SYTHESIS AND CHARACTERIZATION OF SHAPE MEMORY

POLYMER FOAMS WITH IMPROVED MECHANICAL PROPERTIES

An Undergraduate Research Scholars Thesis

by

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ABSTRACT

Synthesis and Characterization of Shape Memory Foams with Improved Mechanical Properties

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Vascular aneurysms are a significant source of morbidity and mortality, affecting 3 to 5 million Americans annually. Current treatments often require either highly invasive strategies to surgically occlude the aneurysm or endovascular occlusion via metal coils. While endovascular coils are safer, there are distinct limitations to this treatment path, including a lack of stable blood clot formation and a risk of the coil intruding into the arteries. Endovascular coils that are integrated with shape memory polymers (SMPs) have the potential to improve occlusion and reduce coil risks; however, there are some limitations on mechanical performance and homogeneity of SMP physical properties. To address this issue, SMP foams were synthesized using the monomer diethanolamine (DEA) in place of triethanolamine (TEA) to provide the mechanical properties required for medical device applications. The incorporation of DEA was confirmed spectroscopically, as demonstrated by the urethane peak that is the hallmark of this chemistry and the urea peak associated with the DEA-isocyanate reaction. The utility of the DEA foam was demonstrated via mechanical testing and shape recovery analysis, in comparison to the TEA SMP formulation. DEA foams had a comparable modulus, or stiffness, and an increased toughness compared to the control. Preliminary shape recovery experiments indicate that the incorporation of DEA increases the rate of recovery compared to that of the control. This work

presents the utility of DEA in SMPs to improve mechanical toughness and enable the production

of safer medical devices for use in aneurysm treatment.

ACKNOWLEDGMENTS

This thesis is the result of my Undergraduate Research Scholar project at Texas A&M University. First, I would like to express my appreciation to my advisor, Dr. Duncan Maitland, for sharing his experience and wisdom with me during my research. I also would like to thank Dr. Mary Beth Browning Monroe, Dr. Brandis Keller, and Dr. Marziya Hasan for their help in the experiment and writing process. Finally, I would like to thank the remaining Biomedical Device Laboratory members for their support during the research process.

NOMENCLATURE

BDL   Biomedical Device Laboratory

DEA   diethanolamine

DI   deionized

DSC   differential scanning calorimetry

FTIR   Fourier transform infrared spectroscopy

HDI   hexamethylene diisocyanate

HPED   N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylene-diamine

Nitinol   Nickel Titanium

RO   reverse osmosis

SEM   scanning electron microscopy

SMP   shape memory polymer

TEA   triethanolamine

TGA   thermogravimetric analysis

TMHDI   trimethyl-1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4- mixture

CHAPTER I

INTRODUCTION

Approximately 3 to 5 million Americans suffer from cerebral aneurysms.[1] An aneurysm occurs when a blood vessel weakens and balloons out, which most commonly occurs in the aorta, cerebral arteries, the popliteal artery, the mesenteric artery, and the splenic artery. [2] As the aneurysm expands, the blood vessel wall thins, which leads to rupture. A cerebral aneurysm rupture often results in a subarachnoid hemorrhage, which can lead to a hemorrhagic stroke.[3] Approximately 46% of patients do not survive the first hemorrhage, and if the ruptured aneurysm is not repaired, a second hemorrhage can occur. Approximately 80% of patients do not survive the second hemorrhage.[3]

Current treatments to prevent blood flow to the aneurysm include invasive microsurgical clipping and minimally-invasive endovascular coiling. Microsurgical clipping involves placing a small metal clip at the base of the aneurysm to block blood flow.[3] This procedure requires a craniotomy, or surgical removal of part of the skull to expose the brain, to access the aneurysm for clip placement.[4] The craniotomy procedure presents significant risks, such as hemorrhage, thrombus formation, brain swelling, and seizures.[4] During the procedure, the clip may also be placed incorrectly, causing partial blockage or complete restriction of blood flow through a normally functioning artery.[5]

Endovascular coils were first used clinically in 1990 to reduce the risk associated with aneurysm occlusion *via* microsurgical clipping.[6] This method utilizes a catheter that is inserted into the

femoral artery and maneuvered to the aneurysm site.[7] After the catheter is properly positioned,

endovascular coils are deployed using a guide wire.[7] Relative to surgical clipping, endovascular

coils reduce procedural risks, but have higher incidences of retreatment and lower rates of

complete aneurysm occlusion due to incomplete healing.[8,9]

The Biomedical Device Laboratory (BDL) at Texas A&M aims to improve the function and

safety of endovascular coils by utilizing an innovative integration of coils with shape memory

polymers (SMPs). SMPs are materials that have the ability to transition between a primary and

secondary shape *via* a thermally induced transition. The device utilizes the same concept as the

endovascular embolization coils, but introduces a shape memory polymer (SMP) foam crimped

over a nickel-titanium (nitinol) and platinum wire backbone.[10] These devices are delivered in

their secondary, crimped shape to the aneurysm *via* a micro-catheter, as shown in Figure 1. Once

deployed in the aneurysm sac, the foam will expand to its primary shape, promoting rapid
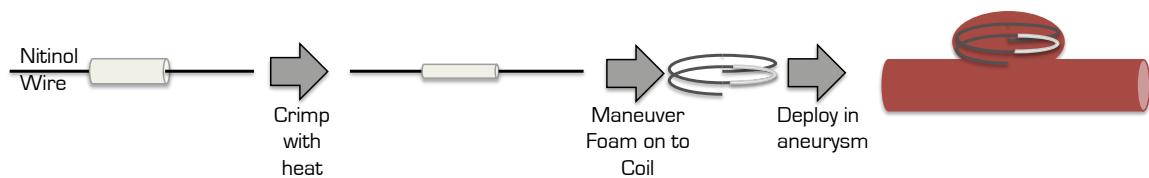
occlusion.[10]

Figure 1. Schematic representation of the process of crimping a SMP onto a nitinol wire, maneuvering the foam onto a coil, and deploying to SMP/coil system into an aneurysm.

Although the main focus of the BDL is the foam-over-wire embolization device, there are other

potential applications of the SMP foams, including clot removal devices, vascular stents, and

scaffolds for tissue engineering applications.[11] All of these devices rely on the shape memory

property of the polymers to return the foams to the original, expanded shape once deployed in

the body. One limitation of the SMP foams is the anisotropic pore geometries, or pores that are elongated in the foaming direction. The elongated pores are more susceptible to mechanical deformation, such as cell collapse and strut fracture.[12,13] These deformations reduce the mechanical properties and inhibit total volume recovery (strain recovery) of the material, as shown in Figure 2.
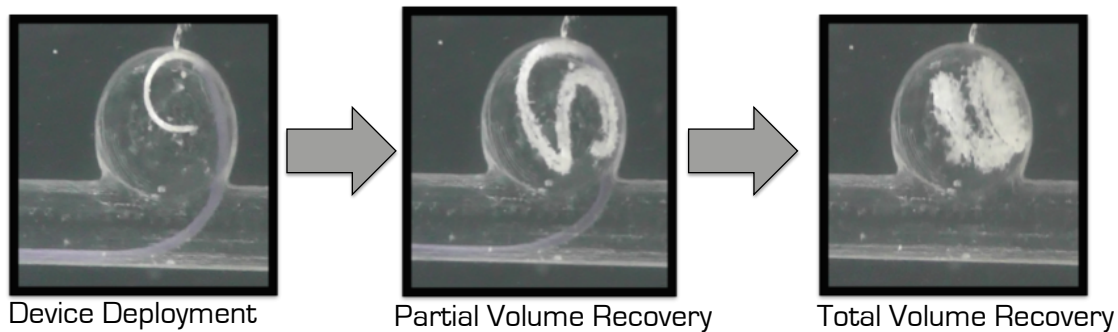

Device Deployment   Partial Volume Recovery   Total Volume Recovery

Figure 2. *In vitro* device deployment and primary shape recovery.

Research objectives

To address these issues, I will chemically modify the foams with dieathanolamine (DEA) in an attempt to enhance their mechanical properties by yielding isotropic pores. Mechanically robust foams are hypothesized to be more resilient to deformation, which will improve their ability to occlude the aneurysm and reduce device complications of recanalization and perforation compared to currently available endovascular embolization coils. Additionally, changing the chemical component of the polymer will potentially increase the working time of the device (time until the diameter is larger than the microcatheter delivery system). We hypothesize that the chemically-modified-DEA foams are suitable for SMP integration, and propose the following experiments:

AIM 1: Fabricate DEA foams and characterize their pore isotropicity and mechanical properties relative to previously developed triethanolamine (TEA)-based SMP foams.

AIM 2: Compare volume recovery and working time of DEA and TEA SMP foams.

CHAPTER II

METHODS

Material synthesis

The following chemicals were obtained and used as received: diethanoleamine (DEA, 99%; Sigma-Aldrich Inc., St. Louis, MO), triethanolamine (TEA, 99%; Sigma-Aldrich Inc., St. Louis, MO), N,N,N′,N′-tetrakis(2-hydroxypropyl)ethylene-diamine (HPED, 99%; Sigma-Aldrich Inc., St. Louis, MO), trimethyl-1,6-hexamethylene diisocyanate, 2,2,4- and 2,4,4- mixture (TMHDI, 97%; TCI America Inc., Portland, OR), hexamethylene diisocyanate (HDI, 98% ; TCI America Inc., Portland, OR), and deionized (DI) water (Millipore water purifying system, Millipore Inc., Billerica, PA). To achieve the objectives defined above, the foaming protocol was altered to ensure that DEA reacted properly with the other monomers.[15]

The pre-polymer mix was made by first reacting HPED and TMHDI with an excess of isocyanate. Once the HPED and TMHDI reaction was complete, the DEA was added, and the jar was shaken until the mixture became clear. The pre-polymer mix was cured using a heating cycle of 6 hours at room temperature, heating at 20°C per hour until the temperature reached 50°C, and holding at 50°C for 16 hours.[15] The hydroxyl premix was made after the pre-polymer had cured by combining the remaining stoichiometric amounts of DEA and HPED with surfactants, tin catalyst, amine catalyst, and DI water.[14] The pre-polymer mix, the hydroxyl premix and physical blowing agent were combined to produce a foam, which was cured for 20 minutes at 90°C. The first series of 32 gram foams (TEA:DEA ratio series) contained varying amounts of DEA added at 0%, 10%, 20%, 30%, and 40% (Table 1). The isocyanate content for all foams

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was 100% TMHDI, and the remaining percent of alcohol groups came from HPED. The second series of 32 gram foams (TMHDI: HDI ratio series) contained 20% DEA and 80% HPED for the alcohol groups. The isocyanate content was varied at 0%, 30%, 50%, 70%, and 100% HDI, with the remaining percent of isocyanate groups from TMHDI (Table 1). A control foam was synthesized containing 20% TEA, 80% HPED, and 100% TMHDI (H60:T40 control foam). The density, pore size, and mechanical properties of all of the foams were characterized before the cleaning process.[15} Foams were cleaned to remove unreacted monomers and excess foaming agents *via* washing with isopropyl alcohol wash and reverse osmosis (RO) water. After cleaning, the remaining characterizations were performed.

Material characterization

Density

Sample cubes were cut from three different horizontal positions within the foam using a hot wire cutter. The length, width, and height of the cubes were measured in triplicate for accuracy. The masses of the cubes were taken, and the densities were calculated in grams per centimeter cubed.

Pore size

Slices were cut from the center of the foam in the axial and transverse directions. The samples were mounted onto a stage and sputter coated with gold using a Cressington Sputter Coater (Ted Pella, Inc., Redding, CA) for 60 seconds at 20 milliamperes. The samples were then imaged using a Joel NeoScope JCM-5000 Scanning Electron Microscope (SEM) (Nikon Instruments Inc., Melville, NY) at 10X to 15X magnification at 5 kilovolts under high vacuum. The pore size was measured from the images using ImageJ software (National Institute of Health, Bethesda,

MD). The pore size was calculated as the average of the major axis length of ten pores found within the image.

Spectral characterization

A foam slice was taken from cleaned foam and was placed into a Brunker ALPHA Infrared Spectrometer (Bunker, Billerica, MA). Thirty-two backgrounds scans were performed on each sample before sixty-four sample scans were performed. The FTIR spectrum was collected in absorption mode with a resolution of 4 cm^{-1}. The background scan was subtracted from the sample scan, a baseline correction, and atmospheric compensation was applied using OPUS software. This process was repeated three times for each composition.

Mechanical properties

Samples (n=10) were prepared by cutting 3 mm thick slices of foams into a dog-bone shape (ASTM standard IV). After the samples were cut, they were secured onto wooden stubs using epoxy to prevent sample damage from the clamps. The samples were then secured into the Insight 30 Material Tester (MTS Systems Corporation, Eden Prairie, MN), and were tested using a uniaxial tensile loading test protocol. The samples were stretched at a constant strain rate of 5 mm per minute. The resulting stress-strain curve was used to determine toughness, tensile strength, and strain at break.

Thermal properties

Dry samples (n=5, ~10 mg) were cut and placed in a TA Tzero aluminum hermetic pan for differential scanning calorimetry (DSC) using a Q200 TA DSC with a TA Refrigerated Cooling

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System 90 (TA Instruments, New Castle, DE). The pans were sealed and loaded into the test cell at room temperature. The dry samples were equilibrated at -40°C and then ramped to 120°C at a rate of 10°C per minute. The samples were held isothermally at 120°C for 2 minutes and then cooled to -40°C at a rate of 10°C per minute. The samples were held isothermally at -40°C for 2 minutes and then heated back to 120°C at a rate of 10°C per minute.

Five additional samples were prepared by adding approximately 1 mg of deionized (DI) water at 50°C to each sample. The samples were re-weighed, sealed into a TA pan at room temperature, and vented before being loaded into the Q200 DSC. The wet samples were equilibrated at -40°C and held isothermally for 5 minutes, then ramped to 120°C at a rate of 5°C per minute. The glass transition temperature (T_g) for both wet and dry samples was identified as the half-height transition point from the last heating cycle using TA Universal Analysis software (TA Instruments, New Castle, DE).

Samples (n=3) weighing approximately 10 mg were placed into a clean alumina pan. The pan was loaded into the TA Q50-0408 thermogravimetric analyzer (TGA) (TA Instruments, New Castle, DE). The samples were heated from room temperature to 800°C at 10°C per minute. The % mass remaining was plotted against the temperature, and the temperature of thermal degradation onset was found using TA Universal Analysis software (TA Instruments, New Castle, DE).

Working time characterization

Volume recovery profiles were determined by expanding crimped samples (n=3) in a heated water bath. Cylindrical samples were cut to 4 mm in diameter and 1 cm in length. The samples were then threaded onto a nickel-titanium (nitinol) wire with a diameter of 203.20 microns (Nitinol Devices and Components Inc., Fremont, CA). Using a ST 150-42 stent crimper (Machine Solutions, Flagstaff, AZ), the samples were heated to 100°C held isothermally for 15 minutes, radially compressed to the smallest possible diameter, and then cooled to room temperature. An image was taken before and after radial crimping. Once the samples were crimped, they were stored in a dry container for 24 hours to ensure complete shape-setting of the foam and allow for any relaxation to occur. After 24 hours, a reverse osmosis (RO) water bath was heated to 37°C. The samples were submerged in the water bath, and images were taken at set time points for 30 minutes. After 30 minutes, the samples were removed from the water bath, dried with compressed air for approximately 5 minutes and were placed back into a container, at room temperature, to dry for 24 hours. After the samples were dry, the RO water bath was heated to 50°C. The samples were submerged in the water, and images were taken at set time points for 30 minutes.

CHAPTER III

RESULTS

Material characterization

Density

There was minimal change in the density of the foams with increasing amounts of DEA or with varied isocyanate monomer ratios, as seen in Table 1. Thus, these materials still display the ultralow density (< 0.093 g cm^{-3}) characteristic of the cross-linked SMP system.[16]

Table 1. Effects of isocyanate and alcohol monomer ratios on foam density. The TEA:DEA ratio series was fabricated with 100% TMHDI, and the TMHDI:HDI ratio series was fabricated with 20% DEA.

TEA:DEA Ratio	ρ (g cm^{-3})	TMHDI:HDI Ratio	ρ (g cm^{-3})
T100:D0	0.023 ± 0.005	TM100:H0	0.020 ± 0.001
T90:D10	0.020 ± 0.001	TM70:H30	0.017 ± 0.001
T80:D20	0.020 ± 0.001	TM50:H50	0.018 ± 0.001
T70:D30	0.018 ± 0.001	TM30:H70	0.015 ± 0.001
T60:D40	0.020 ± 0.001	TM0:H100	0.020 ± 0.001

Pore size

The axial pore size of the foams remained relatively constant with changes in alcohol and isocyanate monomer ratios, as seen in Figure 3. In the TEA:DEA ratio series, incorporation of DEA resulted in isotropic pores, or pores that have similar diameters in the axial and transverse directions; this trend is particularly apparent with lower concentrations of DEA and correlates with previous studies that utilized DEA in which a similar result was qualitatively shown using SEM images.[17] In the TMHDI:HDI ratio series, decreasing the amount of TMHDI present in the foam led to more anisotropic pores, or pores that have different diameters in the axial and transverse directions.
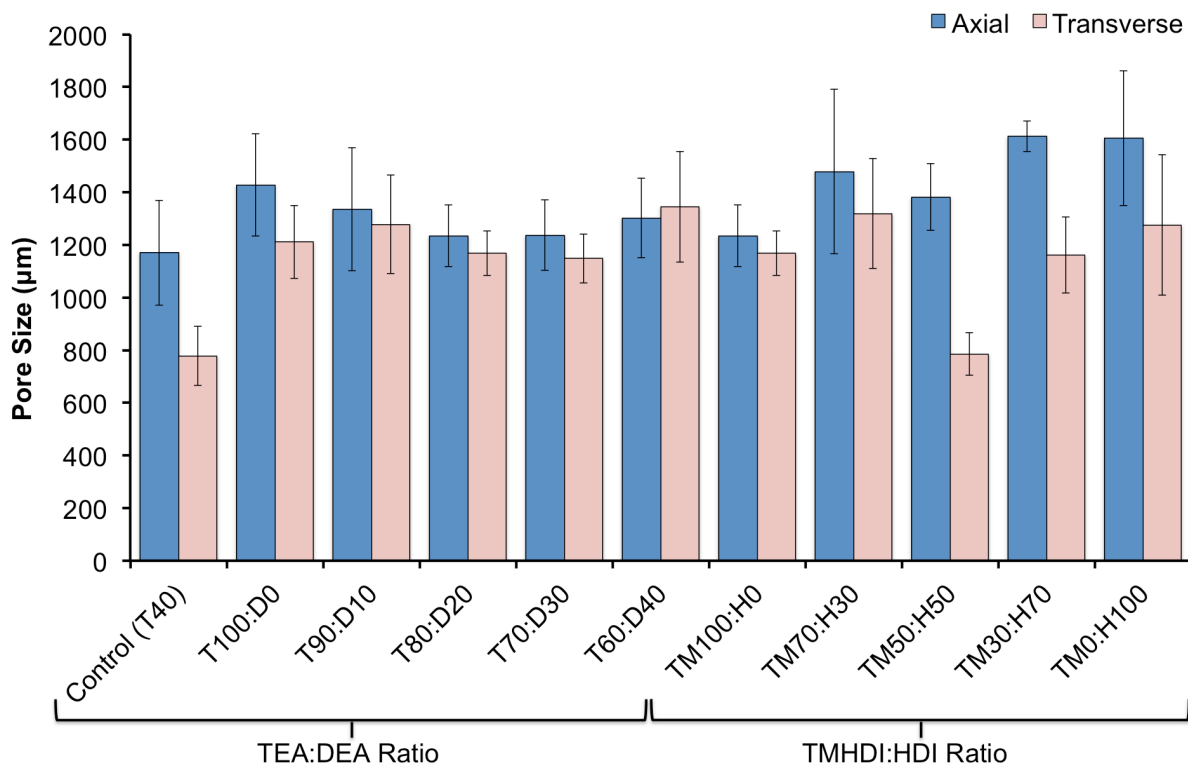

Figure 3. Effect of changes in alcohol and isocyanate monomer ratios on pore sizes measured on axial and transverse slices. The TEA:DEA ratio series was fabricated with 100% TMHDI, and the TMHDI:HDI ratio series was fabricated with 20% DEA.

Spectral characterization

Selected FTIR spectral regions are identified in Figure 4. The hydrogen-bonded urethane, C=O stretch (1698 cm^{-1}), identifies a polyurethane system.[14] The increases in the relative peak height for the hydrogen-bonded urea, C=O shoulder (1647 cm^{-1}), confirms the successful incorporation of DEA. The amine group in DEA reacts with the isocyanate functional groups to form a urea linkage.
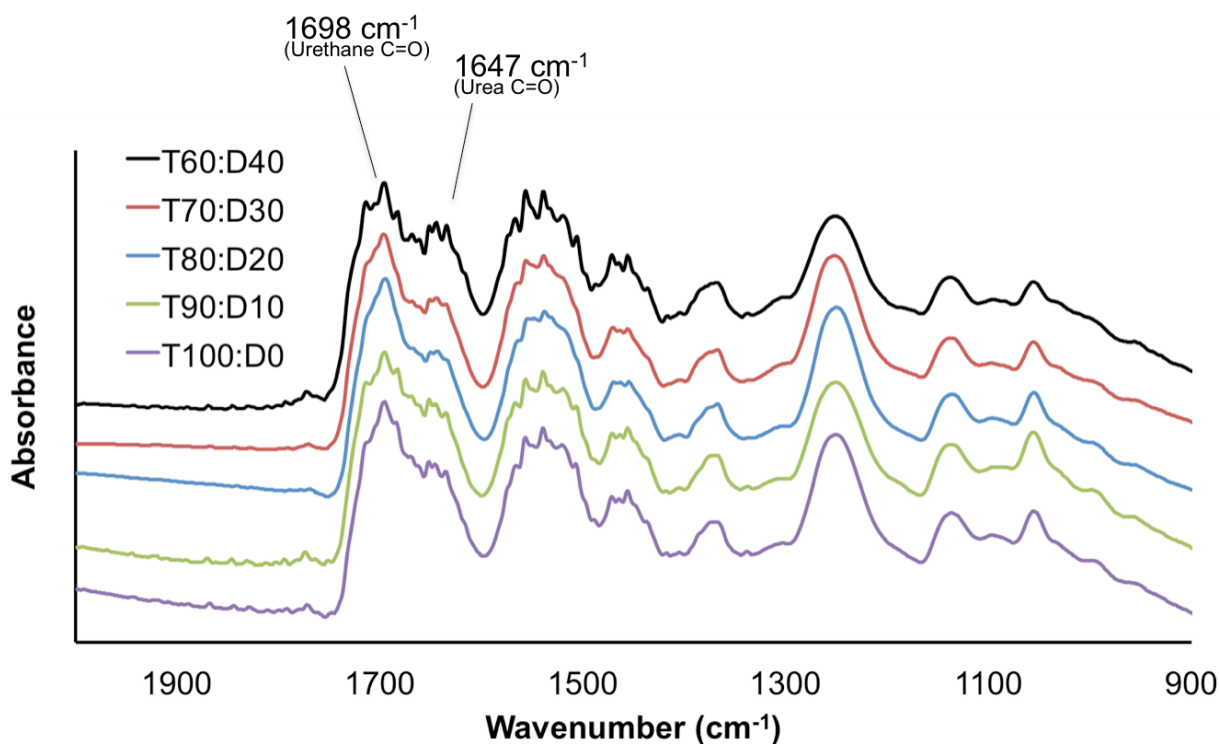

Figure 4. Effects of TEA:DEA ratio on FTIR spectra.

Mechanical properties

The foams containing DEA exhibited similar Young's modulus, or slope of the linear region, as the control, as seen in a representative stress-strain curve of T70:D30 and the control, while ultimate tensile strength, toughness, and strain at break differed with monomer variables. In general, the addition of HDI led to a decrease in ultimate tensile strength, as seen in Figure 5c.

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The TM30:H70 foams exhibited a large increase in ultimate tensile strength that is attributed to the anisotropic pores that allow for larger deformation in the direction of applied force. Increasing the amount of DEA in the foam up to 30% increased the ultimate tensile strength as compared to T100:D0 and H60:T40, which is the current (control) formulation, Figure 5b. The T60:D40 foam ultimate tensile strength is reduced, which is attributed to the premix reaching maximum loading of DEA at 30% (T70:D30). Overall, the addition of HDI decreased the toughness (Figure 5e), while increasing the amount of DEA increased the toughness compared to the H60:T40 control foam (Figure 5d). Overall, strain at break decreases with increasing amounts of HDI, as seen in Figure 5g. The addition of DEA leads to a minimal changes in strain at break compared to the control H60:T40 foam, as seen in Figure 5f.
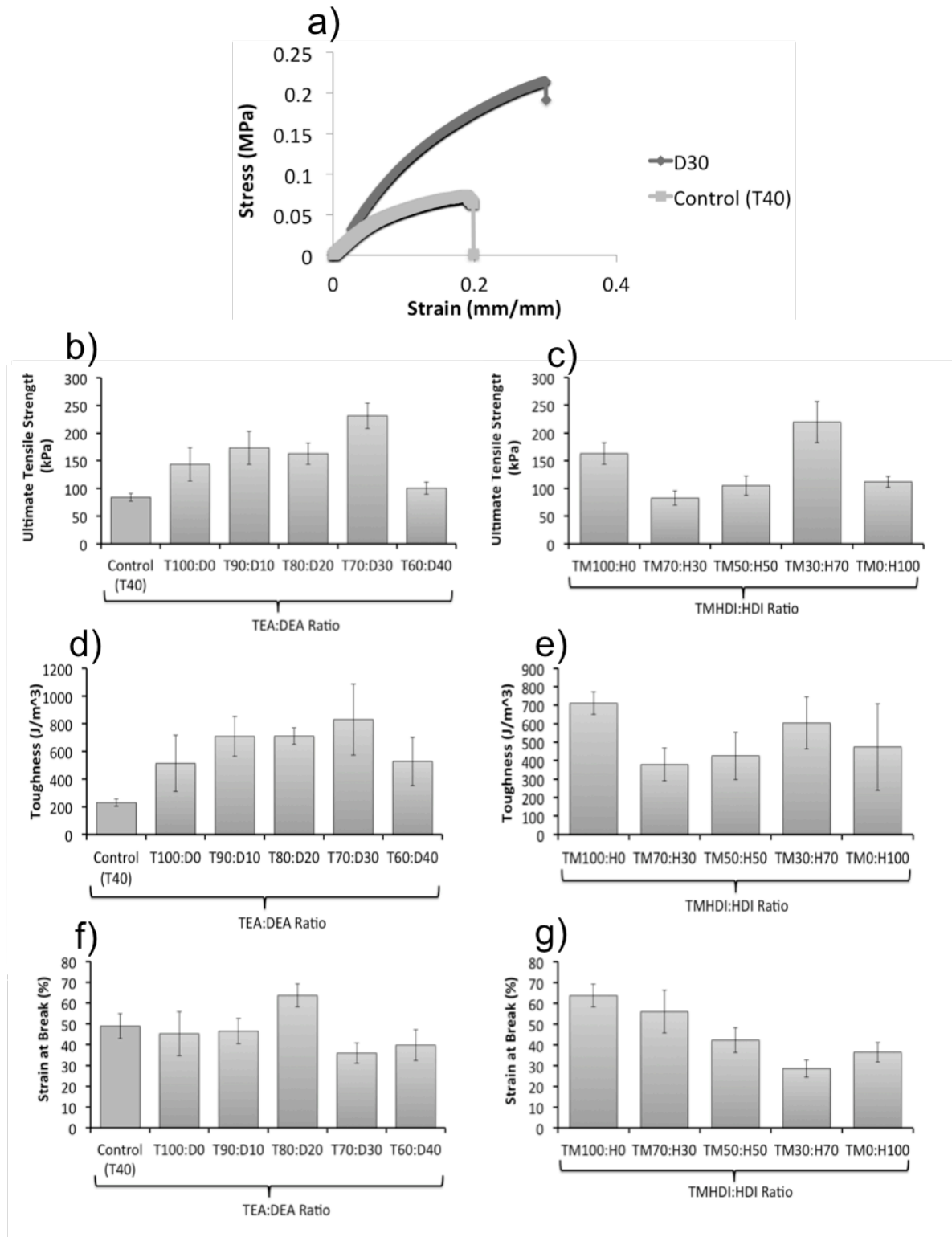
Figure 5. Effects of monomer variables on foam mechanical properties. a) Stress vs. strain curve; ultimate tensile strength of b) TEA:DEA series and c) TMHDI:HDI series; toughness of c) TEA:DEA series and d) TMHDI:HDI series; and strain at break of f) TEA:DEA series and g) TMHDI:HDI series.

Thermal properties

All foam compositions exhibited a dry T_g that was greater than the wet T_g, as seen in Figure 6. Increasing the amount of DEA in the foams had minimal effects on both the wet and dry T_g. Increasing the amount of HDI in the foam decreased dry T_g while the wet T_g was unaffected.
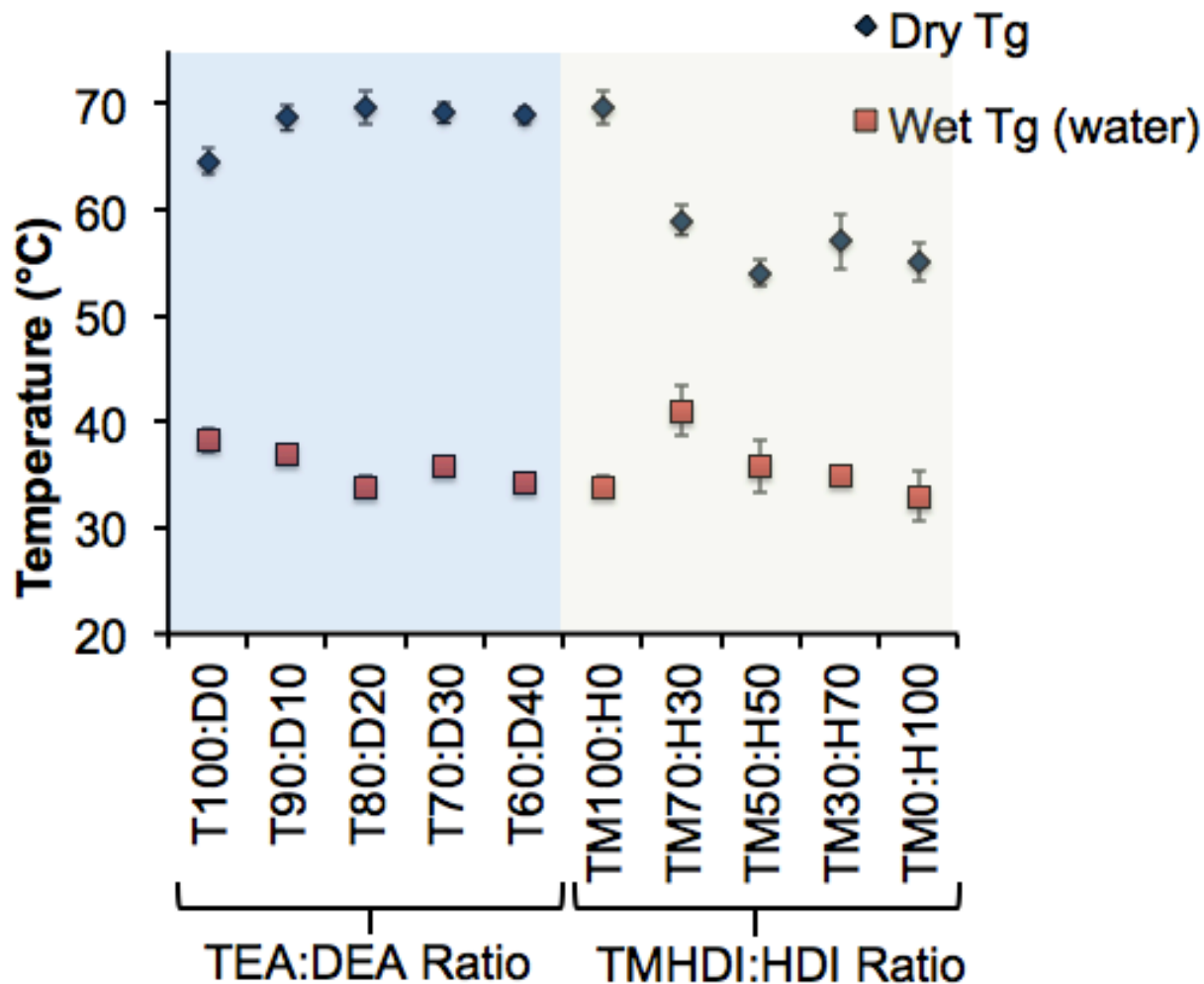

Figure 6. Effects of monomer variables on wet and dry T_g. The TEA:DEA ratio series was fabricated with 100% TMHDI, and the TMHDI:HDI ratio series was fabricated with 20% DEA.

TGA of the foams was performed, and the thermal degradation onset for the foams is seen in Figure 7. The thermal degradation onset varies slightly with increasing amounts of DEA, as seen

in Figure 7a. With varying amounts of HDI the thermal degradation onset temperature was relatively constant, as seen in Figure 7b.
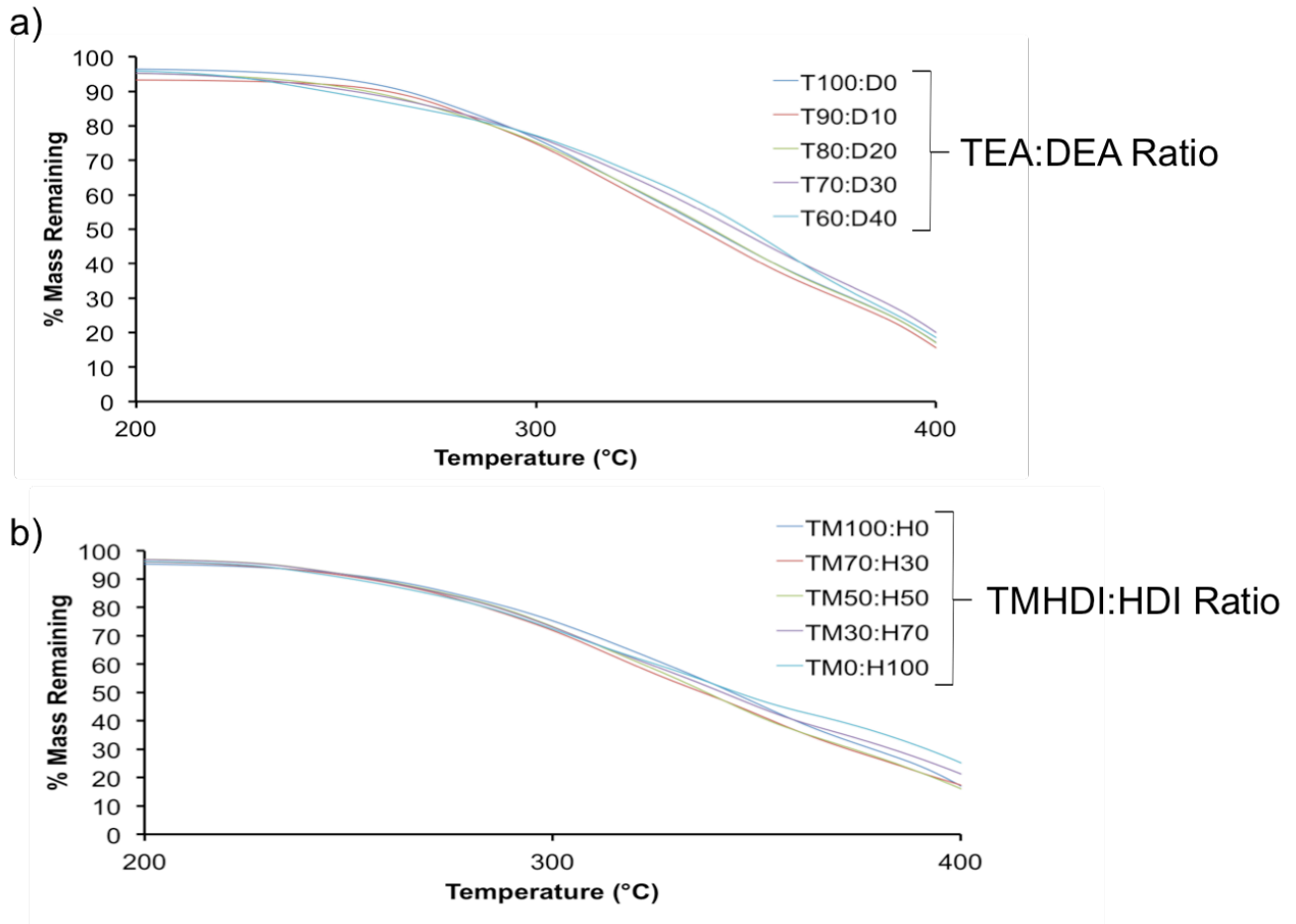

Figure 7. Effects of monomer variables on thermal degradation profiles. The TEA:DEA ratio series was fabricated with 100% TMHDI, and the TMHDI:HDI ratio series was fabricated with 20% DEA.

Working time characterization

The working time is defined as the time until the foam diameter is larger than the inner diameter of the catheter, preventing its further delivery. Foam expansion of the TEA:DEA series demonstrated that working time decreases as DEA concentration increases, as seen in Figure 8.

Analysis of foam expansions with varying TMHDI:HDI showed that the working time decreased as HDI concentration was increased, as seen in Figure 9.
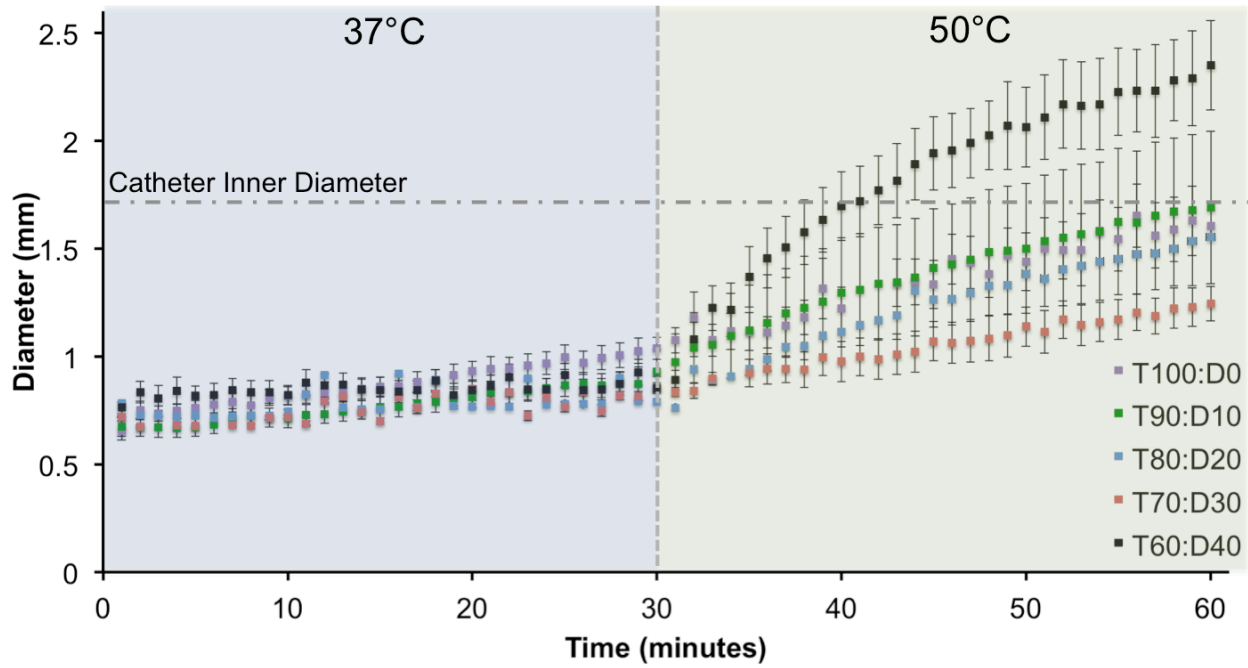

Figure 8. Effect of TEA:DEA alcohol monomer ratios (isocyanate is 100 TMHDI) on device working time. Catheter diameter is indicated by gray dotted line (1.7 mm).
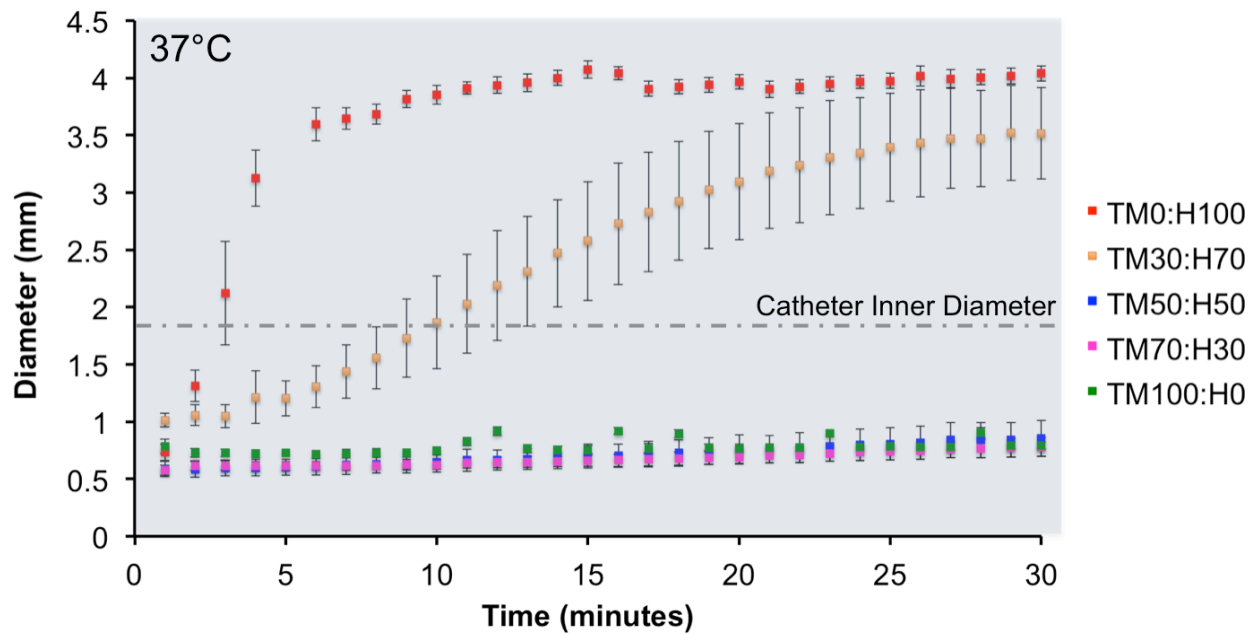
Figure 9. Effect of TMHDI:HDI isocyanate monomer ratios on device working time (alcohol is 20% DEA). Catheter diameter is indicated by gray dotted line (1.7 mm).

CHAPTER IV

CONCLUSION

In conclusion, we demonstrate the successful inclusion of DEA into shape memory polymer foams with the intent of improving the mechanical properties and forming isotropic pores. We confirmed the incorporation of DEA using FTIR and TGA. Our examination of the foam revealed more isotropic pores as the DEA concentration was increased. This method also allows for the tailoring of working time despite the inherent upper threshold of 40% DEA loading. These results indicate the inclusion of DEA works to improve the mechanical properties and processing potential of shape memory polymer foams. The new DEA containing foams are more mechanically robust which will lead to fewer device failures.

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