DIELECTRIC PROPERTIES OF MULTILAYER POLYMER FILMS FOR HIGH ENERGY DENSITY CAPACITORS & PREDICTING LONG-TERM CREEP FAILURE OF A BIMODAL POLYETHYLENE PIPE FROM SHORT-TERM FATIGUE TESTS

by

Zheng Zhou

Submitted in partial fulfillment of the requirements
For the degree of Doctor of Philosophy

Dissertation Advisors: Prof. Eric Baer and Prof. Anne Hiltner

Department of Macromolecular Science and Engineering
CASE WESTERN RESERVE UNIVERSITY

August, 2013
We hereby approve the thesis/dissertation of

Zheng Zhou

candidate for the Ph.D. degree *.

(signed) Prof. Eric Baer

(chair of the committee)

Prof. Lei Zhu

Prof. Donald Schuele

Prof. Alex Jamieson

(date)

May 8, 2013

*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedication

To my wife, Ying Chen, and my parents, Baihua, and Jieshui
TABLE OF CONTENTS

LIST OF TABLES iii
LIST OF FIGURES iv
ACKNOWLEDGEMENTS xi
ABSTRACT xiii

PART A 1

CHAPTER 1 2
INTERPHASE/INTERFACE MODIFICATION ON THE DIELECTRIC PROPERTIES OF PC/P(VDF-HFP) MULTILAYER FILMS FOR HIGH ENERGY DENSITY CAPACITORS

CHAPTER 2 51
MULTILAYERED POLYCARBONATE/POLY(VINYLIDENE FLUORIDE-CO-HEXAFLUOROPROPYlene) FOR HIGH ENERGY DENSITY CAPACITORS WITH ENHANCED LIFETIME

CHAPTER 3 92
FRACTURE PHENOMENA IN MICRO- AND NANO-LAYERED POLYCARBONATE/POLY(VINYLIDENE FLUORIDE-CO-HEXAFLUOROPROPYlene) FILMS UNDER ELECTRIC FIELD FOR HIGH ENERGY DENSITY CAPACITORS
LIST OF TABLES

CHAPTER 1

1.1 PC/tie/P(VDF-HFP) multilayer films under investigation 31

1.2 Maximum discharge energy density and hysteresis property values at 500 kV/mm as a function of nominal tie layer thickness for the 65-layer 46/8/46 PC/tie/P(VDF-HFP) multilayer films. 44

1.3 Measured and modeled dielectric constants of PC/tie/P(VDF-HFP) 46/8/46 multilayered films at 20 °C, and effective dielectric constants of P(VDF-HFP) calculated from series model. 46

CHAPTER 2

2.1 Film compositions and nominal layer thicknesses of multilayer PC/P(VDF-HFP) film with overall film thickness of 8 µm. 75

CHAPTER 3

3.1 PC/P(VDF-HFP) multilayer films under investigation 117

CHAPTER 4

4.1 Experimental matrix that was designed to get the stepwise mechanism in order to construct Paris plot at different R-ratios. 151

4.2 Experimental matrix for temperature dependence of stepwise crack growth. 153

4.3 Comparison of modified Paris law and creep factor for different PEs (HDPE, MDPE, and BMPE). 154
LIST OF FIGURES

CHAPTER 1

1.1 Dielectric breakdown strength as a function of nominal tie layer thickness for 65-layer PC/PMMA/P(VDF-HFP) films. The 33-layer PC/P(VDF-HFP) film was also included and taken as the film with 0 nm tie layer thickness (indicated as the dashed line).

1.2 Representative unipolar D-E hysteresis loops for 65-layer PC/PMMA/P(VDF-HFP) films with various PMMA layer thicknesses/compositions. In addition, the 50/50 PC/P(VDF-HFP) 33-layer film was also included for comparison. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 µm.

1.3 a ) Charge energy density, b ) discharge energy density, and c ) loss energy density as a function of electric field for 65-layer PC/PMMA/P(VDF-HFP) films with various layer thicknesses/compositions. In addition, the 50/50 PC/P(VDF-HFP) 33-layer film was also included for comparison.

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

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

1.6 Dielectric loss tangent of 65-layer PC/PMMA/P(VDF-HFP) films in addition to 33-layer PC/P(VDF-HFP) and PMMA controls as a function of frequency at 100 °C. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 µm.

1.7 a ) AFM images of selected PC/PMMA/P(VDF-HFP) 65-layer samples. Example PMMA thicknesses are 25 nm, 63 nm, and 103 nm. PC/P(VDF-HFP) control is included for comparison. b )
Schematic of the layered structure in the PC/PMMA/P(VDF-HFP) 65-layer samples as a function of tie layer thickness.

1.8 Breakdown field as a function of nominal tie layer thickness for the various PC/tie/P(VDF-HFP) 65-layer films. The 33-layer PC/P(VDF-HFP) film was also included and taken as the film with 0 nm tie layer thickness and indicated as the dashed line. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 µm.

1.9 AFM images (upper) and their gray value profiles (lower) of select PC/tie/P(VDF-HFP) 65-layer samples with 25 nm tie layer thickness. Example tie layers are PMMA (left column), PETG (middle column), and SAN30 (right column).

1.10 AFM images (upper) and their gray value profiles (lower) of select PC/tie/P(VDF-HFP) 65-layer samples with 103 nm tie layer thickness. Example tie layers are PMMA (left column), PETG (middle column), and SAN30 (right column).

1.11 Representative unipolar D-E polarization hysteresis loops for selected 46/8/46 PC/tie/P(VDF-HFP) 65-layer films. The selected tie layers were PMMA, SAN30, and PETG. In addition, the 50/50 PC/P(VDF-HFP) 33-layer film was also included for comparison. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 µm.

1.12 a) Charge energy density, b) discharge energy density, and c) loss energy density as a function of field for the various 46/8/46 PC/tie/P(VDF-HFP) 65-layer films in addition to the 50/50 PC/P(VDF-HFP) 33-layer film.

1.13 Measured a) Dielectric constant, and b) Dielectric loss tangent of various 46/8/46 PC/tie/P(VDF-HFP) 65-layer films. The 50/50 PC/P(VDF-HFP) 33-layer was also included for comparison. All tests are done at 20 °C.

1.14 Dielectric loss tangent as a function of frequency for various 46/8/46 PC/tie/P(VDF-HFP) 65-layer films in addition to the 50/50 PC/P(VDF-HFP) 33-layer film. All measurements were conducted at 100 °C.
CHAPTER 2

2.1 a) Dielectric lifetime measurement setup; b) Equivalent circuit of the dielectric lifetime measurement setup; c) Sample preparation for dielectric lifetime measurement.

2.2 Breakdown progression of 32-layer 70/30 PC/P(VDF-HFP) with a thickness of 8 µm under 320 MV/m: a) Current profile during dielectric lifetime test; b) Zoom-in plot of the current profile from 2827s to 2829s. (Modeled data from Equation 2 are included (in red) for comparison); c) Breakdown images at different times indicated in top graph. (The images share the same scale bar in picture (1))

2.3 Film capacitance dependence on the testing time as indicated in Figure 2a for 32 layer 70/30 PC/P(VDF-HFP). The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

2.4 Effect of film composition on the current profile of the 32-layer PC/P(VDF-HFP) films during dielectric lifetime tests. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

2.5 Effect of film composition on the damage sites of the 32-layer PC/P(VDF-HFP) films. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

2.6 Comparison of the number of breakdown holes with the number of spikes for the 32-layer PC/P(VDF-HFP) films. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

2.7 Film capacitance (from fitting of the charge current peak) dependence on the testing time for 32 layer PC/P(VDF-HFP) with different film compositions. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

2.8 a) Weibull analysis of the breakdown data of 32-layer PC/P(VDF-HFP) films with various compositions; b) Characteristic lifetime of the 32-layer PC/P(VDF-HFP) films
from Weibull analysis. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

2.9 Comparison of transition time obtained from capacitance vs. time curves and obtained from bimodal distribution of Weibull analysis.

2.10 Effect of layer number on the leakage current profile of the 70/30 PC/P(VDF-HFP) film. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

2.11 Effect of layer number on the damage sites of the 70/30 PC/P(VDF-HFP) film. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

2.12 Weibull analysis of the breakdown data of PC/P(VDF-HFP) systems with various compositions, a) blend films; b) 2 layer films; c) 32 layer films, c) 256 layer films.

2.13 Characteristic lifetime of PC/P(VDF-HFP) with various numbers of layers and blend films from Weibull analysis. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.

CHAPTER 3

3.1 a) A schematic showing the dielectric lifetime test and the acoustic emission setup for studying breakdown fracture mechanisms; b) Sample preparation for studying breakdown fracture mechanisms.

3.2 Dielectric lifetime as a function of layer thickness for PC/P(VDF-HFP) films with various number of layers. The PC, P(VDF-HFP), and 50/50 blend were also included and indicated as the dashed lines. The number next to the dots are the layer number of the film tested. The dielectric lifetime was obtained using a statistical analysis described in reference 3.
3.3 Cross section images of the 9-layer PC/P(VDF-HFP) film after breakdown at various distances from the breakdown hole; (A) Top view of the breakdown hole; (B) Cross section image right across the breakdown; (B1) Zoom in image of B; (C) Cross section image: 25 µm from the breakdown hole; (D) Cross section image: 50 µm from the breakdown hole. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.

3.4 Cross section images of the 65-layer PC/P(VDF-HFP) film after breakdown at various distances from the breakdown hole; (A) Top view of the breakdown hole; (B) Cross section image right across the breakdown; (B1) Zoom in image of B; (C) Cross section image: 25 µm from the breakdown hole; (D) Cross section image: 50 µm from the breakdown hole. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.

3.5 Representative images showing the effect of layer thickness on the type of crazing next to the breakdown hole after dielectric breakdown. Layer thickness for the samples are indicated on the top left corner of each image. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.

3.6 The craze density as a function of nominal tie layer thickness for PC/P(VDF-HFP) films with various number of layers. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.

3.7 a.) Types of crazing as a function of PC layer thicknesses for PC/P(VDF-HFP) films with various number of layers for dielectric test. The total film thickness is kept at 10 µm and the applied field is 320 MV/m. b.) Types of crazing as a function of PC layer thicknesses for PC/SAN sheets with various number of layers for mechanical tensile test. The data was from D. Haderski, et al [5].

3.8 a.) Electric current profile and b.) acoustic amplitude data for the breakdown event of the 65-layer 50/50 PC/P(VDF-HFP) film; The total film thickness is kept at 10 µm and the applied field is 320 MV/m.

3.9 Correlation between the acoustic amplitude and the input charge obtained from current profile in the 50/50 PC/P(VDF-HFP)
system with various number of layers. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.

3.10 Effect of layer thickness on the number of acoustic hits during a breakdown event of PC/P(VDF-HFP). The number next to the dots are the layer number of the film tested. The total film thickness is kept at around 10 µm and the applied field is 320 MV/m.

3.11 Figure 11: Schematic representation of the time evolution of a breakdown event. Black, red, and blue colors represent electrodes, PC layers, and P(VDF-HFP) layers, respectively. Solid green lines are electric current.

CHAPTER 4

4.1 Geometry of the compact tension specimens cut from the pipe wall.

4.2 Maximum crosshead displacement versus log time for fatigue tests at 50 °C and KI,mean=0.75 MPa(m)1/2 at different R-ratios (R=0.1, 0.2, 0.3).

4.3 Fracture surfaces of the specimens tested in Figure 2 under KI,mean=0.75MPa(m)1/2 and R=0.1, 0.2 and 0.3. (Only the data for the first step was used to construct modified Paris Law)

4.4 Side views of the damage zone after a prescribed number of cycles for R=0.2, KI,mean=0.75 MPa(m)1/2. (a) 86,000 cycles; (b) 420,000 cycles; and (c) 470,000 cycles.

4.5 Maximum crosshead displacement versus log time for fatigue tests at 50 °C and KI,max=1.17 MPa(m)1/2 at different R-ratios (R=0.1, 0.2, 0.3).

4.6 Effect of KI,mean on the first step jump length for fatigue tests at R=0.1, 0.2, 0.3 and 0.4.
Paris plots of crack growth rate (da/dt versus ΔKI) at 50 °C for different R-ratios. (a) Measured values; and (b) crack growth rate for higher R-ratios calculated from equation (11).

Formulation of the modified Paris plot based on the empirical dependence of crack growth rate on (a) KI,max (constant KI,mean=0.75 MPa(m)1/2 ); and (b) KI,mean (constant KI,max =1.17 MPa(m)1/2 ).

Fit of BMPE test data at 50 °C to the modified Paris law.

Arrhenius plot of the temperature-dependent prefactor B' for BMPE.
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisors, Professor Anne Hiltner and Professor Eric Baer for their guidance, encouragement, and support throughout my PhD study. They have taught me how to do research and think outside of the box. I also would like to thank the other members of my dissertation committee, Professor Lei Zhu, Professor Donald Schuele, and Professor Alex Jamieson for their mentoring and time.

I would also like to thank all the past and present members in Baer/Hiltner group for their collaboration, support, and friendship: Guangming Li, Jong Keum, Matt Mackey, Michael Ponting, Akshay Kamdar, Haopeng Wang, Devang Khariwala, Hyunmin Song, Deepak Langhe, Joel Carr, Chuan-yar Lai, Shannon Armstrong, Shanzuo Ji, Guojun Zhang, Yankai Yang, Ravi Ayyer, Tomasz Kazmierczak, Vishwas Pethe, Madhavi Vadlamudi, Jia Wang, Kezhen Yin, Jiang Du, James Aldridge, Cong Zhang, Hong Xu, William Lenart, Patricia Simmons, and Mariah Miles. Special thanks to Matt Mackey and Ravi Ayyer for his mentorship during my first several years in graduate school. I would also like to thank Prof. Lionel Flandin from Université de Savoie for his help and guidance during his yearly visits to CWRU. Jim Berilla’s help in maintaining the fatigue units is appreciated.

I would like to thank my wonderful wife, Ying Chen, for her love, dedication, understanding, and companionship. Finally, I would like to thank my family, especially my parents and brother Liang, for their inspiration, love, and support. Without them, I would not be the person I am today.
Last but not least, the generous financial and technical support from the Center for Applied Polymer Research (CAPRI), the Office of Naval Research (ONR) and the NSF Center for Layered Polymeric Systems (CLiPS) are gratefully acknowledged.
Dielectric Properties of Multilayer Polymeric Films for High Energy Density Capacitors &

Predicting Long-Term Creep Failure of a Bimodal Polyethylene Pipe from Short-Term Fatigue Tests

Abstract

by

ZHENG ZHOU

Part A: Dielectric properties of multilayer polymeric films for high energy density capacitors

An approach of “forced assembly” multilayer coextrusion was used to produce alternately layered polymeric films for high energy density capacitor applications. The breakdown fracture mechanisms have been studied extensively. Interactive crazing accompanied with delamination and fibril stretching was observed after dielectric breakdown failure. The fracture mechanisms study give us some hint that the adhesion between Polycarbonate , PC, and Poly(vinylidene fluoride-co-hexafluoropropylene), P(VDF-HFP), is not good. In order to minimize the delamination during dielectric breakdown test, and therefore improve dielectric breakdown properties, an “interphase modification” technique--modifying the interphase between PC and P(VDF-HFP) through introducing a third tie layer--was introduced.
The newly designed three component dielectric films (ATBTATBTA, A-PC, B-P(VDF-HFP), T-PMMA) exhibited a 50% enhancement in energy density, 40% decrease in hysteresis, and orders of magnitude slower ion migration relative to the two component control. These property improvements are mainly attributed to the localized interactions at PMMA/P(VDF-HFP) and PMMA/PC interfaces, forming interphase regions. The modified PMMA/P(VDF-HFP) interphase region can effectively hinder the migration of impurity ions in P(VDF-HFP), reducing their mobility within the layer.

In addition to fracture mechanisms study, the long-term dielectric lifetime was probed using homemade setup and it was found out that the layered films of PC/P(VDF-HFP) can have up to 1000X longer lifetime relative to simple PC and P(VDF-HFP) blend films.

**Part B: Predicting long-term creep failure of bimodal polyethylene pipe from short-term fatigue tests**

The so-called third generation of polyethylene pipe resins provides exceptional improvements in environmental stress crack resistance, resistance to rapid crack propagation and creep resistance compared to earlier generations. Short term fatigue testing was used to predict long term creep failure of a bimodal polyethylene (BMPE) pipe with superior creep resistance. The fatigue failure time can be substantially shorter than the failure time in standard creep tests especially for resins that exhibit a high resistance to slow crack growth. This study was
undertaken to determine whether a fatigue-to-creep correlation is applicable to the new generation BMPE pipe resins, and to ascertain whether a lifetime prediction can be obtained within a reasonable time period. The stepwise mechanism of fatigue crack propagation at 50 °C was verified and the crack growth rate was related to the maximum stress and $R$ ratio by a power law relation.

The temperature dependence of slow crack growth followed an Arrhenius relation with a change in slope at 67 °C. The change in slope indicated that extrapolation of creep behavior at temperatures above the $\alpha$-relaxation to ambient temperature requires considerable caution.
PART A: MULTILAYER POLYMER FILMS FOR HIGH ENERGY DENSITY CAPACITOR APPLICATIONS
Chapter 1

Interphase/Interface Modification on the Dielectric Properties of PC/P(VDF-HFP) Multilayer Films for High Energy Density Capacitors
Abstract

Unique 3-component multilayer films with ATBTATBTA configuration were fabricated using forced assembly multilayer coextrusion for novel dielectric systems. The dielectric breakdown strength, displacement – electric field (D-E) hysteresis, and dielectric spectroscopy of 65-layer Polycarbonate (PC)/tie/Poly(vinylidene fluoride-co-hexafluoropropylene) [P(VDF-HFP)] were investigated with various tie materials. Three different tie materials, Poly(methyl methacrylate) (PMMA), Styrene-co-acrylonitrile copolymer with 30% acrylonitrile content (SAN30), and Poly(ethylene terephthalate-co-1,4-cyclohexanediethylene terephthalate) PETG, were chosen due to their various degrees of interaction with either P(VDF-HFP) or PC. The 65-layer PC/PMMA/P(VDF-HFP) films exhibited a 25% enhancement in breakdown properties, 50% higher energy density, 40% smaller hysteresis loop areas, and orders of magnitude slower ion migration relative to the 33-layer PC/P(VDF-HFP) control. These property improvements are mainly attributed to the localized interactions at PMMA/P(VDF-HFP) and PMMA/PC interfaces, forming interphase regions. The modified PMMA/P(VDF-HFP) interphase region can effectively hinder the migration of impurity ions in P(VDF-HFP), reducing their mobility within the layer. Additionally, a small fraction of PMMA can lead to slightly increased dielectric constant of the composite films due to strong interaction between PMMA with P(VDF-HFP). The other two systems with PETG and SAN30 as tie layers exhibited marginal improvements in dielectric properties due to their weaker interactions with the P(VDF-HFP) layers.
Introduction

Polymer films, specifically biaxially oriented polypropylene (BOPP), are widely used in film capacitors due to their high breakdown properties, low loss characteristics, and low cost [1, 2]. New and emerging applications for polymer film capacitors, such as hybrid electric vehicles, grid converters, and pulsed power applications, often require large energy densities in addition to high efficiency (low loss) of the device [3, 4, 5]. These functional requirements have posed new challenges for researchers and engineers to design and develop new materials that can meet these demands. BOPP is not suited to meet these requirements due to its inherent low dielectric constant and reduced performance at elevated temperatures [6].

Our approach to improving the energy density of polymer films used for capacitors is to microlayer a high breakdown strength, insulating polymer [i.e. polycarbonate (PC) and polyethylene terephthalate (PET)] with a high dielectric constant polymer [i.e. polyvinylidene fluoride (PVDF) and its copolymers]. Numerous sets of PC/PVDF (homopolymer and various copolymers) films have been successfully produced using this approach that exhibit enhanced breakdown properties and lifetime characteristics as compared to single component polymer films [7, 8, 9]. Mimicking commercial biaxially oriented polypropylene, multilayer films of PET and poly(vinylidene fluoride-co-tetrafluoroethylene) [P(VDF-TFE)] have also been produced and yield further breakdown property enhancements after biaxial orientation [10]. The enhanced breakdown properties in these multilayered
materials were attributed to a distinct treeing fracture mechanism, observed under a divergent electric field. This fracture mechanism is facilitated by the layer interfaces. These layer interfaces act as “barriers” to impede the breakdown propagation through the film thickness. As a result, the multilayer samples discharged along the layer interfaces, forming tree-like damage zones on the film surface. Since the layer interfaces play such a vital role in the breakdown properties, there is a large opportunity to potentially improve these properties by manipulating the nature of these layer interfaces. The relative impact of variables such as adhesion, interface roughness, and layer interdiffusion on the resulting dielectric properties in multilayer films is not well-understood. All of these variables can be readily manipulated using the forced assembly coextrusion process.

All of the reported multilayer systems for polymer film capacitors consist of only 2-components, where the layers are arranged in an ABABAB configuration. The flexibility of the microlayer coextrusion process offers the potential for more layer configurations, including the addition of a third polymer component [11]. Multilayer films with an ATBTATBTA (T is the tie layer) and ABCABCABC can also be produced using this versatile process. For this application, the addition of a tie layer, in an ATBTA layer configuration, is of considerable interest due the potential to specifically modify the layer interface, adhesion, and level of polymer/polymer interdiffusion. Several 3-component multilayer systems with various tie layers have been used to investigate the adhesion characteristics between polymers [12]. Adding a tie layer in these multilayer dielectric systems, could
potentially change the adhesion characteristics and influence the breakdown properties. Also of interest is the area of layer interdiffusion, where localized mixing of the two layers occurs at the layer interface, creating an interphase region, which essentially acts as an entirely new material [13, 14, 15]. By selecting a tie layer polymer with varying miscibility/interaction with either one or both of the constituent polymers, the amount of interphase can be directly controlled.

In this study, a series of tie layer materials were selected in order to directly influence the adhesion, interaction, and interphase characteristics of PC and P(VDF-HFP) multilayer films. The tie layers include amorphous polymers, such as PMMA, SAN30, and PETG. These materials were chosen based on their compatibility with PC and P(VDF-HFP). For the PC layer, PETG is considered miscible, PMMA is partially miscible or compatible, and SAN30 is immiscible [14]. For the P(VDF-HFP) layer, PMMA is miscible with PVDF-based polymers. Pure poly(acrylonitrile) (PAN) is considered partially miscible; therefore, certain interaction with P(VDF-HFP) is expected for SAN30. PETG is considered immiscible [16]. Based on their thermodynamic interactions, these three tie layers will have a significant impact on the nature of the interphase/interface in PC/tie/P(VDF-HFP) multilayer systems. Their relative impact on the breakdown properties, hysteresis behavior, low field dielectric spectroscopy and layer morphology has been evaluated in this study.
Experimental

Materials

Polycarbonate (PC) was obtained from Bayer Material Science (Makrolon 2207). Polyvinylidene fluoride-co-hexafluoropropylene (P(VDF-HFP)) was provided by Arkema Inc. (Kynar 2500). Poly(methyl methacrylate) (PMMA) was obtained from Arkema Inc. (Plexiglas V826). Styrene-co-acrylonitrile copolymer with 30% acrylonitrile content (SAN30) was supplied by the Dow Chemical Company (Tyril 880). Poly(ethylene terephthalate-co-1,4-cyclohexanedicarboxylate) (PETG) was obtained from Eastman Chemical Co. (Eastar 6763). PC, PMMA, SAN30, and PETG were all dried under vacuum at 80 °C for 12 hours prior to melt processing.

Three component multilayer films with an ATBTATBTA layered structure were produced using a forced assembly multilayer coextrusion process [11]. The coextrusion temperature for all three systems was 250 °C. This temperature was chosen based on the viscosity matching of each polymer, as determined by melt flow index (MFI) at a shear rate that is similar to extrusion condition (10 s⁻¹). The various tie layer systems all contained a total of 65-layers, see Table 1.1. Samples were produced at various tie layer thicknesses (from 6 nm up to 103 nm) by adjusting the relative pump rate of the tie layer extruder. All of the samples had equal volume amount of PC and P(VDF-HFP) and a overall film thickness of 10 µm. For comparison, a 50/50 33-layer PC/P(VDF-HFP) sample without tie layer was also produced with an ABABA layered structure. All samples were laminated
with two sacrificial LDPE skin layers during coextrusion to protect the film from
damage, improve the surface quality, and reduce defects. All skin layers were
removed prior to any subsequent testing.

Dielectric Breakdown Strength Measurements

The breakdown field of the multilayered samples was determined using a
ramped voltage of 500 V/s using needle/plane electrodes. The positive needle
electrodes had a tip radius of 20 \( \mu \text{m} \) and the negative plane consisted of a flat
rectangular piece of aluminum. A Quadtech (Marlborough, MA) Guardian 20kV
HiPot tester was used as the voltage source. All breakdown experiments were
carried out in mineral oil to reduce surface and corona discharging. 20 repetitions
were done on each sample. The needle electrodes were replaced every 10
measurements.

Atomic Force Microscope (AFM)

The multilayer sample cross sections were imaged using AFM. The samples
were first embedded in epoxy, cured overnight, and sectioned at \(-100 \, ^\circ \text{C}\) using a
Leica Microsystems (Buffalo Grove, IL) EM FC6 ultramicrotome. Polished
samples were then imaged using AFM operating in the tapping mode. The phase
and height images were recorded simultaneously using a Nanoscope IIIa
Mutlimode scanning probe (Digital Instruments, Santa Barbara, CA).

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

**Dielectric Hysteresis Measurements**

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

$$U_c = \int_{0}^{D(T)} E(t)dD(t) \quad (1)$$

$$U_d = \int_{D(2T)}^{D(T)} E(t)dD(t) \quad (2)$$

$$U_l = U_c - U_d \quad (3)$$
where $T$ is the time it takes for the voltage waveform to reach maximum from zero, $E(t)$ is the applied electric field and $D(t)$ is the corresponding electric displacement.
Results and Discussion

Dielectric Properties of PC/PMMA/P(VDF-HFP) Multilayer Films with Various PMMA Thicknesses

The dielectric breakdown strength was evaluated for PC/PMMA/P(VDF-HFP) system as a function of PMMA layer thickness, Figure 1.1. The breakdown strength of 33-layer PC/P(VDF-HFP) film was also included and taken as the film with 0 nm tie layer thickness and indicated as the dashed line in Figure 1.1. By comparing the dashed line with the solid line, it is evident that the incorporation of a PMMA tie layer in between PC and P(VDF-HFP) had a substantial impact on the dielectric breakdown properties. Initially, the breakdown strength of PC/PMMA/P(VDF-HFP) increased with increasing PMMA layer thickness. The maximum breakdown strength of 880 kV/mm appeared at 25 nm nominal PMMA layer thickness and represented a 25% improvement in dielectric breakdown strength relative to the 33-layer PC/P(VDF-HFP). For samples, with PMMA tie layer thickness greater than 25 nm, the dielectric breakdown strength began to level off and then slowly decrease. Considering PMMA was miscible with P(VDF-HFP) and compatible with PC, the dielectric breakdown strength was rather interesting. It is believed that the nature of the interdiffusion between PMMA and both PC and P(VDF-HFP) dictates this effect.

The hysteresis properties were also determined for the 65-layer PC/PMMA/P(VDF-HFP) system in addition to the 33-layer 50/50 PC/P(VDF-
HFP) control. Representative unipolar D-E polarization hysteresis curves are shown in Figure 1.2. By comparing the plot (a) for the 33-layer 50/50 PC/P(VDF-HFP) and the plots (b - f) for 65-layer PC/PMMA/P(VDF-HFP) with various PMMA tie layer thicknesses, it is evident that the 33-layer 50/50 PC/P(VDF-HFP) had the largest loop compared with PC/PMMA/P(VDF-HFP) system at the same electric field. The addition of a PMMA tie layer (even as little as 6 nm, 2 v%) reduced the hysteresis D-E loop area dramatically at the same electric field.

To quantify the hysteresis properties, the charge energy density, discharge energy density, and loss energy density were calculated [17] as a function of electric field for all the 65-layer PC/PMMA/P(VDF-HFP) compositions in addition to the 33-layer PC/P(VDF-HFP) control, Figure 1.3. The 33-layer PC/P(VDF-HFP) film sample exhibited maximum charge energy density. However, these samples also contained the lowest discharge energy density, due to the large hysteresis loop areas. The 65-layer PC/PMMA/P(VDF-HFP) samples exhibit much larger discharge energy densities due to the reduced loop areas. In addition, the 65-layer 46/8/46 PC/PMMA/P(VDF-HFP) sample with 25 nm nominal tie layer thickness, possessed the highest breakdown field during D-E loop hysteresis measurements, which correlated well with the needle-plane breakdown data shown in Figure 1.1. To better illustrate the data in Figure 1.3, the values for maximum discharge energy density and the hysteresis properties at a given field, in this case, 500 kV/mm were shown as a function of nominal PMMA tie layer thickness, Figure 1.4. The maximum discharge energy densities for the 33-layer 50/50 PC/P(VDF-
HFP) film and the 65-layer 46/8/46 PC/PMMA/P(VDF-HFP) film were 5.72 J/cc and 8.36 J/cc, respectively. In other words, the 65-layer 46/8/46 PC/PMMA/P(VDF-HFP) sample can store nearly 50% more energy than the 33-layer 50/50 PC/P(VDF-HFP) sample at a given area, which is desirable for capacitor applications.

At 500 kV/mm, the discharge energy density for the 33-layer 50/50 PC/P(VDF-HFP) film was 4.75 J/cc, while the 65-layer 49/2/49 PC/PMMA/P(VDF-HFP) had a discharge energy density of 5.54 J/cc. The discharge energy density increased slightly with increasing PMMA layer thickness, and then dropped gradually when the PMMA thickness was above 25 nm. It is speculated that there are at least two contradictory reasons that dictate the trend in discharge energy density for the 65-layer PC/PMMA/P(VDF-HFP) system with various PMMA tie layer thicknesses. One reason is that a small fraction amount of PMMA can increase the capacitance for storing more electric energy. It was speculated that the slightly increase in dielectric constant was due to either increased content of β-crystal in the P(VDF-HFP) layer [18] or loosening up of the dipole in the amorphous part of P(VDF-HFP) facilitated by PMMA chains [19]. The other reason is that incorporation large fraction of PMMA would decrease the total film dielectric constant of 65-layer PC/PMMA/P(VDF-HFP) based on series model [7]. The dielectric constant of PMMA, 3.71, is lower than the dielectric constant of the 33-layer 50/50 PC/P(VDF-HFP) control, 4.46. Therefore, combing
PMMA with 50/50 PC/P(VDF-HFP) should decrease the dielectric constant of PC/PMMA/P(VDF-HFP).

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

Ion migration in PC/PVDF (and PVDF copolymers) multilayer systems significantly contributes to the resulting hysteresis behavior of the overall films [20]. It was found that by reducing the PVDF layer thickness, this ion motion was inhibited and was effectively probed using low-field dielectric spectroscopy at a wide range of measuring frequencies and temperatures [20,21]. Following this approach, dielectric spectroscopy was measured at 20 °C and 100 °C for the various samples. At 20 °C, one broad peak around 50 Hz was observed and attributed to both $\alpha_c$ of P(VDF-HFP) and $\beta$ relaxation of PMMA [22]. A rise in tan(δ) was observed at very low frequencies (0.1 Hz or below) for the 33-layer 50/50 PC/P(VDF-HFP) samples, Figure 1.5. For the 65-layer PC/PMMA/P(VDF-HFP) samples at 20 °C, no such behavior was observed.
To better probe the ion migration behavior in the 65-layer PC/PMMA/P(VDF-HFP) system, elevated temperatures as high as 100 °C, were used to drive the ion migration peak to higher frequency, Figure 1.6. αc peak was not observed because the peak frequency has drifted above 10^5 Hz. PMMA and the 33-layer 50/50 PC/P(VDF-HFP) sample were included for comparison. β relaxation peak of PMMA, associated with localized motion of methoxy groups, was observed at 10,000 Hz [22]. The 33-layer 50/50 PC/P(VDF-HFP) film exhibited an ion migration peak centered around 30 Hz which was assigned to the ion migration in the P(VDF-HFP) layers. Incorporation of the PMMA tie material into the system shifted the ion migration peak to lower frequencies. The peak frequency of the ion peak decreased with increasing PMMA layer thicknesses. The reduction in the ion migration peak frequency indicated that the ion migration was suppressed in the 65-layer PC/PMMA/P(VDF-HFP), system which correlated to the reduction in the hysteresis loop area shown in Figure 1.3c. One possibility is that the localized mixing of PMMA and P(VDF-HFP) along the layered interphase created ion trap sites that can tie up these ionic species [23] and significantly decrease the ionic species mobility under electric field. The other possibility is that the PMMA chains intermix with amorphous part of P(VDF-HFP), rigidify the amorphous P(VDF-HFP) chains, make ion movement in the interphase region impossible [24], reduce the ion migration distance and mobility [20].
Through breakdown strength, D-E hysteresis and low field dielectric spectroscopy measurements, it was concluded that the 65-layer PC/PMMA/P(VDF-HFP) system exhibited enhanced dielectric breakdown strength, decreased hysteresis loss energy density, and slower ion migration peaks. It was obvious that the improved dielectric properties were attributed to the introduction of the PMMA tie layers. Therefore, the interaction between PMMA and both PC and P(VDF-HFP) was an important structural parameter that might directly influence the resulting dielectric properties. To better visualize these material, AFM was used to quantify the PMMA tie layer thickness and attempt to observe the layer interphase in the 65-layer PC/PMMA/P(VDF-HFP) system with selected PMMA nominal layer thicknesses. Representative AFM images for the 65-layer PC/PMMA/P(VDF-HFP) samples with 25, 63, and 103 nm PMMA tie layers, in addition to the 33-layer 50/50 PC/P(VDF-HFP), are shown in Figure 1.7a. In samples with no PMMA tie layers in between PC and P(VDF-HFP), sharp layer interface boundaries were observed. In the sample with 25 nm PMMA tie layers, no distinct PMMA layers was observed and PMMA was completely interdiffused with both PC (lighter layers) and P(VDF-HFP) (darker layers) layers. In addition, a diffuse interface boundary was observed between PC and P(VDF-HFP) layers. In samples with 63 and 103 nm PMMA tie layers, a distinct portion of the PMMA remained with rich interdiffused regions surrounding it. The measured distinct PMMA tie layer thicknesses were much lower than the nominal tie layer thickness. Based on the AFM images, a schematic of the layer structure in the 65-layer PC/PMMA/P(VDF-HFP) samples is proposed, Figure 1.7b. In these 65-layer
PC/PMMA/P(VDF-HFP) samples, the material between the PC and P(VDF-HFP) layers would consist of a new two-dimensional (2D) interphase material or localized 2D blend of PC/PMMA and P(VDF-HFP)/PMMA [13].

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

The breakdown field was evaluated for the various PC/tie/P(VDF-HFP) multilayer samples as a function of tie layer thickness, Figure 1.8. The breakdown properties of the PC/P(VDF-HFP) 33-layer samples were also evaluated and plotted at 0 nm tie layer thickness. The average value for this sample was plotted as a dashed line for comparison. Three different tie materials, PMMA, SAN30, and PETG, were chosen due to their various degrees of interaction with either PC or P(VDF-HFP). From these data, it is evident that the incorporation of a tie layer in between the PC and P(VDF-HFP) layers had an impact on the resulting dielectric breakdown properties. The nature of the interaction between the tie layer material and both PC and P(VDF-HFP) dictated this effect. For the remaining samples, the films with PETG, and SAN30 tie layers, did exhibit a marginal improvement in the breakdown properties, again with maximums occurring at 25 nm tie layer thickness. The ability to incorporate an additional material in the multilayer dielectric systems and directly influence the breakdown properties is rather interesting from both a scientific and practical perspective.

It is evident that the tie layer materials in addition to the tie layer thickness are critical parameters for the determination of the resulting breakdown properties. Since the tie layers were expected to have different degrees of interaction to the PC and P(VDF-HFP) layers, the nature of the interphase/interface between these
materials is an important structural parameter that may directly influence the resulting breakdown properties. AFM was used to quantify the tie layer thickness and attempt to observe the layer interphase/interface in select PC/tie/P(VDF-HFP) multilayered samples. Representative AFM images for the PC/tie/P(VDF-HFP) 65-layer samples with 25 and 103 nm PMMA, SAN30, and PETG tie layers are shown in Figure 1.9, and Figure 1.10 respectively.

For the samples with 25 nm nominal tie layer thickness, Figure 1.9, the layer interface appeared diffused with no distinct tie layer material being observed for both PMMA and PETG tie layers. As mentioned in the previous section, PMMA layers were fully interdiffused in to both PC (light layers) and P(VDF-HFP) (dark layers). PETG is highly miscible with PC [14] and immiscible with P(VDF-HFP); therefore, for the 25 nm PETG tie layers, it was assumed the PETG was completely interdiffused into the PC layers, with very little material (<5 nm) diffused into the P(VDF-HFP) layers. For the 25 nm SAN30 tie layer sample, the interface appeared sharp with a discrete SAN30 tie layer material being observed between the PC and P(VDF-HFP). The measured layer thickness of the SAN30 tie layers was around 20-30 nm which matched closely to the nominal tie layer thickness. The AFM images were analyzed using Image J software to obtain a contrast profile indicating relative gray values across the images. For the PC/PMMA/P(VDF-HFP) system, the profile exhibits the broadest transition between the PC (high gray value) and P(VDF-HFP) (low gray value) layers. For the PC/PETG/P(VDF-HFP) system, the tie layers are mostly diffused into the PC layers, however, a sharp transition
between P(VDF-HFP) and PC was observed due to poor miscibility between PETG and P(VDF-HFP). For SAN30 system, the SAN30 tie layers (highest gray value) are observed in between PC and P(VDF-HFP) with steep transitions occurring in both PC/SAN30 and P(VDF-HFP)/SAN30 boundaries due to the lower interaction of SAN30 with both PC and P(VDF-HFP).

In samples with larger 103 nm tie layers, Figure 1.10, all of the samples exhibited discrete tie layers from the AFM images, even in the samples with PMMA tie layers. Consistent with AFM images, tie layers were also observed in the gray value profiles. However, the layer interfaces in the 103 nm PMMA tie layer samples did appear quite diffused into both dark P(VDF-HFP) layers and light PC layers, with measured PMMA tie layer thicknesses that are much lower than 103 nm. For the 103 nm PETG tie layer, the PETG tie layers diffused into mainly the PC layers due to its miscibility with PC. In these samples the interface between P(VDF-HFP) and PETG was still rather sharp. The discrete PETG tie layer thicknesses are lower than 103 nm. For the 103 nm SAN30 tie layer, the layer interface appeared rather sharp on both PC and P(VDF-HFP) interfaces. In addition, the measured tie layer thicknesses was around 100-130 nm which matched well to the nominal tie layer thickness. An accurate measurement of the actual PMMA and PETG tie layer thickness in this sample was difficult due to the diffuse nature of the interphase regions; however, the PMMA and PETG tie layers did appear thinner when compared to the SAN30 systems with similar nominal tie layer thicknesses.
The observed structural features in these materials matches the expected thermodynamic behavior/interactions outlined in the introduction. The PMMA tie material was expected to diffuse into both the PC and P(VDF-HFP) layers causing the layer interphase to appear rather diffuse on both sides. The PETG tie material was expected to diffuse into the PC layers rather than P(VDF-HFP) layers causing the layer interphase to appear diffused on PC side and sharp on P(VDF-HFP) side. The SAN30 tie material was not miscible with either PC or P(VDF-HFP), therefore, the layer interface is rather sharp on both sides. Theoretical simulation indicates [26] that a broad interfacial region with gradient dielectric constant distribution along the layer thickness direction could lead to high breakdown strength. The breakdown and dielectric data in addition to the AFM images for PC/tie/P(VDF-HFP) confirms the conclusion. The PMMA tie layers diffuse into both PC and P(VDF-HFP) layers forming a gradient change in PMMA tie layer composition, and gradient dielectric constant distribution along the layer thickness direction. Therefore, the multilayer samples with PMMA as tie layers exhibited the largest enhancement in breakdown properties among all tie materials tested.

The layer interfaces have been reported to influence the hysteresis properties of PC/PVDF and PC/P(VDF-HFP) multilayered films [20, 21]. However, no emphasis has been put to study the effect of the interface/interphase on the resulting properties of these materials. Since these various PC/tie/P(VDF-HFP) systems directly varied the interfacial characteristics, these systems were interesting platforms to probe this phenomenon. The composition of 46/8/46 was
chosen for 65-layer PC/tie/P(VDF-HFP) films for further study, since samples exhibited maximum breakdown strength at this composition. The hysteresis properties were evaluated for the 46/8/46 PC/tie/P(VDF-HFP) 65-layer samples in addition to the 50/50 PC/P(VDF-HFP) 33-layer sample. Representative hysteresis curves are shown for the select systems, Figure 1.11. Both the hysteresis loop area and discharged energy density were calculated as a function of electric field for all of the samples, Figure 1.12. Quantifying the loop area verified that including a tie layer in the PC/P(VDF-HFP) samples effectively reduced the observed hysteresis behavior, Table 1.2. The largest reduction was observed in samples with the PMMA tie layers. Interestingly, the remaining tie layer systems, all exhibited a marginally reduced hysteresis behavior. For the discharged energy density, the 65-layer PC/tie/P(VDF-HFP) samples generally possessed larger discharged energy densities at a constant electric field. The best systems contained PMMA possessed approximately 20% higher energy densities. In general, the PMMA tie layer system could also be measured at much higher electric fields, which also resulted in higher energy densities. These results correlated with the previously determined breakdown properties. In addition, these experiments also revealed that the PC/PMMA/P(VDF-HFP) 65-layer system possessed better hysteresis behavior as compared to the other two systems with PETG and SAN30 as tie layers. The cause of the reduction in hysteresis behavior in these systems was not obvious; however, it was evident that modifying the layer interphase/interface in these systems had an impact on the hysteresis properties. To help clarify this point, low field dielectric
spectroscopy for the various systems was used to probe the ion migration characteristics in these systems with various tie materials.

At 20 °C, the dielectric constant and loss tangent of the dielectric constant was measured for the various 65-layer 46/8/46 PC/tie/P(VDF-HFP) systems in addition to the 33-layer 50/50 PC/P(VDF-HFP) control, Figure 1.13. One major peak was observed and related to $\alpha_c$ of P(VDF-HFP) around 50 Hz in Figure 1.13b. The 65-layer PC/PETG/P(VDF-HFP) and PC/SAN30/P(VDF-HFP) systems in addition to the 33-layer PC/P(VDF-HFP) control exhibited ion migration peak below 1 Hz, however, no ionic peaks were detected in the frequency range tested, Figure 1.13b. Another interesting feature was that the PMMA tie layer system had the highest dielectric constant at 20 °C, Figure 1.13a. A list of the dielectric constants for PC/tie/P(VDF-HFP) systems at 1 Hz is shown in the first column of Table 1.3. 1 Hz was chosen because it is the frequency for D-E hysteresis measurements and is well above the ionic relaxation peak. The second and third columns show the calculated dielectric constant and effective dielectric constant of P(VDF-HFP) based on equations below:

$$\frac{1}{\varepsilon_{calculated}} = \frac{0.08}{\varepsilon_{tie}} + \frac{0.46}{\varepsilon_{PC}} + \frac{0.46}{\varepsilon_{P(VDF-HFP)}}$$  \(4\)

$$\frac{0.46}{\varepsilon_{eff,P(VDF-HFP)}} = \frac{1}{\varepsilon_{Measured}} - \frac{0.08}{\varepsilon_{tie}} - \frac{0.46}{\varepsilon_{PC}}$$  \(5\)

where $\varepsilon_{calculated}$, $\varepsilon_{tie}$, $\varepsilon_{PC}$, $\varepsilon_{P(VDF-HFP)}$, $\varepsilon_{eff,P(VDF-HFP)}$ are the calculated dielectric constant of 65-layer films, tie materials, PC control, P(VDF-HFP)
control, and effective dielectric constant of P(VDF-HFP) layer, respectively. **Equation 4 and 5** do not take consideration into the loss part of the dielectric constant. **Equation 4** assumes that the intermix of tie material with PC and P(VDF-HFP) does not change the dielectric constants of tie materials, PC and P(VDF-HFP). **Equation 5** assumes that the dielectric constants of tie materials and PC in the layered films are the same as in bulk. Dielectric constants of 10 µm PC, P(VDF-HFP), PMMA, SAN30, PETG films were measured to be 2.81, 11.20, 3.71, 2.90, and 3.40, respectively. The calculated effective dielectric constant was highest for PMMA tie system. One speculation is that since PMMA was miscible with P(VDF-HFP), the PMMA material could act as a lubricating agent which loosens up the dipoles in P(VDF-HFP) layers. A similar phenomenon was reported in the literature [19] where polyurethane (PU) chains acted as a lubricant agent and could facilitate easier polar chain rotation in PVDF. Another speculation is that PMMA can induce the formation of β-crystals in P(VDF-HFP) [18], which has higher dielectric constant than α-crystals in bulk P(VDF-HFP). The system with SAN30 tie material exhibited intermediate effective dielectric constant of P(VDF-HFP). Pure poly(acrylonitrile) (PAN) is considered partially miscible with P(VDF-HFP), therefore some level of interaction was expected for SAN30 and may result in a similar behavior although to a much smaller degree. For the system with PETG tie material, the effectively dielectric constant was very close to the series model due to very little interaction between PC and P(VDF-HFP). From the effective dielectric constant of P(VDF-HFP) data of the various tie materials, it is concluded that the
interaction between the P(VDF-HFP) and the tie material played significant role rather than interaction with PC.

To gain a better understanding on the ion migration behavior in these materials, the low frequency dielectric spectroscopy was measured for the various 46/8/46 PC/tie/P(VDF-HFP) 65-layer samples in addition to the 50/50 PC/P(VDF-HFP) 33-layer sample at a measuring temperature of 100 °C to drive the ion migration peak to higher frequencies, Figure 1.14. The data for the 50/50 PC/P(VDF-HFP) sample clearly shows a peak centered at 30 Hz which was assigned to the ion migration in the P(VDF-HFP) layers. Addition of a tie layer had a varying effect on this ionic peak. For the PETG and SAN30 tie layers, the ionic peak was centered around 40 Hz and 25 Hz, respectively. All of the changes were minor in these systems with PETG, and SAN30 tie materials. However, the samples with PMMA tie layers produced a dramatically different result. The ionic peak in these samples shifted to lower frequencies, which was around 4 Hz. This reduction indicated that the ion migration was suppressed in 65-layer PC/PMMA/P(VDF-HFP) which correlates to the reduction in the hysteresis loop area for these 65-layer PC/PMMA/P(VDF-HFP). One possibility is the localized mixing of PMMA into P(VDF-HFP) in the interphase regions may be tying up these ionic species, making them more immobile under an applied electric field. The other possibility is the PMMA molecules intermix with the amorphous part of P(VDF-HFP), making P(VDF-HFP) chains harder to move, and effectively excluding the ions [24] and reducing the ion mobility [20].
Conclusions

The inherent flexibility in the multilayer coextrusion process allows for the production of a wide range of layered structures. Utilizing this flexibility, three-component multilayer films with ATBTATBTA configuration were produced to directly modify the layer interphase/interface between PC and P(VDF-HFP) layers. The tie layer materials were chosen specifically to vary the interaction of these materials. Incorporation of a tie layer between PC and P(VDF-HFP) in multilayers had a significant impact on the dielectric properties of these materials. The 65-layer PC/PMMA/P(VDF-HFP) system exhibited enhanced dielectric breakdown strength, decreased hysteresis loss energy density, and slower ion migration behavior. It was determined that the improved dielectric properties were attributed to the high interactivity between PMMA tie layers and both PC and P(VDF-HFP) layers. The other two systems with PETG and SAN30 as tie layers exhibited marginal improvements in dielectric properties because PETG and SAN30 do not highly interact with P(VDF-HFP). Highly interacting tie layers, in this case PMMA, resulted in enhanced breakdown properties, with approximately a 25% enhancement with only 25 nm PMMA layers as compared to the PC/P(VDF-HFP) films without tie layers. The layered structure in these PC/tie/P(VDF-HFP) multilayer samples was evaluated using AFM. Distinct PMMA tie layers were not seen in the samples with 25 nm nominal PMMA layer thickness with the layer interface appearing rather diffuse into both PC and P(VDF-HFP) layers. It was determined that the PMMA tie layers were completely interdiffused into both the PC and P(VDF-HFP) layers. This interphase region is believed to be responsible
for the enhanced breakdown properties by smoothing dielectric constant
distribution along the film thickness direction. The impact of these materials also
extended to the hysteresis properties, where the PMMA tie layers reduced the
hysteresis loop area and increased the maximum discharged energy density. The
reduction in hysteresis properties in these samples was correlated to a reduction in
the ion migration peak, which was shifted to lower frequencies as a result of the
localized mixing of PMMA and P(VDF-HFP) along the layer boundaries. This
interphase region can effectively reduce the ion mobility within the layer by
creating ion trapping sites in PMMA/P(VDF-HFP) interphase or reducing the ion
migration distance inside P(VDF-HFP). Additionally, a small fraction of PMMA
in P(VDF-HFP) can increase the effectively dielectric constant of P(VDF-HFP)
significantly. One speculation is that since PMMA was miscible with P(VDF-HFP),
the PMMA material could act as a lubricating agent which loosens up the dipoles
in P(VDF-HFP) layers. Another speculation is that PMMA can induce the
formation of β-crystals in P(VDF-HFP), which has higher dielectric constant than
α-crystals in bulk P(VDF-HFP).
Acknowledgement

This research was generously supported by the National Science Foundation through the Center for Layered Polymeric Systems (CLiPS) Science and Technology Center Grant DMR-0425914 and the Office of Naval Research Grant N00014-11-0251.
Table 1.1  PC/tie/P(VDF-HFP) multilayer films under investigation

<table>
<thead>
<tr>
<th>Multilayer Film Compositions</th>
<th>Number of Layers</th>
<th>Tie Layer Thickness (nm)</th>
<th>PC or P(VDF-HFP) Layer Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC/tie/P(VDF-HFP) (vol. %)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50/0/50</td>
<td>33</td>
<td>-</td>
<td>312</td>
</tr>
<tr>
<td>49/2/49</td>
<td>65</td>
<td>6</td>
<td>306</td>
</tr>
<tr>
<td>48/4/48</td>
<td>65</td>
<td>13</td>
<td>300</td>
</tr>
<tr>
<td>46/8/46</td>
<td>65</td>
<td>25</td>
<td>288</td>
</tr>
<tr>
<td>40/20/40</td>
<td>65</td>
<td>63</td>
<td>250</td>
</tr>
<tr>
<td>33/33/33</td>
<td>65</td>
<td>103</td>
<td>206</td>
</tr>
</tbody>
</table>
Fig. 1.1  Dielectric breakdown strength as a function of nominal tie layer thickness for 65-layer PC/PMMA/P(VDF-HFP) films. The 33-layer PC/P(VDF-HFP) film was also included and taken as the film with 0 nm tie layer thickness (indicated as the dashed line).
Fig. 1.2 Representative unipolar D-E hysteresis loops for 65-layer PC/PMMA/P(VDF-HFP) films with various PMMA layer thicknesses/compositions. In addition, the 50/50 PC/P(VDF-HFP) 33-layer film was also included for comparison. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 μm.
Fig. 1.3  a) Charge energy density, b) discharge energy density, and c) loss energy density as a function of electric field for 65-layer PC/PMMA/P(VDF-HFP) films with various layer thicknesses/compositions. In addition, the 50/50 PC/P(VDF-HFP) 33-layer film was also included for comparison.
Fig. 1.4  Maximum discharge energy density and hysteresis property values at 500 kV/mm as a function of PMMA tie layer thickness for the 65-layer PC/PMMA/P(VDF-HFP) multilayer films
Fig. 1.5  Dielectric loss tangent of 65-layer PC/PMMA/P(VDF-HFP) films in addition to the 33-layer PC/P(VDF-HFP) as a function of frequency at 20 °C. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 µm.
Fig. 1.6  Dielectric loss tangent of 65-layer PC/PMMA/P(VDF-HFP) films in addition to 33-layer PC/P(VDF-HFP) and PMMA controls as a function of frequency at 100 °C. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 µm.
Fig. 1.7 (a) AFM images of selected PC/PMMA/P(VDF-HFP) 65-layer samples. Example PMMA thicknesses are 25 nm, 63 nm, and 103 nm. PC/P(VDF-HFP) control is included for comparison. (b) Schematic of the layered structure in the PC/PMMA/P(VDF-HFP) 65-layer samples. Example PMMA thicknesses are 25 nm, 63 nm, and 103 nm, and 0 nm (control).
Fig. 1.8 Breakdown field as a function of nominal tie layer thickness for the various PC/tie/P(VDF-HFP) 65-layer films. The 33-layer PC/P(VDF-HFP) film was also included and taken as the film with 0 nm tie layer thickness and indicated as the dashed line. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 µm.
Fig. 1.9 AFM images (upper) and their gray value profiles (lower) of select PC/tie/P(VDF-HFP) 65-layer samples with 25 nm tie layer thickness. Example tie layers are PMMA (left column), PETG (middle column), and SAN30 (right column).
Fig 1.10 AFM images (upper) and their gray value profiles (lower) of select PClie/P(VDF-HFP) 65-layer samples with 103 nm tie layer thickness. Example tie layers are PMMA (left column), PETF (middle column), and SAN30 (right column).
Fig. 1.11  Representative unipolar D-E polarization hysteresis loops for selected 46/8/46 PC/tie/P(VDF-HFP) 65-layer films. The selected tie layers were PMMA, SAN30, and PETG. In addition, the 50/50 PC/P(VDF-HFP) 33-layer film was also included for comparison. All films had equal amount of PC and P(VDF-HFP), and film thicknesses were maintained at 10 µm.
Fig. 1.12  a) Charge energy density, b) discharge energy density, and c) loss energy density as a function of field for the various 46/8/46 PC/tie/P(VDF-HFP) 65-layer films in addition to the 50/50 PC/P(VDF-HFP) 33-layer film.
Table 1.2: Maximum discharge energy density and hysteresis property values at 500 kV/mm as a function of nominal tie layer thickness for the 65-layer 46/8/46 PC/tie/P(VDF-HFP) multilayer films

<table>
<thead>
<tr>
<th>Tie Material</th>
<th>Maximum Discharge Energy Density (J/cc)</th>
<th>Discharge Energy Density at 500 kV/mm (J/cc)</th>
<th>Loss Energy Density at 500 kV/mm (J/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No tie</td>
<td>5.72</td>
<td>4.75</td>
<td>4.79</td>
</tr>
<tr>
<td>PMMA</td>
<td>8.36</td>
<td>5.62</td>
<td>2.90</td>
</tr>
<tr>
<td>PETG</td>
<td>6.11</td>
<td>5.07</td>
<td>3.79</td>
</tr>
<tr>
<td>SAN30</td>
<td>4.86</td>
<td>4.86</td>
<td>3.85</td>
</tr>
</tbody>
</table>
Fig. 1.13 Measured a) Dielectric constant, and b) Dielectric loss tangent of various 46/8/46 PC/tie/P(VDF-HFP) 65-layer films. The 50/50 PC/P(VDF-HFP) 33-layer was also included for comparison. All tests are done at 20 °C.
<table>
<thead>
<tr>
<th>PC/PMMA/P(VDF-HFP)</th>
<th>Effective Constant</th>
<th>Measured Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.98</td>
<td>4.42</td>
<td>29.60</td>
</tr>
<tr>
<td>PC/SAN30/P(VDF-HFP)</td>
<td>4.56</td>
<td>16.42</td>
</tr>
<tr>
<td>PC/PETG/P(VDF-HFP)</td>
<td>4.49</td>
<td>12.96</td>
</tr>
<tr>
<td>PC/P(VDF-HFP)</td>
<td>4.46</td>
<td>10.80</td>
</tr>
</tbody>
</table>

Table 1.3 Measured and modeled dielectric constants of PC/P(VDF-HFP) 46/8/46 multilayered films at 20 °C, and effective dielectric constants of P(VDF-HFP) calculated from series model. 

1: Based on equation 4: 
$$\frac{\varepsilon_m}{6} = 80 \cdot \frac{\varepsilon_c}{6} \frac{\varepsilon_e}{6} + \frac{\varepsilon_c}{6} + \frac{\varepsilon_e}{6}$$

2: Based on equation 5: 
$$\frac{\varepsilon_m}{6} = 80 \cdot \frac{\varepsilon_c}{6} \frac{\varepsilon_e}{6} + \frac{\varepsilon_c}{6} + \frac{\varepsilon_e}{6}$$
Fig. 1.14  Dielectric loss tangent as a function of frequency for various 46/8/46 PC/tie/P(VDF-HFP) 65-layer films in addition to the 50/50 PC/P(VDF-HFP) 33-layer film. All measurements were conducted at 100 °C.
References


Chapter 2

Multilayered Polycarbonate/Poly(vinylidene fluoride-co-hexafluoropropylene) for High Energy Density Capacitors with Enhanced Lifetime
ABSTRACT

The dielectric lifetime and corresponding damage morphology of polycarbonate/poly(vinylidene fluoride-co-hexafluoropropylene) (PC/P(VDF-HFP)) layered systems are studied under constant direct current (DC) field. Melt blends of the two polymers are also considered for comparison. The dielectric lifetimes of the latter are systematically much shorter than the layered systems. The interfaces between the polymers act as flaws that induce up to two orders of magnitude difference between the layered and blend systems. The capacitance values vs. time during breakdown progression exhibit an inverted S-shape pattern. The three regimes in the S-shape pattern are consecutively attributed to randomly isolated breakdowns, interconnecting breakdowns, and wearing-out of the capacitor film. The film breakdown images during dielectric lifetime test confirmed the transition from randomly isolated breakdowns to interconnecting breakdowns. This transition was further evidenced by a bimodal distribution in the Weibull analysis.

KEYWORDS: Dielectric lifetime, Weibull Analysis, Polycarbonate, poly(vinylidene fluoride-co-hexafluoropropylene), Multilayer Coextrusion, Capacitor,
INTRODUCTION

Polymer films are currently used in a wide variety of electronic applications, including energy storage, electrical insulation, power conditioning, noise suppression, and signal coupling.\textsuperscript{1, 2, 3, 4} Such broad range of applications is made possible by excellent electrical, mechanical, and processing/manufacturing properties.\textsuperscript{1, 2} The electrical properties\textsuperscript{4, 5} include low dissipation factor, high insulation resistance, long dielectric lifetime, and “self-healing” capability.\textsuperscript{5} Polymer film dielectrics\textsuperscript{6} also have better ductility, toughness and flexibility compared with ceramic dielectrics. Polymers are easy to process and can be extruded into thin films continuously.\textsuperscript{7}

In many of these applications, the fundamental components used are capacitors and electrical insulators whose performance is significantly affected by the dielectric lifetime of polymer films. Specifically, improvements in the dielectric lifetime of state-of-the-art materials will translate to improved reliability and longer life span of these components and associated devices.

In the application of energy storage, polymer films play a significant role serving as the capacitor dielectrics. Certain properties are needed for polymer film dielectrics: in particular high energy density and long dielectric lifetime.
Over the last decade, the need for high energy density polymer film capacitors has been driven mainly by the need for fast charging/discharging of electric storage systems in hybrid electric vehicles.\textsuperscript{8} The energy density of linear dielectrics can be expressed as follows:

\[ W = \frac{1}{2} \cdot \varepsilon \cdot \varepsilon_0 \cdot E^2 \]  \hspace{1cm} (1)

where \( E \) is the electric field between the electrodes, \( \varepsilon \) is the relative dielectric constant of the linear dielectrics, and \( \varepsilon_0 \) is the dielectric constant of vacuum and equals \( 8.85 \times 10^{-12} \text{F/m} \). Improving the energy density of a capacitor relies on increasing the dielectric constant, \( \varepsilon \), of the material, and/or the applied electric field, \( E \), it can withstand.

Among the many dielectric properties of polymers, the dielectric lifetime is one that has received little attention. One goal of this paper is to develop a powerful technique which can be used to quantitatively determine the dielectric lifetime of polymer films in a relatively short time scale. Previously, Mackey et. al.\textsuperscript{12, 14, 9} used the needle-plane ramped and pulsed voltage techniques because they provided fast assessment on short-term dielectric breakdown strength and also allowed an easy study of breakdown mechanism. However, a plane-plane, rather than needle-plane, electrode configuration is employed in this paper, because it is more closely related to the configuration in commercial polymer film capacitors.\textsuperscript{12, 14} This technique also has the additional benefit of testing large areas in one measurement.
A second goal is to study the effect of layering on the dielectric lifetime of PC/P(VDF-HFP) films by varying film composition and number of layers. P(VDF-HFP) has been chosen because of its inherent high dielectric constant, namely 12-13. This copolymer, however, suffers from low breakdown strength, short dielectric lifetime, high dissipation factor, and high leakage current. Our approach to increase the dielectric lifetime of P(VDF-HFP) is to multilayer it with a high breakdown strength, long dielectric lifetime, low dissipation factor, and low leakage current polymer such as PC. The micro- and nano-layered structure affects morphology and electric field distributions in the layers; therefore, the dielectric breakdown strength of P(VDF-HFP) can be dramatically improved. It is hypothesized that the layer structure impedes the progress of breakdown through a treeing mechanism not observed in the bulk materials. Therefore, this layering technique is expected to produce a pronounced enhancement in lifetime. Building upon the prior work, it is equally important and of great interest to study the long-term dielectric lifetime of the layered PC/P(VDF-HFP) films with enhanced short-term dielectric breakdown strength; therefore, the constant DC dielectric lifetime of layered films was investigated.
MATERIALS AND METHODS

An approach of “forced assembly” multilayer coextrusion\textsuperscript{15} was used to produce alternately layered films of a Poly(vinylidene fluoride-\textit{co-}
hexafluoropropylene) (P(VDF-HFP), Solef\textsuperscript{®} 21508) and bisphenol A polycarbonate (PC, Makrolon\textsuperscript{®} 2207). The P(VDF-HFP) copolymer had a comonomer content of 15 wt. % HFP. Films with 2, 32, and 256 layers were produced with the total film thickness of approximately 8 $\mu$m. Blend films were also produced by first compounding PC and P(VDF-HFP) in a Haake twin-screw compounder and then extruding with a thickness of 8 $\mu$m (Table \textit{2.1}). The number of layers, film compositions, and nominal layer thicknesses of the film studied in the paper is listed in Table \textit{2.1}. PC was selected based on its excellent dielectric and mechanical properties and adequate adhesion with P(VDF-HFP). P(VDF-HFP) copolymer was chosen for its high dielectric constant and rheological compatibility with PC for coextrusion.\textsuperscript{12} Sacrificial polyethylene (PE) skin layers, which were removed prior to dielectric testing, were coextruded on both sides of the layered and blend films to improve the film surface smoothness and handleability.\textsuperscript{16}

The dielectric lifetime test (\textit{Figure 2.1a}) was carried out with an extremely stable high voltage DC power supply, Fluke\textsuperscript{®} 410B, which has an output voltage of 0 to $\pm$ 10,000 VDC, and an output stability of $\pm$ 0.02\% per day after warm-up. Samples for the dielectric lifetime test were prepared by sputtering 20 nm thick gold electrodes on both sides of the films (\textit{Figure 2.1c}). The plane-plane electrode
configuration could probe large areas in one shot, which was equivalent to running many experiments simultaneously. The testing area was 1 cm by 1 cm. The deposited gold electrodes ensured good electrical contact between the testing sample and high voltage power supply.

Constant DC voltage was applied on the film and held until the film capacitance reached a minimal value of 0.05 nF. Three different methods have been used to obtain the capacitance value. The first method is by directly measuring the film capacitance using dielectric thermal analyzer (DETA) at a constant frequency and electric field (1 kHz, 1 V). The DETA (DE87-04) used is from Polymer Laboratories®. A frequency of 1kHz was chosen because it is above the α-relaxation of P(VDF-HFP)\(^{17}\). The frequency is also in the middle frequency range of the instrument, which ensures high stability and accuracy (±1 pF).

The second method is by fitting the exponential decay of the charging spikes (Figure 2.2b) using the current equation for resistors \(R_1\) and \(R_2\) in series with the sample capacitor film after a voltage step. The capacitor film can be modeled as an ideal capacitor, \(C\), in parallel with a resistor, \(R_p\) (Figure 2.1b), where the resistor accounts for DC conductivity.

\[
I(t) = I(t_0)e^{-\frac{t-t_0}{RC}} + I_c \tag{2}
\]

\[
R = \frac{1}{\left[\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{1}{R_p}\right]} = \frac{R_p(R_1+R_2)}{R_p+R_1+R_2} \tag{3}
\]

\[
R_p = \left(\frac{\nu_{applied}}{I_c}\right) - R_1 - R_2 \tag{4}
\]
The variables are defined as follows: \(I(t)\) is the measured current profile, \(I(t_0)\) is the initial charging current at time \(t_0\), and equals the height of the current spike (Figure 2.2b), \(I_c\) is the conduction current through capacitor films and equals the baseline value under the current spike, \(RC\) is the capacitor time constant, in which \(R\) is defined in Equation 3 and \(C\) is the film capacitance, \(R_1\) is the high voltage resistor (200 M\(\Omega\)), \(R_2\) is the precision sensing resistor (100 k\(\Omega\)), \(R_s\) is the parallel resistance of the layered film sample, and \(V_{applied}\) is the applied high voltage. The conductive current is mainly from the DC conductivity of the P(VDF-HFP) component. A small amount of conduction current does exist in P(VDF-HFP) control and 10/90 PC/P(VDF-HFP), however, the conduction current is negligible for PC/P(VDF-HFP) films with higher PC content. Least square curve fitting method is used to find model curve that best matches the measurements by varying capacitor time constant, \(RC\). Equation 2 is valid for a linear dielectric material. The nonlinearity of the layered system is small enough that a good fit was achieved in all curves. An example is shown in Figure 2.2b.

The third method is through calculating the capacitance from the effective capacitance area by Equation 5:

\[
C = \varepsilon_r\varepsilon_0 \frac{A}{d}
\]

(5)

where \(\varepsilon_0\) is vacuum permittivity (8.854x10\(^{-12}\) F/m), \(d\) is sample thickness (8 \(\mu\)m), \(A\) is effective capacitance area, taken as the dark areas (not the grey or white areas) which still contain metalized electrode on both sides (Figure 2.2c). This effective area was obtained within 2% using Image J\({}^\text{®}\) software. The remaining
variable, $\varepsilon_r$, which is relative dielectric constant of the layered film was calculated from the initial capacitance obtained from method 2. This calculation was carried out using Equation 5 with an effective area of $1\text{cm}^2$ and a thickness of $8\ \mu\text{m}$.

Electrical current with respect to time during the lifetime test was determined by measuring the voltage across a resistor using a data acquisition card (NI AT-MIO-16E-1). To keep voltages within the measurement range ($\pm 10\ V$), two resistors ($200\ \text{M}\Omega$ and $100\ \text{k}\Omega$) were used to form a voltage divider. The voltage across the precision $100\ \text{k}\Omega$ resistor was measured at a sampling rate of $100\ \text{Hz}$ (Figure 2.1a). The current profile was calculated from the voltage profile based on Ohm’s law:

$$I(t) = \frac{v(t)}{R_2} \quad (6)$$

where $R_2$ is the precision $100\ \text{k}\Omega$ resistor, $V(t)$ is the measured voltage across the resistor $R_2$ from the data acquisition card.

After one or more breakdown events have occurred, the fracture surfaces of the breakdown sites were examined under an Olympus® SZH zoom stereo microscope. Features were best resolved in transmission mode using normal incidence illumination.
RESULTS AND DISCUSSION

Breakdown Progression of 32-layer 70/30 PC/P(VDF-HFP) during Dielectric Lifetime Test

An initial dielectric test was carried out on a 32-layer 70/30 PC/P(VDF-HFP) film under 320 kV/mm. The data shown in Figure 2.2 include a current versus time plot as well as optical microscopy images of the damage progression. Each spike in Figure 2.2a corresponded to one individual breakdown event. The current versus time plot consisted of many spikes and was equivalent to running many breakdown experiments simultaneously. The optical microscopy images of the damage progression (Figure 2.2c) indicated that the breakdown damage happened in a fairly random pattern.

Reed and Cichanowski reported5 that dielectric breakdown occurred during the dielectric lifetime test with the formation of a conductive channel across the film resulting in a microsecond discharge event. The quick release of the stored capacitor energy created a localized high temperature and pressure buildup. At the same time, the capacitor film was punctured and the thin layer of gold electrode at the breakdown site rapidly evaporated from the breakdown site. Therefore, the breakdown events were interrupted and the conductive channel inside the capacitor film formed previously was decomposed in this series of rapid occurring events. In such a way, catastrophic damage and failure of the capacitor were prevented.
Afterwards, the power supply charged the capacitor film producing a current spike on the current profile. This phenomenon is described as “self-healing” or “self-clearing”\textsuperscript{18,19, 20} Sometimes, “self-healing” or “self-clearing” could not fully complete, a slightly higher leakage current might be observed in the current profile, seen from 20,000 to 30,000 s in Figure 2.2a.

The breakdown lifetime experiment was stopped at prescribed times and the capacitor film was observed under an optical microscope to observe the breakdown fracture progression (Figure 2.2c). The images demonstrated that the number of breakdown holes increases with time which led to a decrease of film capacitance. The breakdown holes were isolated and randomly distributed before 20,000 s (Figure 2.2c 1-4). After this point, the breakdown sites appeared to interconnect with one another (Figure 2.2c 5-8). The interconnection of the breakdown sites disconnect part of the dark areas from power supply which further reduces the film capacitance.\textsuperscript{18} One interesting feature noticed in Figure 2.2c (8) was that the breakdown occurred mainly along the electrode edge when the film capacitance reached 0.05 nF.

The film capacitance values were recorded for the 32-layer 70/30 PC/P(VDF-HFP) film during the dielectric lifetime test. Three different methods have been used to obtain the capacitance value. One interesting comparison was that the capacitance value obtained by fitting the charging current peak was the same as the value determined from the capacitor area before 20,000 s. After that, the two values
deviated significantly. The deviation resulted from the formation of interconnecting breakdown sites causing additional isolated areas. Another difference observed from Figure 2.3 was that the capacitance obtained by fitting of the charging current peak was consistently (30±10%) higher than the measured value directly from DETA. Two variables that may produce this difference are frequency and applied electric field. Broadband DETA measurements have shown that the capacitance increases significantly at low frequency due to a charge migration relaxation.\textsuperscript{17} Furukawa et. al.\textsuperscript{21, 22} also reported that high electric field can induce additional molecular rotation and polarization, that otherwise will not happen at low electric field.

Energy storage polymer film capacitors usually operate at an electric field of around 100 kV/mm and at low frequency or DC. For the charging peak fitting method, the applied DC electric field was 320 kV/mm; for the DETA method, the applied electric field was only 0.125 kV/mm, and the frequency is 1 kHz. Therefore, the capacitance values obtained from fitting of the charging current decay were used in this paper since they closely represented the end use property.

The capacitance value obtained from the current vs. time plot (Figure 2.2a) for the 32 layer 70/30 PC/P(VDF-HFP) system showed three regimes with different slopes. The inverted S-shape of the capacitance indicated three different regimes with respect to time as the film broke down.
The first regime showed a slow capacitance decrease, which was attributed to randomly isolated breakdowns. These randomly isolated breakdown events appeared early and could be attributed to processing related defects, such as pinholes and/or embedded foreign particles. When an electric field was applied on the film, the external contaminants and film non-uniformity lead to a higher than average local electric field, causing the local current density to increase, and a rapid accumulation of electric heat and trapped local charge, leading to an early breakdown event.\textsuperscript{5,18,23,24}

The second regime signified by a sudden decay of the film capacitance, had the highest slope among the three regimes. The interconnecting breakdowns formed during this regime, which isolated some of the non-fractured area from the applied electric field. Therefore, the capacitance calculated from the effective area was larger than the value obtained from the charging current decay once the breakdown sites began interconnecting.

The capacitance leveled off in the last plateau regime due to the film wearing-out. In this regime, the electrode was disconnected from the power supply because of the massive vaporization of gold resulting from film discharge. Most of the breakdowns in this regime occurred along the electrode edge. The dielectric lifetime experiment was stopped in this regime, when the film capacitance reached a minimal value of 0.05 nF.
Effect of Film Composition on the Dielectric Lifetime Test of 32-layer PC/P(VDF-HFP) Films

Figure 2.4 shows the current profiles for 32-layer PC/P(VDF-HFP) films at various compositions with a total film thickness of approximately 8 µm. The experiments were stopped after the film capacitance reached a minimal value of 0.05 nF. An applied electric field of 320 kV/mm was chosen, because the lifetime of PC and P(VDF-HFP) were both on a reasonable time scale. There are several important features to note from the current profiles. Each spike in Figure 2.4 corresponded to one individual discharge/charge event. Each plot consisted of many spikes and was equivalent to running many breakdown experiments simultaneously. Most of the breakdown events occurred around 100 seconds for the P(VDF-HFP) control. As the PC content increased, the breakdown events shifted to longer times. Therefore, layering with PC increased the DC dielectric lifetime of P(VDF-HFP) significantly. For the P(VDF-HFP) and 10/90 PC/P(VDF-HFP) films, the leakage current between breakdown events was well above zero. This was attributed to poor insulating resistance of P(VDF-HFP), resulting in a significant leakage current after applying a DC field of 320 kV/mm. The peak height distributions of the current spikes for lower PC contents (below 50%) were broader than the peak height distributions for higher PC contents (above 50%).

The damage sites of the 32-layer PC/P(VDF-HFP) films were examined with an optical microscope (Figure 2.5), and found to be interconnected. Edge
breakdowns were observed for all compositions indicating the film capacitance reached the wearing-out regime. The breakdown fracture site grew radially and had a flower-like structure. The flower-like shape was more evident for the layered films compared to the controls. The total number of breakdown holes were counted and plotted as a function of PC composition (Figure 2.6). The number of holes showed a slight increase with increasing PC content after 50%. The total number of current spikes was also counted and found to be greater than the total number of breakdown holes, especially at lower PC contents (Figure 2.4). This indicates that some breakdown events did not form new holes, but rather in preexisting holes. A higher number of amplitude spikes were observed in the layered films with high P(VDF-HFP) content because P(VDF-HFP) is more conductive relative to PC which allows for easier occurrence of surface discharges. To confirm this hypothesis, the number of spikes above certain current thresholds (6.0 and 7.5 µA) from Figure 2.4 were plotted and compared with the total number of breakdown holes determined from optical microscopy (Figure 2.6). The total number of breakdown holes correlated well with the number of spikes above 7.5 µA. The correlation supported that breakdown holes formed when the discharge current was above 7.5 µA and low amplitude spikes did not form new breakdown holes.

Following the same methodology mentioned in the previous section, the breakdown progression experiments were conducted on all 32-layer PC/P(VDF-HFP) films, in addition to both controls. Breakdown progression images for all the films tested revealed that the breakdown holes were isolated distributed followed
by interconnecting breakdowns, which is similar to the behavior described for the 70/30 PC/P(VDF-HFP) film. These two different categories of film breakdown events resulted in a systematic decrease in capacitance following an inverted S-shape.

From the best fitting of the charging current decay peak (Equation 2), the film capacitance values were obtained and plotted against time. The capacitance vs. time plot (Figure 2.7) for 32-layer PC/P(VDF-HFP) system shows three regimes with different slopes for all compositions and controls. One important feature to note from Figure 7 was that the curves shift to longer times with increasing PC content. This is advantageous and desirable for capacitor applications because microlayering with PC indeed increases the dielectric lifetime of the layered capacitor films significantly. The inverted S-shape capacitance change observed for all compositions in Figure 7 indicated three different regimes existed for all layered samples and controls during the dielectric lifetime test.

To determine the effect of composition on the characteristic dielectric lifetime, Weibull analysis was used to analyze the spikes recorded in the current profile. Only current spikes that were above 7.5 µA were taken into consideration, because lower current spikes did not form new breakdown holes. The time to failure for each spike above 7.5 µA was plotted according to Weibull statistics (Figure 2.8a). All compositions exhibited a bimodal Weibull distribution, which indicated that two different categories of breakdown exists with each dominating in a different
time regime. The slope change with time from Weibull distribution were compared with the isolated to interconnecting breakdown transition times obtained from S-shape curves in capacitance vs. time plot (Figure 2.9). The transition times obtained from the two methods were comparable, which supported that the shallow slopes in the Weibull plot were from early isolated breakdowns and the high slopes were from interconnected breakdowns.

The failure time data was fitted using a two-parameter Weibull distribution (Figure 2.8a). Only the interconnecting breakdown regime was used to obtain the characteristic dielectric lifetime since most of the breakdown events occurred in this time-scale. The cumulative two-parameter Weibull distribution function is governed by:

$$P_F(t) = 1 - \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]$$  \hspace{1cm} (7)

where $P_F(t)$ is the cumulative probability of failure, $\tau$ is the characteristic dielectric lifetime to breakdown and represents the 63.2% probability of failure, and $\beta$ is the shape parameter, usually in the range of 0.5 to 3 for time distribution for constant voltage test.\textsuperscript{23}

The characteristic lifetime data calculated from Equation 7 were plotted in Figure 2.8b. The dielectric lifetime data were compared with a weighted average model on a semi-log coordinates. The weighted average model is a linear interpolation between the two controls based on the volumetric composition on semi-log coordinates. The experimental measured dielectric lifetime data of the 32
layer films were significantly higher than the weighted average model. The 30/70, 50/50, and 70/30 show one order of magnitude longer dielectric lifetime compared with the weighted average model, which is in agreement with the enhanced breakdown strengths observed for similar films by Mackey et al.\textsuperscript{12, 14} The shape parameter for each composition ranged from 1.4 to 2 which fell in the range that is typical for a constant voltage test.\textsuperscript{23}

**Effect of Number of Layers on the Dielectric Lifetime Test of PC/P(VDF-HFP) Systems**

Using the same methodology, the breakdown experiments of 2-, 256-layer and blend films of PC/P(VDF-HFP) were tested under constant DC field of 320 kV/mm. A typical current profile and the corresponding optical microscopy images of breakdown sites with a constant sample composition (70/30) of the PC/P(VDF-HFP) is shown in Figure 2.10 and Figure 2.11 respectively.

The blend films always exhibited the shortest dielectric lifetime compared to layered films with the same PC composition. The interfacial area that is parallel to the electric field in the blend films has a weaker dielectric strength compared to the bulk materials.\textsuperscript{25} The PC/P(VDF-HFP) blend films broke down early along the weak interfacial boundary. The breakdown holes of blend films were along elongated phase separated domains which were caused during extrusion process (see Figure 2.11). Since PC and P(VDF-HFP) are immiscible, phase separated
domains will always exist. Domain size can be reduced with different processing
techniques. There will, however, always be a continuous interface path from one
side to the other. In comparison, the interfacial area for the layered film is only
perpendicular to the electric field. No interfacial area is parallel to the electrical
field and all of the breakdown holes have circular shape. The PC layers can deflect
the hot electron propagation and impede the breakdown across the film thickness.12

Besides the enhanced dielectric lifetime of 32- and 256-layer PC/P(VDF-HFP),
it is also important to note that the blend and 2-layer films had leakage current
values higher than 1 µA (Figure 2.10). This implied that the capacitor film did not
fully “self-clear” during testing, which is not desired for capacitor devices.
However, 32- and 256-layer films cleared well, which indicated that microlayer
coextrusion could improve the “self-clearing” capability of the PC/PVDF-HFP
films.

To quantify the DC dielectric lifetime, Weibull analysis was used to extract the
characteristic time to breakdown for the blend, 2-, 32-, and 256-layer films. The
bimodal distribution in Weibull plots, which was attributed to randomly isolated
and interconnecting breakdowns, was observed for all films tested (see Figure
2.12). The characteristic (63.2%) failure lifetimes of 2, 32, 256 layer films in
addition to the blend films were plotted together in Figure 2.13. The dielectric
lifetimes of 32- and 256-layer films are approximately two orders (100 x) of
magnitude longer than the blend films at the same PC composition.
The 256-layer films had slightly shorter dielectric lifetime compared with the dielectric lifetime of 32-layer films at all compositions. It is proposed that PC layers act as barrier layers to slow down or stop the migration of charged species/ions under field in P(VDF-HFP) layer. For 256-layer films, it is speculated the PC layers are too thin to effectively block those charged species. In other words, ionic charges could “penetrate” through the glassy PC layer under high fields.

Compared with 32-layer and 256-layer systems, the beneficial effect of layering the two polymers, however, was revealed less for two layer system. This could be explained by a volume effect which stipulate that the breakdown strength is notably reduced by a film thickness. It can also be thought that the degradation of the P(VDF-HFP) layer would not be impeded with a rather large layer thickness, and when started it went through the PC layer. This suggests that an optimal thickness exists for achieving maximum dielectric lifetime of PC/P(VDF-HFP) systems.

**Proposed Breakdown Mechanism**

Currently, there is no explicit model that can explain the enhanced lifetime seen in multilayered films, especially the 32- and 256-layer PC/P(VDF-HFP) films. However, based on the data presented above, a breakdown mechanism during dielectric lifetime test is proposed. Initially, ions/conductive species are randomly
distributed in P(VDF-HFP) layers. After applying a field, ions/conductive species in P(VDF-HFP) migrate to the polymer layer interface.\textsuperscript{26} The PC layers, in addition to the multiple layer interfaces act as barriers to reduce ionic species migration and bombardment. Alternatively, high purity materials can minimize ionic species migration and bombardment, but are much more expensive. After applying an electric field on the layered film for an extended time, “hot spots” form resulting from a conductive pathway of ionic species migration or accumulation. Breakdown occurs when the heat generated along the hot spot is larger than the film can dissipate.\textsuperscript{2,11} This is termed as hot electron thermal runaway. A main breakdown hole forms after the initial discharge. Subsequent discharges vaporize the gold electrode around the breakdown pinhole, which electrically isolates the breakdown area forming a flower-like breakdown pattern (Figure 2.6).

In order to further understand why layering has such a significant effect on dielectric lifetime, the proposed breakdown mechanism during the dielectric lifetime test is under further investigation. The breakdown mechanism will allow us to better design polymer films for capacitors which have enhanced properties and device reliability.
CONCLUSIONS

A dielectric lifetime test technique was developed and successfully used to analyze the long-term reliability of multilayer and blend films containing PC and P(VDF-HFP). It was determined that layered films, especially 32- and 256-layer PC/P(VDF-HFP) films exhibit enhanced (100 x) dielectric lifetime as compared to the blend films. Another advantage of microlayering is to improve the “self-healing” or “self-clearing” ability of the polymer films after breakdown, which is very important to the manufacturing of safe capacitors.

Breakdown progression data revealed two breakdown categories occurring during long term testing: 1) isolated breakdowns; 2) interconnecting breakdowns. These two different categories of breakdown cause the film capacitance to decrease in an inversed S-shape. By comparing the total number of breakdown holes with the number of spikes above a certain threshold, it is concluded that current spikes above the critical threshold result in the formation of new breakdown holes. Low amplitude current spikes are attributed to surface discharge or expansion of the existing breakdown holes. Weibull analysis of the breakdown current spikes above a critical threshold shows a bimodal distribution confirming the existence of the two breakdown types.

A breakdown mechanism for the dielectric lifetime measurement is proposed based on the data presented to explain the enhanced dielectric lifetime seen in the
layered films. PC layers, in additional to the multiple layer interfaces, act as barrier layers which confine, and slow charge migration and reduce impact ionization and bombardment in the film. By using high purity materials, the electric degradation process will be further minimized and the layered films will last longer. Higher purity materials are, however, much more expensive. The layered film structure can deflect the fracture propagation pathway across the film thickness, thus prolonging the lifetime. However, if the PC layers are too thin, ionic charges could “penetrate” through the glassy PC layer under high fields. Therefore, PC layers and the interfaces will not effectively block those charged species. This suggests that there is an optimal thickness for maximum dielectric lifetimes.
ACKNOWLEDGEMENTS

This research was generously supported by the National Science Foundation through the Center for Layered Polymeric Systems (CLiPS) Science and Technology Center Grant DMR-0423914 and the Office of Naval Research Grant N00014-10-1-0349.
Table 2.1  Film compositions and nominal layer thicknesses of multilayer PC/P(VDF-HFP) film with overall film thickness of 8 µm.

<table>
<thead>
<tr>
<th>Number of Layers</th>
<th>Composition (vol./vol.) PC/P(VDF-HFP)</th>
<th>Layer Thickness (nm) PC/P(VDF-HFP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0/100 (P(VDF-HFP) control)</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>100/0 (PC control)</td>
<td>-</td>
</tr>
<tr>
<td>blend</td>
<td>70/30</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>30/70</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>70/30</td>
<td>5600/2400</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>4000/4000</td>
</tr>
<tr>
<td></td>
<td>30/70</td>
<td>2400/5600</td>
</tr>
<tr>
<td>32</td>
<td>70/30</td>
<td>350/150</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>250/250</td>
</tr>
<tr>
<td></td>
<td>30/70</td>
<td>150/350</td>
</tr>
<tr>
<td></td>
<td>10/90</td>
<td>50/450</td>
</tr>
<tr>
<td>256</td>
<td>70/30</td>
<td>44/19</td>
</tr>
<tr>
<td></td>
<td>50/50</td>
<td>31/31</td>
</tr>
<tr>
<td></td>
<td>30/70</td>
<td>19/44</td>
</tr>
</tbody>
</table>
Sample preparation for dielectric lifetime measurement.

Fig. 2.1  a) Dielectric lifetime measurement setup; b) Equivalent circuit of the dielectric lifetime measurement setup; c)
Fig. 2.2. Breakdown progression of 32-layer 70/30 PC/P(VDF-HFP) with a thickness of 8 µm under 320 MV/m: a) Current profile during dielectric lifetime test; b) Zoom-in plot of the current profile from 2827s to 2829s. (Modeled data from Equation 2 are included (in red) for comparison); c) Breakdown images at different times indicated in top graph. (The images share the same scale bar in picture (1))
Fig. 2.3. Film capacitance dependence on the testing time as indicated in Figure 2.2a for 32-layer 70/30 PC/P(VDF-HFP). The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
Fig. 2.4 Effect of film composition on the current profile of the 32-layer PC/P(VDF-HFP) films during dielectric lifetime tests. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
Figure 5: Effect of film composition on the damage sites of the 32-layer PC/P(VDF-HFP) films. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
Fig. 2.6  Comparison of the number of breakdown holes with the number of spikes for the 32-layer PC/PVDF-HFP films. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
Fig. 2.7 Film capacitance (from fitting of the charge current peak) dependence on the testing time for 32-layer PC/P(VDF-HFP) with different film compositions. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
Fig. 2.8  a) Weibull analysis of the breakdown data of 32-layer PC/P(VDF-HFP) films with various compositions; b) Characteristic lifetime of the 32-layer PC/P(VDF-HFP) films from Weibull analysis. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
Fig. 2.9  Comparison of transition times obtained from capacitance vs. time curves and obtained from bimodal distribution of Weibull analysis.
Fig. 2.10 Effect of layer number on the leakage current profile of the 70/30 PC/P(VDF-HFP) film. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
Fig. 2.11  Effect of layer number on the damage site of the 70/30 PC/P(VDF-HFP) film. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
Fig. 2.12 Weibull analysis of the breakdown data of PC/P(VDF-HFP) systems with various compositions. a) blend films; b) 2-layer films; c) 32-layer films; d) 256-layer films.
Fig. 2.13  Characteristic lifetime of PC/P(VDF-HFP) with various numbers of layers and blend films from Weibull analysis. The total film thickness is kept at 8 µm and the applied field is 320 MV/m.
References


CHAPTER 3

Fracture Phenomena in Micro- and Nano-layered Polycarbonate/Poly(vinylidene fluoride-$co$-hexafluoropropylene) Films under Electric Field for High Energy Density Capacitors
ABSTRACT

The long-term dielectric lifetime properties of multilayered polycarbonate/poly(vinylidene fluoride-co-hexafluoropropylene) [PC/P(VDF-HFP)] films were measured as a function of the layer thickness. An optimum layer thickness of 160 nm was determined with the longest dielectric lifetime. The morphology of the damaged sites after dielectric breakdown was examined using scanning electron microscope (SEM). Acoustic emission detection system was coupled with the dielectric setup to correlate fracture events and dielectric breakdown to thereby elucidate the mechanisms of the enhancements in dielectric lifetime properties. Two types of acoustic signals were always observed during the breakdown process for multilayered films. The high amplitude signals were attributed to the formation of breakdown pinholes caused by the primary discharge from top to bottom electrode. The subsequent low amplitude signals were attributed to internal discharges which could further damage the film. The total number of acoustic hits, in particular low amplitude hits, increased with decreasing layer thickness, indicating more internal discharges occurred along the layered interface. It was concluded that the breakdown event initiated from internal pressure buildup around a defect initiated “hotspot”. The film was punctured when the pressure buildup inside the film overcame the mechanical strength of the film. More number of PC layers and layer interfaces were desirable to slow down and divert the damage propagation through the film thickness direction. The crazes in P(VDF-HFP) can however easily propagate across PC layers with less than 160 nm layer thickness.
KEYWORDS: Dielectric Fracture, Crazing, Acoustic Emission, Polycarbonate, Poly(vinylidene fluoride-co-hexafluoropropylene), Multilayer Coextrusion.
INTRODUCTION

Microlayer coextrusion is a novel polymer processing technique that can tailor readily available polymers into high value-added products for specific purposes. This technique enables fabrication of polymer films that contain up to thousands of alternating two or three polymeric layers with a continuous layer thickness down to 10 nm. The production of nanometer scale polymer layers has been proven to be able to enhance dielectric [1, 2, 3], optical [4, 5], mechanical [6, 7, 8], and gas transport [9] properties.

Polymer films are becoming more and more important in a wide variety of applications ranging from dielectric, optical, and mechanical to gas transport applications. The broad applications are made possible because polymer films have excellent dielectric breakdown strength, high transparency, flexibility, and high barrier to gases and/or moisture. Polymer film capacitors play an important role in energy storage, power conditioning, noise suppression, and signal coupling applications [10, 11, 12, 13]. Among these dielectric applications, energy storage/power conditioning application is becoming more and more essential, driven by the next generation electric vehicles, in which fast charging and discharging of a large amount of the energy is required. For these applications, certain dielectric properties are desired for polymer film dielectrics: high breakdown strength, long dielectric lifetime, low dielectric hysteresis, etc.
Recent studies on the layered polymer capacitor films have focused on dielectric properties, including dielectric lifetime [3], breakdown strength [1,2], and hysteresis [14]. Significant enhancements were observed for dielectric lifetime and breakdown strength, and hysteresis was reduced by decreasing PVDF layer thickness. Wolak [15] and Mackey [2] studied the fracture mechanisms of the layered PC/P(VDF-HFP) under divergent field (needle-plane electrode configuration) conditions. However, little has been done on studying the fracture mechanisms under uniform field which is more close to the actual use condition of capacitor films.

Previous studies [6, 7, 8] of layered polycarbonate/poly(styrene-co-acrylonitrile) PC/SAN sheets demonstrated a significant amount of enhancement in mechanical toughness. Through fracture mechanisms study, it was concluded that the enhancement was attributed to the formation of shear bands in PC layers, which absorbed energy, blunted the tip of the crack in SAN layers, and stopped the crack propagation. Inspired by the previous fracture mechanisms study on mechanical enhancement in layered PC/SAN sheets, it was equally important and of great interest to study the fracture mechanisms of PC/P(VDF-HFP) layered films in the dielectric lifetime test. The dielectric fracture mechanism study would allow us to better design high energy density capacitor films. Acoustic emission detection technique, coupled with dielectric setup, was used to monitor acoustic emissions produced within PC/P(VDF-HFP) films during the dielectric fracture. The acoustic emission signals, in addition to fracture imaging data and electric current profile,
were used to record time evolution of a breakdown event and probe the mechanisms during dielectric fracture. The main goal of this paper was to study the effect of layer thickness on the breakdown/fracture mechanisms in PC/P(VDF-HFP) films. Another goal of this paper was to systematically study the effect of layer thickness on the long-term dielectric lifetime of PC/P(VDF-HFP) films by varying the number of layers while maintaining a constant film thickness and composition, and to determine the optimum layer thickness in term of the dielectric lifetime. It was reported [2, 3] that the 32- and 256-layer system demonstrated an increase in both long-term dielectric lifetime and short-term dielectric breakdown strength relative to control and blend films; however, no optimization has been done on the effect of layered thickness on the dielectric properties of layered PC/P(VDF-HFP) films. In this paper, the PC and P(VDF-HFP) layer thickness was systematically decreased from 5 μm to 20 nm by increasing number of layers from 3 to 513, and the total film thickness and film composition remained essentially constant.
MATERIALS AND METHODS

**Micro- and Nano-layer Film Fabrication Using Multilayer Coextrusion Technology**

An approach of “forced assembly” multilayer coextrusion [16] was used to produce alternately layered films of a poly(vinylidene fluoride-\textit{co}-hexafluoropropylene) [P(VDF-HFP), Kynar® 2500] and a bisphenol A polycarbonate (PC, Makrolon® 2207). The P(VDF-HFP) copolymer had a comonomer content of 19 wt. % hexafluoropropylene content.

Multilayered films with 3, 5, 9, 17, 33, 65, 129, 257, and 513 layers were fabricated with a total film thickness of approximately 10 μm, and a ratio of PC to P(VDF-HFP) of 50/50 vol./vol.. Control films of PC and P(VDF-HFP) as well as a 50/50 blend were extruded with the same film thickness of 10 μm. Corresponding nominal layer thicknesses were calculated and shown in Table 1. One layer of PC with half of the nominal layer thickness was kept on each side of the layered films to maintain low surface resistivity.

PC was chosen based on its excellent dielectric breakdown strength, electronic resistivity, mechanical properties, combined with adequate adhesion with P(VDF-HFP). P(VDF-HFP) copolymer was chosen for its high dielectric constant ($\varepsilon_r=11.2$) and rheological compatibility with PC for coextrusion at 240 °C. Sacrificial low
density polyethylene (LDPE) skin layers with a melt flow index of 5.0, which were removed prior to dielectric testing, were coextruded on both sides of the films to improve the film surface smoothness and handleability [17].

**Long-term Dielectric Lifetime Measurements**

The long-term dielectric lifetime test (Figure 1a) was carried out with a stable high voltage DC power supply, Fluke® 410B, which has an output voltage of 0 to ± 10,000 VDC, and an output stability of ± 0.02% per day after warm-up. The applied electric field was maintained at 320 kV/mm for all samples tested. Four repetitions were performed on each sample. Samples for the dielectric lifetime tests were prepared by sputtering 20 nm thick gold electrodes on both sides of the films (Figure 1b). The plane-plane electrode configuration could probe a large area in one experiment, which was equivalent to running many tests simultaneously. The testing area was 1×1 cm². The deposited gold electrodes ensured good electrical contact between the testing sample and the high voltage power supply.

Electrical current versus time was determined during the lifetime test by measuring the voltage across a resistor using a data acquisition card (NI AT-MIO-16E-1). To keep voltages within the measurement range (±10 V), two resistors (200 MΩ and 100 kΩ) were used to form a voltage divider. The voltage across the precision 100 kΩ resistor was measured at a sampling rate of 100 Hz (Figure 1a). The current profile was calculated from the voltage profile based on Ohm’s law:
\[ I(t) = \frac{v(t)}{R_2} \]  

(1)

where \( R_2 \) is the precision 100 k\( \Omega \) resistor, and \( V(t) \) is the measured voltage across the resistor \( R_2 \) from the data acquisition card.

**Acoustic Emission Detection of the Breakdown Event**

An acoustic emission (AE) detection setup was incorporated with the dielectric lifetime setup to monitor AE signals during film breakdown. The sensor was purchased from Physical Acoustics Corporation (PAC\(^\circledR\)), a member of MISTRAS\(^\circledR\) Group Inc., with a resonant frequency at 150 kHz. Vacuum grease was used to ensure good attachment between the acoustic sensor and a polypropylene sheet on which the dielectric lifetime experiments were carried out. The layered film sample was placed on the polypropylene sheet and was positioned 10 cm away from the sensor. The AE signals were first pre-amplified at a fixed gain of 20 dB through a low noise voltage preamplifier, PAC 2/4/6. The signals were then band pass filtered with a frequency range from 100 to 300 kHz. An acoustic amplitude threshold of 60 dB was chosen to remove all background noise. The acquisition and analysis of the signals were done using PCI/DSP-4P data acquisition card and AEwin\(^\circledR\) software, respectively.

**Experimental Procedure to Observe Breakdown Cross Section of the Breakdown Event**
After the layered film had a breakdown event, the fracture surfaces were examined under an optical microscope (OM). Features were best resolved in transmission mode using normal incidence illumination. The breakdown site of each sample was then sputtered with 10 nm of gold and examined in a JEOL JSM-6510LV scanning electron microscope (SEM) in secondary electron imaging (SEI) mode.

The sample with the breakdown damage site was then embedded into epoxy resin and cured for at least 24 hours. The sample in epoxy was polished to a desired wedge shape with a thickness down to 1 mm. 4000 grit sand paper was used to achieve high transparency across the film thickness direction. The wedge shape specimen was sliced using a Leica® EM UC 7 microtome at -50 °C to get an ultra smooth cross-section. The distance between the microtome knife tip and the breakdown hole can be measured using an OM under transmission mode since the epoxied sample was polished to be transparent. The specimen was cut to a desired distance from the central hole, removed from the microtome, and coated with 10 nm gold and examined in a JEOL JSM-6510LV SEM. 30 kV accelerating voltage and a working distance of 6 mm were chosen to achieve high magnification (>10,000×) images. High magnification SEM images were taken quickly in order to prevent degradation of the samples. This process was repeated a few times to observe the cross-sections at various distances from the central breakdown hole.
RESULTS AND DISCUSSION

Effect of Layer Thickness on the Dielectric Lifetime of Layered PC/P(VDF-HFP) Films

Figure 2 shows the dielectric lifetime of PC/P(VDF-HFP) multilayer films with various layer thicknesses. Values for PC and P(VDF-HFP) controls and 50/50 blend film were included for comparison. The ratio of PC to P(VDF-HFP) was 50/50, and the film thickness was maintained approximately 10 µm for both the layered and blend films. Accurate measurements of the thicknesses allowed applying a constant electric field of 320 kV/mm. The detailed procedure describing the measurement of dielectric lifetime was reported before [3].

The 50/50 blend film exhibited the shortest dielectric lifetime of all tested films. It was even below both controls of individual polymers. On the structural standpoint, PC and P(VDF-HFP) are immiscible and physical blending induces phase separated domains. It thus appears that the interface between the two polymers is sensitive to the high electrical field and responsible for earlier failure of the blends. The reduction of lifetime may also partly result from the electric field enhancement caused by the large contrast in electrical properties of the two polymers. In any case, the blending strategy is not desirable to improve the lifetime of polymers subjected to high electric field.
In contrast, the dielectric lifetime increased substantially for PC/P(VDF-HFP) multilayer films, where the interfaces are arranged perpendicular to the electric field. As previously suggested [2, 15], the layered interfaces seem to delocalize the damage tip, prevent its propagation, and disfavor the breakdown across the film thickness. The lifetime varied from 200 to 30,000 seconds with decreasing the layer thickness from 5 µm to 160 nm. The 65-layer PC/P(VDF-HFP) film with a layer thickness of 160 nm exhibited the longest dielectric lifetime under the testing conditions.

For films with layer thickness thinner than 160 nm, the beneficial effect of layering two polymers, however, dropped gradually. A reasonable hypothesis to describe this limitation is related to the mechanical fracture damage that necessarily can propagate through the tough PC layers easily when the layers are too thin. Another hypothesis is that ultrathin PC layers fail to develop an electrical barrier effect. In other words, the charges trapped at the interfaces carry out internal discharges within thin PC layers. This means that electrons could tunnel through the glassy PC layers thinner than 160 nm under the applied electric fields. In order to further understand the major effect of layering on dielectric lifetime, the breakdown mechanisms during the dielectric lifetime test were investigated in more details through the observation of the damage areas.

**SEM Imaging of 9-layer and 65-layer PC/P(VDF-HFP) Films under Constant DC Field of 320 MV/m**
Figure 3 and Figure 4 are top-view and cross-section images of the multilayer films at several distances from the central breakdown hole for 9- and 65-layer films, respectively. Crazing, micro cavitation, and delamination are evidenced on the B images. The cross-sectional images B and C gave some indications on nature of the breakdown event. Initially, high pressure built up in the central part of the layered film due to the vaporization of materials around the “hot spot” [18]. When the internal pressure overwhelmed the mechanical strength of neighboring layers, the mechanical breakdown occurred, inducing micro-cavitation, delamination, and crazing in the film. The breakdown of the PC layer allowed the discharge of the charged species, simultaneously released the electric tension between layers.

Picture B1 is a zoom-in image of picture B in both Figure 3 and Figure 4. P(VDF-HFP) layers were brighter relative to PC under SEM because of its higher dielectric constant. Crazes with a width of around 400 nm were observed only in bright P(VDF-HFP) layers. PC layers remained intact. A smooth and featureless delamination tip was observed, indicating that the adhesion between PC and P(VDF-HFP) layers was overcome by the amount of energy released during breakdown.

The lateral delamination, which was also observed in the dielectric breakdown under divergent field [2, 15], deflected the propagation pathway and impeded the breakdown process, therefore, contributed to the enhanced dielectric lifetime. In
addition, the textured nature of cross-section image B across the breakdown hole implied that crazing and dilation was also involved in the breakdown process to dissipate the input electric energy.

**Effect of the Layer Thickness on SEM Cross-section Images after Dielectric Breakdown**

The cross-section images were taken for each sample with various layer thicknesses. It was first observed on the macroscopic scale that all breakdown damage zones extended approximately 50 µm from the center of the main breakdown hole. *Figure 5* contains the representative images showing the effect of layer thickness on the breakdown fracture pattern across the breakdown hole under an electric field of 320 MV/m.

Three types of crazing were observed for all samples tested. Crazes were not interconnected when the layer thickness was above 450 nm. The crazes were confined within a single P(VDF-HFP) layer. The height of the crazes was therefore the same as the layer thicknesses. The average width of the crazes was of around 400 nm. Additionally, stretched fibrils with a diameter close to 50 nm developed within those crazes (see the sketch in the images with layer thickness of 630 nm in *Figure 5*). In contrast, PC layers remained essentially intact. In addition to crazes, smooth delaminations with sharp tips occurred along the PC/P(VDF-HFP) interfaces, indicating weak interlayer adhesion.
When the layer thickness was in the range of 100 to 450 nm, parts of the crazes were interconnected across the film thickness direction. The craze density, defined as the number of crazes in a given area, increased drastically with decreasing layer thickness. The total amount of single crazes and craze arrays increased from 20 per 10 µm² for the film with PC layer thickness of 1.3 µm to 160 per 10 µm² for the film with PC layer thickness of 160 nm PC layers (Figure 6). The majority of the crazes were single crazes for all samples with layer thickness above 100 nm.

All crazes penetrated through many PC layers and interconnected with each other when the layer thickness decreased below 100 nm. The type of crazing in the film with 80 nm film was specific and qualitatively different from that observed with thicker PC layers. PC layers were so thin that the crazes propagated rapidly through many PC layers. An example of the craze arrays was indicated inside the rectangular box in the image with layer thickness of 80 nm in Figure 5.

To quantify the single craze and interconnected crazes, the craze densities and the percentage of interconnected crazes were counted and plotted as a function of PC layer thickness for the PC/P(VDF-HFP) films with various number of layers, Figure 6 and Figure 7a. The total number of crazes including both single craze and interconnected crazes were counted in the images. The number of crazes gradually increased with the number of layers until the PC layer thickness reached 160 nm. For thinner PC layer this amount dropped significantly because of a result of the
development of the craze interconnectivity. In summary, Figure 5 follows a bell curve very similar in nature to that describing the dielectric lifetime in Figure 2. It is desirable to have more PC layers and interfaces to divert or delocalize the breakdown damages for the 10 µm layered capacitor films. However, when the PC layers are too thin, the crazes can propagate rapidly through PC layers. These craze arrays indicate thinner PC layers are not as effective as thicker PC layers in terms of slowing down or stopping the craze propagation. This could explain the existence of an optimum thickness of 160 nm for achieving longest dielectric lifetime.

Similar phenomenon described as "interactive crazing" was observed in mechanical tensile test of PC/SAN layered sheet, Figure 7b [6, 7]. Similar three types of crazing: single crazes, partially craze arrays, and craze arrays were observed as a function of PC layer thickness. The transition region, partially craze arrays region, had a PC thickness of 1.3 to 6 µm during mechanical tensile test. The transition region, partially craze arrays region, for dielectric lifetime test had a PC thickness of 100 nm to 450 nm. The difference in the transition PC layer thickness was from the difference in testing conditions, specifically testing frequency. The dielectric lifetime test had a breakdown frequency of approximately $10^6$ Hz, and the testing frequency of tensile test was approximately 1 Hz. It is also shown that the crazes tend not to connect when increasing testing speed or frequency [6]. In addition, the damage zones tend to become smaller when increasing testing frequency during fatigue testing of a polymeric sample [19, 20]. And the glass transition temperature shifts to higher temperature and the material becomes harder.
as increasing testing frequency. The PC tested at $10^6$ Hz is stronger and harder for crazes to penetrate through. All of the above statements could explain that the layer thickness for the transitional region was smaller for dielectric test which had a higher testing frequency.
Acoustic Emission Signals and Electric Current Profile of 65-Layered PC/P(VDF-HFP) Films under Constant DC Field of 320 MV/m

Acoustic emission technique was incorporated with dielectric lifetime setup to monitor acoustic emission signals emitted from PC/P(VDF-HFP) films during dielectric fracture process. The layered films were stressed under a DC field of 320 kV/mm until a breakdown event occurred. A threshold of 60 dB was chosen to eliminate the background noise.

Under these conditions, no current spikes or acoustic hits was detected until film breakdowns happened. For each breakdown event, a series of current peaks and acoustic hits were observed for all samples. For all the observed events, a current peak corresponded to an acoustic hit. The monolithic control films qualitatively differed from the layered films in the acoustic amplitude profile. For the controls, all acoustic amplitudes were similar and relatively high (above 75 dB). If the layered films also exhibited a high initial acoustic amplitude (above 75 dB), the subsequent acoustic amplitude always was significantly lower (~65 dB). The third and subsequent events increased again to high amplitude (above 75 dB).

The energy charged into the capacitor films is expressed based on equation

\[ E_c = \frac{1}{2} CV^2 = \frac{1}{2} \frac{Q^2}{c} \]  \hspace{1cm} (2)

\[ \log E_c = 2 \log Q - \log (2C) \]  \hspace{1cm} (3)
where $E_c$ is the energy charged into the capacitor film, $C$ is the film capacitance, $V$ is the voltage across the resistor, $Q$ is the charge input into the capacitor film. Assuming that $C$ remains constant before and after the breakdown event, $lgQ$ has a linear relationship with $lgE_c$. The acoustic amplitude can be expressed as equation

$$A = 10 lg \frac{E_a}{E_{ref}}$$  \hspace{0.5cm} (4)

$$A = 10 lg E_a - 10 lg E_{ref}$$  \hspace{0.5cm} (5)

where $A$ is the acoustic amplitude, $E_a$ is the acoustic energy, and $E_{ref}$ is the reference energy and equals $10^{-12}$ J/m$^3$. Therefore, acoustic amplitude $A$ has a linear relationship with $lgE_a$.

The input charge calculated from the integration of the current peak and acoustic amplitude was plotted (Figure 9). The logarithmic charge calculated from the area under the current profile increased linearly with acoustic amplitude for layered PC/P(VDF-HFP) films, which indicated that $lgQ$ has a linear relationship with $A$. $lgQ$ had a linear relationship with $lgE_c$ and $A$ has a linear relationship with $lgE_a$; therefore, $lgE_c$ and $lgE_a$ were linearly related. The linear relationship indicated the acoustic signals were intercorrelated with electric signals for all acoustic hits.

For monolithic PC and P(VDF-HFP) controls, all acoustic amplitude signals were above 75 dB (solid rectangles and circles in Figure 9). The different trends for controls and layered PC/P(VDF-HFP) films in amplitude vs. logarithmic charge
gave us indirect proof that the breakdown mechanisms were different for controls and layered films. It is proposed that the initial high amplitude acoustic emission was from the discharge from the top to the bottom electrode, and subsequent low amplitude acoustic emissions were from internal discharges along the layer interfaces. The controls only exhibited high amplitude signals because there was no discharge along the layered interfaces.

Figure 10 shows the effect of the layer thickness on the number of acoustic hits during a breakdown event of layered PC/P(VDF-HFP) films. The number of acoustic hits for PC and P(VDF-HFP) monolithic controls was shown as arrows on the right side of the plot. The total number of acoustic hits, mainly the low amplitude acoustic hits produced by the discharge along the layered interfaces, increased gradually with decreasing the layer thickness. In other words, the discharge along the layered interfaces happened more easily within films with thinner layers.
Proposed Breakdown Mechanism based on the Fracture Images, Acoustic Signals and Electrical Current Profile

Currently, there is no explicit model that can explain the lifetime data seen in multilayered films with various layer thicknesses, Figure 2. However, based on the fracture images, acoustic signals and electrical current profile, a breakdown mechanism during the dielectric lifetime test is proposed, Figure 11.

After applying electric field for some time, a "hot spot" forms along a conductive pathway [18]. High pressure builds up inside the layered film due to the vaporization of materials around the "hot spot". The film is punctured when the pressure buildup at the hot spot overcome the mechanical strength of layered films. Main breakdown hole forms, and film discharges. Crazing, micro-cavitation, and delamination happen during the puncture of the film, inducing the loudest acoustic hit. The subsequent acoustic hits, with lower amplitudes, happen because of internal discharge along the layered interfaces. These hits further damage the film and evaporate the electrodes. The breakdown events are interrupted and the conductive pathway inside the capacitor film formed previously is decomposed in this series of rapid occurring events. In such a way, catastrophic damage and failure of the capacitor are prevented. As long as the PC layers remain tough enough to mechanically hold the structure, the lifetime is enhanced by the increase of amount of interface. For very large number of layers, however, the barrier effect is partially lost because of the lack of strength of thin PC layers. In summary, an optimum layer
thickness of about 160 nm is observed corresponding to the longest dielectric lifetime.
CONCLUSIONS

The forced assembly approach of microlayering lead to alternate layers of polymers with enhanced dielectric lifetime properties. The lifetime increased from 200 to 30,000 s by increasing the number of layers within the films from 3 to 65. An optimum layer thickness of 160 nm was found for achieving the longest dielectric lifetime.

Dielectric fracture image analysis revealed that the damages were delocalized by the blocking electrode PC layers and the interfaces. Three types of crazing were observed in P(VDF-HFP) layers for PC/P(VDF-HFP) systems with a wide range of layer thicknesses. The crazes were non-interconnecting and confined in only one P(VDF-HFP) when the PC layer thickness was above 450 nm. Those crazes started to interconnect when the layer thickness decreased. A partially craze arrays region was found in between 450 nm and 100 nm. When the layer thickness was further reduced to down below 100 nm, crazes could penetrate PC layers and interconnect with each other. The total number of crazes also followed a bell curve as a function of the PC layer thickness. The two properties (lifetime and number of crazes) were closely interrelated with maxima at about 160 nm.

A similar phenomenon on the types of crazing was observed in the mechanical tensile test of PC/SAN layered sheets. A difference was observed in the layer thickness of the transition region from single craze to partial craze arrays. The PC
layer thickness of the transition region for tensile test was 1.3 to 6 µm, and the PC layer thickness of the transition region for dielectric test was 100 to 45 nm. The difference in the PC layer thickness lies in the testing frequency. High frequency testing disfavors the interconnection between the crazes shifting the transition to lower thicknesses.

The acoustic signals indicated that the high amplitude signals were from the main breakdown hole formation caused by the pressure buildup inside the film. The subsequent smaller amplitude signals were from the internal discharges along the layered interfaces. The film with thinner layers discharged along the layered interfaces more easily because of smaller interlayer distances, which was not desirable for capacitor applications.

A breakdown mechanism for the dielectric lifetime measurement is proposed based on the data presented to explain the optimum layer thickness observed in the dielectric lifetime data. PC layers, in additional to the multiple layer interfaces, acted as barrier layers to slow down or divert damage propagation through the film thickness direction, thus prolonging the lifetime. However, if the PC layers were too thin, the crazes formed in P(VDF-HFP) layers can penetrate rapidly through the PC layers and the damage can propagate rapidly across the film. In addition, the film discharge happened more easily when the thickness of PC layers was thin, which was also not desirable for energy storage applications.
ACKNOWLEDGEMENTS

This research was generously supported by the National Science Foundation through the Center for Layered Polymeric Systems (CLiPS) Science and Technology Center Grant DMR-0425914 and the Office of Naval Research Grant N00014-11-0215.
<table>
<thead>
<tr>
<th>Number of Layers</th>
<th>PC or P(VDF-HFP) Layer Thicknesses (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>5000</td>
</tr>
<tr>
<td>5</td>
<td>2500</td>
</tr>
<tr>
<td>9</td>
<td>1250</td>
</tr>
<tr>
<td>17</td>
<td>630</td>
</tr>
<tr>
<td>33</td>
<td>310</td>
</tr>
<tr>
<td>65</td>
<td>160</td>
</tr>
<tr>
<td>129</td>
<td>80</td>
</tr>
<tr>
<td>257</td>
<td>40</td>
</tr>
<tr>
<td>513</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 3.1: PC/P(VDF-HFP) multilayer films under investigation. All multilayer films have a composition of 50/50 and film thickness of 10 µm.
Figure 3.1. a) A schematic showing the dielectric lifetime test and the acoustic emission setup for studying breakdown fracture mechanisms; b) Sample preparation for studying breakdown fracture mechanisms.
Figure 3.2: Dielectric lifetime as a function of layer thickness for PC/P(VDF-HFP) films with various number of layers. The PC, P(VDF-HFP), and 50/50 blend were also included and indicated as the dashed lines. The number next to the dots are the layer number of the film tested. The dielectric lifetime was obtained using a statistical analysis described in reference 3.
Figure 3.3: Cross section images of the 9-layer PC/P(VDF-HFP) film after breakdown at various distances from the breakdown hole. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.
Figure 3.4: Cross section images of the 65-layer PC/P(VDF-HFP) film after breakdown at various distances from the breakdown hole. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.
Figure 3.5: Representative images showing the effect of layer thickness on the type of crazing next to the breakdown hole after dielectric breakdown. Layer thickness for the samples are indicated on the top left corner of each image. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.
Figure 3.6: The craze density as a function of nominal tie layer thickness for PC/P(VDF-HFP) films with various number of layers. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.
Figure 3.7: a.) Types of crazing as a function of PC layer thicknesses for PC/P(VDF-HFP) films with various number of layers for dielectric test. The total film thickness is kept at 10 µm and the applied field is 320 MV/m. b.) Types of crazing as a function of PC layer thicknesses for PC/SAN sheets with various number of layers for mechanical tensile test. The data was from D. Haderski, et al [6].
Figure 3.8: a. ) Electric current profile and b.) acoustic amplitude data for the breakdown event of the 65-layer 50/50 PC/P(VDF-HFP) film; The total film thickness is kept at 10 µm and the applied field is 320 MV/m.
Figure 3.9: Correlation between the acoustic amplitude and the input charge obtained from current profile in the 50/50 PC/P(VDF-HFP) system with various number of layers. The total film thickness is kept at 10 µm and the applied field is 320 MV/m.
Figure 3.10: Effect of layer thickness on the number of acoustic hits during a breakdown event of PC/P(VDF-HFP). The number next to the dots are the layer number of the film tested. The total film thickness is kept at around 10 µm and the applied field is 320 MV/m.
Figure 3.11: Schematic representation of the time evolution of a breakdown event. Black, red, and blue colors represent electrodes, PC layers, and P(VDF-HFP) layers, respectively. Solid green lines are electric current.

More discharges to "self-clearing"

Subsequent internal discharges

Main breakdown hole formation

Hotspot

Breakdown initiation

As-extruded Film

Initiation

Breakdown

Film
References


PART B: FAITUGE TO CREEP PREDICTION IN BIMODAL POLYETHYLENE PIPES
CHAPTER 4

Predicting long-term creep failure of bimodal polyethylene pipe
from short term fatigue tests
Abstract

Short term fatigue testing was used to predict long term creep failure of a bimodal polyethylene (BMPE) pipe with superior creep resistance. The stepwise crack propagation was studied by increasing the $R$-ratio (defined as the ratio of the minimum to the maximum stress intensity factor in the fatigue loading cycle) at 50 °C from 0.1 approaching creep ($R = 1$). Crack growth rate $(\frac{da}{dt})$ was related to the maximum stress intensity factor $K_{1,max}$ and $R$-ratio by a power law relationship

$$\frac{da}{dt} = B'K_{1,max}^4 (1 + R)^{-8.5}.$$  

The correlation in crack growth kinetics allowed for extrapolation to creep fracture from short-term fatigue testing. The temperature dependence of crack growth rate was contained in the prefactor $B'$. A change in slope of the Arrhenius plot of $B'$ at 67 °C indicated that at least two mechanisms contributed to crack propagation, each dominating in a different temperature region. This implied that a simple extrapolation to ambient temperature creep fracture from elevated temperature tests might not be reliable.
1. Introduction

The so-called third generation of polyethylene pipe resins provides exceptional improvements in environmental stress crack resistance, resistance to rapid crack propagation and creep resistance compared to earlier generations. The enhanced performance derives from the molecular architecture of the new resins. The structural origin of the polyethylene fracture toughness is thought to reside in the tie molecules [1,2]. The processes of tie molecule disentanglement and pullout that lead to fracture are severely hampered by incorporation of short chain branches (SCBs) [3,4]. However, in conventional polyethylenes, the SCB content decreases with molecular weight. The SCBs are concentrated in the chains that are least likely to serve as tie molecules. The new resins with bimodal molecular weight distribution redistribute the SCBs to the high molecular weight chains. The SCBs retard disentanglement and pullout of the tie molecules and increase the topological disorder at the crystal lamella surface. The low molecular weight chains are essentially homopolymer. They provide crystalline anchors for the branched tie molecules. The ratio of the high weight average molecular weight chains to the low weight average molecular weight chains ($M_{wH}/M_{wL}$) is 30 or more [5].

The superior creep resistance of BMPE challenges the accelerated tests that are used to predict long term behavior. The PENT test (ASTM F1473) is an elevated temperature test (80°C) that is designed specifically for predicting the long term failure of polyethylene natural gas pipe resins [6,7,8]. However, some of the BMPE resins are reported to have failure times longer than 10,000 hours (>1 year) in the PENT test [9].
Short term fatigue testing is another approach to predicting long-term creep performance [10,11,12]. To accurately predict long-term failure, the creep failure mechanism must be maintained in fatigue while the crack growth rate is substantially enhanced. Tests in which the stepwise crack propagation mode observed in creep is conserved in fatigue show that the failure time at ambient temperature is up to three orders of magnitude shorter in fatigue compared to creep [4,13].

The relationship between fatigue and creep is quantitatively examined by systematically decreasing the dynamic component of fatigue loading. This is accomplished by varying the $R$-ratio (the ratio of $K_{I,\text{min}}$, the minimum stress intensity factor, to $K_{I,\text{max}}$, the maximum stress intensity factor) so that $R$ gradually approaches unity (creep loading). It is convenient to vary the $R$-ratio under conditions of constant mean stress intensity factor $K_{I,\text{mean}}$ or constant $K_{I,\text{max}}$. This approach was previously used to examine the relationship between fatigue and creep in high density polyethylene (HDPE) [14], and in a medium density polyethylene (MDPE) pipe [15]. Stepwise crack propagation was observed in tests under fatigue and creep, and a power law relation described crack growth rate over the entire range of fatigue and creep loading conditions studied

$$\frac{da}{dt} = B'K_{I,\text{max}}^m (1 + R)^n$$

(1)
where \( m = 4 \) for polyethylene and the prefactor \( B' \) and the power \( n \) vary depending on the specific resin. In creep (\( K_1 = K_{1,max} \) and \( R = 1 \)), **equation (1)** reduces the conventional Paris relation for creep

\[
\frac{da}{dt} = BK_1^m
\]  

(2)

where \( B = 2^n B' \). Correspondence between the values of \( B \) obtained from fatigue (**equation (1)**) and the values obtained directly from creep (**equation (2)**) for HDPE at ambient temperature \([14,16]\), and MDPE at 50 °C \([17]\), confirm that short-term fatigue testing can be used to predict long-term creep failure.

The goal of this investigation is to extend the fatigue approach given by **equation (1)** to predict the creep lifetime of a BMPE pipe material. Due to the superior creep resistance of BMPE, an elevated temperature of 50 °C is used. The temperature dependence of fatigue crack growth is also studied in order to predict the lifetime at ambient temperature. Comparisons are made with the previous studies of HDPE and MDPE.
2. Materials and methods

2.1. Specimens

A gas transportation pipe with an outer wall diameter of 32 cm was obtained from the Silver-Line Plastic Pipe Company. The pipe had a wall thickness of 30 mm and a wall thickness to diameter ratio of about 11. The pipe was extruded from carbon black-filled (<4wt%) DOW Continuum DGDA-2490 BK BMPE resin with a reported density of 0.959 kg/m$^3$. The resin was reported to have a PENT (ASTM F1473) lifetime longer than 10,000 hr by The Dow Chemical Company.

The specimens were cut from the real pipe, rather than from compression molded plaques, because it has been found that the thermal history during compression molding strongly affects the fracture kinetics [13]. MF Kanniene et al. [18] reported that pipe field failures occur about equally in both circumferential and radial directions. In addition, A. Shah [19] in our group showed that crack propagation in a non-standard specimen cut from real pipe can be effectively simulated using a standard compact tension specimen. Therefore, standard compact tension specimens with dimensions in accordance with ASTM D5045 were cut parallel to the radius of the pipe so that the crack propagated in the radial direction as shown in Figure 4.1. A thickness of 13 mm ensured plane strain conditions and also was the limit due to the pipe dimensions. V-shaped side grooves 1 mm in depth were cut into the specimen to minimize the plane stress condition near the edge. The notch was prepared in two steps. An initial 9.5 mm cut was made with a band saw on the inner side of the pipe and a final 2.5 mm cut was achieved by
pushing a fresh razor blade at a controlled speed of 1 μm/s. A fresh razor blade was used for each specimen.

2.2. Fatigue tests

Fatigue tests were performed with mechanical fatigue units equipped with a heated air chamber. The mechanical fatigue units were capable of applying a stable (±0.5N) and accurate sinusoidal load in a fatigue loading cycle. The temperature in the chamber was maintained at 50 °C for most of the fatigue tests. The mean stress intensity, $K_{I,\text{mean}}$, defined as the average of the maximum stress intensity, $K_{I,\text{max}}$, and the minimum stress intensity, $K_{I,\text{min}}$, was varied from 0.65 to 0.95 MPa(m)$^{1/2}$. The $R$-ratio, defined as $K_{I,\text{min}}/K_{I,\text{max}}$, was also varied. All the fatigue experiments were performed at a frequency of 1 Hz. The applied load, crosshead displacement and time were recorded by computer every 1000 s during the tests. A manual zoom macro lens attached to a monochrome video camera was used to observe the crack tip and to measure the crack depth during crack propagation. The camera was focused on the root membrane formed at the crack tip. The output of the camera was routed through a VCR to a black and white video monitor, and when necessary, the experiment was recorded onto a videocassette for later analysis.

Additional tests were performed at 21, 40, 50, 60, 70, 80, 90 °C. In these tests, $K_{I,\text{mean}}$ was varied from 0.75 to 0.40MPa(m)$^{1/2}$ in order to conserve stepwise discontinuous crack propagation at each temperature. All of the tests were performed at a frequency of 1Hz.
After each experiment, the fracture surfaces were examined under the optical microscope. Features were best resolved in reflection mode using normal incidence illumination. Some of the fatigue fracture surfaces were coated with 10 nm of gold and examined in a JOEL JSM-6510LV scanning electron microscope (SEM). The accelerator voltage did not exceed 10 kV in order to minimize radiation damage to the specimens.

Some specimens were fatigued for a predetermined number of cycles, removed from the fatigue unit, and sectioned using a low speed Isomet diamond knife to obtain a side view of the craze damage zone ahead of the crack tip. The sectioned pieces were coated with 10 nm of gold and viewed under a SEM in the secondary electron imaging (SEI) mode.

2.3. Mechanical Tensile Testing and Dynamic Mechanical Thermal Analysis

Dog bone shape specimens in accordance to the geometry of ASTM D1708 were cut from plaques compression molded directly from pipe. The plaques were rapidly cooled using the conditions that have been shown to best reproduce the crack-resistant properties of pipe [13]. 1000% strain rate was chosen for the tensile testing. The stress-strain response was determined with an MTS Alliance RT/30 testing machine. Five repetitions were done for tensile testing.

The dynamic mechanical response was determined with a Rheometrics DMA Q800 in the tensile mode. The dynamic measurement was subject to a small strain amplitude of 0.2% at a sample length of 15 mm (distance between the clamps) and a small static force of 0.01 N at a sample geometry of $15\times8\times0.2$ mm$^3$. 
(length×width×thickness) to ensure tension mode. The experiments were performed at frequencies of 0.1, 1, 10, and 50 Hz. The temperature was increased at a rate of 3 K/min.

The frequency dependence of the maximum in the tensile loss modulus $E''$ was used to determine the activation energy $E_a$ of the $\alpha$-relaxation according to the Arrhenius equation.

$$f(T) = Ae^{\frac{E_a}{RT}}$$  \hspace{1cm} (3)

$$\ln f(T) = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln(A)$$  \hspace{1cm} (4)
3. Results and discussion

3.1. Effect of $R$-ratio on slow crack growth

The effect of R-ratio on fatigue crack propagation at 50 °C was probed under constant $K_{I,\text{mean}} = 0.75 \text{ MPa(m)}^{1/2}$. The time dependence of the maximum crosshead displacement is shown in Figure 4.2 for $R = 0.1$, 0.2, and 0.3 and the corresponding fracture surfaces are shown in Figure 4.3. The typical stepwise character of crack propagation, which is due to sequential formation and fracture of a crack tip damage zone, was easily observed on the crosshead displacement plot and on the fracture surface for $R = 0.1$. The plateau regions of the displacement curve corresponded to crack arrest periods, during which a craze damage zone formed to alleviate the stress concentration at the crack tip [19]. Failure of the damage zone began with fracture of the craze fibrils followed by fracture of the crack tip membrane. A sharp step in the crosshead displacement curve occurred when the membrane fractured and the crack jumped through the fractured craze to begin a new craze damage zone. Remnants of the broken membranes produced the periodic striations on the fracture surface.

When the $R$-ratio was increased to 0.2 or 0.3, the step jumps were not as obvious on the crosshead displacement curve and well defined striations were not as apparent on the fracture surface under $K_{I,\text{mean}} = 0.75 \text{ MPa(m)}^{1/2}$. To confirm the stepwise nature of crack propagation, fatigue experiments under $K_{I,\text{mean}} = 0.75 \text{ MPa(m)}^{1/2}$ and $R = 0.2$ were stopped after a prescribed number of cycles and the specimens were sectioned to obtain side views of the damage zone,
Figure 4.4. After about 10% of the first step lifetime (point a in Figure 4.4), a typical damage zone for stepwise crack propagation in polyethylene was observed [19]. It consisted of a main craze with a continuous membrane at the crack tip. Subsidiary shear crazes emerged from the membrane region at an angle of about 30º with respect to the primary craze. The crack tip main craze had reached 80% of the first step length after about 10% of the first step lifetime. At about 90% of the craze lifetime (point b in Figure 4.4) examination of the crack tip opening revealed that the membrane ahead of the crack tip had formed some elliptical holes, and voids could be seen behind the membrane. A side view confirmed that part of the craze had fractured but the membrane remained intact. After the shallow step in the displacement curve (point c in Figure 4.4), the membrane was fully ruptured, the main craze was completely broken, and a new craze damage zone had begun to form. From these observations, it appeared that the membrane and the main craze fractured concurrently. As a consequence, the stepwise propagation was not revealed as clearly in the displacement curve or on the fracture surface. The stepwise crack growth through a crack tip craze zone was similarly confirmed for all the $R$-ratios studied, Table 4.1. Despite the modification in fracture mode from sequential fracture of the main craze and the membrane to concurrent fracture, the damage zone, as characterized by the length of the main craze and shear crazes, followed the same dependence on loading parameters, and the crack growth rate followed the same kinetics [15]. The length of the craze damage zone as measured from the fracture surfaces and the side views was about 1 mm for $R$-ratios of 0.1, 0.2 and 0.3 under $K_{I, \text{mean}} = 0.75$ MPa(m)$^{1/2}$. 
An additional series of fatigue experiments was performed at constant \( K_{I,\text{max}} = 1.17 \text{ MPa(m)}^{1/2} \) and \( R \)-ratios of 0.1, 0.2 and 0.3, **Figure 4.5**. Both the first step lifetime and the overall lifetime increased significantly with increasing \( R \)-ratio. The step jumps were clearly visible in the displacement curve for \( R = 0.1 \). However the step jumps were not as apparent in curves for \( R \)-ratios of 0.2 and 0.3. Nevertheless, it was confirmed from the fracture surfaces and side views of the damage zone that the stepwise crack propagation mode was conserved for all \( R \)-ratios under constant \( K_{I,\text{max}} = 1.17 \text{ MPa(m)}^{1/2} \).

Increasing \( K_I \) resulted in ductile fracture (\( R = 0.1, K_{I,\text{mean}} = 0.85, 0.95 \text{ MPa(m)}^{1/2} \) [20], or crack propagation through a shear craze (\( R=0.2, K_{I,\text{mean}} = 0.80, 0.84, 0.91 \text{ MPa(m)}^{1/2} \) [15], instead of stepwise propagation through a main craze, **Table 4.1**. Fatigue under lower \( K \) or higher \( R \)-ratio resulted in impractically long lifetimes. Data for \( R \)-ratios of 0.1, 0.2, 0.3 and 0.4 obtained at intermediate \( K \) values where stepwise crack propagation was observed were used to predict fatigue failure at higher \( R \)-ratios and creep failure (\( R = 1 \)) in BMPE.

Analysis of experiments performed under constant \( K_{I,\text{max}} \) and constant \( K_{I,\text{mean}} \) revealed that the crack jump length was determined primarily by \( K_{I,\text{mean}} \). The dependence of damage zone length on \( K_{I,\text{mean}} \) rather than on \( K_{I,\text{max}} \) resulted from the time scale of craze growth. The time for completion of a single fatigue loading cycle was negligible compared to the duration of craze growth. Therefore the stress that controlled the craze length was the average stress, i.e. the mean stress.
The Dugdale model is widely used to relate craze zone length to the applied stress intensity factor

\[ l = \frac{\pi K_1^2}{8 \sigma_y} \]  \hspace{1cm} (5)

where \( K_1 \) is the stress intensity factor for mode I and \( \sigma_y \) is the yield stress which depends on strain rate and temperature. Because the craze length was controlled by \( K_{1,\text{mean}} \), this quantity was used to represent the stress intensity in eq (1). The step length \( l \) was shown to be proportional to \( K_{1,\text{mean}}^2 \) for all \( R \)-ratios studied, Figure 4.6. From the linear fit in Figure 4.6, the yield stress for BMPE at 50 °C was 14.6 MPa, which agreed well with the measured yield stress of 16 MPa.

3.2. Kinetics of fatigue crack propagation

The crack growth rate \((da/dt)\) for stepwise crack propagation is conventionally calculated from the step jump length \((da)\) and the duration of the step jump \((dt)\). For a given \( R \)-ratio, the dependence of crack growth rate in fatigue on the stress intensity factor is usually described by the Paris relation

\[ \frac{da}{dt} = A\Delta K_1^m \]  \hspace{1cm} (6)

where \( \Delta K_1 = K_{1,\text{max}} - K_{1,\text{min}} \) in the fatigue cycle and the prefactor \( A \) and the power \( m \) are material constants. In numerous studies, the power \( m \) was determined to be independent of temperature and \( R \)-ratio, and equal to 4 for polyethylene resins
The prefactor $A$ depends on the specific resin and is a measure of the resistance to fatigue crack propagation. A plot of log ($da/dt$) versus log $\Delta K_1$ for the various $R$-ratios shows that the fatigue data conform to equation (4) with $m = 4$, Figure 4.7a. However, the Paris relation and other Paris-type relations where stress intensity factor is represented by $\Delta K_1$ are not applicable to creep testing where $\Delta K_1 = 0$.

For fatigue at constant temperature and frequency, there are five loading variables that can be used to describe the fatigue cycle: $R$-ratio, $\Delta K_1$, $K_{I,\text{max}}$, $K_{I,\text{min}}$ and $K_{I,\text{mean}}$, however only two of these are independent. Because the Paris relation relates crack growth rate only to $\Delta K_1$, one of the other variables, usually the $R$-ratio, is held constant. In order to express data for various $R$-ratios in a form that could be extrapolated to creep loading ($R = 1.0$), the dependencies on $K_{I,\text{max}}$ and $K_{I,\text{mean}}$ were determined independently. Figure 4.8a shows log ($da/dt$) for the first step jump plotted versus log $K_{I,\text{max}}$ for $K_{I,\text{mean}} = 0.75 \text{ MPa(m)}^{1/2}$. A linear relationship was obtained over the entire range of $K_{I,\text{max}}$ with a slope of 12.5. Increasing $K_{I,\text{max}}$ decreased $dt$ without affecting $da$, and therefore $da/dt$ was strongly dependent on $K_{I,\text{max}}$. Similarly, the effect of $K_{I,\text{mean}}$ was obtained by plotting log ($da/dt$) versus log $K_{I,\text{mean}}$ for tests under $K_{I,\text{max}} = 1.17 \text{ MPa(m)}^{1/2}$, Figure 4.8b. Again, a linear relationship was observed over the entire range of $K_{I,\text{mean}}$, in this case with a slope of -8.5. Increasing $K_{I,\text{mean}}$ increased the step jump length ($da$), but also increased the step jump lifetime ($dt$). The net result was that the crack growth rate was less dependent on $K_{I,\text{mean}}$ than on $K_{I,\text{max}}$. 
The dependencies of crack growth rate on $K_{I,\text{max}}$ and $K_{I,\text{mean}}$ led to a power law relationship for crack growth rate

$$\frac{da}{dt} = BK_{I,\text{max}}^{12.5} K_{I,\text{mean}}^{-8.5}$$ (7)

where the prefactor $B$ is a material constant that depends on temperature and frequency. In creep ($K_{I,\text{max}} = K_{I,\text{mean}} = K_i$) equation (7) reduces to the conventional Paris relation for creep in polyethylene as given by

$$\frac{da}{dt} = BK_{i}^4$$ (8)

For convenience, equation (7) was reformulated as

$$\frac{da}{dt} = B'K_{I,\text{max}}^4 (1 + R)^{-8.5}$$ (9)

where $B' = 2^{8.5} B$. Equation (9) follows a general form that has been observed for other polyethylene resins [14,15,17]

$$\frac{da}{dt} = B'K_{I,\text{max}}^4 (1 + R)^n$$ (10)

where the prefactor $B'$ and the power $n$ depend on the specific resin. Although $B'$ depends on temperature, the power $n$ appears to be independent of temperature [15, 17]. The term $(1+R)^n$ is a measure of the sensitivity of the resin to $R$-ratio in fatigue. The prefactor $B'$ is a temperature-dependent material parameter. In creep, equation (10) reduces to equation (8).
All the fatigue data for BMPE are plotted according to equation (7) in Figure 4.9. The data followed a straight line fit with a slope of 1. The prefactor $B'$ extracted from the linear regression was $5.0 \times 10^{-5} \text{mm/m}^2 (s)^{-1} (\text{MPa}^{-4})$, which gave a creep prefactor $B = 1.4 \times 10^{-8} \text{mm/m}^2 (s)^{-1} (\text{MPa}^{-4})$. The Paris plots for $R$-ratios as high as 0.9 were calculated for $m = 4$ by rearranging equation (9) using the extracted value of $B'$

$$\frac{da}{dt} = \left[ B'(1 - R)^{-4} (1 + R)^{-8.5} \right] \Delta K_i$$

(11)

Although the Paris plots for lower $R$-ratios appeared to follow a single linear relationship, substantial deviation was predicted as the $R$-ratio increased approaching creep ($R = 1$), Figure 4.7b.

3.3. Temperature dependence of the prefactor $B'$

The temperature dependence of the crack growth rate is contained in the prefactor $B'$. The crack growth rate was obtained at various temperatures between 21 and 90 °C using values of $K_{\text{I,mean}}$ and $R$-ratio that produced stepwise crack propagation, Table 4.2. The prefactor $B'$ was calculated from equation 9 using the crack speed ($da/dt$) of the first crack jump and the fatigue loading conditions. An Arrhenius plot of $\ln B'$ versus $1/T$ was constructed, Figure 4.10. The data were described by two straight lines with a slope change at 67 °C. The extracted activation energies were 89 kJ(mol)$^{-1}$ for the high temperature region and 22 kJ(mol)$^{-1}$ for the low temperature region. A similar slope change was observed in the temperature dependence of $B'$ for a conventional medium density.
polyethylene pipe resin (MDPE) with similar activation energies of 125 kJ(mol)$^{-1}$ and 25 kJ(mol)$^{-1}$ [15]. The high temperature process was related to the $\alpha$-relaxation. The activation energy obtained from Figure 4.10 correlated with the activation energy of the $\alpha$-relaxation, and the temperature of the slope change in the Arrhenius plot coincided with the temperature of the $\alpha$-relaxation as defined by DMTA. It is noteworthy that both the slope change and the $\alpha$-relaxation temperature for BMPE occurred at a temperature about 12 °C higher than for MDPE. Below 67 °C, a much lower activation energy was obtained. The low temperature process was ascribed to the amorphous entanglement network.

For the lifetime prediction, the lifetime depends on the pipe wall thickness and the stress intensity that the pipe is subject to. If the pipe wall thickness and the stress intensity are known, then the lifetime of the bimodal pipe can be calculated using Equation 1 (a modified Paris Law). The modified Paris Law parameters and the creep prefactors for various polyethylene resins are compared in Table 4.3. By comparing the creep factors, $B$, for different pipes, the relative performance of those pipes can be ranked. The comparison of $n$ indicated that the dependence of fatigue on $R$-ratio as expressed in the parameter $n$ became stronger as the resin became more resistant to slow crack growth. A qualitative comparison made in a previous study also suggested that fatigue was more effective in accelerating slow crack growth in resins with higher creep resistance [13]. Our longest experiment on first steplifetime at the condition of $R=0.4$, $K_{\text{L,mean}}=0.70\text{MPa(m)}^{1/2}$ for BMPE took about one month (7,00hrs). The PENT test would have taken around a year or more (10,000hrs) to make this prediction.
The creep crack growth rate in BMPE is predicted to be more than an order of magnitude slower than in MDPE. The structural origin of the fracture toughness of polyethylene is thought to reside in the interlamellar tie molecules. Upon loading, the tie molecules stretch as they take up the applied stress and form taut links between crystals. This leads to local yielding and breakup of the crystals, and formation of highly oriented fibrils. These fibrils form the damage zone at the crack tip. For creep and fatigue, fibril fracture is ascribed primarily to chain disentanglement, which requires chain slippage and pullout [13]. Both the density of tie molecules and the rate of chain pullout depend on the molecular weight and the branch content. As molecular weight increases, more tie chains form and more time is required to disconnect a tie chain from a crystal. Introducing chain branches dramatically improves the fracture toughness. Short branches act as protrusions along the chain that significantly hamper chain disentanglement. By impeding a tie chain from sliding through a crystal, the short chain branches considerably increase the disentanglement time. In conventional polyethylene copolymers, the chain branch content decreases with molecular weight. Thus, the branch content is highest in the chains that are least likely to be involved in intercrystalline links. One way to make the branches more efficient is to redistribute them to the high molecular weight chains. This approach is realized in BMPE. The lower molecular weight chains are essentially homopolymer. They increase the crystallinity, thereby providing more crystalline anchors for the tie molecules. The higher molecular weight copolymer chains provide the tie chains that link the crystals. The short chain branches hamper slippage and pullout.
4. Conclusions

The exceptionally high resistance of modern BMPE pipe resins to slow crack growth challenges the practicality of conventional creep failure tests for predicting the service lifetime. Short term fatigue testing is another approach to predicting long-term creep performance. The fatigue failure time can be substantially shorter than the failure time in standard creep tests especially for resins that exhibit a high resistance to slow crack growth. This study was undertaken to determine whether a fatigue-to-creep correlation previously developed for an earlier generation of pipe resins is applicable to BMPE pipe resins, and to ascertain whether a lifetime prediction can be obtained within a reasonable time period. The stepwise mechanism of fatigue crack propagation at 50 °C was verified and the crack growth rate was related to the maximum stress and $R$-ratio by a power law relation. The dependence on $R$-ratio was a measure of the fatigue acceleration. Comparison with results for other polyethylene resins indicated a stronger dependence on $R$-ratio as the resin became more resistant to slow crack growth. Thus, fatigue was more effective in accelerating slow crack growth in resins with higher creep resistance. The temperature dependence of slow crack growth followed an Arrhenius relation with a change in slope at 67 °C. The change in slope indicated that extrapolation of creep behavior at temperatures above the $\alpha$-relaxation to ambient temperature requires considerable caution.
Table 4.1
Experimental matrix that was designed to get the stepwise mechanism in order to construct Paris plot at different R-ratios.
Experiment was stopped before the sample was completely ruptured.
<table>
<thead>
<tr>
<th>Kmax (MPa(m)(^{1/2}))</th>
<th>KImean (MPa(m)(^{1/2}))</th>
<th>First step length (mm)</th>
<th>First step lifetime (x10(^3)s)</th>
<th>Prefactor B' (mm(m(^2))(s(^{-1})(MPa(^{-4})×10(^5)))</th>
<th>Yield stress* (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.75</td>
<td>1.36</td>
<td>0.93</td>
<td>0.73</td>
<td>0.40</td>
</tr>
<tr>
<td>0.1</td>
<td>1.77</td>
<td>0.31</td>
<td>0.93</td>
<td>0.40</td>
<td>0.00</td>
</tr>
<tr>
<td>0.1</td>
<td>2.72</td>
<td>0.72</td>
<td>1.60</td>
<td>0.39</td>
<td>0.00</td>
</tr>
<tr>
<td>0.1</td>
<td>2.03</td>
<td>0.96</td>
<td>1.81</td>
<td>0.85</td>
<td>1.00</td>
</tr>
<tr>
<td>0.1</td>
<td>2.41</td>
<td>0.80</td>
<td>1.36</td>
<td>0.75</td>
<td>0.00</td>
</tr>
<tr>
<td>0.1</td>
<td>2.04</td>
<td>0.80</td>
<td>1.36</td>
<td>0.35</td>
<td>0.00</td>
</tr>
<tr>
<td>0.1</td>
<td>1.72</td>
<td>0.82</td>
<td>1.86</td>
<td>0.75</td>
<td>0.00</td>
</tr>
<tr>
<td>0.1</td>
<td>1.04</td>
<td>1.01</td>
<td>1.82</td>
<td>0.00</td>
<td>1.00</td>
</tr>
<tr>
<td>0.1</td>
<td>1.39</td>
<td>0.72</td>
<td>1.85</td>
<td>0.85</td>
<td>0.00</td>
</tr>
<tr>
<td>0.1</td>
<td>2.08</td>
<td>0.95</td>
<td>1.75</td>
<td>0.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*Calculated from equation (5).

**Table 4.2** Experimental matrix for temperature dependence of stepwise crack growth.
<table>
<thead>
<tr>
<th>Reference</th>
<th>$B' = \frac{n}{n-1} (mm^2/s-1(MPa)^{-4} \times 10^{5})$</th>
<th>Creep Parameter $B$</th>
<th>$\nu$</th>
<th>$m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.28</td>
<td>0.40</td>
<td>0.05</td>
<td>4</td>
</tr>
<tr>
<td>15</td>
<td>0.0255</td>
<td>0.72</td>
<td>0.06</td>
<td>4</td>
</tr>
<tr>
<td>17</td>
<td>0.026</td>
<td>1.7</td>
<td>0.06</td>
<td>4</td>
</tr>
</tbody>
</table>

Generalized Modified Paris Law: $u' = \frac{B' I_{max} (1 + B)}{B'}$

Table 4.3 Comparison of modified Paris law and creep factor for different PE (HDPE, MDPE, and BMPE).
Fig. 4.1  Geometry of the compact tension specimens cut from the pipe wall
Fig. 4.2  Maximum crosshead displacement versus log time for fatigue tests at 50 °C and $K_{I,\text{mean}}=0.75 \text{ MPa(m)}^{1/2}$ at different $R$-ratios ($R=0.1, 0.2, 0.3$).
Fracture surfaces of the specimens tested in Figure 2.2 under $K_{1,\text{mean}}=0.75\text{MPa(m)}^{1/2}$ and $R=0.1$, 0.2 and 0.3. (Only the data for the first step was used to construct modified Paris Law)
Fig 4.4  Side views of the damage zone after a prescribed number of cycles for $R=0.2$, $K_{1,\text{mean}}=0.75 \text{ MPa(m)}^{1/2}$. (a) 86,000 cycles; (b) 420,000 cycles; and (c) 470,000 cycles.
Fig 4.5  Maximum crosshead displacement versus log time for fatigue tests at 50 °C and $K_{I,max}=1.17 \text{ MPa(m)}^{1/2}$ at different $R$-ratios ($R=0.1, 0.2, 0.3$).
Fig. 4.6 Effect of $K_{I,\text{mean}}$ on the first step jump length for fatigue tests at $R=0.1$, 0.2, 0.3 and 0.4.
Fig. 4.7  Paris plots of crack growth rate \((\frac{da}{dt} \text{ versus } \Delta K_i)\) at 50 °C for different \(R\)-ratios. (a) Measured values; and (b) crack growth rate for higher \(R\)-ratios calculated from equation (11).
Fig. 4.8  Formulation of the modified Paris plot based on the empirical dependence of crack growth rate on (a) $K_{I,\text{max}}$ (constant $K_{I,\text{mean}}=0.75$ MPa(m)$^{1/2}$); and (b) $K_{I,\text{mean}}$ (constant $K_{I,\text{max}}=1.17$ MPa(m)$^{1/2}$).
Fig. 4.9  Fit of BMPE test data at 50 °C to the modified Paris law.
Fig. 4.10  Arrhenius plot of the temperature-dependent prefactor $B'$ for BMPE.
Reference

BIBLIOGRAPHY

Chapter 1


Chapter 2


**Chapter 3**


