CASE WESTERN RESERVE UNIVERSITY
SCHOOL OF GRADUATE STUDIES

We hereby approve the thesis/dissertation of

Shanzuo Ji

candidate for the Ph.D. degree *.

(signed)  Prof. Eric Baer

(Chair of the committee)

Prof. Alexander Jamieson

Dr. Andrew Olah

Prof. Donald Schuele

(date)  8/25/2015

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

To my parents, Meizhu, and Baosuan, and my wife, Shuang
TABLE OF CONTENTS

LIST OF TABLES ............................................................................................................ ii

LIST OF FIGURES ......................................................................................................... iii

ACKNOWLEDGEMENTS .............................................................................................. vii

ABSTRACT ...................................................................................................................... ix

CHAPTER 1 A BIO-INSPIRED POLYMERIC GRADIENT REFRACTIVE INDEX (GRIN) HUMAN EYE LENS .......................................................................................... 1

CHAPTER 2 POLYMERIC NANOLAYERED GRADIENT REFRACTIVE INDEX (GRIN) LENSES: TECHNOLOGY REVIEW AND INTRODUCTION OF SPHERICAL GRIN BALL LENSES ................................................................................. 26

CHAPTER 3 CORRELATION BETWEEN EXPERIMENTAL AND SIMULATED SHAPE DEFORMATION OF A BIO-INSPIRED TUNABLE POLYMER LENS. 68

CHAPTER 4 TRIPLE SHAPE MEMORY POLYMER FILMS CREATED BY FORCED ASSEMBLY MULTILAYER FILM COEXTRUSION ............................ 88

BIBLIOGRAPHY ......................................................................................................... 120
LIST OF TABLES

CHAPTER 1

Table 1.1  Polynomial coefficients of an “Age=5” human eye lens used in Code V model ........................................................................................................................................................................ 17

Table 1.2  Polynomial coefficients of the bio-inspired anterior and posterior lenses . 18

CHAPTER 2

Table 2.1  Properties of GRIN lenses of aquatic creatures and air-dwelling animals. 51

Table 2.2  Geometric parameters of “Age=5” and bioinspired human eye lenses. ..... 52

Table 2.3  Design specification for the f/2.25 GRIN lens.................................................. 53

CHAPTER 4

Table 4.1  Characteristics of 257 layered PU/PVAc/EVA multilayered films .......... 106

Table 4.2  Fixity and recovery ratios calculated for triple shape memory 257 layered PU/EVA/PVAc (20/60/20) multilayered films with different thickness. All of the numbers represent the percentage (%).................................................. 107

Table 4.3  Fixity and recovery ratios calculated for triple shape memory 100 μm 257 layered PU/EVA/PVAc multilayered films with different composition. All of the numbers represent the percentage (%).................................................. 108
LIST OF FIGURES

CHAPTER 1

Figure 1.1 Refractive index distribution of the anterior and posterior lenses of an “Age=5” human eye lens represented in the Diaz’s and Code V models. ........................................ 19

Figure 1.2 Design of a bio-inspired polymeric gradient refractive index (GRIN) human eye lens. a) Fabrication illustration to create the bio-inspired GRIN anterior and posterior lenses. b), refractive index distribution of “Age=5” human eye and buildable bio-inspired GRIN lenses. c), RMS wave error of bio-inspired GRIN lenses with two different sets of aspheric coefficient for anterior and posterior lenses simulated by Zemax software: (Top) Q_{anterior}=-5, and Q_{posterior}=-4; (Bottom)Q_{anterior}=0.5, and Q_{posterior}=-5. ........................................ 20

Figure 1.3 Stacking recipes of anterior (left) and posterior (right) lens sheets with buffer layers. ....................................................................................................................... 21

Figure 1.4 Refractive index distribution of anterior (left) and posterior (right) lens sheets measured by µATR-FTIR. ................................................................. 22

Figure 1.5 Fabricated lens images (a and d) and measured geometry surface profiles (b/c and e/f) of the aspheric anterior and posterior bio-inspired human eye GRIN lenses. ............................................................. 23

Figure 1.6 Comparison plot of experimentally measured and simulated wavefront for as built bio-inspired aspheric posterior lenses. a-b, Measured (a) and numerical simulated (b) wavefront of aspheric posterior GRIN lens. c-d, Measured (c) and numerical simulated (d) wavefront of aspheric posterior PMMA reference lens. Vertical axis in units of waves (633nm). Planar values are unit less measures of aperture across the wavefront sensor. ....................... 24

Figure 1.7 Experimentally obtained image of a Case Western Reserve University logo taken through a bio-inspired “age=5” human eye GRIN lens. The logo was placed about 33 cm from a bare CCD camera. The Case logo was laser printed onto standard letter paper, illuminated by an external light source, and imaged onto the camera by a bio-inspired “age=5” human eye GRIN lens. ........................................................................ 25
CHAPTER 2

Figure 2.1  (a) Layout of two component forced assembly multilayer system: extruders, polymer melt pumps, feedblock, multilayering dies, surface layer extruder (not shown), and exit die. Layer multiplication from two to four layers is illustrated by cutting, squeezing, spreading, and recombining polymer melt streams. (b) Procedure to build a GRIN lens: stacking, consolidation, shaping, and diamond turning................................................................. 54

Figure 2.2  (a) Films with tailored refractive index. (b) Refractive indices of PMMA/SAN17 films.......................................................... 55

Figure 2.3  A schematic showing the flexibility of the nanolayered GRIN technique of making sheets with different refractive index distributions: linear and/or non-linear. ......................................................................................... 56

Figure 2.4  Hierarchical layered structure of the human eye lens ......................... 57

Figure 2.5  (a) Process schematic for producing anterior and posterior bio-inspired GRIN lenses. Refractive index distribution of the “Age=5” human eye lens (anterior and posterior) represented in the Diaz’s and Code V models. (b) Refractive index plot of the designed bio-inspired GRIN lens in comparison to the Age=5 lens. (c) RMS wave error of bio-inspired GRIN lenses with two different aspheric coefficients simulated by Zemax software: (Top Point) Q anterior=-5, and Q posterior=-4; (Bottom Point) Q anterior=0.5, and Q posterior=-5. .................................................................................................................. 58

Figure 2.6  Images of bio-inspired GRIN lenses (Top) and the corresponding cross-sectional profiles of anterior and posterior GRIN lenses (Bottom). ........ 59

Figure 2.7  Plots of experimentally measured and simulated wavefronts for as built bio-inspired aspheric posterior lenses. (a) Measured data of GRIN lens (b) Numerically simulated values of GRIN lens (c) Measured data of PMMA reference lens (d) Numerically simulated data of PMMA reference lens. Vertical axis in units of waves (633nm). Planar values are unit less measures of aperture across the wavefront sensor................................................................. 60

Figure 2.8  A Case Western Reserve University logo image that was focused using a bio-inspired “age=5” human eye GRIN lens and captured with a CCD camera. ........................................................................................................ 61
Figure 2.9  Refractive index distribution of the PMMA/SAN17 polymer GRIN lens (in the z direction) ................................................................. 62

Figure 2.10  (a) Experimental setup of minimum spot size measurement. (b) Spot size of glass lens and PMMA/SAN17 polymer GRIN lens. (c) 1D intensity plot of focal spot image. ................................................................. 63

Figure 2.11  USAF test chart imaged through a PMMA/SAN17 polymer GRIN lens (left) and a glass lens (right). ................................................................. 64

Figure 2.12  (a) Schematic representation of a hemispherical GRIN lens. (b) Refractive index distribution design of a hemispherical GRIN lens in the Z direction. (c) Procedure of thermoforming a hemispherical GRIN lens. (d) Cross-sectional profile of the hemispherical GRIN lens acquired with placido-cone topography. ................................................................. 65

Figure 2.13  (a) Experimental setup for focal length measurements. (b) Focal length for PMMA control and hemispherical GRIN lenses as a function of distance between two pinholes: Hemispherical GRIN lens (Triangle) and PMMA control lens (Square). ................................................................. 66

Figure 2.14  Method of adhering two hemispherical GRIN lenses (Top). Image of a GRIN ball lens (Bottom). ................................................................. 67

CHAPTER 3

Figure 3.1  Schematic representation of producing a tunable polymer lens (a); design (b) and image (c) of the compression unit; and schematic of the mechanism for variable focal length (d). ................................................................. 81

Figure 3.2  The measured lens curvature and calculated focal length of the tunable lens in the first and second compression cycles as a function of distance: (a) 0.1mm; (b) 0.2mm; (c) 0.3mm; and (d) 0.4mm. ................................................................. 83

Figure 3.3  (a) the first loading and unloading cycle and the four subsequent cycles of lens materials EO at a strain of 10%; (b) Experimental and simulated stress-strain curves for the elastomer material. The simulation was performed using Mooney-Rivlin model. ................................................................. 84

Figure 3.4  Comparison of the deformed lens shapes generated by the experiments and simulation. ................................................................. 85
Figure 3.5  Total mechanical strain intensity results for the lenses with compression distances of (a) 0.1 mm, (b) 0.2 mm, (c) 0.3 mm, and (d) 0.4 mm. ........... 87

CHAPTER 4

Figure 4.1  A typical schematic layout of 3-component forced assembly multilayer film coextrusion system utilized to fabricate shape memory polymer materials. .................................................. 109

Figure 4.2  Definition of shape fixity and recovery ratios in triple shape memory polymer. ................................................................. 110

Figure 4.3  AFM images of continuous PU/EVA/PVAc layer structure in 100 μm multilayer films at different composition: a) 20/60/20; b) 15/65/20; and c) 10/60/30. ................................................... 111

Figure 4.4  Quantitative evaluation of triple shape memory properties of 4 mils 257 Layered 20/60/20 PU/EVA/PVAc Films by DMTA. ......................... 112

Figure 4.5  5 consecutive triple shape memory testing of 4 mils 257 layered 20/60/20 PU/EVA/PVAc multilayer films. ............................. 113

Figure 4.6  Effect of layer thickness on shape fixity ratio (a) and shape recovery ratio (b) of 20/60/20 PU/EVA/PVAc films in the first temporary shape. .......... 114

Figure 4.7  Effect of layer thickness on shape fixity ratio (a) and shape recovery ratio (b) of 20/60/20 PU/EVA/PVAc films in the second temporary shape. .......... 115

Figure 4.8  Strain evolution of different compositional PU/EVA/PVAc multilayer films in 5 consecutive thermo-mechanical cyclic testing. ..................... 116

Figure 4.9  Effect of composition on shape fixity ratio (a) and recovery ratio (b) of PU/EVA/PVAc multilayered films in the first temporary shape. ........... 117

Figure 4.10  Effect of composition on shape fixity ratio (a) and recovery ratio (b) of PU/EVA/PVAc multilayered films in the second temporary shape. ........... 118

Figure 4.11  Visual demonstration of triple shape memory properties of 100μm 257 layered PU/EVA/PU (20/60/20) multilayered films. .......................... 119
ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisors, Professor Eric Baer and Professor Anne Hiltner for their guidance, patience, encouragement, and support throughout my graduate study. They have taught me how to do good research and how to enjoy the fun of research. I would also like to thank my dissertation committee, Prof. Alexander Jamieson, Dr. Andrew Olah, and Prof. Donald Schuele, for their time, support, and advice.

I would also like to thank all the past and present members in Baer-Hiltner group for their collaboration, support, and friendship: Yijian Lin, Zheng Zhou, Haopeng Wang, Hyunmin Song, Jong Keum, Devang Khariwala, Deepak Langhe, Matt Mackey, Joel Carr, Chuan-yar Lai, Shannon Armstrong, Guojun Zhang, Madhavi Vadlamudi, Jia Wang, Kezhen Yin, Cong Zhang, James Aldridge, Arifur Rahman, Sunsheng Zhu, Zhenpeng Li, Jingxing Feng, Yuanzhe Liang, Xinting Wang, Ci Zhang, Patricia Simmons, Pamela Bligh-Glover, and Mariah Miles. Special thanks to Yankai Yang and Michael Ponting for their mentorship during my first several years in graduate school. The important discussions from Professor Lionel Flandin (Université de Savoie) and Howard Fein (PolymerPlus) are appreciated.

I would like to thank my wonderful wife, Shuang Qin, for her love, dedication, understanding, and companionship. Finally, I would like to thank my parents Meizhu Ye and Baosuan Ji, my brother Shangkao Ji and my sister Yeru Ji, for their constant encouragement, unflinching support and love. Without them, I would not be the person I am today.
Last but not least, the generous financial support from the Defense Advanced Research Projects Agency (Contract HR0011-10-C-0110) and the NSF Center of Layered Polymeric Systems (Grant DMR-0423914) are gratefully acknowledged.
CHAPTER 1: A synthetic polymeric lens was designed and fabricated based on a bio-inspired, “Age=5” human eye lens design by utilizing a nanolayered polymer film-based technique. The internal refractive index distribution of an anterior and posterior GRIN lens were characterized and confirmed against design by μATR-FTIR. 3D surface topography of the fabricated aspheric anterior and posterior lenses was measured by placido-cone topography and exhibited confirmation of the desired aspheric surface shape. Furthermore, the wavefronts of aspheric posterior GRIN and PMMA lenses were measured and simulated by interferometry and Zemax software, respectively. Their results show that the gradient index distribution reduces the overall wavefront error as compared a homogenous PMMA lens of an identical geometry. Finally, the anterior and posterior GRIN lenses were assembled into a bio-inspired GRIN human eye lens through which a clear imaging was possible.

CHAPTER 2: A nanolayered polymer films approach to designing and fabricating gradient refractive index lens (GRIN) lenses with designer refractive index distribution profiles and an independently prescribed lens surface geometry has been demonstrated to produce a new class of gradient index optics. This approach utilized nanolayered polymer composite materials from polymethylmethacrylate (PMMA) and a styrene-co-acrylonitrile
copolymer (SAN) with a tailorable refractive index intermediate to bulk materials to fabricate discrete gradient refractive index profile materials. A process to fabricate nanolayered polymer GRIN optics from these materials through thermoforming and finishing steps is also described. A review of a collection of technology-demonstrating nanolayered GRIN case studies is which include: optical performance of an f/# 2.25 spherical GRIN plano-convex singlet 1/10 the weight of a similar BK7 lens and a bio-inspired aspheric human eye lens. Original research on the fabrication and characterization of a Luneburg inspired GRIN ball lens is presented as a developing application of the nanolayered polymer technology.

CHAPTER 3: Compact and adaptive-focus tunable lenses have drawn increasing attention in the field of imaging applications including cellphone cameras, video endoscopes, and optical fiber components. This study demonstrated an all-solid-state thermoplastic elastomer tunable lens where the focal length was altered by the lens radius variation under a compressive pressure. The elastic behavior of the lens material was also investigated in the hysteresis study, which indicated that the conditioned lens material possessed a better elastomeric properties after the first cycle of loading and unloading. The radius of curvature of the tunable lens was simultaneously measured by a corneal topographer during compression. The results showed at a 0.4 mm compression, the lens curvature decreased from 12.86 mm down to 10.41 mm, which resulted in 19% of focal length change in the tunable lens. An ANSYS finite element analysis (FEA) model was used to predict shape deformation of the tunable lens during compression, which correlated well with the experimental results.
CHAPTER 4: Triple shape memory polymers are capable of memorizing two temporary shapes and sequentially recovering from the first temporary shape to the second temporary shape, and eventually to the permanent shape upon exposure to heat. In this paper, unique three component multilayered films with ATBTATBTA configuration were produced by using a forced assembly multilayer film coextrusion process for a novel triple shape memory system. The films consisted of 65 polyurethane (PU) layers and 64 ethylene vinyl acetate (EVA) layers and separated by 128 poly(vinyl acetate) (PVAc) layers. The resulting films have two well separated thermal transition temperatures, one from the melting temperature of EVA and the other from the glass transition temperature of PVAc, which were used to subsequently fix two temporary shapes. The cyclic thermo-mechanical testing results showed that 257-layered PU/EVA/PVAc films possessed outstanding triple shape memory performance in term of shape fixity and shape recovery ratios. This approach allows greater design flexibility to some specific applications that are in need of simultaneous adjustment of the mechanical and shape memory properties.
CHAPTER 1

A BIO-INSPIRED POLYMERIC GRADIENT REFRACTIVE INDEX

(GRIN) HUMAN EYE LENS

1.1 Introduction

Many biological optical systems utilize a gradient refractive index (GRIN) lens, an optic that possess an internal refractive index, to enhance focusing power, increase field of view, and correct for optical aberrations [1]. Biological examples of GRIN lenses include spherical eye lenses found in aquatic creatures such as fish, octopus, squid, and jellyfish [2-5] while aspheric shaped lenses found in air dwellers include humans, lions, and cows [6,7]. In contrast to the compact single or dual lens designs of naturally occurring GRIN eye systems, modern multi-element synthetic lens designs are commonly larger and heavier. A homogenous glass or plastic spherical singlet lens is the simplest, most compact optic used for imaging. Images produced solely from a single homogeneous lens commonly suffer from significant chromatic and geometrical aberrations [8]. The human eye is an optical system consisting of only two lens elements: a cornea and a crystalline lens. Though constructed from only two lens elements, the human eye produces nearly aberration-free imaging [9]. The crystalline human lens functions as an aspheric compensator correcting the corneal induced-spherical aberrations while avoiding any major off-axis coma generation [9]. The superior optical aberration correction of the GRIN lens results from a synergistic dual compensator mechanism comprised of an aspheric lens surface shape and
an internal lens GRIN distribution. The refractive index distribution of the human eye lens is constructed of non-planar protein layers, which vary from a maximum refractive index, n=1.42, at the lens core to a refractive index minimum, n=1.37, at the lens surface [8, 10]. Constructing a lens with a refractive index distribution shape and magnitude similar to the human eye lens, $\Delta n=0.05$, requires substantial power and flexibility in materials construction previously unavailable in synthetic optics. Polymeric based GRIN material fabrication techniques, including interface-gel copolymerization [11] and plasmonics [12] approaches have the necessary magnitude in available refractive index gradient, a $\Delta n$ up to 0.08 is possible; however, they are limited by the internal refractive index distribution control, or the overall lens size due to fabrication techniques, or material diffusion coefficients. Recently, a more flexible alternative to producing polymeric GRIN materials comprised of limitless internal refractive index distribution control was reported based on optic fabricated from nanolayered films [13, 14]. This nanolayered polymers material approach was selected to satisfy the design criteria for producing a polymeric-based, bio-inspired aspheric human eye GRIN lens.

The following work introduces a new material approach that allows for the fabrication of synthetic polymer lenses with geometric and gradient refractive index distributions similar to those of naturally occurring biological animal eyes. A bio-inspired example which utilizes nanolayered polymer films to fabricate an aspheric shaped GRIN lens with the shape and magnitude of a refractive index distribution modeled from a (chronologically equivalent, “Age=5”) human lens was fabricated. This work represents the first published attempt to produce a synthetic copy of an aspheric GRIN synthetic eye
lens with a geometry and refractive index distribution similar to those of the human eye lens.
1.2 Design of a bio-inspired human eye lens

Though the geometry of an aging human eye has been extensively studied and reported by several independent sources [15-17], an optical design for constructing a synthetic, bio-inspired version of the human eye GRIN anterior and posterior lens was based on the geometry and an internal refractive index profile reported by Díaz et al. [16]. In this work, Díaz provides a complete description of age dependent eye geometry as well as the internal human eye lens refractive index distribution profile accounting for age-dependent vision deterioration and eye chromatic aberrations [16]. As a result of human growth and age-related lens deterioration, an optical copy of the human eye is a function of age. To fabricate a bio-inspired GRIN lens, described by the Díaz’s model in Equation 1.1, an age dependent lens thickness and surface curvature relationship for a rotationally symmetric concoid lens shape was utilized.

\[ d_L = 2.93 + 0.0236 \times \text{age} \]  \hspace{1cm} (1.1)

The curvature radii of anterior, Equation 1.2, and posterior, Equation 1.4, human eye lenses, as well as their aspheric shape coefficient, are given by Equation 1.3 and Equation 1.5, respectively.

\[ R_{\text{anterior}} (mm) = 12.7 - 0.058 \times \text{age} \]  \hspace{1cm} (1.2)

\[ Q_{\text{anterior}} = -5 \]  \hspace{1cm} (1.3)

\[ R_{\text{posterior}} (mm) = -5.9 - 0.0015 \times \text{age} \]  \hspace{1cm} (1.4)

\[ Q_{\text{posterior}} = -4 \]  \hspace{1cm} (1.5)
The crystalline lens was considered as one element with a single continuous GRIN distribution and its refractive index distribution given by

\[ n(\lambda, x, y, z) = n_0(\lambda) + n_1(\cos(n_2 z) - 1) + n_3 \sin(n_4 z) + n_5 (x^2 + y^2) \]  
(1.6)

Here, \( z \) represents the lens optical axis; with \( x^2 + y^2 \) modeling the elliptical shape of the isoindicial surfaces, and the function \( \sin \) accounts its asymmetry along the lens axis.

Adopting the “Age=5” human eye lens design maximized the magnitude of the internal lens refractive index distribution, however, any age human eye lens and refractive index distribution could have been fabricated. The “Age=5” lens was, therefore, selected as an initial materials capability demonstrator of the nanolayered polymer GRIN lens fabrication technique flexibility.

A ray tracing model based on the geometry and internal refractive index distribution of the “Age=5” GRIN lens was created in Code V software, to verify the refractive index with Diaz’s published model, as shown in Equation 1.6 and Figure 1.1. The spherical, rather than ellipsoidal contours of the model capture the salient optics of the nested protein layers while allowing for improved computational and fabrication efficiency. Large differences due to the different geometries would be expected only for rays entering at the edges of the lens, which would be blocked by the iris in all but dark conditions. The polynomial coefficients used in this model are listed in Table 1.1.

\[ n(r) = n_0 + n_1 (r - R) + n_2 (r - R)^2 + n_3 (r - R)^3 + n_4 (r - R)^4 \]  
(1.7)

Where \( r = \frac{R}{R} \sqrt{x^2 + y^2 + (R - z)^2} \)  
(1.8)
Fabricating a nanolayered polymer film-based GRIN lenses required two alternations to Diaz’s model: (1) segmentation of the bi-convex human eye lens into two plano-convex GRIN halves that resulted in the creation of anterior and posterior parts segmented at the maximum internal refractive indexes of the lens, Figure 1.2a, and (2) utilizing existing coextruded PMMA/SAN17 nanolayered optical film, with an available range of refractive index from 1.489 to 1.573 as compared to the internal 1.37 to 1.41 biological refractive index distribution of the human eye. To compensate for the difference in the biological and polymer material refractive index, the internal refractive index design of the “Age=5” lens was offset by a refractive index of +0.12 as shown in Figure 1.2b. Since this offset existed, and because the lens was tested in air, rather than the naturally occurring aqueous environment, holding the lens to its naturally occurring shape would result in blurred test images. As such, the polynomial coefficients for the bio-inspired anterior and posterior lenses, Table 1.2, was utilized.

The lens surfaces were optimized independently of their original shape for better in-air imaging. The optimization was performed at a single wavelength (the d-line at 587.6 nm) and used on-axis light. The improved performance represented by Figure 1.2c was obtained with radii curvatures of 12.40 and -5.90 mm, respectively, for the anterior and posterior lens surfaces. Furthermore, an aspheric conic constant was adopted for each surface, with values of 0.5 (anterior) and -5.0 (posterior). Results from these values result in a simulated monochromatic, diffraction-limited performance on-axis, with off-axis aberrations dominated by coma. This change was not a required design change based on material nor fabrication limitations, but was a conscious decision by the authors to display
an aspheric GRIN optic capable of evaluation in a conventional air based, n=1.0, laboratory environment.
1.3 Experimental

Utilizing the nanolayered polymer coextrusion technique, a set of transparent polymer films, each with a specified refractive index, were fabricated. Each film contains 4097 alternating layers of PMMA and SAN17 with individual layer thickness less than a quarter of visible lights wavelength as previously described [13, 14]. A series of 51 compositions of nanolayered films, differing in refractive index by about 0.0016, were produced by systematically varying the constituent ratios during coextrusion. Each nanolayered film had a thickness of approximately 50 ± 4 μm. The nanolayered films were extruded with protective peel-off layers of low density polyethylene, which improved the surface quality of these films and made it easier to exclude contaminants during the stacking process [14].

Based on the synthetic eye lens design refractive index distribution, 1.49 to 1.54 (see Figure 1.3), anterior and posterior lens sheets were stacked from 64 and 76 individual 50 μm nanolayered films, respectively, in a class 10,000 clean room. Nanolayered films were selected based on a closest match refractive index with the design refractive index distribution. The nanolayered film stacks of the anterior and posterior GRIN distribution were thermoformed into 2.6 and 3.1 mm thick GRIN sheets in a heated hydraulic compression molder at 135 °C and 17,000 lbf.

The anterior and posterior GRIN sheets were shaped into spherical pre-forms in a compression press against a pair of convex and concave glass lenses with radii of 10.9 and -12.4 mm, as well as, 3.3 and -5.9 mm, respectively, at 130°C and 500 lbf.
thermoforming, the spherical anterior and posterior lens pre-forms were diamond turned into the prescribed aspheric surface shape.

The wavefront measurements were performed with a commercial sensor based on lateral shearing interferometry, with a maximum 3.6 mm diameter aperture sampled at 120 x 120 points. The test lenses were placed in a broad area collimated laser beam with a 633 nm wavelength, far enough away from the sensor to focus the light in air and have the beam expand back up to a 3 mm diameter in the measurement plane. Over the full aperture of the lenses, the aspheric coefficients were high enough to create caustics near the edges of the beam. To combat this effect, irises placed before the test lenses reduced the input beam diameters to slightly under the radii needed to ensure smooth intensity variations for wavefront analysis. The apertures reduced the beam diameters to 80% of the full lens diameters. The aperture sizes were taken into account in the comparisons between data and simulations.
1.4 Results and discussion

In a previous work, it was reported that the PMMA/SAN17 spherical GRIN lens exhibited better optical performance than commercial glass singlets in terms of energy concentration and image quality [13, 14]. Here, fabricated aspheric anterior and posterior GRIN lenses were characterized to determine geometric and optical compliance against the Code V model. Characterizing the anterior and posterior lens included the following: (1) verification of the internal lens refractive index distribution and shape, (2) an aspheric surface curvature measurement, (3) wavefront measurements, and (4) an imaging test collected through the bonded GRIN lens.

To ensure the stacked and compressed GRIN sheet contained the desired refractive index distribution, the refractive index distribution in both of the anterior and posterior lens blanks were characterized by a µATR-FTIR examination by exhuming cross sections of adjacent sheet material. The µATR-FTIR technique can map the relative composition across the cross-sectioned sheet surface, which is directly related to the refractive index distribution of the piece [18]. A plot of the design and µATR-FTIR-measured GRIN sheet refractive index distribution displays good agreement with the fabricated anterior and posterior GRIN sheets, shown in Figure 1.4.

An image and 3D profile of the fabricated aspheric anterior and posterior GRIN lens are shown in Figure 1.5a,d. For this lens, the surface profiles satisfy the Equation 1.9 below [19],

\[ h^2 + (1 + Q)z^2 - 2zR = 0 \]  (1.9)
Where $h^2 = x^2 + y^2$, the $z$ axis is the optical axis, $R$ is the vertex radius of curvature, and $Q$ is the surface aspheric coefficient. Cross-sectional profiles of an aspheric lens and a spherical lens with consistent geometries as the aspheric anterior and posterior GRIN lens were calculated and plotted in Figure 1.5c,f. These values show good agreement between the measured profiles of aspheric anterior and posterior GRIN lenses and calculated profiles.

Optical wavefront measurements were conducted on the posterior GRIN lens and tested with light incident to the planar lens surfaces, i.e. from the same direction as their design. Figure 1.6a shows the wavefront measured at the sensor plane after the posterior GRIN lens, next to Figure 1.6b, which predicts a theoretical ray trace through the design lens at the same location. Both wavefronts were fit to a series of Zernike polynomials [20]. These results were plotted in Figure 1.3b and represent the residual wavefronts after low-order terms for offset, tilt, and power were subtracted. In the lens design there were no contributions due to tilt. However, in the measured lens there were tilt contributions at the sensor plane of 7.6 waves (peak-to-valley) across the field of view, indicative of the level of parallelism achieved in the diamond turning process. The remaining data show excellent agreement between the measured and predicted wavefronts. Qualitatively the shapes are the same, and quantitatively the wavefronts agree to within a RMS error of 0.10 waves.

Figure 1.6c,d show analogous wavefront data for the non-GRIN, PMMA version of the posterior lens, but are displayed with different vertical scales to Figure 1.6a,b. Designed to the same shape as the GRIN lens, differences between the two highlight the effect of the gradient index distribution on the wavefront. As can be seen from a
comparison between Figure 1.6d,b, the gradient index distribution reduces the overall wavefront error. The RMS wavefront error is reduced by the gradient index distribution from 0.41 down to 0.20 waves. A surface figure error in the diamond turned PMMA part produced a radial asymmetry in the measured wavefront, shown in Figure 6c. Subtracting the tilt contribution to the wavefront, shown in Figure 6c, produced 18.8 waves, peak-to-valley, across the measured aperture. The wavefronts displayed in Figure 6c,d agree to one another within a RMS variation of 0.18 waves.

The aspheric anterior and posterior GRIN lenses were reversibly assembled into a human eye lens. This lens captured an image of Case Western Reserve University logo, shown in Figure 1.7. The image was clear and sharp, confirming the focusing ability of the singlet, bio-inspired human eye lens. As expected from the design, on-axis imaging is seen to be superior to off-axis imaging in the figure.
1.5 Conclusions

The design and fabrication flexibility afforded by the nanolayered film-based GRIN lens technology enabled successful demonstration of an “Age=5” bio-inspired, aspheric human eye GRIN lens. Characterizing the polymer lenses demonstrated an ability to fabricate the nanolayered polymer materials to an external aspheric design shape, with an internal refractive index distribution to specification. Demonstrated in the design of the human eye GRIN lens, are additional freedoms, previously unavailable to optical designers, but available with this technology. The ability to independently select arbitrarily shaped refractive index distributions and optic surface shapes, spherical or aspheric, allows for advances and potential element reductions in modern high resolution and complex zoom, optical systems. Though a first generation design, the polymeric nanolayered GRIN lens technology, demonstrated in this work, enables many potential advances toward fabrication of more compact optical systems, similar to one or two lens biological systems. Other opportunities to apply this technology include lightweight, miniaturized imaging or surveillance systems, conventional glasses, contacts, or potentially customizable gradient refractive index distribution lens implants.
References


Table 1.1 Polynomial coefficients of an “Age=5” human eye lens used in Code V model.

<table>
<thead>
<tr>
<th>Lens</th>
<th>$n_0$</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$n_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anterior</td>
<td>1.3680</td>
<td>-0.0817</td>
<td>-0.0280</td>
<td>0.0075</td>
<td>0.0031</td>
</tr>
<tr>
<td>Posterior</td>
<td>1.4190</td>
<td>0.0006</td>
<td>-0.0300</td>
<td>0.0100</td>
<td>-0.0012</td>
</tr>
</tbody>
</table>
**Table 1.2** Polynomial coefficients of the bio-inspired anterior and posterior lenses.

<table>
<thead>
<tr>
<th>Lens</th>
<th>$n_0$</th>
<th>$n_1$</th>
<th>$n_2$</th>
<th>$n_3$</th>
<th>$n_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anterior</td>
<td>1.4890</td>
<td>-0.0817</td>
<td>-0.0280</td>
<td>0.0075</td>
<td>0.0031</td>
</tr>
<tr>
<td>Posterior</td>
<td>1.5403</td>
<td>0.0006</td>
<td>-0.0300</td>
<td>0.0100</td>
<td>-0.0012</td>
</tr>
</tbody>
</table>
Figure 1.1 Refractive index distribution of the anterior and posterior lenses of an “Age=5” human eye lens represented in the Diaz’s and Code V models.
Figure 1.2 Design of a bio-inspired polymeric gradient refractive index (GRIN) human eye lens. a) Fabrication illustration to create the bio-inspired GRIN anterior and posterior lenses. b), refractive index distribution of “Age=5” human eye and buildable bio-inspired GRIN lenses. c), RMS wave error of bio-inspired GRIN lenses with two different sets of aspheric coefficient for anterior and posterior lenses simulated by Zemax software: (Top) $Q_{\text{anterior}}=-5$, and $Q_{\text{posterior}}=-4$; (Bottom)$Q_{\text{anterior}}=0.5$, and $Q_{\text{posterior}}=-5$. 
Figure 1.3 Stacking recipes of anterior (left) and posterior (right) lens sheets with buffer layers.
Figure 1.4 Refractive index distribution of anterior (left) and posterior (right) lens sheets measured by µATR-FTIR.
Figure 1.5 Fabricated lens images (a and d) and measured geometry surface profiles (b/c and e/f) of the aspheric anterior and posterior bio-inspired human eye GRIN lenses.
**Figure 1.6** Comparison plot of experimentally measured and simulated wavefront for as built bio-inspired aspheric posterior lenses. a-b, Measured (a) and numerical simulated (b) wavefront of aspheric posterior GRIN lens. c-d, Measured (c) and numerical simulated (d) wavefront of aspheric posterior PMMA reference lens. Vertical axis in units of waves (633nm). Planar values are unit less measures of aperture across the wavefront sensor.
Figure 1.7 Experimentally obtained image of a Case Western Reserve University logo taken through a bio-inspired "age=5" human eye GRIN lens.
CHAPTER 2

POLYMERIC NANOLAYERED GRADIENT REFRACTIVE INDEX (GRIN) LENSES: TECHNOLOGY REVIEW AND INTRODUCTION OF SPHERICAL GRIN BALL LENSES

2.1 Introduction

Optimized for survival, biological species evolved internal gradient refractive index (GRIN) lenses for maximizing their visual performance. Homogeneous lenses, consisting of a material of a uniform refractive index, alter light’s direction only at its surfaces as a function of geometry and incident and emergent light angles. On the other hand, GRIN lenses are constructed from materials whose refractive indices continually refract propagating light. The optical power of GRIN lenses is not only determined by its surface geometry, but also by the spatial distribution of refractive index occurring along through the thickness of the optic. As an example, a GRIN optic with spherical refractive index profile decreasing from a center maximum to a surface minimum refractive index can slow centrally propagating light so peripheral light can intersect it at the same point along the lens’ optical axis.\(^1\) Combining this effect with surface geometry equips visual systems using GRIN lenses with enhanced focusing power and increased view fields, all while minimizing optical aberrations, lens size and complexity. [1-3]
Animals or vertebrates with simple camera-type eyes focus an image onto a single photoreceptor on the organism’s retina. Aquatic creatures, such as the fish [4], octopus [5], squid [6], and jellyfish [7] have camera-type eyes which contain GRIN lenses to compensate for low contrasts between water \((n = 1.33)\) and proteins’ refractive indices. [8] Since biological GRIN lens’ refractive indices range between 1.33 and 1.52, values similar to water, aquatic eyes need to exploit strongly curved surface geometries and GRIN to derive stronger optical power. Without GRIN optics, spherically curved and homogenous lenses could still focus light and offer large fields of view, however, would exhibit significant spherical aberrations and focused light would not intersect at one point along the lens’s optical axis, causing image blur. [1-3] In contrast, air-dwelling creatures [9-12], such as the lion, cow, rat, and human, utilize GRIN lenses to correct for significantly larger geometric aberrations stemming from a large difference in environment (air \(n = 1.0)\) to lens material \((n = 1.33 – 1.43)\) refractive index and contributions from aspheric shaped lenses.

Table 2.1 A bi-product of nature’s incorporation of GRIN into eye lens optics has resulted in most biological imaging systems containing a low, typically one to three, number of lenses, which minimizes the size necessary for an organism’s eyes to exhibit a powerful accommodating image system.

In contrast to nature, state-of-the-art synthetic optical designs typically utilize a series of homogenous refractive index elements to form images. Aberrations are corrected by including aspheric optical surface geometries and combining multiple dispersion materials in the system design. Typically consisting of glass or plastic lenses, it is not uncommon for high definition optical zoom systems to consist of five or more elements. This traditional multi-material, multi-element design approach has been successfully
applied by optical engineers for decades. However, these result in systems with larger element counts, larger size and higher weight than naturally occurring GRIN analogs. [13]

The technological limitations of successfully demonstrated GRIN lens fabrication techniques, such as ion exchange [14], partial polymerization [15], interface-gel copolymerization [16], chemical vapor deposition [17], and plasmonics [18] have minimized their application. Specifically, these lenses are limited by their refractive index distribution magnitudes (Δn), refractive index profiles (linear, Gaussian, and Lorentzian), and their small apertures. [19] While these technologies have their limitations, another approach discovered in 2004 by Case Western Reserve University and the Naval Research Laboratory produces GRIN lenses through nanolayering of polymeric films. [20] This unique materials approach has enabled the fabrication of GRIN lenses with an unprecedented variety of GRIN profiles, index distribution magnitudes, geometries, and lens apertures. [21-26] This paper reviews the enabling technology and describes unique nanolayered polymeric GRIN lenses, including original research demonstrating fabrication of a polymeric layered GRIN ball lens. These GRIN lenses demonstrate the technology’s potential to utilize unrestricted lens geometries and refractive index profiles in their performance, optical element savings, and weight reductions.
2.2 GRIN optic fabrication technique based on nanolayered polymeric films

2.2.1 Enabling technology: Polymer films with layer thickness < λ/4

The technological basis for creating nanolayered polymer GRIN optics lies in the fabrication of polymer films with a tailored refractive index, **Figure 2.1**. When two polymer materials with a sufficient difference in their refractive indices are arranged in alternating layers, the resulting layered material has a refractive index modulation whose period corresponds to layer thicknesses. [21] These layered polymer materials have interesting optical properties when their layer thickness is similar to or shorter than a wavelength of visible light. In the first case, where the wavelength of light is one quarter (λ/4) of the film’s repeating layer thicknesses, the material shows high reflectivity. This high reflectivity makes it a one dimensional photonic crystal. [27,28] In the second case, when the layer thickness is less than one quarter the wavelength of light, the layered polymeric material transmits light. [23] But the bulk layered structure exhibits a refractive index, which is a function of the volumetric average of the two component materials, **Figure 2.2**. It is under this second condition, where the layered materials have individual layer thicknesses less than λ/4, that nanolayering polymeric materials enables a unique, polymer film coextrusion based approach to GRIN lens fabrication.

2.2.2 Enabling technology: forced assembly multilayer coextrusion

The initial step in fabricating GRIN optics is the production of a series of polymer films via a forced assembly multilayer coextrusion process. Multilayer coextrusion is a continuous processing technique creating films composed of tens to thousands of
micrometer to nanometer thick layers. Utilizing a two-component coextrusion system, two single screw extruders with melt metering pumps separately supply two polymers, “A” and “B”, into a layered feedblock. The metering pumps add a degree of volumetric control over the relative materials, which enables variation in the nanolayered film’s composition, which defines its bulk refractive index. Using this system, polymers A and B are layered so polymer B is sandwiched between two A layers in an A/B/A vertical stack. This occurs in a three layer coextrusion feedblock. Starting at this feedblock, the A/B/A polymer layers flow into a series of layer multiplying die elements. Each layer multiplier die doubles the initial feed’s layer count through a process of flow splitting, compression, and vertical stacking, shown in Figure 2.1a and described in Ponting et. al. [29] Thus one A/B/A layered flow stack is placed on another creating an A/B/A/A/B/A layered stack. When combined in series, $n$ number of multiplier elements produces multilayered films consisting of $2^{(n+1)}+1$ alternating layers. Figure 2.1a represents a two-component coextrusion system and a series of eleven multiplier elements that increases the number of layers from 3 to 4097. This coextrusion process produced 4097 nanolayered polymer films with an overall bulk film thicknesses of 50 microns. The 50 micron target was selected to ensure each of the 4097 intra-film layers were significantly below the $\lambda/4$ limitation. This criterion satisfies the physical requirement for the volumetric additive refractive index rule of mixtures applied to nanolayered films.

2.2.3 Tailored refractive index nanolayered polymer films

Polymer films of 4097 poly(methyl methacrylate) (PMMA, Arekema Plexiglas V920) and poly(styrene-co-acrylonitrile) with 17mol% acrylonitrile (SAN17, Ineos
Lustran Sparkle) layers were coextruded for constructing GRIN optics. The volumetric contribution of PMMA to SAN17 was varied in 2% steps, so their respective contributions were 100/0, 98/2, 96/4, continuing through 50/50, and ending at 0/100, respectively. Together, this series produced 51 separate films of PMMA/SAN17, volumetrically varied in 2% steps, each engineered so their total film thickness was 50 µm. As an example, a 50/50 volumetric ratio of PMMA/SAN17 nanolayered films with an overall thickness 50 µm will have about a 12 nm individual intra-film layer thickness (50 µm divided by 4097 layers) because each polymer is volumetrically proportional. The refractive indices of these 51 layered films processed at 2% compositional step intervals were measured via a Metricon refractometer and exhibited a 0.0016 difference in their bulk film refractive index, which was predicted, Figure 2.2a. [21,22] These results are plotted as a function of overall PMMA film volume percentage in Figure 2.2b. Theoretically, it is possible to make polymer films of any refractive index value between its constituent polymers, such as PMMA or SAN17. These 51 compositional films were selected based on computational simulations suggesting the 0.0016 refractive index step size in the GRIN lens was sufficient to demonstrate a satisfactory optical performance. Next, these 51 nanolayered films were utilized to construct a gradient refractive index.

2.2.4 Construction of a gradient refractive index profile

A fundamental strength of the polymeric nanolayered approach is the removal of refractive index profile shape restrictions since any value in between the constituent polymer absolute refractive index values can be used. Thus, constructing a refractive index gradient is accomplished by sequentially stacking nanolayered PMMA/SAN17 polymer
films whose refractive indices vary, Figure 2.1b. The nanolayered polymer film stacks can be arranged so their refractive index profiles are linear, second order, third order, and so on, as shown in Figure 2.3. Typically stacks consist of between 75 to 300 individual nanolayered films. Once the desired refractive index distribution profile is stacked, typically in a cleanroom environment to prevent contamination, a thermoforming, hydraulic press consolidation process at elevated temperatures and pressures locks-in the desired axial GRIN profile. This GRIN stack is usually a 3 to 7 mm thick, flat sheet.

2.2.5 GRIN optics finishing

Subsequent polishing or diamond turning steps to the consolidated axial GRIN sheet enable the construction of axial or radial GRIN optics. Converting an axial GRIN sheet to a radial or spherical GRIN distribution is accomplished by a second thermoforming operation. With this operation, an axial GRIN sheet is formed into a meniscus-like lens, or GRIN preform. This is done by molding against a concave-convex mold pair. Spherical refractive index contours are created by maintaining the thickness of the curved GRIN preform equal to the difference in the convex and concave mold radii of curvature, also described elsewhere. [22] The curved GRIN preforms can be further transformed into a variety of finished optics by additional diamond turning.

Using this methodology, a variety of GRIN optical geometries could be formed: meniscus lenses, plano-convex, plano-concave, plano optics with a radial GRIN distributions, such as the Wood lens [20]; basically any machineable, spherical or aspheric shaped optic. Due to the formability of polymer materials, GRIN optics can be fabricated with a large range of radii and diameters. These radii could be as sharp as 3 mm nearly
infinite. GRIN optics with diameters ranging from 6 mm to 60 mm have been fabricated. As compared to conventional GRIN sol-gel, deposition, or interdiffusion techniques, this nanolayering approach provides many fabrication freedoms enabling breadth, not only in the shape of the optic’s refractive index distribution (axial, radial, or aspheric), but also in the optical diameter, optic thickness, and surface curvatures. None of these freedoms significantly change the optical fabrication process. Therefore, grounded in provided optical designs an additional degree of freedom, nanolayered GRIN optical systems offer a materials and fabrication path toward demonstrating previously unattainable optical designs. Indeed, these methods have produced GRIN optics that out-performed similarly powered homogenous optical lens systems.
2.3. Review of demonstrator lens design

2.3.1 Aspheric Human eye lens

The human eye, constructed from a two element cornea and GRIN lens, Figure 2.4, represents one of the most widely studied naturally occurring gradient refractive index optical systems. The human eye produces a nearly aberration-free image [30]. The high performance of the two lens optical system is due to the GRIN lens dual compensator optics which derive corrective power from an aspheric surface geometry and an internal gradient refractive index distribution. Together these correct for corneal induced-spherical aberrations while avoiding off-axis coma. [30] This corrective power originates from the nearly 22,000 non-planar protein layers that constitute an approximately parabolic shaped optic refractive index gradient. The GRIN decreases from a value of 1.42 at the lens center to n=1.37 at its surface. [11,33] The ability of the human eye lens protein layers to vary its refractive index results from a dynamic chemical make-up, i.e. volumetric ratio of protein to water concentration proportional to the material refractive index, within the layers.

Although the shape and GRIN distribution of the human eye lens has been extensively studied [12,32,33], traditional Interdiffusion [19] and sol-gel GRIN fabrication techniques [15,16] have not produced equivalent refractive index distributions. However, the design freedom from combining polymer nanolayered films with thermoforming offers a materials and fabrication pathway capable of producing a bio-inspired synthetic GRIN human eye lens. A summary of the recently published bio-inspired human GRIN eye lens is included to demonstrate that the nanolayered film GRIN optic fabrication technique has
the ability to build a lens with any arbitrary refractive index distribution and lens shape.

[25]

An optical design based on the geometry and internal refractive index distribution of the human eye lens was selected based on previously published works. One caveat to designing a synthetic version of the human eye lens is an age dependent GRIN distribution and lens geometry. [12,32,33] Based on one such age dependent human lens model for the refractive index distribution and geometry developed by Diaz et al., [25] an “Age=5” human eye lens was selected as a design case. The “Age=5” model eye possess a maximum gradient refractive index magnitude in the lens, estimated at Δn=0.05, which illustrates the maximum corrective contribution of the GRIN to the lens performance.

The fabrication pathway for construction of the inspired copy of the human eye lens required fabrication of two aspheric, plano-convex lenses. Both the anterior and posterior lens followed Diaz’s model for the refractive index distribution and were translated into a Code V spherical ray tracing model for improved computational and fabrication efficiency, as shown Figure 2.5. A refractive index shift by +0.12 was required in the synthetic eye due to the available polymer material refractive index as compared to the water-biological protein layers of the human eye. This shift in the refractive index value, not in the shape, was accounted for in the design simulations. A final lens design change to the aspheric coefficients of both the anterior and posterior lens of 0.5 and -5.0 were made. This change allowed for the final optic performance to be measurable in a n=1.0 (air) vs. a n=1.33 (water) environment, Table 2.2 and Figure 2.5c.
Construction of the nanolayered polymer bio-inspired human eye lens was accomplished following the previously described procedure utilizing PMMA/SAN17 nanolayered films. The films were stacked, consolidated, shaped, and diamond turned into anterior and posterior GRIN lens according to geometry and GRIN distribution shown in Figure 2.5. Nanolayered anterior and posterior refractive index distributions were confirmed through attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR).25 Diamond turned aspheric anterior and posterior lenses surface curvatures were mapped and compared to the prescribed surface profiles by non-contact profilometry with a placido-cone topographer, Figure 2.6. Confirmation of the nanolayered polymer GRIN lens geometric and internal refractive index distribution allowed for optical measurements to demonstrate the effect GRIN has on the optical lens performance as compared to an identically shaped homogenous PMMA lens.

The optical performance of the synthetic GRIN optics were measured and compared against a simulated transmission wavefront at the Naval Research Laboratory, Figure 2.7. Wavefront measurements of the posterior GRIN and PMMA control lenses were tested with light incident to the planar lens surfaces, i.e. from the same direction as their design. [25] In the lens design, there was no tilt contribution to the wavefront measurement, however, the finished lens possessed a tilt contribution that indicated a level of parallelism was achieved in the diamond turning process. The tilt contribution of the wavefront for the posterior GRIN and PMMA control lenses was determined to be 7.6 and 18.8 waves (peak-to-valley) respectively across the measured aperture, Figure 2.7a and (c). These measured results had a good agreement with the numerical simulations, Figure 2.7b,d. The RMS wavefront was reduced from 0.41 in the PMMA reference lens down to
0.2 in the GRIN lens; **Figure 2.7b,d.** Since the posterior PMMA control and GRIN lenses have the same physical dimensions, the incorporation of GRIN distribution effectively exhibited smaller wavefront error in an identical geometric lens. It is noted that by holding the optic geometry constant, the PMMA wavefront may not represent an optimized minimum value. However, the reduction in fabricated optic wavefront distortion in optics with identical geometries through introduction of a bio-inspired intra-lens refractive index distribution was validated.

Both anterior and posterior GRIN lenses were reversibly assembled into a biconvex human eye GRIN lens with an optical gel. The assembled lens imaged a print logo placed about 33 cm from the bare camera, **Figure 2.8.** Illuminated by an external light source, the camera imaged the logo through the nanolayered bio-inspired “age=5” human eye GRIN lens. The resulting image was clear and sharp, confirming the focusing ability of the bio-inspired human eye lens.

The added optical design flexibility provided by the novel nanolayered fabrication process demonstrated in the “Age=5” bio-inspired, aspheric human eye GRIN lens provides optical engineers an additional design variable, GRIN distribution, to optimize optical systems for enhanced properties and reduction in the optical elements. This technology has demonstrated the feasibility of making spherical and aspheric lenses with a non-linear and nonsymmetrical GRIN distribution. This technique may also enable future potentially implantable, intraocular (IOL) polymer GRIN lenses to replace the deteriorated or destroyed human eye lens. As a material for IOLs, PMMA, a component of the described aspheric human eye lens, has a long history of use as a result of its high light
transmission, hydrophobic surface, and ease to add an UV absorber to the monomer with the earliest implantable PMMA IOL tracked back to 1950s. [34,35] Although PMMA IOLs are still used in some countries, usage is waning due to its lack of mechanical flexibility in comparison to the deformable IOL now available. Adoption of a nanolayered GRIN IOL is challenged with introducing material flexibility, as well as an understood deformable optical performance, for medical community adoption of the technology.

2.3.2 Spherical GRIN lens for size and weight reduction

The flexibility of the polymeric nanolayering approach to GRIN lens fabrication allows for additional design freedom to improve performance over a similar f/# conventional homogenous plastic or glass optics. To demonstrate this advantage, a plano-convex nanolayered GRIN singlet was designed, fabricated, and characterized against a commercial glass optic while simultaneously reducing the optic size and weight. A plano-convex nanolayered GRIN lens was designed by the Naval Research Laboratory to minimize spherical aberration using custom designed ray-tracing software incorporated into ZEMAX (Zemax Development Corporation, Bellevue, WA). Constructed from the previously described family of PMMA and SAN17 nanolayered films, a lens with a spherical refractive index distribution ranging from 1.53 to 1.57, Figure 2.9, was fabricated by stacking and consolidating 128 individual nanolayered films. The films were molded into a meniscus perform, a requirement to establish a spherical refractive index distribution, and diamond turned into a plano-convex singlet as described in Table 2.3.

The optical properties of the nanolayered GRIN lens were compared against a commercial bi-convex BK7 (Newport Optics Inc., Irvine, CA, part # KBX049) glass lens.
The bi-convex BK7 glass lens was chosen to exhibit a similar f/# 2.2 to the f/# 2.4 plano-convex GRIN singlet when the optics were apertured to 17 mm. That a bi-convex BK7 lens was required to match the f/# of the nanolayered plano-convex lens was a result of the added optical power of the GRIN distribution singlet. In addition to GRIN eliminating one of the glass lens convex surfaces to achieve the target f/#, the lens weighed significantly less, approximately ¼ that of glass optic, even at normalizing the lenses for an identical optical aperture and removing weight contributions of lens material edge thickness. The large weight reduction resulted from the lower PMMA/SAN17 material density (1.12 g/cm³) compared to BK7 (2.5 g/cm³) and the reduction in lens center thickness in the polymer GRIN lens. It is worth noting that the significant weight reduction demonstrated in the 20 mm aperture optics in this study represent a GRIN advantage that will only widen as the comparative optic diameter and thickness increase in larger optic designs.

Simplifying the optic’s geometry and reducing its weight can be realized only if the GRIN optic can exhibit performance similar to a homogenous lens. To characterize and compare the optical performance, spot size and contrast measurements were completed on both optics. Spot sizes of the GRIN and BK7 lens were characterized by focusing a collimated HeNe laser beam with a wavelength of 632.8 nm and measuring maximum transmission through 50µm pin hole at the lens focus point (Figure 2.10a). Next, a one dimensional intensity scan of the focused HeNe spot size was measured for both lenses, Figure 2.11c. The polymer GRIN lens exhibited a sharper decrease in spot size intensity and a higher image contrast. One dimensional intensity scans of these spots was accomplished by measuring the full width at half maximum peak height of the GRIN and BK7 lens. The half maximum peak heights were measured at 100 microns and 200 microns
for the polymer GRIN and BK7 lenses, respectively. As expected, with a tighter focal spot, the comparison of a USAF test chart image of the nanolayered polymer GRIN lens displayed a greater contrast and higher intensity than the BK7 lens, Figure 2.11. The USAF air force patterns were imaged through the polymeric GRIN and BK7 glass at 630 nm using an identical CCD camera and lens to image spacing. [23]

The combined superior optical performance and order of magnitude weight savings of the nanolayered GRIN lens over a commercial BK7 optic demonstrates the technology potential to improve lens performance, through reduction of spherical aberration, while simultaneously reducing the size of conventional imaging systems. Additional optical modeling and fabrication studies have demonstrated the extension of this lens singlet performance in an optical system. Incorporation of two nanolayered GRIN optics in a five lens night vision imaging system was designed and characterized to exhibit similar optical performance while encompassing only 1/7 the weight of the homogenous optic system. The corrective power of the nanolayered GRIN technology is not limited solely to spherical aberration corrections, and has been demonstrated to also affect chromatic aberrations.

Traditional achromatic optic elements are doublets comprised of highly dispersive flint glass and lower dispersion crown glass arranged with geometric surface curvatures selected to balance material chromatic affects. Optical design equations have recently demonstrated the ability of a model nanolayered polymer material system to achieve a red-blue achromatic singlet utilizing spherical and/or aspheric surfaces. [26] Chromatic correction of the nanolayered optics was achieved by de-coupling the internal spherical GRIN contours with the surface curvature of the optics. The highest powered achromat
lenses were demonstrated when the GRIN contours were created in the opposite direction to the lens surface curvature, i.e. bulk polymer layers possessing a convex internal refractive index contour in a concave optic. A specific design case was presented that demonstrated a 0.1 micron focal shift over 470 – 660 nm operating band for a 19 mm diameter nanolayered plano-convex achromat singlet optic.

Though a significant achievement, the simulated ability of the nanolayered GRIN technology to produce achromatic singlet elements is not without challenges. Materials utilized in the previously referenced effort utilized, “typical polymer” optical properties in designing the achromatic singlet. The universe of existing nanolayered polymer material systems need be expanded to account for a high refractive index (n~1.70) and highly disperse (abbe number ~ 20) material candidate. It should be stated that polyester type polymer materials with similar optical properties exist; however, optics utilizing the polymer nanolayering process for production of achromatic optics is still under development. An additional polymer material pair containing a fluoropolymer and acrylic material are under development to expand the available nanolayered material ∆n to encompass values from 1.40 – 1.57. An opportunity to combine the new optical polymer materials with GRIN correction for chromatic aberration with unconventional, or even aspheric, geometries would yield a singlet optic simultaneously corrected for spherical and chromatic aberrations. An original research effort toward a non-traditional, GRIN ball lens is described in the next section as a potential path toward future efforts to explore potential GRIN optical advantages.
2.3.3 New GRIN Development: Layered GRIN ball lens

Spherical or ball lenses have been a source of optical designs for hundreds of years. Full sphere lenses are attractive due to their low f/# and potential for wide field of views. Optical ball lens designs from Maxwell and Rudolf Luneburg proposed incorporating large gradient refractive index distributions with a core refractive index of 2.0 reducing radially to 1.0 refractive index at its lens surface, to reduce or eliminate aberrations. [24,36] Though some ball lenses are applied in microwave technology [37,38], many GRIN ball lens solutions have remained elusive in optics systems due to the GRIN material or fabrication limitations. Limitations of the current GRIN technologies arise from the depth of gradient, magnitude of gradient refractive index change (Δn), and refractive index distribution control. The design flexibility of the novel nanoalayered polymer GRIN technology was utilized to demonstrate a basic capability to fabricate GRIN ball lens with arbitrary refractive index profiles and up to a 12 mm diameter.

A path to fabricating a ball GRIN lens was derived through a creation of a series of spherical nesting shells which could be adhered together into the ball optic. As illustrated in Figure 2.12, a small SAN17 half ball was adhered inside three nesting GRIN shells of different radii, labeled GRIN shell 1, GRIN shell 2 and GRIN shell 3. The three nesting GRIN shells were fabricated with the full available refractive index range of the nanolayered optical PMMA/SAN17 films, which spanned 1.49 to 1.57. This refractive index distribution, Δn of 0.08, was divided equally throughout the three shells. The three nesting GRIN shells and half ball were compressed into a hemispherical GRIN lens with a diameter of 12mm, as illustrated in Figure 2.12c. The cross-sectional profile of the
hemispherical GRIN lens near the vertex was characterized confirming the desired geometric design radius via non-contact profilometry with a placido-cone topography, as shown in Figure 2.12d. Measurements far from the ball lens vertex were not measurable due to the limited field of view and depth-of-focus of placido-cone topography.

Radial half ball focal lengths of the GRIN lens, Figure 2.13, were compared against a hemispherical homogenous PMMA control lens and simulated performance of a homogenous SAN17 lens. A lens hemispherical geometry was utilized for focal length measurements to ensure that optic focal length was outside the lens surface enabling characterization through conventional optical metrology techniques. As expected, the change in focal length as a function of optical aperture of the half ball GRIN lens was significantly less than an identically shaped homogenous PMMA (measured) or a simulated SAN17 lens result following Equation 2.1.

\[
\frac{1}{F} = \left( \frac{1}{\sqrt{R^2 - r^2}} + \frac{r}{\tan^{-1} \left( \frac{n_{\text{air}} R - n_{\text{san}} R}{R} \right)} - R \right)^{-1}
\]

(2.1)

Where R is the radius of the SAN17 hemispherical lens; r is the distance from the optical axis; is \( n_{\text{san}} \) refractive index of the SAN17 hemispherical lens; and \( n_{\text{air}} \) is the refractive index of air. This result confirmed the added power of the GRIN to correct for spherical aberration in a hemispherical optic construction as the radially dependent optic focal length (\( \Delta F/\Delta r \)) value of GRIN lens is much smaller than those of both PMMA and
SAN17 homogenous lenses. A final step to create a full spherical GRIN ball lens was accomplished by adhering the two hemispherical GRIN lenses as shown in Figure 2.14.

The nanolayering polymer materials system was utilized to demonstrate a production path toward fabrication of spherical GRIN ball lenses with up to a Δn=0.08. Beyond this accomplishment, the nanolayering fabrication technology allows for almost any shape refractive index distribution to be created in future designs. Potential applications for incorporation of a novel GRIN ball lens include the wide field-of-view solar concentrators and compact imaging systems such as UAV cameras, surveillance and panoramic imaging systems.
2.4 Conclusion and projected future impacts

Inspired by the structure of biological optic systems, the nanolayered polymer film approach to designing and fabricating GRIN lenses with arbitrary refractive index distribution profiles along with an independently prescribed lens surface geometries has enabled the design and fabrication of a whole new class of gradient index optics. Nanolayered polymer coextrusion processing has been demonstrated to produce an inventory of materials with a tailored refractive index that were utilized to construct a discretely stepped gradient refractive index distribution. Thermoforming of these gradient refractive index materials was utilized to create axial, radial, or spherical distributions in spherical, aspheric, or planar optics. Topography, spectroscopy and optical wave front or contrast imaging confirmed the ability of the nanolayered polymer GRIN lenses fabrication process to create optics with the desired shape, internal refractive index distribution, and optical performance.

First generation nanolayered polymer GRIN lens designs and optics were fabricated to demonstrate the unique ability to construct optics previously rendered un-buildable due to a combination of materials and/or fabrication restrictions which include: optic size, lens surface shape, and/or magnitude and shape of the gradient refractive index profile. A polymeric, nanolayered aspheric gradient refractive index optic was fabricated which mimicked the refractive index distribution and layered construction of a human eye lens. This optic demonstrated an improved performance with inclusion of the gradient refractive index over a homogenous PMMA aspheric lens with an identical optic geometry. A plano-convex nanolayered polymer GRIN lens was designed, fabricated, and demonstrated to
show an optical GRIN performance advantage over a similar $f/#$ homogenous BK7 bi-
convex lens while also significantly reducing the optic weight. Finally a new class of GRIN
ball lenses was fabricated as proof-of-concept to show a path toward the production of
classically studied, but never built Maxwell or Luneburg-like spherical GRIN lenses. The
ability to create ball lenses with an arbitrary spherical refractive index distribution
represents a potential to realize optics with a wide field of view optics and minimal
gerometric induced aberrations. The nanolayered fabrication approach to the GRIN ball
lenses will also allow scalability of lens diameters from small, 6 mm in diameters, to large,
approaching an inch or more, enabling potential applications in handheld or equipment
mounted surveillance or light concentrating applications.

We believe the demonstrator nanolayered GRIN optics fabricated to-date capture
the spirit of the advantages afforded by the highly flexible fabrication process, however,
are but a sampling of the potential application space for this technology. All of the
described optics in this work were built utilizing a PMMA/SAN17 material systems,
whereas the nanolayering technology is not restricted to these materials. The vast array of
available polymer materials provides an opportunity for research and development of
additional polymer material systems with contrasting or complementary refractive index
ranges, dispersion properties, operating temperature, and physical properties for GRIN
optic construction. On-going research at CWRU hopes to exploit the nature of polymer
materials to potentially expand the nanolayered GRIN technology into areas of elastically
deformable polymers which may even produce variable focal length optics as a function of
an external pressure or electronic/chemical stimulus.
References


Table 2.1 Properties of GRIN lenses of aquatic creatures and air-dwelling animals.

<table>
<thead>
<tr>
<th>Environment</th>
<th>Animal</th>
<th>Δn</th>
<th>GRIN Distribution</th>
<th>Lens Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aquatic</td>
<td>Trout⁴</td>
<td>0.22</td>
<td>Parabolic</td>
<td>spherical</td>
</tr>
<tr>
<td></td>
<td>Octopus⁵</td>
<td>0.15</td>
<td>Parabolic</td>
<td>spherical</td>
</tr>
<tr>
<td></td>
<td>Squid⁶</td>
<td>0.21</td>
<td>Parabolic</td>
<td>spherical</td>
</tr>
<tr>
<td></td>
<td>Jellyfish⁷</td>
<td>0.14</td>
<td>Parabolic</td>
<td>spherical</td>
</tr>
<tr>
<td>Air</td>
<td>Rat⁹,¹⁰</td>
<td>0.11</td>
<td>Parabolic</td>
<td>Aspheric</td>
</tr>
<tr>
<td></td>
<td>Cow⁹,¹⁰</td>
<td>0.08</td>
<td>Parabolic</td>
<td>Aspheric</td>
</tr>
<tr>
<td></td>
<td>Lion⁹,¹⁰</td>
<td>0.04</td>
<td>Modified Parabola</td>
<td>Aspheric</td>
</tr>
<tr>
<td></td>
<td>Human¹¹,¹²</td>
<td>0.05</td>
<td>Modified Parabola</td>
<td>Aspheric</td>
</tr>
</tbody>
</table>
### Table 2.2 Geometric parameters of “Age=5” and bioinspired human eye lenses.

<table>
<thead>
<tr>
<th>Lens</th>
<th>Thickness (mm)</th>
<th>R_anterior (mm)</th>
<th>Q_anterior</th>
<th>R_posterior (mm)</th>
<th>Q_posterior</th>
<th>Diameter (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Age=5</td>
<td>3.048</td>
<td>12.4</td>
<td>-5</td>
<td>-5.90</td>
<td>-4</td>
<td>6</td>
</tr>
<tr>
<td>Bioinspired</td>
<td>3.048</td>
<td>12.4</td>
<td>0.5</td>
<td>-5.90</td>
<td>-5.0</td>
<td>6</td>
</tr>
</tbody>
</table>
Table 2.3 Design specification for the f/2.25 GRIN lens.

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lens diameter</td>
<td>20 mm</td>
</tr>
<tr>
<td>Clear aperture</td>
<td>18 mm</td>
</tr>
<tr>
<td>Form factor</td>
<td>Plano-convex</td>
</tr>
<tr>
<td>Radius of curvature</td>
<td>23.5 mm</td>
</tr>
<tr>
<td>Center thickness</td>
<td>2.87 mm</td>
</tr>
<tr>
<td>Focal length</td>
<td>41.2 mm</td>
</tr>
<tr>
<td>f/#</td>
<td>2.25</td>
</tr>
<tr>
<td>Minimum index</td>
<td>1.53</td>
</tr>
<tr>
<td>Maximum index</td>
<td>1.57</td>
</tr>
</tbody>
</table>
Figure 2.1 (a) Layout of two component forced assembly multilayer system: extruders, polymer melt pumps, feedblock, multilayering dies, surface layer extruder (not shown), and exit die. Layer multiplication from two to four layers is illustrated by cutting, squeezing, spreading, and recombining polymer melt streams. (b) Procedure to build a GRIN lens: stacking, consolidation, shaping, and diamond turning.
Figure 2.2 (a) Films with tailored refractive index. (b) Refractive indices of PMMA/SAN17 films.
**Figure 2.3** A schematic showing the flexibility of the nanolayered GRIN technique of making sheets with different refractive index distributions: linear and/or non-linear.
Figure 2.4 Hierarchical layered structure of the human eye lens.
coefficients simulated by Zemax software: (Top Point) Q anterior = -5, and Q posterior = -5, and (Bottom Point) Q anterior = 0.5, and Q posterior = 4. (a) Process schematic for producing anterior and posterior bio-inspired GRIN lenses with two different aspheric bio-inspired GRIN lenses in comparison to the Age=5 lens. (b) RMS wave error of bio-inspired GRIN lenses with two different models. (c) RMS wave error of bio-inspired GRIN lenses. Refractive index plot of the designed "Age=5" human eye lens (anterior and posterior) represented in the Dizia's and Code V models. (d) Refractive index plot of the designed "Age=5" human eye lens (anterior and posterior) represented in the Dizia's and Code V models. (e) Refractive index distribution of the anterior and posterior bio-inspired GRIN lenses.
Figure 2.6 Images of bio-inspired GRIN lenses (Top) and the corresponding cross-sectional profiles of anterior and posterior GRIN lenses (Bottom).
Figure 2.7 Plots of experimentally measured and simulated wavefronts for as built bio-inspired aspheric posterior lenses.  (a) Measured data of GRIN lens (b) Numerically simulated values of GRIN lens (c) Measured data of PMMA reference lens (d) Numerically simulated data of PMMA reference lens.  Vertical axis in units of waves (633nm). Planar values are unit less measures of aperture across the wavefront sensor.
Figure 2.8 A Case Western Reserve University logo image that was focused using a bio-inspired “age=5” human eye GRIN lens and captured with a CCD camera.
**Figure 2.9** Refractive index distribution of the PMMA/SAN17 polymer GRIN lens (in the z direction).
Figure 2.10 (a) Experimental setup of minimum spot size measurement. (b) Spot size of glass lens and PMMA/SAN17 polymer GRIN lens. (c) 1D intensity plot of focal spot image.
Figure 2.11 USAF test chart imaged through a PMMA/SAN17 polymer GRIN lens (left) and a glass lens (right).
Figure 2.12 (a) Schematic representation of a hemispherical GRIN lens. (b) Refractive index distribution design of a hemispherical GRIN lens in the Z direction. (c) Procedure of thermoforming a hemispherical GRIN lens. (d) Cross-sectional profile of the hemispherical GRIN lens acquired with placido-cone topography.
Figure 2.13 (a) Experimental setup for focal length measurements. (b) Focal length for PMMA control and hemispherical GRIN lenses as a function of distance between two pinholes: Hemispherical GRIN lens (Triangle) and PMMA control lens (Square).
Figure 2.14 Method of adhering two hemispherical GRIN lenses (Top). Image of a GRIN ball lens (Bottom).
CHAPTER 3

CORRELATION BETWEEN EXPERIMENTAL AND SIMULATED SHAPE DEFORMATION OF A BIO-INSPIRED TUNABLE POLYMER LENS

3.1 Introduction

Compact and adaptive-focus lenses have drawn increasing attention in the field of imaging applications, such as cell phone cameras, video endoscopes, and optical fiber components. [1-4] In traditional optical systems, focal length tuning is accomplished by mechanically translating the optical lens group back and forth along the optical axis which needs a complex transmission mechanism and space. [5] This kind of mechanical lens motion sharply contradicts the biological examples found in nature. For example, the human eye changes its refractive index and shape to focus objects at different distances instead of moving the lens forwards or backwards within the eye. [3,6]

By leveraging principles based on biological examples, researchers have developed a variety of tunable focal length lenses by varying either the refractive index of the optical lens or the lens shape. [2,3,7] Refractive index variation is mainly limited to liquid crystal materials of which molecular orientation can be changed under an electric field. [7] While, lens shape variation takes advantage of either electrowetting mechanisms to alter the radius of the meniscus between two immiscible fluids with different refractive indices [8-10] or deform flexible membranes encapsulating a liquid. [2,9,11,12] As for the flexible
membrane lenses, the lens shape is altered in the following two ways: (a) lens periphery actuation to generate shape deformation in the optical path; or (b) internal volume change through liquid mass transfer. However, these liquid based tunable lenses are susceptible to gravity, temperature fluctuation, and external vibration, and also have low optical axis stability. [3,5,13]

To overcome those drawbacks in liquid based tunable lenses, more and more attention has been paid to the development of all-solid-state tunable lenses, which more closely mimics the nature of the human eye lens. Adaptive-focus can be achieved in all-solid-state tunable lenses through a controlled deformation of their shape, which has been demonstrated by different approaches including mechanical [3,5], thermal[13,14], and electromagnetic [15] actuations. Furthermore, all-solid-state tunable lenses, in contrast to liquid based tunable lenses, do not have any potential sealing and liquid evaporation issues.

In this work, we demonstrate an all-solid-state tunable lens of which focal length can be altered through shape deformation under a compressive stress. A detailed description of the design, material, lens fabrication, and characterization is presented in the following sections. An ANSYS finite element analysis (FEA) model is established to predict shape deformation of the tunable lens, the results of which correlated well with the experimental results.
3.2 Experimental

Ethylene octene copolymer (EO) was provided by Dow Chemicals, Inc. (ENGAGE 8180). EO was selected based on excellent elasticity and optical clarity.

Tunable EO lenses were fabricated via compression molding of EO pellets as shown in Figure 3.1a. Several EO pellets were placed between a glass cylinder lens and a plano-concave glass lens with radius of 13.00 mm which were housed and aligned in a metal holder. The assembly was heated at 180˚C for 10 minutes under minimal pressure, for 5 minutes at 500 lbf, and cooled down to ambient temperature in the press.

The adaptive focus of the tunable lens was accomplished via deforming the lens curvature with applied pressure. To achieve this, a ring compression unit was designed and fabricated as shown in Figure 3.1b,c. The tunable lens was aligned in the center of the piston. When the piston moved the lens towards fixed ring by a micrometer drive, a compressive ring pressure was applied to the lens. This compressive pressure resulted in a symmetrical shape deformation of the tunable lens. As the piston moved the lens towards the rigid ring, the radius of curvature of the tunable lens was sequentially decreased as shown in Figure 3.2d.

The surface profile of the tunable lens was simultaneously captured by a corneal topographer (MM-1 Magellan Mapper, NIDEK Inc.). A non-curing optical coupling gel with a refractive index of 1.46 (OG-1001, Luxlink, Hicksville, NY) was utilized to minimize reflection at the air gap between the tunable lens and compression unit.
The refractive index of the compression molded EO sheet was measured at three different spots by using a commercial refractometer (Model 2010 Prism Coupler, Metricon Corporation, Pennington, NJ).

Stress–strain behavior in uniaxial tension was measured with ASTM1708 microtensile specimens cut from the compression molded sheet at ambient temperature. The separation between the grips was 22.3 mm. Specimens were stretched in an Instron 5965 testing machine. In the hysteresis study, the specimens were cyclically loaded and unloaded in uniaxial tension at a rate of 1.11 mm/min. The hysteresis experiment was conducted at various strains from 10 to 60%.

The model of the entire set-up was simulated using ANSYS Mechanical with 1-to-1 magnification factor. SOLID187 element was used to mesh the compression ring, the lens, and the lens holder. For accurate and efficient solution, the mesh was set fine for the lens and coarse for the compression ring.

Contact surfaces for the simulation were created between the compression ring and the lens, and between the lens and the holder, so that no normal penetration was allowed between these surfaces. And only sliding movements in the tangential direction were allowed. Their counterpart target elements (TARGE170) were created on the surfaces of the ring in contact with the lens. The CONTACT material model was defined for these contact and target elements to have the friction coefficient of 0.1.

A second material model, the linear elastic isotropic model, was defined for the aluminum ring. The Young’s modulus and Poisson’s ratio were set as 7x10^4 MPa and 0.33,
respectively. [16] Mooney-Rivlin model was utilized to simulate the mechanical behavior of the elastic material. The strain energy density was calculated using the two-termed Equation 3.1[17].

\[
W = C_{10}(I_1 - 3) + C_{01}(I_2 - 3)
\]  

(3.1)

Whereas \(C_{10}\) and \(C_{01}\) are two empirically determined material constants, and \(I_1\) and \(I_2\) are first and the second invariant of the unimodular component of the left Cauchy–Green deformation tensor determined by Equation 3.2 [17]:

\[
I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2
\]  

(3.2.1)

\[
I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2
\]  

(3.2.2)

\[
I_3 = \lambda_1^2\lambda_2^2\lambda_3^2
\]  

(3.2.3)

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

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

3.3.1 Characterization of the lens curvature

Figure 3.2 shows the measured radii of curvature as a function of compression distance $\Delta L$. In this study, the lenses had different initial radii of curvatures as measured by corneal topography. The lenses were initially compressed 2 cycles to vary their radii of curvature. The tunable lens was “conditioned” by first compressing to a predetermined strain during the first cycle, and then releasing and repeating the compression. A micrometer was advanced at 0.05 mm increments, and the radius of curvature of the tunable lens was measured by a corneal topographer. When compression is 0.1 mm, the radii of curvature during the 1st cycle nearly overlap those that occurred in the 2nd cycle as shown in Figure 3.2a. With increasing compression, the difference between the radius of curvature of the first cycle and the second cycle increases, which is consistent with the results of the hysteresis study. When compression is 0.4 mm during the 2nd cycle, the radius of curvature decreases from 12.86 mm to 10.41 mm as shown in Figure 3.2d. It was reported that for a 29 year old human eye during accommodation stimulus, the radius of anterior lens can change from 11.9 mm to 7.2 mm; while the radius of posterior lens can change from 6.0 mm to 5.0 mm. [6] So the bioinspired tunable lens can generate a comparable radius change to the human eye lens when compression is 0.4 mm.

To investigate the effect of change in radius of curvature on the focusing properties of the tunable lens, the focal length of the tunable lens can be calculated by using the thin lens Equation 3.3:
\[
\frac{1}{F} = (n - 1) \frac{1}{R} \quad (3.3)
\]

When \( R \) is the radius of curvature of the plano-convex lens, and \( n \) is the refractive index of lens material. The refractive index of EO materials is 1.48 measured by Metricon Refractometer. **Figure 3.2** shows the calculated focal length of the tunable lens plotted as a function of compression distance \( \Delta L \). As the compression distance increases, the calculated focal length also increases. When the compression distance is 0.4 mm, the calculated focal length decreases from 26.8 mm down to 21.7 mm, which results in 19% focal length change in the tunable lens.

### 3.3.2 Elastic Strain Recovery

The effect of repeated cyclic loading on the elastic behavior of EO material at a strain of 60% is shown in **Figure 3.3a**. In this example, the specimen was continuously cycled 5 times to 60% strain, based on the initial gauge length with no time lapse between cycles. A considerable change in stress response was observed between 1\(^{st}\) and 2\(^{nd}\) cycles. However, there were small but consistent decreases in the stress response for all subsequent cycles. The specimen showed a certain amount of unrecovered strain or “permanent set” after the 1\(^{st}\) cycle; however, there is only a small amount of change in the “permanent set” for all the subsequent cycles. Apparently, a significant and permanent structural change occurs during the 1\(^{st}\) cycle that creates a “conditioned” material with better elastomeric recovery. [18-19] After the 1\(^{st}\) cycle, the structural changes during the subsequent cycles were negligible, as indicated by almost overlapping stress-strain curves. It is demonstrated
that the “conditioned” EO material can be used to make tunable lens due to the fact that it possess excellent elastomeric strain recovery after the 1st cycle.

### 3.3.3 Correlation between experimental and simulation results

EO is a rubber-like thermoplastic elastomer which is nearly or purely incompressible. Among all the hyperelastic models, the Mooney-Rivlin (M-R) model is one of the most frequently used models for such a material. Under uniaxial tension conditions, the engineering stress of the Mooney-Rivlin model can be expressed as

**Equation 3.4** [20]:

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

(3.4)

Where the two invariants \( C_1 = C_{10} \), and \( C_2 = C_{01} \).

To best simulate the behavior of the compressed elastomeric material, the 2nd cycle stress-strain curve of EO after being shifted to zero strain (**Figure 3.3a**) was utilized in the simulation work. Successful fitting was achieved below strain of 0.5 using the Mooney-Rivlin model as shown in **Figure 3.3b**. The fitting was based on minimizing the sum of the squares of the offsets, and the invariants \( C_{10} \) and \( C_{01} \) were determined as -0.25 and 1.25, respectively.

To confirm that these two parameters are physically meaningful, Equation 2 was transformed based on the relationship of \( \lambda = \varepsilon + 1 \) using Taylor expansions for \(|\varepsilon| < 1\). The obtained stress-strain relationship for this Mooney-Rivlin model is:
\[ \sigma = 6(C_{10} + C_{01})\varepsilon - 6(C_{10} + 2C_{01})\varepsilon^2 \quad (3.5) \]

In the linear regime of the stress-strain curve (below \( \varepsilon < 2\% \)) in Figure 3.3b, the elastic modulus of the material can be expressed as \( E = 6(C_{10} + C_{01}) \approx 5.98 \text{ MPa} \), which falls in the acceptable region for the EO 8180 elastomeric material. [21] As shown in Figure 3.3b, the stress-strain curve of this Mooney-Rivlin model fits the experimental data below 20% strain.

After ring compression to 0.1, 0.2, 0.3, and 0.4 mm in the –z direction, the lens profile was deformed as shown in Figure 3.5a,b,c,d. As the perimeter area of the lens was compressed, the lens exhibited smaller radius. As the compression increased, the convex shape of the lens became more pronounced with decreasing radius of curvature. The quantitative comparison between the experimental and simulation results are plotted in Figure 3.4. For the samples at each level of compression, the simulated lens shape curve was found to overlap with the experimental data reasonably well, particularly in the lens center region, where the majority of lens functions rely. The lens shape changes generated from the experimental and simulative work are in agreement with each other, confirming the accuracy of the result.

The total mechanical strain density of the elements were examined to confirm that the strains for all the lens samples were within the range of the input material stress-strain curve for valid results. The Von Mises strain is defined based on the strain energy determined from the principle strains in all three (x, y, and z) directions. As shown in Figure 3.5, the maximum mechanical strain intensity for the center parts of these lenses,
which are the lens’s functional area, increased from 0.038 to 0.19 as the compression distance increased from 0.1 to 0.4 mm. All of these strain values fall below 20% strain, where the stress-strain data has satisfactory fitting with the experimental data for the elastomeric material. It is confirmed that the simulated results of the shape change of the lens material are reliable.

In Figure 3.5d, it was exhibited that the total mechanical strain density the center area of the tunable lens is below 9.8% when the compression is 0.4 mm. Meanwhile, when the compression is 0.4 mm, the radius of the tunable lens changes after the 1st cycle from 13.00 mm to 12.86 mm, which is approximately a 1.2% unrecovered radius change. On the other hand, as demonstrated in the previous repeated loading and unloading test at a strain of 10%, the EO material has a hysteresis of 1.2% after the 1st cycle. Therefore, a similar hysteresis behavior was observed in compression tests as well as in the repeated loading and unloading experiment.
3.5 Conclusions

In summary, we have demonstrated an all-solid-state thermoplastic elastomer tunable lens of which focal length was altered by the lens curvature variation under a compressive pressure. The elastic behavior of the lens material was investigated in the hysteresis study. After the first cycle of loading and unloading, the conditioned lens material possesses a complete elastic strain recovery for all subsequent cycles. A permanent and significant structural change occurs during the first cycle that creates a material having better elastic recovery properties. The radius of curvature of the tunable lens was simultaneously measured by a corneal topographer during compression. The results showed that at 0.4mm compression, the lens curvature decreased from 12.86 mm down to 10.41 mm, which resulted in 19% of focal length change in the tunable lens. Furthermore, an ANSYS finite element analysis (FEA) model was established to predict shape deformation of the tunable lens during compression. The simulated results of the models are consistent with the experimental results. In the current study, the adaptive focus was accomplished via altering the radius of curvature of the tunable lens by a micrometer. The micrometer can provide an even and symmetrical pressure to change the radius of curvature of the tunable lens; however, it also blocks the light along the optical axis. In the future, the micrometer can be replaced by motor driven assemblies. The all-solid-state tunable lens is of interest for developing a compact, low-cost, and adaptive-focus imaging systems.
References


Figure 3.1 Schematic representation of producing a tunable polymer lens (a); design (b) and image (c) of the compression unit; and schematic of the mechanism for variable focal length (d).
Figure 3.2 The measured lens curvature and calculated focal length of the tunable lens in the first and second compression cycles as a function of distance: (a) 0.1mm; (b) 0.2mm; (c) 0.3mm; and (d) 0.4mm.
Figure 3.3 (a) the first loading and unloading cycle and the four subsequent cycles of lens materials EO at a strain of 10%; (b) Experimental and simulated stress-strain curves for the elastomer material. The simulation was performed using Mooney-Rivlin model.
Figure 3.4 Comparison of the deformed lens shapes generated by the experiments and simulation.
Figure 3.5 Total mechanical strain intensity results for the lenses with compression distances of (a) 0.1 mm, (b) 0.2 mm, (c) 0.3 mm, and (d) 0.4 mm.
CHAPTER 4

TRIPLE SHAPE MEMORY POLYMER FILMS CREATED BY FORCED ASSEMBLY MULTILAYER FILM COEXTRUSION

4.1 Introduction

Shape memory polymers (SMPs) are a class of smart materials that can memorize temporary shapes and recover to their permanent shape upon exposure to an external stimulus such as heat, light, solvent, magnetic field, or electric field. SMPs have some appealing features compared with the widely used shape memory alloys and shape memory ceramics, such as low cost, large strain recovery, low density, easy shape programming, broad operation temperature, and potential biocompatibility as well as biodegradability. [1-9] These attractive properties of SMPs have enabled numerous applications including sensors, smart fabrics, intelligent packaging, biomedical devices, and aerospace deployable structures. [4,9]

Traditionally, thermoplastic dual SMPs are polymer blends block or copolymers whose shape memory mechanism has already been ascribed to the cooperation of two distinct phases (hard and soft domains) induced by phase separation. However, it is highly composition dependent to produce this kind of two co-continuous domains in both block copolymers and polymer blends, which limits some specific applications that require the turning of the mechanical and shape memory properties. [10-12] A previous study [13,14] on polyurethane (PU)/ polycaprolactone (PCL) shape memory materials using a continuous
multilayer film coextrusion process showed that multilayered PU/PCL films possess dual-shape memory properties which were comparable to or better than PU/PCL blends in terms of strain fixing rate, strain recovering rate, and recovering force. Unlike the PU/PCL blends, the layered film maintained continuous PU and PCL layer structure across all the compositions. This unique advantage allowed multilayered shape memory materials to have a broad window to simultaneously adjust the mechanical properties and shape memory performance.

In order to fully explore the potential applications of SMPs, more and more attention has been paid to the development of triple SMPs. For a dual SMP, which possesses one permanent shape and one temporary shape, only has one thermal transition temperature where the temporary shape will recover to the permanent shape. Unlike dual SMPs, triple SMPs have two well separated thermal transition temperatures. When exposed to heat, triple shape polymers will recover from one temporary shape to another at the first transition temperature, and then bounce back to the permanent shape at another higher transition temperature. In 2006, Lendlein et al. reported that two distinct thermal transitions in a cross-linked network could be independently utilized to fix and recover two temporary shapes. [15] Subsequently, many different strategies including both chemical and physical methods have been proposed to produce triple SMPs. [15 - 20] Furthermore, co-continuous structure plays a vitally important role in triple SMPs as well. [21] It was reported that when the volume fraction of polyethylene (PE) is 30-70% in immiscible PE/polypropylene (PP) blends, chemically cross-linked PE/PP blends have co-continuous structure exhibiting triple shape memory behavior. [22]
In this work, 257 layered polyurethane (PU)/ethylene vinyl acetate (EVA)/poly(vinyl acetate) (PVAc) multilayered films are fabricated by utilizing a 3-component forced assembly multilayer film coextrusion process. The prepared PU/EVA/PVAc films have two well separated thermal transition temperatures, from the melting temperature of EVA and glass transition temperatures of PVAc, which were used to sequentially fix two temporary shapes. Cyclic thermo-mechanical testing was used to study the triple shape memory behavior of PU/EVA/PVAc multilayered films. The effect of layer thickness and film composition on triple shape memory performance was also investigated.
4.2 Experimental

Carbothane PC-3595A polyurethane (PU) and Bynel 38E536 ethylene vinyl acetate (EVA) were obtained from Lubrizol and DuPont, respectively. Polyvinyl acetate (PVAc), VINNAPAS® UW 4 FS, of $M_w = 270000 - 310000$ g/mol, was obtained from Wacker Chemie AG, München Germany. EVA and PVAc were all dried under vacuum at 40°C for 48 hours before extrusion to remove any moisture that may have been absorbed during storage. PU was dried under vacuum at 80°C for 24 hours prior to extrusion.

Multilayered films with 257 alternating ATBTA layers of PU/PVAc/EVA/PVAc/PU were coextruded using 3-component multilayer coextrusion technology described previously. [23] A schematic representation of a 3-component multilayer coextrusion process is shown in Figure 4.1. The coextrusion was conducted at 210°C to ensure viscosity matching among all three polymers. The multilayer films were co-extruded with a polyethylene (PE) skin layer to improve the film quality and protect the film from damage. Films extruded through a 14” sheet die were collected on a film casting takeoff chill-roll set at 50°C. The films consisted of 65 PU layers and 64 EVA layers separated by 128 PVAc layers. The volumetric composition of PU/EVA/PVAc films are 20/20/60, 10/30/60, and 15/20/65. The total PU/EVA/PVAc film thickness varies from 50 μm to 200 μm.

The detailed characteristics of 257 layered PU/EVA/PVAc films is shown in Table 4.1. The nominal layer thickness of PU, EVA, and PVAc layers for each film sample was calculated from the composition and the overall film thickness.
Before evaluating its shape memory behavior, the skin layer PE was removed, and the as-extruded multilayered film annealed at 80 °C for 10 minutes followed by slow cooling to 20 °C to remove the residual stress from the polymer processing step.

Atomic Force Microscopy (AFM) was used to characterize the PU/EVA/PVAc films for layer thickness and integrity. The films were embedded in epoxy and cured overnight at room temperature. The cross section of the embedded film was micromotomed at -120 °C. The AFM images were obtained at ambient temperature in air using the tapping mode of the Nanoscope IIIa Multi Mode scanning probe (Digital Instruments, Santa Barbara, CA).

All quantitative shape memory properties evaluation was performed on a TA instruments Q800 dynamic mechanical analyzer in a tensile and force controlled mode under ambient humidity conditions. Rectangular samples with dimensions of 38 mm by 5.5 mm were cut from the annealed PU/EVA/PVAc multilayered films in the extrusion direction. The tested length in the DMTA was approximately 10 mm for all samples.

Shape fixity and recovery ratios are the two important quantities to describe shape memory effects. The fixity ratio is the ability of switching segments to fix the temporary shape; while, the recovery ratio is the ability of the material to memorize its permanent shape. Figure 4.2 is a schematic representation of a cyclic thermo-mechanical experiment to quantitatively characterize triple shape memory effect. Fixity ratio \( R_f \) and recovery ratio \( R_r \) for each step deformation and overall deformation were calculated by Equation 4.1 and Equation 4.2, respectively. [17,24]
\[ R_f(x \rightarrow y) = 100\% \times \frac{(\varepsilon_y - \varepsilon_x)}{(\varepsilon_{y,load} - \varepsilon_x)} \]  
\[ (4.1) \]

\[ R_r(x \rightarrow y) = 100\% \times \frac{(\varepsilon_y - \varepsilon_{x,rec})}{(\varepsilon_y - \varepsilon_x)} \]  
\[ (4.2) \]

Where \( x \) and \( y \) stand for two different shapes, respectively, \( \varepsilon_{x,load} \) is the maximum strain under load, \( \varepsilon_x \) and \( \varepsilon_y \) represent fixed strains after cooling and unloading, and \( \varepsilon_{x,rec} \) is the strain after recovery.
4.3 Results and Discussion

4.3.1 Morphology and structure of layered films

It is known that morphology and structure play a significant great role in the shape memory properties of multilayered films. The cross-section of the annealed 100 μm 257-layered PU/EVA/PVAc film was imaged and observed under AFM. The alternating layered structure of PU, EVA, and PVAc maintain continuous and regular in the films as shown in Figure 4.3.

4.3.2 Triple shape behavior

Unlike the traditional dual shape memory polymer materials having one thermal transition temperature when a temporary shape recovers back to a permanent shape, triple shape polymers will have two separated thermal transition temperatures. When exposed to heating, triple shape polymers will switch from one temporary shape to another at the first transition temperature, and then back to the permanent shape at another higher transition temperature.

For the PU/EVA/PVc multilayered films, these two well separated thermal transition temperatures are 55 °C and 80 °C. The triple-shape memory behavior of the 100 μm 257-layered PU/EVA/PVAc film was quantitatively evaluated by DMTA and the results are shown in Figure 4.4. The film was first deformed at 80 °C, a temperature above both glass transition temperature Tg of PVAc and melting point Tm of EVA by ramping the force at 0.05 N/min until a stress of 0.05 MPa was reached. The sample was then cooled to
55 °C at 3 °C/min while holding the external stress constant, followed by an isothermal hold for 10 min. The external load was released, and continued to have an isothermal hold for 10 min. This finished the fixing of the first temporary shape S₁ illustrated in Figure 4.4. The shape memory testing continued by reloading the sample at 55 °C using the same force rate of 0.05 N/min until a stress of 0.2 MPa was achieved. The temperature was further reduced to 20 °C at 3 °C/min while holding the external stress constant, followed by an isothermal hold for 10 min. The external load was released, and continued to have an isothermal hold for 10 min. This led to fixing of the second temporary shape S₂ shown in Figure 4.4. The two fixed temporary shapes sequentially recover to permanent shapes when the film was heated to 80 °C at 3 °C/min. It has been reported that polymer shape memory effect is predominantly an entropic phenomenon. [2,20] Changes in temperature and shape in a triple shape memory thermo-mechanical cyclic testing of a 257-layered PU/EVA/PVAc film are as elucidated in the following three steps.

(1) **Programming the first temporary shape (S₁).** In its permanent macroscopic shape (S₀), the molecular chains of PU, EVA, and PVAc layers adopt conformations with the highest entropy, therefore the chains are in a thermodynamically stable state. Upon heating to 80 °C above both T_g of PVAc, and T_m of EVA, both PVAc and EVA’s chain mobility are significantly activated and can move freely while PU chain mobility is low. When an external stress is applied, the PU chain conformation is changed, leading to a lower entropy state and macroscopic change. When the PU/EVA/PVAc film is cooled down to 55 °C, this lower entropy state in PU layer is kinetically trapped due to the crystallization of the EVA molecular chain segment, resulting in the macroscopic shape fixation (S₁).
(2) Programming the second temporary shape ($S_2$). When another external stress is further applied, both EVA and PU chain conformation are changed, leading to a lower entropy state and macroscopic change. When the PU/EVA/PVAc film is cooled down to 20 °C, this lower entropy state in both EVA and PU layer is kinetically trapped due to the vitrification of the PVAc molecular chain segment, resulting in the macroscopic shape fixation ($S_2$).

(3) Shape recovery. Upon reheating to 55°C above $T_g$ of PVAc under a stress free condition, the PVAc chain mobility is reactivated, which allows both EVA and PU chains to return to their highest entropy state at this temporary shape, and macroscopically recover to $S_{1,\text{rec}}$. When the temperature is further heated up to 80°C above $T_m$ of EVA, the EVA chain mobility is also reactivated, so PU chains return to its highest entropy state, resulting in macroscopic change to $S_{0,\text{rec}}$.

In order to study the effect of hysteresis on shape memory properties of the 100 μm 257-layered PU/EVA/PVAc (20/60/20) film, a 5 consecutive cycles of thermo-mechanical testing was conducted as illustrated in Figure 4.5. During the 2$^{\text{nd}}$ cycle, the strain response to the same external stress slightly increases compared with strain response in the 1$^{\text{st}}$ cycle. However, the strain response to the same amount of external stress is nearly identical for the last three cycles. Meanwhile, with increasing thermo-mechanical testing cycles, the recovered strain slightly increases during the first 2 cycles, and then levels off at around 4% strain for the last three cycles. Therefore, it is confirmed that there is no effect of hysteresis on shape memory behavior of PU/EVA/PVAc multilayered film after two thermo-mechanical testing cycles.
4.3.3 Effect of layer thickness on shape fixity and recovery ratios

The effect of layer thickness on triple shape memory properties of PU/EVA/PVAc (20/60/20) multilayered films is investigated. For a 100 μm PU/EVA/PVAc (20/60/20) film, $R_f(S_0 \rightarrow S_1)$, which quantifies shape fixity ratio in the first deformation step, depends on the stress balance between PU and EVA at a temperature of 55˚C. EVA component becomes much stronger after crystallization, which enables the multilayered PU/EVA/PVAc film to achieve a $R_f(S_0 \rightarrow S_1)$ of 74% in the first cycle as shown in Figure 4.6a. The $R_f(S_0 \rightarrow S_1)$ slightly decreases with increasing number of thermo-mechanical cycles. On the other hand, the recovery ratio for the first temporary shape $S_1$ back to its permanent shape $S_0$, $R_r(S_1 \rightarrow S_0)$, increases from 84.57% to 97.6% with the increasing number of thermo-mechanical testing cycles, as shown in Figure 4.6b. At a temperature of 80˚C which is above the glass transition temperature of PVAc and melting temperature of EVA, so $R_r(S_1 \rightarrow S_0)$ is mainly determined by elastic recovery properties of PU. It has been reported that PU has a permanent and significant structural change in the first deformation step, which results in a certain amount of hysteresis after loading was removed. [25] After the first cycle, the PU becomes a better elastomeric material, which confirmed by the decreasing hysteresis. The same phenomenon has also been observed in previous PU/PCL layered shape memory materials. [13,14] Furthermore, it is also noticed that there is no significant effect of layer thickness on shape fixity and recovery ratios of PU/EVA/PVAc films. Thinner film tends to have a slightly better shape fixity and recovery ratios as indicated in Figure 4.6a,b.
Figure 4.7a shows the effect of layer thickness on \( R_f(S_1 \rightarrow S_2) \) in the second shape deformation step. PU/EVA/PVAc multilayered films achieve a shape fixity ratio of 99% in the second shape deformation step for all three different samples with different layer thickness. As described earlier, \( R_f(S_1 \rightarrow S_2) \) mainly depends on the stress balance between PVAc after vitrification and the total strength of EVA and PU. At room temperature, PVAc has much higher modulus than these of EVA and PU. When temperature is cooed down to 25˚C, the vitrification of the PVAc component completely freezes the second temporary shape yielding an outstanding shape fixity ratio in the second shape deformation step.

The effect of layer thickness on shape recovery ratio, \( R_f(S_1 \rightarrow S_2) \), in the second shape deformation step is as shown in Figure 4.7b. \( R_f(S_1 \rightarrow S_2) \) is determined by the stress by balance between EVA and PVAc at 55 °C. It is noticed that \( R_f(S_1 \rightarrow S_2) \) is around 88% and for the first and all subsequent cycles. This is due to the fact that as with the PU material, EVA also has a certain amount of hysteresis in the first cycle, which is generated by the permanent structural change during shape deformation. However, since EVA will be re-melted and then re-crystallized at 55 and 80˚C, respectively, the hysteresis still exists after every thermo-mechanical testing cycle. The amount of hysteresis is theoretically the same in each cycles, which results in nearly the same shape recovery ratio for all 5 thermo-mechanical testing cycles in the second shape deformation. Thinner film also tends to have a slightly better shape fixity and recovery ratios as indicated in Figure 4.7a,b.

\( R_f(S_2 \rightarrow S_0) \) and \( R_r(S_2 \rightarrow S_0) \) are shape fixity and recovery ratios to quantify the overall shape deformation for all three film thickness and are calculated as shown in Table
4.2. Shape fixity ratio, $R_f(S_2 \rightarrow S_0)$, is around 99% for all three films with different thickness, which is very close to shape fixity performance of an ideal shape memory material. While, the shape recovery ratio significantly increases 4-5 % after the first thermo-mechanical testing cycle for all three samples, and then it levels off at around 98%. The multilayered PU/EVA/PVAc films show outstanding triple shape memory behavior in terms of shape fixity and recovery ratios.

4.3.4 Effect of film composition on shape fixity and recovery ratios

Figure 4.8 shows the strain evolution of 100 μm PU/EVA/PVAc multilayered films with different film composition in one round of 5 consecutive thermo-mechanical cyclic testing. With decreasing compositional volume of PU, the strain response to the same stress dramatically increases. Especially, for a 10/60/30 PU/EVA/PVAc composition, the strain response to the same stress increases from 70% in the first thermo-mechanical cycle up to 117% in the fifth cycle. That is because the PU content in 10/60/30 PU/EVA/PVAc multilayered film is not strong enough to keep its permanent shape. For 15/65/20 compositional PU/EVA/PVAc multilayered films, the strain response is slightly higher than 20/60/20 PU/EVA/PVAc films. Therefore, PU plays a very important role in the strain response to the external stress while maintaining the permanent shape.

Shape fixity and shape recovery ratio of all three different composition in the first shape deformation step, $R_f(S_0 \rightarrow S_1)$ and $R_r(S_1 \rightarrow S_0)$ are calculated and plotted as shown in Figure 4.9. The 10/60/30 PU/EVA/PVAc film exhibits the highest shape fixity ratio among all three samples with different compositions as shown in Figure 4.9a. That’s
because the shape fixity in the first shape deformation is dominated by stress balance between EVA and PU at 55°C, which indicates that film having the highest concentration ratio between EVA and PU will have the highest shape fixity ratio in the first step. Obviously, 10/60/30 multilayered film has the highest concentration ratio between EVA and PU. However, shape recovery is always a tradeoff to achieve a high shape fixity ratio. As shown in Figure 4.9b, with the increasing concentration ratio between EVA and PU, the shape recovery in the first shape deformation decreases.

Shape fixity and recovery ratios of all three different compositions in the second shape deformation step, $R_f(S_1 \rightarrow S_2)$ and $R_r(S_2 \rightarrow S_1)$, are calculated and plotted as in Figure 4.10. According to the stress balance mechanism described previously, 10/60/30 compositional PU/EVA/PVAc multilayered film has the best shape fixity ratio in the second shape deformation step because of having the highest concentration ratio between PVAc and EVA among all three compositional samples. However, the shape recovery, $R_r(S_1 \rightarrow S_0)$, in the second shape deformation step shows this film composition has the lowest shape recovery ratio.

$R_f(S_2 \rightarrow S_0)$ and $R_r(S_2 \rightarrow S_0)$, which are shape fixity and recovery ratios to quantify the overall shape deformation for all three film compositions, are calculated as shown in Table 4.3. The 10/60/30 PU/EVA/PVAc multilayered film containing a relatively high concentration of PVAc possesses a slightly better shape fixity ratio than the other two composition. However, all three samples achieve a shape fixity ratio as high as 99%. On the other hand, shape recovery ratio significantly increases 4-5% for all three samples after the first thermo-mechanical testing cycle, then levels off at around 98%.
4.3.5 Visual demonstration of triple shape effect

The triple-shape memory behavior for a 4 mils PU/EVA/PVAc (20/60/20) multilayered film is visually demonstrated in Figure 4.11. A rectangular sample was cut from the annealed PU/EVA/PVAc films along the extrusion direction. The sample was first immersed in a water bath at 80 °C, and then was wound around a brass rod to achieve a loose helical coil structure. Cooling the sample to 55 °C fixes the first temporary shape S1. This temporary shape S1 was further wound into a tight and curved helical coils at 55 °C, and fixed at 20 °C to yield a second temporary shape S2. When immersed in a water bath at 55 °C, the sample quickly returns to the first temporary shape S1, rec. Further heating to 80 °C yielded the recovered permanent shape S0, rec. The recovered permanent shape S0, rec is slightly longer than the original shape S0 due to the fact that there is a certain amount of hysteresis in the first cycle, which correlates well with the previous thermo-mechanical testing results. Therefore, the triple shape memory behavior of PU/EVA/PVAc films is successfully demonstrated.
4.4 Conclusions

Forced assembly multilayer film coextrusion is a continuous, solvent-less, and environmentally friendly process. By utilizing this technique, 257-layer PU/EVA/PVAc films with ATBTATBTA configuration were produced for a novel triple shape memory system. The PU, EVA, and PVAc maintain continuous layered structure in the multilayered films. The resulting PU/EVA/PVAc films have two well separated transition temperatures, one from the melting temperature of EVA and the other from the glass transition temperature of PVAc, which were used to subsequently fix two temporary shapes. The thermo-mechanical cyclic testing results showed that 257 layered PU/EVA/PVAc films possessed outstanding triple shape memory performance in term of shape fixity and shape recovery ratios. It was determined that film composition has an important impact on the triple shape memory performance of the prepared multilayered films. A variety of commercially available polymers can be employed by forced assembly multilayer film coextrusion technique to produce triple shape memory devices with desired shape memory and mechanical properties.
References


Table 4.1 Characteristics of 257 layered PU/PVAc/EVA multilayered films.

<table>
<thead>
<tr>
<th>PU/PVAc/EVA Comp. (vol%/vol%/vol%)</th>
<th>film thickness (μm)</th>
<th>nominal thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>PU</td>
</tr>
<tr>
<td>PU Control</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>EVA Control</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>PVAc Control</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>20/60/20</td>
<td>50</td>
<td>157</td>
</tr>
<tr>
<td>20/60/20</td>
<td>100</td>
<td>315</td>
</tr>
<tr>
<td>20/60/20</td>
<td>200</td>
<td>720</td>
</tr>
<tr>
<td>10/60/30</td>
<td>100</td>
<td>157</td>
</tr>
<tr>
<td>15/65/20</td>
<td>100</td>
<td>236</td>
</tr>
</tbody>
</table>
Table 4.2 Fixity and recovery ratios calculated for triple shape memory 257 layered PU/EVA/PVAc (20/60/20) multilayered films with different thickness. All of the numbers represent the percentage (%).

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Film Thickness (μm)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>100</td>
<td>200</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>1&lt;sup&gt;st&lt;/sup&gt;</td>
<td>R&lt;sub&gt;f&lt;/sub&gt;(S&lt;sub&gt;2&lt;/sub&gt;→S&lt;sub&gt;0&lt;/sub&gt;)</td>
<td>99.3</td>
<td>92.8</td>
<td>99.4</td>
<td>92.3</td>
<td>99.4</td>
</tr>
<tr>
<td>2&lt;sup&gt;nd&lt;/sup&gt;</td>
<td>R&lt;sub&gt;r&lt;/sub&gt;(S&lt;sub&gt;2&lt;/sub&gt;→S&lt;sub&gt;0&lt;/sub&gt;)</td>
<td>99.3</td>
<td>96.4</td>
<td>99.4</td>
<td>96.5</td>
<td>99.7</td>
</tr>
<tr>
<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>R&lt;sub&gt;f&lt;/sub&gt;(S&lt;sub&gt;2&lt;/sub&gt;→S&lt;sub&gt;0&lt;/sub&gt;)</td>
<td>99.3</td>
<td>97.7</td>
<td>99.4</td>
<td>98.1</td>
<td>99.4</td>
</tr>
<tr>
<td>4&lt;sup&gt;th&lt;/sup&gt;</td>
<td>R&lt;sub&gt;r&lt;/sub&gt;(S&lt;sub&gt;2&lt;/sub&gt;→S&lt;sub&gt;0&lt;/sub&gt;)</td>
<td>99.2</td>
<td>98.7</td>
<td>99.4</td>
<td>98.5</td>
<td>99.2</td>
</tr>
<tr>
<td>5&lt;sup&gt;th&lt;/sup&gt;</td>
<td>R&lt;sub&gt;r&lt;/sub&gt;(S&lt;sub&gt;2&lt;/sub&gt;→S&lt;sub&gt;0&lt;/sub&gt;)</td>
<td>99.2</td>
<td>98.6</td>
<td>99.4</td>
<td>99.1</td>
<td>99.1</td>
</tr>
</tbody>
</table>
Table 4.3 Fixity and recovery ratios calculated for triple shape memory 100 μm 257
layered PU/EVA/PVAc multilayered films with different composition. All of the numbers
represent the percentage (%).

<table>
<thead>
<tr>
<th>Cycle</th>
<th>PU/EVA/PVAc (vol%/vol%/vol%)</th>
<th>10/60/30</th>
<th>20/60/20</th>
<th>15/65/20</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rf (S2→S0)</td>
<td>Rr (S2→S0)</td>
<td>Rf (S2→S0)</td>
<td>Rr (S2→S0)</td>
</tr>
<tr>
<td>1st</td>
<td>99.3</td>
<td>95.8</td>
<td>99.4</td>
<td>92.3</td>
</tr>
<tr>
<td>2nd</td>
<td>99.7</td>
<td>97.0</td>
<td>99.4</td>
<td>96.5</td>
</tr>
<tr>
<td>3rd</td>
<td>99.7</td>
<td>97.8</td>
<td>99.4</td>
<td>98.1</td>
</tr>
<tr>
<td>4th</td>
<td>99.7</td>
<td>98.0</td>
<td>99.4</td>
<td>98.5</td>
</tr>
<tr>
<td>5th</td>
<td>99.7</td>
<td>98.3</td>
<td>99.4</td>
<td>99.1</td>
</tr>
</tbody>
</table>
Figure 4.1 A typical schematic layout of 3-component forced assembly multilayer film coextrusion system utilized to fabricate shape memory polymer materials.
Figure 4.2 Definition of shape fixity and recovery ratios in triple shape memory polymer.
Figure 4.3 AFM images of continuous P/P/UV/EVA/PVAc layer structure in 100 μm multilayer films at different composition: a) 20/60/20; b) 15/65/20; and c) 10/60/30.
Figure 4.4 Quantitative evaluation of triple shape memory properties of 4 mils 257 Layered 20/60/20 PU/EVA/PVAc Films by DMTA.
Figure 4.5: Consecutive triple shape memory testing of 4 mils 257 layered 20/60/20 PU/EVA/PVAc multilayer films.
Figure 4.6 Effect of layer thickness on shape fixity ratio (a) and shape recovery ratio (b) of 20/60/20 PU/EVA/PVAc films in the first temporary shape.
Figure 4.7 Effect of layer thickness on shape fixity ratio (a) and shape recovery ratio (b) of 20/60/20 PU/EVA/PVAc films in the second temporary shape.
Figure 4.8 Strain evolution of different compositional PU/EVA/PVAc multilayer films in 5 consecutive thermo-mechanical cycles.
Figure 4.9   Effect of composition on shape fixity ratio (a) and recovery ratio (b) of PU/EVA/PVAc multilayered films in the first temporary shape.
Figure 4.10 Effect of composition on shape fixity ratio (a) and recovery ratio (b) of PU/EVA/PVAc multilayered films in the second temporary shape.
Figure 4.11
Visual demonstration of triple shape memory properties of 100μm 257 layered PU/EVA/PU (20/60/20) multilayered films.
BIBLIOGRAPHY

CHAPTER 1:


CHAPTER 2:


**CHAPTER 3:**


**CHAPTER 4:**


