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Electron Beam Crosslinked Polyurethane Shape Memory Polymers with Tunable Mechanical Properties

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Abstract

Novel electron beam crosslinked polyurethane shape memory polymers with advanced processing capabilities and tunable thermomechanical properties have been synthesized and characterized. We demonstrate the ability to manipulate crosslink density in order to finely tune rubbery modulus, strain capacity, ultimate tensile strength, recovery stress, and glass transition temperature. This objective is accomplished for the first time in a low-molecular-weight polymer system through the precise engineering of thermoplastic resin precursors suitable for mass thermoplastic processing. Neurovascular stent prototypes were fabricated by dip-coating and laser machining to demonstrate processability.

Keywords

electron beam curing; polyurethanes; processing; stimuli-sensitive polymers; structure–property relations

1. Introduction

The stimuli-responsive geometric transformations exhibited by shape memory polymers (SMPs) have drawn increasing interest from diverse audiences in the scientific community. The biomedical device industry has traditionally been regarded as one of the most promising avenues to achieving future developments in SMP-related research.^[1,2] This industry drives multidisciplinary efforts in areas ranging from materials engineering to microelectronics, in addition to actively calling for the fabrication of SMP medical devices.^[3–8] The aerospace industry has likewise driven SMPs research and development,^[9,10] and a significant number of aerospace studies have investigated SMPs as potential actuators for atmospheric and outer space applications.^[11–15] Recently, new SMP applications have been proposed for a highly diverse array of industries, including the fabric and clothing industry,^[16] the culinary industry,^[17] and the water filtration industry.^[18]

With this increasing number of proposed SMP applications comes an increased need for SMP versatility. From a materials engineering standpoint, it is important that SMPs be easily processable into a wide range of desired geometries and that the thermomechanical properties of these SMPs be tailorable to meet various application demands.^[19,20] Covalently crosslinked SMPs have sometimes been shown to have superior mechanical properties to those of physically crosslinked SMPs, including higher recovery stresses and higher cyclic recoverable strains.^[21–24] Furthermore, while numerous factors influence a polymer's material properties, enhanced crosslinking has been shown to have a significant impact on multiple properties, generally limiting strain capacity, improving ultimate tensile strength, raising glass transition temperature, and increasing recovery stress.^[25]

Consequently, one method of tuning the thermomechanical properties of SMPs for specific applications is tailoring crosslink density.^[26,27]

Although significant work has been done in the development and characterization of crosslinked SMPs, certain issues have emerged that limit the application range of thermoset SMP-based devices. One such issue is limited thermoset SMP processing capability.^[28] Thermoset polymers do not flow and cannot be processed by thermoplastic processing methods such as injection molding or extrusion, and the mass production of covalently crosslinked SMPs into complex geometries has consequently been limited.^[24,29] One approach to improving thermoset SMP processability has been the development of thermoplastic SMPs that can be processed into complex geometries as thermoplastics and subsequently crosslinked in a secondary step while in the bulk state. Multiple studies have reported post-polymerization crosslinking of various thermoplastic polymers.^[30–32] However, these studies have generally relied on high-molecular-weight polymers for robust crosslinking and associated thermomechanical properties.

Radiation crosslinking—in particular, electron beam crosslinking, has been reported for numerous polymers, including polyethylene,^[33] poly(ϵ -caprolactone),^[34] poly(vinyl chloride),^[35] poly(methyl acrylate),^[36] and various polyurethanes.^[37–39] The random radiation crosslinking of thermoplastic polymers is described in the classical Charlesby-Pinner equation,

$$s + s^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 \mu_1 d} \quad (1)$$

where s is sol fraction, p_0 is degradation density, q_0 is crosslinking density, μ_1 is initial molecular weight (M_n), and d is dose. Electron beam irradiation of polymers results in both random chain scission and random inter-chain bond formation (i.e., crosslinking), and the ratio of scission to crosslinking, p_0/q_0 , describes the inverse crosslinking efficiency of a given polymer system at a specific dose. In a classical Charlesby-Pinner analysis plot, $s + s^{1/2}$ is plotted against $1/d$, and a linear fit of the data yields a positively sloping trend line with intercepts at $s + s^{1/2}$ equals two and $1/d$ equals zero. The $s + s^{1/2}$ equals two intercept represents the inverse crosslinking efficiency, represented by the ratio p_0/q_0 , and the $1/d$ equals zero intercept represents d_0 , the minimum dose to gelation.^[36,40] One method of controlling the crosslink density of electron beam crosslinked polymers to tune mechanical properties is to blend radiation sensitizer monomers with thermoplastic polymers before irradiation. Radiation sensitizers, which are often poly-functional (meth) acrylate or allyl molecules, were first reported by Pinner and others in the 1950s.^[41] These molecules have high mobility in comparison with bulky polymer chains and are highly reactive with polymer radicals induced during irradiation. Radiation sensitizers have been shown to reduce the amount of energy required for crosslinking, which is represented by the d_0 parameter, and to decrease the random nature of radiation crosslinking by making it more favorable.^[24]

In a previous study, we reported a polyurethane SMP system with novel processing capabilities that could be crosslinked in the bulk state using electron beam irradiation after

thermoplastic processing.^[42] This SMP system was made from 2-butene-1,4-diol (2-but) and trimethyl-hexamethylene diisocyanate (TMHDI) and contained C=C double bonds in its polymer backbone repeat units. In this study, our objective was to demonstrate control of crosslink density in this 2-but-*co*-TMHDI SMP system, with our underlying motivation being to synthesize, characterize, and report a novel SMP system with highly tunable and versatile thermomechanical properties, including tailorable strain capacities, ultimate tensile strengths, glass transition temperatures, rubbery moduli, and recovery stresses.

The effects of four independent parameters on electron beam crosslinking were investigated: radiation sensitizer composition, radiation dose, carbon-carbon double bond composition, and thermoplastic molecular weight. The ratio of sensitizer to polymer was varied over the wide range of 2.5 to 25 mol% for the purpose of maximizing achievable variations in crosslink density. A dose range of 25 to 500 kGy was selected because numerous previous studies have demonstrated successful electron beam crosslinking of various polymer systems over this dose range.^[32,34] To determine the effect of carbon-carbon double bond composition on radiation crosslinking, 2-butene-1,4-diol was copolymerized with nonolefinic monomers, including its saturated analog 1,4-butane-diol, and radiation crosslinking studies were carried out on the various polymers. In the molecular weight study, M_w was varied from 3.7 to 160 kDa by copolymerizing diisocyanate and diol monomers with monofunctional methanol. 160 kDa was the maximum molecular weight achievable under the synthetic conditions utilized in this work. Crosslinking was quantified using sol/gel analysis and dynamic mechanical analysis (DMA), and further thermomechanical characterizations were performed using differential scanning calorimetry (DSC), strain-to-failure, and shape memory characterization experiments.

To demonstrate the processability of this SMP system, a neurovascular stent prototype was fabricated using dip-coating, CO₂ laser machining, and subsequent crosslinking by electron beam irradiation. From a processing proof-of-concept standpoint, an SMP neurovascular stent was selected as the target medical device prototype because the geometry of a small stent is in many ways ideal for fabrication by dip-coating, which is a very effective thermoplastic processing method for producing hollow or thin-walled prototypes.^[43] From a medical device standpoint, a stent application falls in line with our previous studies, in which we reported the fabrication of neurovascular stents from other poly-urethane materials.^[44,45] In these former studies, we investigated the collapse pressure of similar laser-etched SMP stents and solid tubular stents, fabricated using the Mitsubishi MM7520 SMP. The solid tubular stent (expansion ratio ≈ 2.1) was able to withstand the maximum pressure expected to be exerted by an artery, while the laser-etched stent (expansion ratio ≈ 2.7) was possibly susceptible to collapse at temperatures higher than normal body temperature (i.e., a fever). In this materials engineering study, we aim to demonstrate the successful fabrication of a post-polymerization crosslinkable SMP neurovascular stent in order to provide an avenue for future biomedical device engineering studies, including the continuing development of neurovascular SMP stents.

2. Experimental Section

2.1. Materials

The polyurethane shape memory polymers synthesized in this work were generally based on TMHDI and 2-butene-1,4-diol (2-but). Diethylene glycol (DEG) and 1,4-butanediol (1,4-but) were copolymerized with select samples to study the effect of polymer backbone C=C composition on electron beam crosslinking. Methanol (MeOH) was added in varying amounts to select polymerization batches to control molecular weight in order to determine the effects of molecular weight on e-beam crosslinking. Two acrylic sensitizer monomers were also solution blended with select thermoplastic polymers to determine the effect of sensitizer composition on e-beam crosslinking.

All reagents and starting materials were used as received unless otherwise stated. TMHDI (97%), 2-butene-1,4-diol (97%), and DEG (99%) were purchased from TCI America. Anhydrous tetrahydrofuran (THF) (> 99.9%, inhibitor free), anhydrous MeOH (>99.8%), tris[2-(acryloyloxy)ethyl] isocyanurate (TAcIC) (97%, inhibited, 100 ppm monomethyl ether hydroquinone), and 1,4-butanediol (99%) were purchased from Sigma-Aldrich. Pentaerythritol triacrylate (PETA) (97%, inhibited, 400 ppm 4-methoxyphenol) and Zirconium(IV) 2,4-pentanedionate catalyst (Zr Cat) (99%) were purchased from Alfa Aesar. This catalyst was chosen because it has been shown to favor urethane formation over urea formation when moisture is present.^[46] All starting materials were stored in a glove box under dry air until use to prevent moisture absorption. The chemical structures of the monomers and sensitizers used in this study are provided in Table 1.

2.2. Thermoplastic Polyurethane Synthesis

All thermoplastic urethanes were synthesized in a 33.0 vol% solution of anhydrous THF in 100 g-scale reaction conditions. To enhance experimental accuracy, the Zr catalyst was first diluted by making 0.100 wt% stock solution in THF. All solvents, alcohol and isocyanate monomers, and catalysts were stored, massed, and mixed under dry air in a LabConco glove box. 100 g samples (total monomer mass, 1.01 NCO excess) were massed in the glove box in 225 mL glass jars that were previously flame dried, after which the THF and Zr catalyst solution (0.010 total wt%, unless otherwise noted) were added. The jars were sealed, and the polymerizations were carried out in a LabConco RapidVap instrument at 80 °C for 24 h at a vortex setting of 150 RPM. The RapidVap was used to heat and mix the monomer solutions. After 24 h, the viscous polymer solutions were poured into 12" × 9" rectangular polypropylene (PP) dishes, which were placed under vacuum at 80 °C for 72 h to remove solvent.

2.3. Molecular Weight Characterization

Gel permeation chromatography (GPC) characterization was carried out on a Viscotek GPCmax VE-2001 instrument, equipped with twin LT5000L mixed medium organic columns. The detector system was a Viscotek Model 302 Triple Detector Array system, simultaneously operating differential pressure, refractive index, and light-scattering detection modes. All GPC analyses were carried out at a constant column temperature of 40 °C. The carrier solvent was THF and the carrier flow-rate was 1 mL min⁻¹. Each

polyurethane sample was prepared as a 4 mg mL⁻¹ solution in spectroscopy grade THF, filtered through a 2 µm PTFE Millipore filter to remove gel/particulate matter, and injected into the GPC system. For each sample, number and weight average molar mass (M_n and M_w) distributions were obtained and the polydispersity index (PDI) was determined. Triplicate analyses were performed for each polyurethane system.

2.4. Radiation Sensitizer Blending, Film Casting, and Irradiation

After the solvent was evaporated, the optically clear thermoplastic films were cut into strips and placed in 40 mL glass vials in masses of 4–5 g. All masses were recorded, and amounts of radiation sensitizer (TAcIC and PETA) necessary to make 2.5–25 mol% samples were calculated based on these masses. The thermoplastic strips were then redissolved in THF (0.14 g mL⁻¹ solution) using the heat and vortex features of the RapidVap at 50 °C and 150 RPM for 12 h. The new polymer solutions were allowed to cool to ambient temperature, after which the radiation sensitizers were solution blended in desired amounts. Each blended polymer solution was then poured out evenly into three 2" × 4" polypropylene dishes to give final films of about 0.30 mm thickness. The PP dishes were placed at ambient temperature in a fume hood for 72 h and then in a vacuum oven at 25 °C at 1 Torr for an additional 2 weeks. The resulting amorphous thermoplastic films were then placed in 2" × 3" × 2 mil polyethylene bags. The samples were then irradiated at 25, 50, 100, 150, 200, 300, and 500 kGy using a 10 MeV electron accelerator located at the Texas A&M University National Center for Electron Beam Research.

2.5. Sol/Gel Analysis

To determine the extent of network formation in irradiated samples, a sol/gel analysis was conducted. Since the thermoplastic urethanes were synthesized in 33% THF solutions and remained in solution after polymerization, THF was chosen as the solvent. Fifty milligrams samples were dried at 80 °C for 24 h, massed in triplicate, put in 150:1 THF mixtures in 40 mL glass vials, and heated at 50 °C on in a LabConco RapidVap at 150 RPM for 24 h. The solvent was then changed, and the process was repeated for another 24 h. The swollen samples were then vacuum-dried at 90 °C at 1 Torr for 48 h, after which no further mass change from solvent evaporation was measurable.

2.6. Differential Scanning Calorimetry

To ensure that the irradiated polyurethane samples were amorphous, DSC was run on the irradiated 2-but-160 sample series. Experiments were run using a TA Instruments Q200 DSC under at nitrogen atmosphere. Five milligrams samples were cut from the irradiated films and placed in standard TA aluminum DSC pans with TA hermetic lids. Two-cycle runs were performed on each sample, in which the temperature range was –20 to 200 °C, the ramp rate was 20 °C min⁻¹, and an isothermal time of 2 min was added to the end of each heating/cooling cycle. The initial ramp cycle was run for each sample to relieve thermal stress and allow any residual solvent, monomer, or sensitizer to evaporate or react.

2.7. Dynamic Mechanical Analysis

All DMA experiments were run using a TA Instruments Q800 Dynamic Mechanical Analyzer. $25 \times 4 \times 0.3$ mm rectangular samples were laser cut using a Gravograph LS100 40W CO₂ laser cutter. All plots generated were recorded by QSeries software and analyzed using Universal Analysis graphing software. In the “DMA Multifrequency/Strain” mode, DMA experiments were run to determine the effects of sensitizer content, radiation dose, thermoplastic C=C composition, and molecular weight on the rubbery modulus and glass transition temperature (T_g) of the irradiated urethanes. The frequency was set to 1 Hz, the Preload Force to 0.01 N, the Strain to 0.1%, and the Force Track to 150%. All experiments were run from 0–200 °C with a ramp rate of 2 °C min⁻¹ in a nitrogen environment. T_g is measured as the peak of tangent δ , unless otherwise indicated.

2.8. Strain-to-Failure Experiments

ASTM Type V dog bone samples were machined from irradiated polymer films using the Gravograph CO₂ laser cutter and then carefully hand-sanded using 600-grit sandpaper. Strain-to-failure experiments were performed at a displacement rate of 10 mm min⁻¹ at T_g using an Instron 5965 electromechanical, screw-driven test frame, which was equipped with a 500N load cell, 1kN high temperature pneumatic grips, and a temperature chamber that utilizes forced convection heating. An Instron Advanced Video Extensometer with a 60 mm field-of-view lens was used to optically measure the deformation of the samples by tracking parallel lines applied at the ends of the gauge length. The samples were heated to T_g under zero load (bottom grip unclamped). The temperature was held at T_g for 30 min to reach thermal equilibrium, after which the bottom grip was clamped, and the experiments were started thereafter. Data were recorded and processed using Instron Bluehill 3 software.

2.9. Shape Memory Characterization Experiments

Shape memory tests were performed on ASTM Type V dog bone samples using the same Instron 5695 instrument assembly described in the previous experimental section. This assembly also used liquid nitrogen for cooling. The shape memory tests were performed in tension for select compositions according to ASTM D638 standards for Type V dogbone samples.^[47] The samples were heated to 80 °C under zero load (bottom grip released). The temperature was held at 80 °C for 30 min to reach thermal equilibrium, and then the bottom grip was closed and the samples were loaded to nominal strains of 0.30 mm/mm (for free strain recovery) or 0.25 mm/mm (for constrained recovery) at a displacement rate of 50 mm/min. The crosshead displacement was held constant and the temperature was reduced, at a rate of 1 °C min⁻¹, to 25 °C. The temperature was held at 25 °C for 30 min to reach thermal equilibrium. After cooling to the glassy phase, the specimen was unloaded at a displacement rate of 5 mm/min until zero load was applied to the sample. For the free strain recovery tests, the bottom grip was pneumatically released, and the specimen was allowed to hang freely from the top grip to ensure zero applied load. For the constrained recovery tests, the bottom grip was reattached to ensure zero displacement. The temperature was then ramped at a rate of 1 °C min⁻¹ to the original temperature of 80 °C while maintaining the zero load or constant displacement conditions for the free or constrained recovery tests, respectively.

2.10. Neurovascular Stent Prototype Fabrication

In order to demonstrate the novel processing capabilities of the polyurethane SMP system reported in this study, a neurovascular stent prototype was fabricated using a dip-coating procedure. Cylindrical pins were dip-coated in a polymer solution, crosslinked using electron beam irradiation, and then machined into complex stent geometries using CO₂ laser machining.

2.11. Dip-Coating

The dip-coating solution was prepared in a 60 mL glass vial by dissolving 22 g of 2-but-160 in 27 g THF. This concentration of polymer and solvent was qualitatively optimized in multiple dip-coating trials to achieve desirable viscosity and volume for dip-coating. Brass rods initially measuring 1 m in length and 4 mm in diameter were cut into 80 mm long pins. These pins were mounted in a drill press and sanded to a smooth, tarnish-free finish using 400 and 2000 grit sandpaper. To minimize adhesion between the dip-coated polyurethanes and the brass pins, a thin coating of PTFE mold release spray was applied to each pin and sintered using a butane torch. Using a linear translating platform, a set of four pins was mounted on a custom fixture and dipped into the polymer solution over a 51 mm range at a rate of 0.67 mm s⁻¹. The pins were held at the bottom of the dip for 20 s and removed from the solution at 0.67 mm s⁻¹. Before another dip-coating layer was applied, the pin fixtures were placed in an oven at 45 °C for 20 min to facilitate solvent evaporation. The dipping process was repeated 6 to 10 times to vary the wall thickness of the polymer tubes that formed on the outside surface of the brass pins. In order to remove residual THF without causing bubbling to occur in the dip-coated tubular samples, the pins were left at ambient temperature for 24 h, heated to 45 °C in an oven at ambient pressure for 72 h, and then heated to 50 °C for 48 h at 1 Torr. The dried tubes, which varied in wall thickness from 140–220 μm, were transferred from the brass pins to 4 mm OD high density polyethylene tubing and irradiated at 150 kGy. The tubes were transferred back to the brass pins and post-cured at 80 °C for 24 h at 1 Torr.

2.12. CO₂ Laser Machining

Complex stent patterns were designed using SolidWorks 2011 software and were converted to the .eps file format before stent machining. The stent patterns were machined on the e-beam crosslinked tubes using a Gravograph LS100 CO₂ laser machining assembly in its cylindrical engraving mode. After laser machining, the stents were carefully removed by hand from the brass pins and stored under desiccation.

3. Results and Discussion

3.1. Molecular Weight Characterization Results

The GPC results for all thermoplastic polyurethanes synthesized are provided in Table 1. Without the addition of methanol (MeOH), all thermoplastic polyurethanes had molecular weights (M_w) in the range of 60–160 kDa. As MeOH content was increased from 0 to 10 mol% for 2-but-co-TMHDI SMPs, molecular weight decreased from 85 kDa to 3.6 kDa. Polydispersity index (PDI) values were in the range of 2.0–3.0 and generally decreased as molecular weight decreased, although the variation in PDI was large. The monofunctional

methanol molecules limited the polyurethane step-growth polymerization by introducing chain ends at sites that would otherwise have been available for step growth. As methanol content increased, the average functionality, f_{av} for the polymerization decreased, and polymer dispersity also decreased. This relationship between molecular weight and polymer dispersity was expected and follows reported trends.^[48] It is noteworthy that the sample 2-but-160, which had an M_w of 160 kDa, was prepared using 0.1 wt% Zr Cat (all other samples were prepared using 0.01 wt% Zr Cat). This increased amount of catalyst resulted in an increased reaction rate. Since urethane polymerization reactions are exothermic, an increased reaction rate enabled an increased amount of heat to be generated simultaneously during polymerization, and the increased kinetic energy in the system drove the polymerization reactions to greater completion.

3.2. Sol/Gel Analysis Results

Gel fraction was most strongly dependent on the ratio of sensitizer to polymer, but it also increased with increasing dose, increasing C=C double bond composition, and increasing molecular weight. Plots of gel fraction (GF) versus dose for 2-but-co-TMHDI samples with varying molecular weights are provided in Figure 1a, b, and c for 0%, 10%, and 20% PETA samples, respectively. Figure 1d shows plots of GF versus dose for 2-but-40 samples containing varying amounts of PETA sensitizer. Figure 1 indicates that increasing the amount of sensitizer has the most drastic influence on increasing GF, although GF also increases with increasing dose and molecular weight. Figure 2a–d show Charlesby-Pinner analysis plots of $s + s^{1/2}$ versus $1/d$ for the gel fraction data provided in Figure 1. A linear fit of each data series in Figure 2 was used to calculate d_0 and p_0/q_0 values for each sample, and these calculated Charlesby-Pinner parameters are provided in Table 2.

The trends in Figure 2b–d are consistent with reported results from other radiation crosslinking studies in which molecular weight was varied in the presence of sensitizer.^[34] Increasing molecular weight in the presence of sensitizer in Figure 2b and 2c resulted in a downward vertical shifting of the Charlesby-Pinner trend lines without causing a significant change in trend line slope. In 2(c), the 2-but-40 sample had gel fractions approaching 1.0 for all doses tested, so plotting $s + s^{1/2}$ versus $dose^{-1}$ resulted in a straight line with a slope and y-intercept of zero. In 2(d), the slope of the trend lines approaches zero with increasing sensitizer composition, and this trend is also consistent with data reported in other studies.^[46] In Figure 2a, which contains Charlesby-Pinner data for sensitizer-free 0% PETA samples, a more pronounced change in the slope of the trend lines was observable as M_w increased from 20 to 40 to 85 kDa. This trend line behavior resembles that of the increasing sensitizer series, shown in Figure 2d, which contains samples with varying sensitizer and a constant M_w of 40 kDa. Figure 2a contains data only for the 2-but-20, 2-but-40, and 2-but-85 samples because no gel fractions occurred for the lower molecular weight samples at any dose tested.

As indicated in Table 2, minimum dose to gelation (d_0) decreased with increasing sensitizer composition and increasing molecular weight, in accordance with trends reported in previous works.^[47,48] Since the molecular weights in this study are much lower than those reported in many other studies,^[23,33,49,50,51] the d_0 values in this study are generally higher

than those in other studies that used higher-molecular-weight polymers (this study's lowest d_0 value was 4.82 kGy for the 10% PETA, 2-but-40 sample, although a d_0 value for the 2-but-40, 20% PETA could not be calculated because all gel fraction values were 1.0). The scission-to-crosslinking ratio, p_0/q_0 , appeared to be highly dependent on molecular weight, especially for low-molecular-weight samples. Since the lowest molecular weight samples had no gel fractions for 0% PETA, and the highest molecular weight samples had only gel fractions of 1.0 for 20% PETA, a four data-point trend was only complete for 10% PETA. However, for the other PETA compositions, this same trend was still evident. P_0/q_0 did appear to decrease slightly with increasing PETA, especially in the case of 0% versus 10% PETA. Also, p_0/q_0 appeared to remain relatively constant as PETA composition was increased from 10% to 20%, and this trend is consistent with data reported in previous studies.^[24,52,53]

3.3. DSC Results

DSC results for 2-but-160 samples containing varying PETA and TAcIC sensitizer and irradiated at 50 kGy are provided in Figure 3 and are indicative of the DSC results of all samples. All samples appeared to be amorphous with glass transitions in the range of 37 to 80 °C. Samples containing TAcIC generally appeared to have glass transitions approximately 10 to 15 °C higher than those containing PETA, although the trend was less pronounced for samples containing low sensitizer compositions.

3.4. DMA Results

Rubbery modulus increased significantly with increasing sensitizer composition and also increased with increasing dose, increasing C=C double bond composition, and increasing molecular weight. DMA storage modulus plots for 50 kGy, 2-but-160 samples containing varying PETA and TAcIC sensitizer are provided in Figures 4a and b, respectively, and Figure 4c and 4d contain the corresponding tan delta plots. Figure 4a shows that for 2-but-160 samples irradiated at 50 kGy, as PETA sensitizer increased from 2.5 to 25 mole%, rubbery modulus (E_r) increased from 0.5 MPa to 30 MPa. Figure 4b shows a very similar trend for otherwise identical samples containing TAcIC sensitizer. As TAcIC composition increased from 5 to 25 mole%, rubbery modulus increased from ≈ 5.0 to ≈ 39 MPa. In contrast to the irradiated samples, the thermoplastic sample in Figure 4b did not exhibit a significant rubbery plateau after its glass transition. Above T_g , its storage modulus tailed off and approached zero as the polymer began to flow, as is characteristic of amorphous thermoplastic polymers. The rubbery moduli of samples containing TAcIC were approximately 15% to 25% higher than the moduli of samples containing PETA. One explanation for this trend could be that the TAcIC sensitizer contained approximately 100 ppm monomethyl ether hydroquinone inhibitor, while the PETA sensitizer contained approximately 400 ppm 4-methoxy-phenol inhibitor. Since our working hypothesis, which is discussed in later in this section, states that electron beam crosslinking proceeds by a free radical mechanism, the presence of free radical inhibitor could potentially have an inverse influence on radiation crosslinking.^[54] For practical systems, increasing inhibitor helps the balance of enhanced resin shelf life (to avoid premature polymerization and crosslinking) at the expense of ease of crosslinking under a given dose. Thus, a nonlinear optimization among radiation dose, inhibitor content, sensitizer content, and polymer molecular weight

can be used in real systems to pinpoint desired thermomechanical properties and resin shelf life.

Peaks of tangent δ , seen in Figure 4c and d, correspond to the viscoelastic changes around T_g seen in Figure 4a and b and indicate that T_g increased with increasing sensitizer composition. Glass transition has often been shown to increase with increasing crosslink density because crosslinking can reduce chain mobility,^[55] so the general T_g trends in Figure 4c and d are in accordance with previously published trends. As shown in 4(c), T_g increased from approximately 52 to 65 °C as PETA increased from 5% to 25%. The TAcIC samples shown in 4(d) generally had higher T_g than the PETA analogs: T_g increased from approximately 62 to 78 °C as TAcIC increased from 5% to 25%. The central isocyanurate ring structure of TAcIC is expected to be more rigid than the more flexible PETA structure, so a higher T_g for TAcIC samples was expected.^[56]

Figure 5, which contains a large series of DMA storage modulus plots, illustrates that rubbery modulus was also dependent on dose, repeat unit C=C composition, and thermoplastic molecular weight. This figure represents the breadth of control that can be exerted on thermomechanical properties by altering both the underlying chemistry and the processing parameters. As **5(a)** shows, as dose was increased from 25 to 100 kGy, E_r increased from 2.5 to 14.0 MPa for 2-but-160, 5% TAcIC samples. As **5(b)** shows, as C=C double bond composition per repeat unit was increased from 50% (DEG-60) to 80% (DEG-78) to 100% (2-but-40), E_r increased from 1.5 to 3.0 to 7.0 MPa, respectively for 100 kGy, 10% PETA samples. As **5(c)** shows, as M_w increased from 7.0 to 160 kDa, E_r increased from 10.8 to 23.5 MPa for 50 kGy, 20% PETA samples. The positive correlations observed in this study between gel fraction and sensitizer, dose, and molecular weight are in accordance with observed trends reported in previous electron beam crosslinking studies.^[34] It is noteworthy, however, that a comparatively significant positive correlation between these same three variables and rubbery modulus was also observed in this study.

We have hypothesized previously that it may be possible to increase the electron beam crosslinking susceptibility of a polymer by tailoring its chemistry to favor such crosslinking reactions.^[42] As illustrated in Scheme 1, the alpha hydrogen theory of electron beam crosslinking, which has been supported in the literature since the 1950s, states that one of the dominant mechanisms of e-beam crosslinking may be the hydrogen extraction and ensuing radical formation at carbons in positions *alpha* to electron-withdrawing groups (EWGs) during irradiation. Crosslinking is then proposed to occur via radical graft polymerization by radical-radical coupling.^[40,57] Also illustrated in Scheme 1 is our working hypothesis, which states that, assuming that the processes described in alpha hydrogen theory do play some role in e-beam crosslinking, then the incorporation of a C=C double bond in the *beta* position to an EWG in a polymer may enhance a polymer's susceptibility to radiation crosslinking by providing resonance stabilization of e-beam-induced α -carbamate radicals. This delocalization could increase radical life, and longer radical life could increase the probability of crosslinking events' occurring, therein enhancing a polymer's susceptibility to radiation crosslinking.

The powerful effect of C=C double bond presence on radiation crosslinking is illustrated in Figure 5d, which shows DMA storage modulus plots of two polymers with identical dose (100 kGy) and sensitizer (20% PETA) conditions. One sample is composed of 2-butene-1,4-diol (2-but-40), and the other of 1,4-butanediol (1,4-but-98). The 2-butene-1,4-diol sample, which contains C=C double bonds in the *beta* positions to electron-withdrawing carbamate groups in addition to alpha hydrogens, appears significantly crosslinked. This sample has a minimum rubbery modulus of 25.8 MPa and exhibits a slight increase in E_r with increasing temperature, which is characteristic of ideal elastomeric behavior. In contrast, 1,4-butanediol sample, which does contain α -carbamate hydrogens, but lacks β -carbamate C=C motifs, appears only lightly crosslinked. This sample maintains a temporary rubbery plateau modulus of approximately 3.0 MPa, and its modulus begins to slope downward above 150 °C.

Although the results provided in 5(b) and 5(d) clearly indicate that a correlation exists between thermoplastic carbon-carbon double bond composition and electron beam crosslinking, alternative crosslinking processes other than the hypothesized radical graft polymerization mechanism should also be considered. For example, radiation crosslinking could instead proceed by free radical chain growth polymerization, or it could involve a combination of multiple chemical processes. As Dannoux and others have reported, numerous chemical reactions occur during the high-energy irradiation of polymers, and the most dominate of these processes dictate whether scission and/or crosslinking events occur.^[58] The hypothesis presented in this study appears sound, but it should be regarded only as a working scientific theory.

One major implication resulting from the data in 5(d) is that this SMP system is very well-suited for processing by thermoplastic melt-processing techniques such as injection molding because high crosslink densities are achievable upon irradiation of even low-molecular-weight thermoplastics. High-molecular-weight thermoplastics can be difficult to process, and molecular weights often must be lowered before thermoplastics can be injection molded or extruded on a mass scale.^[59] Figure 5e shows storage modulus plots for a very low molecular weight sample ($M_w = 7.0$ kDa) containing varying PETA and irradiated at 50 kGy. While the 0% PETA sample exhibits no rubbery plateau, the 10% PETA sample appears to have undergone some degree of molecular weight increase during irradiation and exhibits a small rubbery plateau region. The 20% PETA sample appears to have undergone a network formation during irradiation and has a rubbery modulus of roughly 11.0 MPa. Considering that the starting M_w of this polymer was only 7.0 kDa, this rubbery modulus value is considerably high. In 5(d), even with 20 mol% triacrylate sensitizer, high crosslink densities were not achievable in the 1,4-butanediol sample, even though its molecular weight (98 kDa) was more than twice that of the 2-butene-1,4-diol sample (40 kDa).

The crosslink density of this polyurethane SMP system can thus be controlled by varying four factors: sensitizer, dose, carbon-carbon double bond composition, and molecular weight. There are inherent advantages to having multiple methods of achieving a particular material design criterion. For example, if a particular application were to require that a specialty monomer (such as an ionomeric motif for filtration) replace some of the 2-butene-1,4-diol monomer content, a target crosslink density could still be achievable by

compensatively increasing sensitizer, dose, molecular weight, or any combination of the three. If an application should instead require an SMP with a low crosslink density, but should also require a high electron beam dose (e.g., for sterilization purposes), C=C composition, sensitizer composition, or molecular weight could be lowered to compensate for the increased dose. In this study, these four parameters were varied in order to create materials that met two design criteria: (1) the ability for glass transition to be controlled independently of rubbery modulus, and (2) the ability for rubbery modulus to be controlled independently of glass transition. As Yakacki and others have reported, since actuation temperature and recovery stress are two of the most important properties in an SMP system, the ability to control each of these properties independently of the other could be extremely important from an application-based standpoint, and demonstrating control over these parameters can broaden the material application range.^[25,26] In Figure 5f, DMA for samples with glass transitions of 45 and 62 °C and a constant rubbery modulus of 5.0 MPa are shown. In Figure 5g, DMA for samples with rubbery moduli of 3.0, 7.0, and 26.0 MPa and a glass transition of approximately 60 °C are shown. The various plots in Figure 5 highlight different approaches to manipulate the thermo-mechanical properties of radiation crosslinked SMPs.

3.5. Tensile Testing Results

The tensile testing results followed anticipated trends: stress-at-failure increased with increasing crosslink density, and strain-to-failure decreased with increasing crosslink density. The experiments were performed at T_g (as measured from DMA tangent δ peaks) on the 2-but-160, 50 kGy, varying PETA series, for which DMA data is provided in Figure 4. Stress/strain plots for strain-to-failure experiments are provided in Figure 6a, and a summary plot of ultimate tensile stress and strain versus PETA composition is provided in 6(b). As PETA composition was increased from 2.5% to 25%, average strain-to-failure decreased from 2.1 mm/mm to 0.4 mm/mm, and average stress-at-failure increased from 8.1 to 29.3 MPa. The tensile tests indicate sample strengths and toughness that could make these systems appealing candidates for engineering applications traditionally selecting from moldable thermoplastics.

3.6. Shape Memory Characterization Results

Free strain recovery results, which are provided in Figure 7a, demonstrated 100% recoverable strains for the 2-but-160, 50 kGy, 10% PETA sample selected for the test (0.30 mm/mm applied strain). Since high percent recoverable strains are generally thought to be an advantage of covalent crosslinking, this sample's ability to fully recover its strain was anticipated. The constrained recovery results in Figure 7b indicate that the recovery stresses of samples strained to 0.25 mm/mm increased with increasing sensitizer composition (i.e., increasing crosslink density). For PETA compositions of 0% (thermoplastic), 2.5%, 5.0%, and 10%, peak recovery stress values were measured to be 0.0, 0.9, 1.3, and 2.3 MPa, respectively. This observed positive correlation between crosslink density/rubbery modulus and recovery stress of SMPs confirms trends noted in previous investigations by Yakacki and others^[60]

The primary objective of this study was to demonstrate control of the crosslink density of electron beam crosslinked SMPs using low-molecular-weight thermoplastics. Although the DMA results in Figure 4–5 are the best experimental evidence that this specific objective was met, the stress-strain data in Figure 6 and shape memory characterization data in Figure 7 provide compelling validation that the strategy of controlling crosslink density is an effective method of tuning thermomechanical properties. By controlling crosslink density, control over stiffness, ultimate strain capacity, and ultimate tensile strength was also achieved, and the stress-strain data in Figure 6 illustrate this point. The constrained recovery data in 7(b) then serve as a fitting parallel conclusion to the DMA data in 4(a), as this figure brands the tangible concept of physical force onto an otherwise intangible concept of crosslink density.

3.7. Stent Fabrication Results

The purpose of fabricating a medical device from the poly-urethane SMPs in this study was to demonstrate their novel capability to be processed into desired geometries by dip-coating and subsequently crosslinked after processing using electron beam irradiation to tune thermomechanical properties. From a medical device standpoint, an SMP neurovascular stent was selected as the target medical device prototype because we have investigated similar polyurethane neurovascular SMP stents in previous studies.^[44,45] The stents in these studies were determined to have collapse pressures above (tubular) or very near (laser etched) the maximum expected pressures to be exerted by an artery, and the expansion ratios of the tubular and etched stents were approximately 2.1 and 2.7, respectively. In this study, our objective was to introduce a new SMP system that could potentially offer improved processing capability and better tunability of thermomechanical properties for numerous medical device applications, including neurovascular stents.

The automated assembly used to dip-coat sets of four 80 mm long, 4 mm diameter brass pins is pictured in Figure 8a. Figure 8b shows a brass pin that was dip-coated in 2-but-160 polyurethane SMP, irradiated at 150 kGy, and engraved using CO₂ laser machining. The SEM images in Figure 8c, taken after the stent's removal from the brass pin, provide a close-up view of the complex, laser-engraved stent geometry.

3.8. Crimping

The final stent prototypes were approximately 25 mm in length, with wall thicknesses ranging from 150 to 220 μm and outer diameters (ODs) of approximately 4.30 mm. To qualitatively demonstrate the ability of these SMP stent devices to store temporary, compressed geometries, the stents were crimped from their original 4.30 mm ODs to final diameters of 1.40 mm using a Machine Solutions, Inc. SC150-42 Stent Crimper, which is pictured in Figure 8d. Each stent was heated to 55 °C ($T_g + 15$ °C) and given 1 h to equilibrate. The stents were then crimped to final diameters of 1.4 mm using a constant applied pressure of 45 psi. Figure 8e shows a crimped stent and a stent in its primary geometry. Ongoing and future work involves stent-specific thermomechanical characterization and testing on the bench top and in vivo. The engineering of this polyurethane SMP system will also continue, with device-specific material demands largely driving this engineering process.

4. Conclusion

As the shape memory polymer community continues to diversify, a broadening application range demands that SMPs have more versatile material capabilities. Covalent crosslinking can improve certain thermomechanical properties and act as an avenue to finely tune these properties, but it also creates major processing difficulties for complex thermoset SMP prototypes. This work introduces novel polyurethane SMPs with highly tunable mechanical properties that can be processed into desired geometries as thermoplastics and then crosslinked using electron beam irradiation at significantly lower molecular weights than previously described in the literature. The potential impacts of this study span the confines of multiple disciplines. From a radiation physics standpoint, the observed dependence of e-beam crosslinking on carbon-carbon double bond composition suggests that a “polymer chemistry” factor could be missing from the classical radiation crosslinking model. Furthermore, while classical theory has sought to quantify radiation crosslinking in terms of gel fraction trends, this study suggests that exploring an alternative model that uses both rubbery modulus and gel fraction to define crosslinking may be an interesting future course of study. From a materials engineering standpoint, the demonstrated ability to control crosslink density and the material properties that depend on it by varying dose, sensitizer composition, C=C composition, or molecular weight may be very useful when application-specific requirements limit what factors can be varied to control crosslink density. For example, for a hypothetical medical device that requires processing by injection molding but also requires high crosslink density, molecular weight could be kept low to facilitate injection molding, and high crosslink density could still be achieved by varying other factors. Finally, from a biomedical engineering standpoint, new SMP medical devices with highly tunable mechanical properties may now be able to be fabricated and characterized, and current devices already being investigated may now be fabricated in a more efficient manner. The demonstrated use of dip-coating and laser machining to fabricate an SMP neurovascular stent is promising evidence that other devices can also be made using this novel SMP system. As intelligent polymer systems continue to gain attention in the scientific community, materials engineers bear the responsibility of ensuring that these materials remain relevant for increasingly complex applications.

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Figure 1.

The effect of increasing radiation dose on gel fraction for samples with M_w varying from 3.6 to 40 kDa. Plots for samples containing 0% (a), 10% (b) and 20% (c) PETA are shown. 1d) shows gel fraction data for samples 2-but-40 samples with varying PETA. Gel fraction is most highly dependent on the presence of sensitizer but also increases with increasing molecular weight and increasing radiation dose.

Figure 2.

Charlesby-Pinner analysis plots of $s + s^{1/2}$ versus $1/\text{dose}$ for irradiated samples with varying molecular weights and (a) 0% PETA, (b) 10% PETA, and (c) 20% PETA; in (d), $M_w = 40$ kDa, and PETA is varied.

Figure 3. DSC results for samples with increasing (a) PETA and (b) TAcIC composition irradiated at 50 kGy. The samples were amorphous, and this DSC data is indicative of DSC data for all samples. DSC traces were shifted vertically to facilitate viewing.

Figure 4.

Changing storage modulus, 4(a) and 4(b), and tangent δ , 4(c) and 4(d), as a function of temperature from DMA for samples containing varying amounts of PETA and TAcIC. The thermoplastic sample is included in 4(b) for comparison. Maximum rubbery moduli of 30 MPa (PETA) and 45 MPa (TAcIC) were achieved.

Figure 5.

The thermomechanical effects of (a) dose, (b) the presence of double bonds in the polyurethane backbone, and (c) molecular weight on electron beam crosslinking. The effects of repeat unit C=C composition of radiation crosslinking for samples made from 2-butene-1,4-diol and 1,4-butanediol (d). A rubbery modulus of approximately 10 MPa was achievable upon irradiation of a sample with an M_w of 7.0 kDa (e). DMA results for select samples with varying polymer structure, sensitizer composition, and/or radiation dose demonstrate the tunability of the thermomechanical properties of this SMP system where glass transition is controlled independently of rubbery modulus (f); and where rubbery modulus is controlled independently of glass transition (g).

Figure 6.

(a) Stress-strain data for strain-to-failure tests run on samples with varying PETA irradiated at 50 kGy. Testing was performed at tan delta peak. (b) The effect of PETA composition strain-to-failure (negative correlation) and stress-at-failure (positive correlation) of 2-butene-1,4-diol samples irradiated at 50 kGy.

Figure 7.

Shape memory characterization: (a) Free strain recovery demonstrated fully recoverable strains of 0.30 mm/mm for 2-but-160, 50 kGy, 10% PETA samples; (b) Constrained recovery tests at 0.25 mm/mm demonstrated that recovery stress increased with increasing PETA composition (i.e., crosslink density, rubbery modulus) for 2-but-160, 50 kGy samples with varying PETA.

Figure 8.

(a) Dip-coating assembly use to fabricate stents; (b) Brass pin surrounded by thin SMP tube, after dip-coating, drying, electron beam crosslinking, and CO₂ laser machining; (c) SEM image of the stent after removal from brass pin. (d) Author: change the image to d and e (Already insert comment in the doc file.). Machine Solutions, Inc. SC150-42 Stent Crimper; (e) SMP neurovascular stent in primary geometry and crimped geometry.

Scheme 1.

Schematic of hypothesized radiation crosslinking mechanism for polyurethane SMPs made from 2-butene-1,4-diol and TMHDI. **1:** Thermoplastic samples are irradiated, radicals form at α -carbamate carbons; **2:** If C=C groups are present at β -carbamate sites, resonance may stabilize the radicals; **3:** Crosslinking then proceeds by radical graft polymerization, and crosslinking may be enhanced by the resonance stabilization effects described in 2; **4:** If mobile, reactive radiation sensitizer molecules are blended with the thermoplastic, these sensitizers can also enhance a polymer susceptibility to radiation crosslinking.

Table 1

GPC quantifies thermoplastic polyurethane behavior of synthesized samples.

Sample	Equiv. TMHDI	Equiv. 2-but	Equiv. 2x MeOH	Equiv. DEG or 1,4-but	M_n [kDa]	M_w [kDa]	PDI
2-but-160*	1.000	1.000	–	–	46	160	3.5
2-but-85	1.000	1.000	–	–	33	85	2.5
2-but-40	1.000	0.990	0.010	–	18	40	2.5
2-but-20	1.000	0.975	0.025	–	5.2	20	3.2
2-but-7	1.000	0.950	0.500	–	2.8	7.0	2.4
2-but-3.6	1.000	0.900	0.100	–	1.7	3.6	2.0
DEG-60	1.000	0.500	–	0.500	27	60	2.2
DEG-78	1.000	0.800	–	0.200	29	78	2.7
1,4-but-98	1.000	–	–	1.000	42	98	2.3

TMHDI

PETA

1,4-butanediol

diethylene glycol

TAcIC

* Note: 0.1 wt% Zr catalyst was used in the synthesis of the 2-but-160 polymer sample, while 0.01 wt% Zr catalyst was used in the synthesis of all other samples. Increasing the catalyst resulted in increased molecular weight and increased polydispersity index.

Table 2

Values for p_0/q_0 and d_0 for samples with varying sensitizer composition and varying molecular weight. These parameters were calculated from Charlesby-Pinner plots of $s + s^{1/2}$ versus $1/\text{dose}$, such as the ones shown in Figure 2.

Sample information		p_0/q_0	d_0 (kGy)
0% PETA	2-but-85	0.539	10.95
	2-but-40	0.583	35.04
	2-but-20	1.005	106.84
10% PETA	2-but-40	0.098	4.82
	2-but-20	0.293	9.98
	2-but-7.0	0.897	22.51
	2-but-3.7	1.246	53.66
20% PETA	2-but-20	0.311	8.44
	2-but-7.0	0.654	12.74
	2-but-3.6	1.049	17.85