20]. In this process, two polymers are multilayered in a film to create a structure with many parallel alternating layers [21]. This is advantageous for capacitors because the properties of two different materials can be combined and each interface of the two polymers works to bolster the overall dielectric properties [12-13]. One of the polymers, the insulating layer with low dielectric constant, is chosen to have high breakdown strength and low loss, e.g. poly(ethylene terephthalate)
polycarbonate [12-18], or polysulfone [20]. The other polymer has a high dielectric constant such as poly(vinylidene fluoride) [13,17,20] or it's copolymers that can increase the energy density [12,14-16,18,19]. The layered structure leads to build-up of Maxwell-Wagner-Sillars interfacial polarization at the interfaces. The charge buildup at these interfaces allows the films to discharge along the interfaces and thus results in higher breakdown strengths [19].

In this work, four different poly(arylene ether)s were synthesized to compare symmetric and asymmetric fluorine-containing structures versus their non-fluorinated counterparts. Prior work on low dielectric polymers as insulators showed that asymmetric versus symmetric fluorination could affect a material's overall polarization[22]. Therefore, this paper describes poly(arylene etherketone)s (PAEKs) with systematic fluorine- and non-fluorinecontaining geometries that could be melt processed for use in capacitors (Figure A1). In the future, they could be layered with poly(-vinylidene fluoride) to explore the effect that fluorination and symmetry have on the interfaces of the microlayer film architecture. Literature shows that increasing the strength of the interface can increase the breakdown strength of layered dielectric films [23]. It was reasoned that added fluorine structures in the polymers may improve interactions with fluorinated high dielectric constant materials such as PVDF.

A. 2 Experimental

Material synthesis and film casting (courtesy of Andrew Shaver)

The procedure for all four polymers was the same. A representative synthesis of the BPA polymer was adapted from previous literature [25-29]. For example, bisphenol A (67.713
g, 296.6 mmol), 4,4’-difluorobenzophenone (65.643 g, 306.4 mmol), and DMAc (600 mL) were charged to a three-neck flask equipped with a N₂ inlet, mechanical stirrer, and Deane-Stark trap. Toluene (300 mL) and K₂CO₃ (48.352 g, 349.8 mmol) were added to the flask and the Deane-Stark trap was filled with toluene. The apparatus was placed in a silicone oil bath that was heated to 155°C to begin azeotropic removal of water. After 4 h the toluene and water were removed from the Deane-Stark trap. The oil bath was maintained at 150°C for 12 h, and then the reaction was allowed to cool to room temperature. The polymer solution was filtered to remove any excess K₂CO₃ or by-product salts. The polymer solution was precipitated into deionized water, and then the polymer was stirred in deionized water at 80°C to further assist the removal of salts and solvents. The white polymer was filtered and dried at 110°C under vacuum. Yield was 81%.

The values for the remaining three reactions were as follows. For the 6FBPA polymer the amounts of the materials were: 4,4’-Hexafluoroisopropilenediphenol (2.733 g, 8.128 mmol), 4,4’-difluorobenzophenone (1.814 g, 8.468 mmol), DMAc (24 mL), toluene (12 mL), and K₂CO₃ (1.3800 g, 9.985 mmol). Yield was 92%. For the 3FBPAP polymer the amounts of the materials were: 1,1-bis(4-hydroxyphenyl)-1-phenyl-2,2,2-trifluoroethane (9.960 g, 28.93 mmol), 4,4’-difluorobenzophenone (6.481 g, 30.25 mmol), DMAc (24 mL), toluene (12 mL), and K₂CO₃ (6.4370 g, 46.57 mmol). Yield was 82%. For the BPAP polymer the amounts of the materials were: 4,4’-(1-phenylethyldene)bisphenol (2.081 g, 7.167 mmol), 4,4’-difluorobenzophenone (1.600 g, 7.469 mmol), DMAc (24 mL), toluene (12 mL), and K₂CO₃ (1.2300 g, 8.899 mmol). Yield was 89%.

The polymer (0.4 g) was weighed into a small glass vial with a magnetic stir bar. Chloroform (11 mL) was added to the vial to obtain a 2.5 wt% solution. The solution was
filtered using a 1-mm syringe filter into a clean glass vial. A 5 x 5” glass plate was placed in a base bath for 30 min for surface treatment. The glass plate was rinsed and dried, then placed on a level surface for casting. The solution was poured onto the plate and the solution was spread to the edges of the plate until it covered the whole glass plate. A glass dome with 2 outlets was used to cover the plate. One outlet was fitted with a syringe filter and the other was connected to the house air stream running at 2 SCFH. The plate was left undisturbed for a minimum of 30 min, and then transferred to an oven at 110°C for an additional 30 min. The film was removed from the glass plate using a razor blade by slowly lifting the edges until the film came off.

**Breakdown strength**

Breakdown strengths of the PAEK films were measured with a needle-plane electrode. The needle electrode was the positive side and the diameter of the needle tip was 40 mm. The negative electrode was a 3 x 10 cm rectangular aluminum plate. A Quadtech (Marlborough, MA) Guardian 20-kV HiPot tester was used as the voltage source and the voltage ramp speed was 500 V/s. The breakdown strength measurements were carried out in an oil bath at 25, 75, 125, 150, and 175°C with twenty repetitions for each film.

**Dielectric thermal analysis (DETA)**

Dielectric spectroscopy was measured with a frequency sweep from 0.01 Hz to 10000 Hz at 25 °C at a constant voltage of 1 V using a Novocontrol (Hundsangen, Germany) spectrometer. Electrodes on each side of the film were sputtered-coated with gold using an EMS Q300 T sputter coater (Electron Microscopy Science, Quantum Technologies, Ashford, Kent, England). The diameter of the gold electrode was 1 cm. Prior to testing, the
films were dried for 24 h at 120 °C. The frequency sweep measurements were carried out at room temperature and the temperature sweep heating rate was 5°C/min.

**Refractive indices**

The refractive indices of PAEK films were characterized using a 2010 Metricon instrument with a 633 nm laser at room temperature. The PAEK films were brought into contact with the base of a prism with a known refractive index. The laser beam began horizontal (90°) to the prism/polymer interface so all light was totally reflected, and then it rotated until it was normal to the prism/polymer interface (0°). At some angle between 90° and 0° the reflected laser light intensity decreased which indicated the critical angle. The refractive indices of the films were calculated by Snell's Law (equation (1))

\[ n_p \sin \theta_p = n_f \sin \theta_f \]  

(1)

where \( n_p \) and \( n_f \) are the refractive indices of the prism and the film, respectively, \( \theta_p \) is the critical angle and \( \theta_f \) equaled 90° [30].

**A. 3 Results and discussion**

The calculated breakdown strengths of each of the materials as functions of temperature are listed in Table A1. At 25°C, the trend is 3FBPAP > BPAP > 6FBPA > BPA with a difference of approximately 20 V between each. This can also likely be correlated to stiffness because breakdown strength has been shown to increase with Young’s modulus [31-32]. As the temperature is increased, the two asymmetric polymers maintain higher calculated breakdown strengths, most likely due to their higher Tg's and stiffer backbones. Even at 175°C, the calculated breakdown strengths of the asymmetric polymers are greater than those of the symmetric polymers at 125°C.
The relative permittivity ($\varepsilon$) was measured from $10^1$ to $10^4$ Hz (Figure. A2). The trend in relative permittivity for the four polymers is BPAP > BPA > 3FBPAP > 6FBPA. The differences can be attributed to their fluorine content, introduction of a phenyl ring, and their symmetric versus asymmetric structures. Increased fluorine content in the polymer increases the fractional free volume, and an increase in fractional free volume decreases the amount of polarizable content per unit volume. With less material to be polarized, the relative permittivity will be lower [33]. Thus, it is reasonable to expect that 6FBPA and 3FBPAP would have lower relative permittivities than BPA and BPAP, respectively. Xie et al. made a series of poly(arylene ether ketone)s using 4,4’-difluorobenzophenone which showed comparable results to our own. Their nonfluorinated poly(arylene ether ketone) had an $\varepsilon$ of 2.95 at 1 MHz where as our BPA-based poly(arylene ether ketone) had an $\varepsilon$ of 2.94 at 0.1 MHz [34]. Further literature shows that the $\varepsilon$ of both our fluorinated and non-fluorinated PAEK polymers are in the expected value range. [35-37].

Introduction of a phenyl ring in the bisphenol linking group increases the relative permittivity because its polarizability to weight contribution is higher than for the methyl or trifluoromethyl groups. This can be explained using the Vogel model polarization group contribution values [38]. The phenyl group has a polarization contribution of 123.5 and a M$_w$ of 77 to give a polarizability/weight ratio of 1.604. In comparison, the methyl group has a polarization contribution of 17.66 and a M$_w$ of 15 to give a ratio of 1.177. The trifluoromethyl group has a polarization contribution of 86.4 and a M$_w$ of 69 to give a ratio of 1.252. The phenyl group contributes more polarization to the relative permittivity than the methyl or trifluoromethyl groups, and this can be correlated to its easily polarized aromaticity [33]. Other poly(ether ketone)s with highly aromatic structures and ketones
have high $\varepsilon$ values, thus showing their structural importance to the polymer $\varepsilon$ for dielectric films [11, 39, 40].

The higher performance of BPAP and 3FBPAP over their symmetric counterparts, BPA and 6FBPA, can be linked to their asymmetric methyl or trifluoromethyl groups. In the symmetric polymers the methyl or trifluoromethyl groups have an opposing group with the same composition so the dipole will be canceled. Without the opposing group, the asymmetric polymers have a net dipole and any group with a net dipole will contribute to orientation polarization (dipole polarization). Orientation polarization is one of the three main types of polarization that can contribute to the overall polarizability, which is one of the main factors in determining the relative permittivity. The three types are electronic, atomic, and orientation polarization [33].

In order to examine the contribution of incorporating fluorine in an asymmetric geometry, relative permittivities ($\varepsilon$) measured by dielectric spectroscopy were compared with the squares of the refractive indices, also known as the Maxwell $\varepsilon$. Equation (2) shows the relationship between the refractive index and relative permittivity.

$$\varepsilon_{\text{Maxwell}} = n^2$$

(2)

The difference between the measured and Maxwell $\varepsilon$ provides some understanding of the contributions of orientation polarization to the permittivities in the polymer systems. This is because the Maxwell model represents the $\varepsilon$ at high frequencies, which is dominated by electronic polarization. The measured $\varepsilon$ by dielectric spectroscopy was at lower frequencies and has orientation polarization contributions. Therefore the difference gives an indication of the orientation contribution of the material.
In Figure A3 the left graph compares the measured \( \varepsilon \) at 1 kHz to the Maxwell \( \varepsilon \) of the symmetric PAEK structures. The dashed line is included to make a better comparison between the two \( \varepsilon \) values. The measured \( \varepsilon \) and Maxwell comparison were extremely close since BPA and 6FBPA are both symmetric and therefore have no orientation polarization. The right graph makes the same comparison but with the two asymmetric structures. In this case there is a difference between the measured \( \varepsilon \) and the Maxwell comparison lines. This is expected since the orientation polarization due to the asymmetric trifluoromethyl group will be greater than for the asymmetric methyl. This is confirmed since the measured \( \varepsilon \) by dielectric spectroscopy has a less negative slope than the Maxwell comparison. This indicates that orientation polarization contributes more to the 3FBPAP measured \( \varepsilon \) than it contributes to the BPAP \( \varepsilon \).

### A. 4 Conclusion

In summary, we were able to make high molecular weight BPA, 6FBPA, BPAP, and 3FBPAP based poly(arylene ether ketone)s via nucleophilic aromatic substitution step growth polymerization. The breakdown strengths of the asymmetric PAEK's were higher than for the symmetric polymers. The trend in \( \varepsilon \) was BPAP > BPA > 3FBPAP > 6FBPA and this was attributed to fluorine content, replacement of the methyl or trifluoromethyl in the bisphenol linking groups with the phenyl ring, and the asymmetric structure. Introduction of fluorine in place of hydrogen results in increased fractional free volume, and this reduces the polarizable content per unit volume. The phenyl ring has a superior polarizability to weight ratio. The asymmetric structure results in larger dipoles which contribute to orientation polarization. This was confirmed by comparing the relative permittivities measured at 1 kHz to the Maxwell model relative permittivities (squares of
the refractive indices). This suggests that asymmetric structures with higher relative permittivities would be advantageous for multilayer capacitors with PVDF or its copolymers.

It is reasoned that energy storage density would be improved in multilayer films with increased interaction at the interface between the two materials. Thus, our approach has been to design engineering polymers that contain fluorinated groups so that they will interact positively with PVDF at the interfaces between the layers. The maximum energy storage density in an insulating material is proportional to the dielectric constant times the square of the breakdown strength. The breakdown strengths of these amorphous poly(arylene ether ketone)s are higher than the aromatic polycarbonates that were studied previously. For example, at 125°C, bisphenol A polycarbonate had a calculated breakdown strength of 540 kV/mm [13] while 3FBPAP PAEK has a calculated breakdown strength of 622 kV/mm. Moreover the Tg of bisphenol A polycarbonate is 150°C whereas the Tg of 3FBPAP PAEK is 183°C, and both have excellent mechanical properties. Thus, we believe that these poly(arylene ether ketone)s have potential for incorporation into multilayered (thin-film) capacitors with PVDF as a high dielectric constant layer. The processing parameters for making multilayered capacitors through forced assembly microlayer coextrusion and the dielectric properties of those materials with poly(arylene ether ketone)s and high dielectric constant fluorinated polymers will be a major focus of a forthcoming publication.

A. 5 Reference


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Table A1 Calculated breakdown strengths measured via a needle-plane electrode method.

The units of breakdown strength are volts/film thickness (kV/mm).

<table>
<thead>
<tr>
<th></th>
<th>25°C</th>
<th>75°C</th>
<th>125°C</th>
<th>150°C</th>
<th>175°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPA PAEK</td>
<td>782±35</td>
<td>563±44</td>
<td>412±52</td>
<td>365±22</td>
<td>-</td>
</tr>
<tr>
<td>6FBPA PAEK</td>
<td>803±55</td>
<td>583±20</td>
<td>410±34</td>
<td>396±28</td>
<td>-</td>
</tr>
<tr>
<td>BPAP PAEK</td>
<td>821±45</td>
<td>753±33</td>
<td>651±50</td>
<td>615±27</td>
<td>511±36</td>
</tr>
<tr>
<td>3FBPAP PAEK</td>
<td>840±45</td>
<td>765±33</td>
<td>662±49</td>
<td>641±26</td>
<td>523±31</td>
</tr>
</tbody>
</table>
Figure A1. The polymer chemical structures.
Figure A2. The relative permittivity of each material over varying frequency at 25°C.
Figure A3. Comparison of the measured relative permittivity by dielectric spectroscopy versus the squared refractive indices. The left graph is the comparison of the symmetric PAEK structures and the right graph is the comparison of the asymmetric structures. Relative permittivities were measured by dielectric spectroscopy at 1 kHz.
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