1 Title: Thermo-mechanical Behavior and Structure of Melt Blown Shape-Memory Polyurethane Nonwovens
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20 Abstract:

21 New processing methods for shape-memory polymers allow for tailoring material properties for numerous
22 applications. Shape-memory nonwovens have been previously electrospun, but melt blow processing has yet
23 to be evaluated. In order to determine the process parameters affecting shape-memory behavior, this study
24 examined the effect of air pressure and collector speed on the mechanical behavior and shape-recovery of
25 shape-memory polyurethane nonwovens. Mechanical behavior was measured by dynamic mechanical
26 analysis and tensile testing, and shape-recovery was measured by unconstrained and constrained recovery.
27 Microstructure changes throughout the shape-memory cycle were also investigated by micro-computed
28 tomography. It was found that increasing collector speed increases elastic modulus, ultimate strength and
29 recovery stress of the nonwoven, but collector speed does not affect the failure strain or unconstrained
30 recovery. Increasing air pressure decreases the failure strain and increases rubbery modulus and
31 unconstrained recovery, but air pressure does not influence recovery stress. It was also found that during the
32 shape-memory cycle, the connectivity density of the fibers upon recovery does not fully return to the initial
33 values, accounting for the incomplete shape-recovery seen in shape-memory nonwovens. With these
34 parameter to property relationships identified, shape-memory nonwovens can be more easily manufactured
35 and tailored for specific applications.
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39 Keywords: nonwoven; shape-memory; melt blown; microcomputed tomography; structure; mechanical
40 behavior
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43 Introduction
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45 Shape-memory polymers (SMP)s are a class of mechanically active polymers that change from a
46 temporary programmed shape to an original permanent shape when exposed to a stimulus. These stimuli may
47 be direct heat or indirect heat (e.g. current, magnetic field), solvent or water uptake, light, or mechanical force
48 [1-6]. Acrylates, urethanes, and biodegradable esters represent only a handful of the eclectic chemistries used
49 in SMPs, which typically rely upon either physical or chemical crosslinking for the shape-memory effect [7-10].
50 Studies have shown that the recovery behavior is highly tunable under different programming conditions and
51 recovery environments [9, 11]. For thermoplastic polyurethanes, the recovery ratio is highly dependent upon
52 the programming temperature, strain, strain rate, and recovery temperature [12]. This allows for the SMPs to be
53 tailored to specific applications including medical devices, aerospace structures, and composites [13-16]. In
54 particular, SMP polyurethanes and their foams have attracted attention for use as minimally invasive tools for
55 treatment of aneurysms, stents, and thrombectomy devices [17-22].
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58 A growing part of the SMP field is the work on processing shape-memory polymers into textiles either
59 as wovens or as nonwovens [23]. Some of the earliest work started with shape-memory polyurethanes being
60 wet-spun into individual fibers with shape recovery as high as 92% [24]. Manufacturing technique considerably
61 impacts the shape-recovery of the textile product. When generating SMP fibers, melt-spun SMP fibers have
62 improved shape-recovery over wet-spun fibers because of a higher degree of phase separation [25]. Shape-
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memory fibers' recovery is also greatly affected by post-spinning thermal treatments. Recovery increased from 80% to 90% as heat treatment temperature increased because of further phase separation of the hard and soft segments and increased hard segment stability [26, 27]. More recently, SMPs have been processed into nonwovens by electrospinning. Nonwovens are advantageous for applications where a very fine fiber structure on the nano or micro-scale is desired and can be fabricated faster than wovens. Shape-memory polyurethanes fabricated by electrospinning, often PCL-based, have had fiber diameters ranging from 50 nm-3 μ m and 80-98% shape recovery [28-30]. These electrospun SMP nonwovens can recover at a lower temperature compared to their bulk film because the pore structure allows for more rapid heating [31].

To the authors' best knowledge, only nonwovens fabricated by electrospinning have been characterized for their shape-memory performance. Electrospinning is often limited to small quantities, and requires use of a solvent that complicates the production and poses a health hazard for the manufacturing operator. In contrast, melt blowing can be used to produce larger quantities and does not require a solvent and thus serves as an attractive alternative for making SMP nonwovens. Melt blowing currently produces nonwovens for many applications, such as filtration, insulators, hygiene products, and protective apparel [32]. A wide variety of SMPs could be processed using this technique because it is possible for nearly all thermoplastics [33]. Specifically, melt blowing produces nonwovens by using hot, high speed air to attenuate molten thermoplastic into fibers. The fiber diameters often range from 2 to 6 μ m, but more advanced dies have produced submicron fibers [33, 34]. The melt blowing structure formation is highly complex due to the large numbers of variables, such as air pressure, collector speed, die to collector distance, melt throughput rate, air temperature, and die temperature. However, there have been no previous reports evaluating the effects of the melt blown process on the shape-memory properties of the final material.

The objective of this work was to determine the effect of processing parameters on the microstructure, the resulting thermo-mechanical behavior, and the shape-memory performance of a melt blown shape-memory polyurethane nonwoven. The main processing parameters of air pressure and collector speed were varied to alter microstructure. Tensile behavior at varying test temperatures was examined to determine the relationships with processing parameters and microstructure. Shape-memory recovery and recovery stress were thoroughly examined for varying melt blown processing parameters and shape-memory programming parameters. In addition, microcomputed tomography was used to determine microstructural changes throughout the shape-memory cycle. The results of this study are (i) determination of the relationships between melt blown processing parameters, microstructure, mechanical behavior, and shape-memory performance and (ii) characterization of the structural changes occurring during the shape-memory cycle for these melt blown nonwovens.

2. Materials and Methods

2.1 Melt blown processing

A proprietary shape-memory aromatic polyether polyurethane was used for this study. The thermomechanical properties of the neat resin are detailed in the supplemental information. The polyurethane was dried in a hopper drier for 2 hours at 105°C prior to use. The 6" melt blow line at the University of Tennessee Knoxville Nonwoven Research Laboratory was used under the following conditions to produce the nonwovens: die temperature was set at 230°C, air temperature was set to 260°C, air pressure varied from 10 to 30 psi (68.9 to 206.8 kPa), collector speed varied from 0.3 to 1.0 m/min, and die-to-collector distance was set to 13.5 cm. Nine nonwovens were produced by using combinations of collector speeds of 0.3, 0.6, 1.0 m/min and air pressures of 10, 20, and 30 psi (68.9, 137.9, 206.8 kPa).

2.2 Bulk density and porosity

Bulk density was determined by measuring the mass (Ohaus Pioneer) and taking the dimensions with digital calipers (Mitutoyo Absolute) of each nonwoven that was cut to 4 cm x 2 cm rectangles (n=9/nonwoven), Equation 1. Porosity was determined by using the bulk density of the nonwoven and the density of the raw polymer, 1.19 g/cm³, Equation 2.

Equation 1.

$$\text{Bulk Density} = \frac{\text{Mass}}{\text{Volume}}$$

Equation 2.

$$\text{Porosity} = 1 - \frac{\text{Bulk density}}{\text{Polymer density}}$$

2.3 Scanning electron microscopy

Nonwovens were imaged with a Hitachi S-3700N VP-SEM at 70 Pa and 10 kV. Samples were not sputter coated since variable pressure mode was used. Five images of each nonwoven were used to measure fiber diameter (n=20/image, n=100/nonwoven) (Image J, NIH).

2.4 Micro-computed tomography (MicroCT)

Samples of 20 psi 0.6 m/min nonwoven (6 mm x 2 mm x 1 mm) were scanned using micro-computed tomography (μCT 50, Scanco Medical) prior to programming, after programming 200% strain at 55°C, and after recovery at 90°C (n=4/stage). Samples were scanned at 2 μm voxel resolution with the scanner set at a voltage of 55 kVp, a current of 145 μA, and an integration time of 1200 ms. Nonwovens were manually contoured tightly to the edges to minimize inclusion of non-nonwoven volume. A global threshold was applied to segment nonwoven from open space and kept consistent throughout all evaluations. Fiber morphometrics were evaluated using direct distance transformation methods [35, 36]. Structural model index (SMI) is used to measure how rod-like or plate-like the structure is and ranges from 0 (plate-like) to 3 (rod-like) [37]. The degree of anisotropy (DA) is defined as the ratio between the maximal and minimal radius of the MIL ellipsoid [35] and provides a measure of the alignment of the structure, where an isotropic structure would have a value of 1 and an anisotropic structure a value greater than 1.

2.5 Dynamic mechanical analysis

Dynamic mechanical analysis was run on each nonwoven (n=3/nonwoven) (Q800, TA Instruments). Rectangular samples (20 mm x 5 mm) were tested **in tension** under the following conditions: equilibrate at -50°C, isotherm for 2 minutes, ramp 5°C/min to 175°C with a strain of 0.1% at 1 Hz. Glass transition temperature was defined at the peak of tan δ. The rubbery modulus is defined as the storage modulus at the beginning of the rubbery plateau.

2.6 Tensile behavior

Each nonwoven was strained to failure at three temperatures (25, 55, 90°C) using an Instron 5567 load frame and an Instron SFL Heatwave environmental chamber. Rectangular samples (4 cm x 2 cm) with a gage length of 2 cm were pulled at a strain rate of 1%/s. The ultimate stress and failure strain were recorded for each test (n=3/nonwoven/temperature). The elastic modulus was calculated from the initial slope of the stress-strain curve.

2.7 Unconstrained recovery

Unconstrained recovery was measured using a digital video camera (Canon HG10) and Image J software to track strain recovery. Rectangular samples (4 cm x 2 cm) were strained at 1%/s to a predetermined strain at a defined programming temperature, then cooled to 0°C for 10 minutes. Samples were unclamped from lower grip and were then heated to 90°C for 10 minutes. To determine what variables affect unconstrained recovery, programming strain (50, 100, 200%), programming temperature (55, 75, 95°C), air pressure (10, 20, 30 psi), and collector speed (0.3, 0.6, 1.0 m/min) were varied while holding other variables constant (n=3/test).

2.8 Constrained recovery

Recovery stress was measured using the Instron 5567 load frame. Rectangular samples (4 cm x 2 cm) were strained at 1%/s to a predetermined strain at a defined programming temperature, then cooled to 0°C for 10 minutes. **Samples were unclamped from lower grip to relieve any remaining stress. Samples were reclamped** and were then heated to 90°C for 10 minutes. To determine what variables affect recovery stress, programming strain (50, 100, 200%), programming temperature (55, 75, 95°C), air pressure (10, 20, 30 psi), and collector speed (0.3, 0.6, 1.0 m/min) were varied while holding other

variables constant (n=3/test). Recovery stress is given in engineering stress and also as tenacity [38], where tenacity is given by the Equation 3 and corrects for the void fraction of the nonwoven.

Equation 3.

$$\text{Tenacity} = \frac{\text{Force}}{\text{Width} \times \text{Thickness}} \times \frac{\text{Polymer Density}}{\text{Bulk Density}}$$

2.9 Statistical Analysis

One-way ANOVA with Tukey's HSD package in Igor Pro (Wavemetrics) was used to determine if any statistically significant difference was present. $p < 0.05$. The mean $\pm$ standard deviation is given, where the sample number is given above for each test. For those measurements that are representative of an average value (such as fiber diameter or inter-fiber spacing), the reported value from the microCT was taken as an individual value. This approach was chosen by the authors given the substantial data set (10^6), making statistical comparisons of the experimental groups difficult. Tukey's HSD was chosen to control for EER.

3. Results

Porosity (Table 1) and bulk density (Table S1) were calculated for each of the nine nonwovens. Porosity ranged from 0.57 to 0.75 as air pressure and collector speed were varied. Porosity increased and density decreased as collector speed increased for nonwovens of a given air pressure. At 0.3 and 0.6 m/min, nonwovens made at 20 and 30 psi exhibited lower porosities and higher densities than nonwovens made at 10 psi. At 1.0 m/min, porosity and density were not affected by changes in air pressure. Thickness increased as collector speed decreased (Table S2). Representative SEM images of nonwoven collected at 0.6 m/min at each air pressure are shown in Figure 1. As the air pressure increased, the fiber diameter visually decreased with the 10 psi nonwoven having thicker fibers and larger points of contact with each other than the 20 psi or 30 psi nonwovens. The 20 psi nonwoven has a wide range of fiber diameters. The 30 psi nonwoven has a large number of thin fibers that overlap at a higher frequency. Fiber diameters were quantified from SEM imaging (Figure 2A). The average fiber diameter was found to be dependent upon air pressure, but not the collector speed. There was a significant difference between the average fiber diameter of the 10 psi nonwovens and average fiber diameters of the 20 psi and 30 psi nonwovens at a given collector speed. There was no significant difference between the average fiber diameter of nonwovens made at varying collector speeds at a given air pressure. However, from Figure 2B, it was seen that the average fiber diameters were similar between the 20 psi and 30 psi nonwovens; the distribution of fiber diameters was distinct for each air pressure (Figure 2B). The 30 psi nonwoven had a majority of fibers falling between 2 and 5 μm with a very small number of fibers ranging up to 10 μm . The 20 psi nonwoven contained mostly fibers between 2 and 7 μm , and fewer fibers up to 16 μm . This graph also revealed that the 10 psi nonwoven has the broadest distribution of fiber diameters, peaking around 10 μm and ranging from 2 μm to 20 μm .

Representative dynamic mechanical analysis curves are shown in Figure 3. Each nonwoven showed a defined glassy region followed by the glass transition, a rubbery plateau, and finally melting. The glass transition temperature (Table S3) ranged from 63°C to 72°C as processing conditions were varied. The glass transition temperature increased as collector speed decreased for the 20 psi and 30 psi nonwovens. The rubbery modulus ranged from 0.89 MPa to 5.50 MPa as processing conditions were varied, and increased as collector speed decreased for each nonwoven (Table S4). In addition, the 20 psi and 30 psi nonwovens had higher rubbery moduli than the 10 psi nonwoven at a given collector speed. Similar to the rubbery modulus, the storage modulus at 25°C in the glassy regime increased as collector speed decreased at a given air pressure (Table S5). At each given collector speed, the 10 psi nonwoven had the lowest modulus, followed by the 30 psi nonwovens, then the 20 psi nonwovens with the highest modulus.

Tensile tests were performed to determine how the processing conditions affect the mechanical properties. Representative stress-strain curves are shown in Figure S2 and Figure S3 with corresponding elastic modulus, ultimate stress, and failure strain data for all nonwovens in Tables S6, S7, S8, respectively. For all collector speeds and air pressures, the modulus and strength decreased as test temperature increased while the failure strain increased with increasing test temperature. At constant test temperatures, changing the

collector speed and air pressure affected the modulus, strength, and failure strain. Further details can be found in the supplemental information.

Unconstrained recovery tests were conducted in order to determine if air pressure, collector speed, programming temperature, and programming strain affect the amount of recovery. One parameter was varied while the other three parameters were held constant for a total of four sets of tests. As programming strain increased, a decrease in recovery from 83.3% to 72.3% was observed (Figure 4A). As programming temperature increased, recovery decreased from 72.3% to 39.5% (Figure 4B). As air pressure increased, recovery increased from 65.3% to 92.1%. As seen in Figure S2B, the 30 psi nonwoven cannot reach 200% programming strain at 55°C. Therefore, these samples were programmed at 50%. Collector speed did not have noticeable effect on unconstrained recovery. Air pressure and collector speed data, along with programming temperature and programming strain data can be found in Table 2.

Constrained recovery tests were conducted in order to determine if air pressure, collector speed, programming temperature, and programming strain affect the amount of recovery stress generated during the shape-memory cycle. One parameter was varied while the other three parameters were held constant for a total of four sets of tests (Table 3 for engineering stress, Table S9 for tenacity). As programming strain increased, max recovery stress and final recovery stress increased (Figure 5A). Regardless of the amount of programming strain, stress relaxation occurred, ranging from 43-57%. The 50% strain and 100% strain samples had similar average final recovery stresses, but were lower than the 200% strain sample final recovery stress. As programming temperature increased, max recovery stress decreased (Figure 5B). At 55°C and 75°C, average final recovery stress values were near 0.3 MPa, but at 95°C, the average final recovery stress was lower at 0.15 MPa. At 55°C, the recovery stress profile displayed near 49% stress relaxation after reaching the max recovery stress. Nonwovens programmed at 75°C or 95°C did not display significant stress relaxation and held stress at 93% of max recovery stress. The 0.3 m/min nonwoven had higher recovery stress values than the 0.6 m/min or 1.0 m/min nonwovens, which showed similar recovery stress values. The 30 psi nonwoven had higher recovery stress values than both 10 psi and 20 psi nonwovens. The 30 psi nonwoven cannot reach 200% programming strain at 55°C, thus the samples were programmed to 50% strain. The 10 psi and 20 psi nonwovens had similar max and final recovery stress values.

MicroCT scans were taken of 20 psi, 0.6 m/min nonwoven samples before programming, after programming 200% strain at 55°C, and after recovery at 90°C (Figure 6). The color map shows the fiber diameter as the nonwoven undergoes programming and recovery. Prior to programming, the fibers appear evenly distributed and are patterned randomly. In comparison to the preprogrammed sample, the programmed sample contains fewer thick fibers. Additionally, the fibers are elongated and more aligned than the preprogrammed nonwoven. After recovery, the fibers return to a random patterning and evenly distributed state. Fiber diameter, porosity, interfiber spacing, connectivity density, structural model index (SMI), and degree of anisotropy (DA) were calculated from microCT images of 20 psi, 0.6 m/min nonwoven samples (n=4) to quantify structural differences in the stages of the shape memory process (Table 4). The average fiber diameter showed a significant decrease between preprogrammed and programmed states, and then showed a significant increase between programmed and recovered states. There was a not significant difference between the average fiber diameter of the pre-programmed and recovered states. The SMI and DA showed a significant increase between pre-programmed and programmed states, and then showed a significant decrease between programmed and recovered states. A higher SMI value indicates a more rod-like structural architecture, while a higher DA value indicates a more oriented (i.e. anisotropic) structural architecture. There was not a significant difference between the SMI and DA of the pre-programmed and recovered states. The porosity showed a significant increase between pre-programmed and programmed states, and a significant decrease between programmed to recovered state, but a significant increase remained in the porosity from the pre-programmed to recovered state. The connectivity density showed a significant decrease between pre-programmed and programmed states, and a significant increase between programmed to recovered state, but a significant decrease remained in the connectivity density from the pre-programmed to recovered state. Thus, the porosity and connectivity density values show partial recovery, such that the recovered value for both parameters is between the pre-programmed and programmed value. Once programming occurs, the interfiber

spacing increases significantly, and the recovered interfiber spacing value shows no progression to return towards the pre-programmed value from the programmed value.

The fiber diameter distribution from microCT was determined for each stage of the shape-memory cycle divided into 2 μm bins (Figure 7A) ($n=4$) [39]. There are similar patterns in the distribution of fiber diameters across the stages. The pre-programmed, programmed, and recovered stages all have 23% of their fibers at a diameter of 10 μm . However, the programmed nonwovens have a higher count percentage compared to both the pre-programmed nonwovens and the recovered nonwovens below 10 μm . Also, the programmed nonwovens have a lower count percentage compared to both the pre-programmed nonwovens and the recovered nonwovens at and above 12 μm . Figure 7B quantifies the changes between the stages of the shape-memory cycle in Figure 7A for each fiber diameter distribution. It shows that as the nonwoven goes through the shape-memory cycle, the fiber diameter shifts towards overall smaller fiber diameter. The number of fibers with a diameter above 10 μm decrease relative to the pre-programmed counts, and the number of fibers with a diameter below 10 μm increase relative to the pre-programmed counts. After recovery, the fibers remain smaller than the pre-programmed nonwoven, since the ratio of recovered to pre-programmed fiber diameters does not match the theoretical line for 100% recovery. Even though the average fiber diameter has not significantly changed between the recovered and the pre-programmed nonwovens, the nonwoven structure has shifted to smaller fiber diameters.

4. Discussion

SMPs are being processed into fibers, fabrics, and nonwovens to gain multi-functionality and increase usage. Melt blowing is a potentially attractive alternative to electrospinning because it offers faster production rates and does not require use of a solvent. In order to evaluate the feasibility of using this processing method to produce shape-memory nonwovens, this study sought to determine the relationship between processing parameters, microstructure, mechanical behavior, and shape-memory performance of a shape-memory polyurethane nonwoven. Furthermore, microCT analysis was used to characterize how the microstructure of the nonwoven changes throughout the shape-memory cycle.

Melt blowing is a complex process due to the multitude of parameters that can be varied. For this study, the processing variables were limited to the collector speed and the air pressure, which can both be readily changed during the production run. Simultaneous control of these two process variables allows for control of the structure across multiple length scales from microns to millimeters (e.g. the porosity/density, fiber diameter, fiber diameter distribution) [33, 40, 41]. The collector speed controls the belt speed such that a faster moving belt collects less material than a slow moving belt. This dictates the number of fibers per unit area, the density, and porosity of the nonwoven. Increasing the air pressure subjects the fibers to higher forces, causing them to undergo more elongation and thus form a smaller fiber diameter. The 2 to 20 micron range of fiber diameters observed in this study are similar to the fiber diameters of elastomeric melt blown thermoplastic polyurethanes reported in a previous study [24].

Understanding an SMP's thermo-mechanical behavior is critical in tailoring its performance for specific applications. In order to successfully program the shape-memory and maximize the recovery, a material should have a distinct transition from a glassy state to a rubbery state and exhibit a defined rubbery modulus plateau as determined through DMA. This thermal transition was observed for the SMP nonwovens, but at overall lower moduli than that reported for solid SMPs due to the inherent porosity introduced into the nonwoven structure. As would be expected, the storage modulus is highly dependent upon the collector speed as the collector speed affects the porosity. At a given collector speed, the rubbery modulus increases at higher air pressure because of the decreased fiber diameter, which also produces a less porous structure. For solid amorphous SMPs, the glass transition temperature (T_g) is generally governed by the chemical structure, and the rubbery modulus is governed by the crosslinking density. The T_g shows a slight increase as the collector speed decreases because the SMP samples are less porous, thicker, and take longer to heat at the 5°C/min

1 ramp rate. If a 1°C/min ramp rate is used, the T_g align at 65°C (data not shown). Regarding the nonwoven's
2 rubbery modulus, it is first governed by the collector speed, then the air pressure.

3
4 The tensile behavior was examined in order to determine the relationship between the processing
5 parameters and mechanical properties during programming. The results show that elastic modulus and
6 ultimate strength are mainly governed by the collector speed, as might be expected since the collector speed
7 primarily dictates the density of the nonwoven. Within a given collector speed, the elastic modulus is then
8 affected by the air pressure where by increasing the air pressure results in smaller fiber diameters that
9 contribute to a higher density, stiffer material. This is in agreement with previous studies on the tensile
10 behavior of melt blown elastomeric thermoplastic polyurethanes, which found that thickness and tear strength,
11 increase as collector speed decreases [33, 40, 41]. The observed decrease in modulus and strength and
12 increase in failure strain at test temperatures above the nonwoven's glass transition temperature, but below the
13 melt temperature is consistent with other plastics in their rubbery regime [42, 43]. No apparent trend exists
14 between collector speed and failure strain [38]. However, the failure strain is affected by changing the air
15 pressure with nonwovens produced at lower air pressures exhibiting higher failure strain. This relationship may
16 be due to the wider distribution of fiber diameters, the changes in interfiber spacing, or the manner in which the
17 fibers are entangled with each other. It has been previously shown that fiber entanglement decreases as air
18 pressure increases for melt blowing[44]. For this study, the die to collector distance was minimized in order to
19 increase the number of entanglements, which can include interlacing, thermal bonding, and branching [45]. At
20 such a short die to collector distance, the effect of air pressure on entanglements is more pronounced because
21 fiber travel time is dramatically decreased, which limits the formation of entanglements at higher air pressures
22 [44].

23
24 The shape-recovery of solid SMPs is highly dependent upon the programming temperature [46]. For
25 chemically crosslinked, amorphous SMPs, shape-recovery starts at a lower temperature when programmed at
26 a low temperature below T_g compared to a high temperature above T_g because more mechanical energy is
27 stored along with the entropic energy [47]. However, the amount of shape-recovery is equivalent regardless of
28 programming temperature and should approach 100% as the recovery temperature is near or above T_g. In
29 contrast, the SMP nonwovens show a decrease in shape-recovery as programming temperature increases,
30 mainly due to the chemical structure and then the fiber structure. For solid shape-memory polyurethanes
31 similar to the one used in this study, shape-recovery decreases as programming temperature increases above
32 T_g. When programming temperature nears T_g, the modulus of the soft-segment, reversible phase has
33 decreased, while the hard-segment, physical crosslinks are stable and allow for high shape-recovery. As
34 programming temperature increases above T_g, the hard-segment, physical crosslinks become less stable and
35 serve as poor crosslinks [12]. This trend is further compounded because these melt blown nonwovens are
36 composed of a mixture of fiber-fiber bonding and fiber entanglements, which more easily deform at higher
37 temperatures. Increasing the programming strain permanently deforms the hard-segment phase and
38 decreases the network points in the structure by debonding the fibers, undoing the entanglements, and
39 breaking short fibers, which all limit the recovery upon heating [12, 41, 48]. This is similar in nature to the
40 permanent elongations seen in elastomeric melt blown polyurethanes (i.e. glass transition below room
41 temperature), which shows increasing permanent elongation as the tensile elongation increases [48], thus non-
42 ideal recovery is to be expected regardless of the composition. Electrospun shape-memory nonwovens
43 underwent multiple shape-memory cycles with increasing programming strains of 25%, 35%, 50% and showed
44 a recovery ratios of 49%, 76%, 80% by the third cycle [49]. The recovery of these melt blown shape-memory
45 nonwovens shows higher recovery on the first cycle with equivalent or higher programming strains, which
46 suggests that the recovery ratio may approach values above 90% with proper cyclical programming. Besides
47 tuning programming conditions, the shape recovery of SMP nonwovens can be further tailored by the air
48 pressure during the melt blowing process. As air pressure decreases, a limited increase in shape recovery
49 occurs, presumably due to a higher entanglement density being formed under higher air pressures.
50 Interestingly, collector speed does not have a noticeable effect on the shape recovery; however, this may be
51 an artifact of using 200% programming strain.

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53 Recovery stress is affected by the collector speed because the collector speed changes the resulting
54 porosity, density, and modulus of the nonwoven. However, air pressure does not influence recovery stress
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because the 10 psi and 20 psi had nearly equivalent values; thus, fiber diameter does not govern recovery stress. At programming temperatures at or above the glass transition temperature (75°C and 95°C), the recovery stress profile displays the typical sigmoidal shape due to a combination of inherent thermal expansion and release of the stored strain energy. When the SMP nonwoven is programmed below the glass transition temperature (55°C), it displays a peak in the recovery stress, which has been associated with the higher levels of strain energy required to program at this lower temperature. Following the peak in recovery stress, the material softens and relaxes to an equilibrium stress value similar to the 75°C programming conditions. Similar behavior has been seen in crosslinked acrylic networks [46]. For ideal crosslinked networks, the recovery stress is proportional to the rubbery modulus and the programming strain above the glass transition temperature [1]. Interestingly, the programming strain shows the expected trend that increasing the programming strain increases the recovery stress because more strain energy is stored in the nonwoven; however, the recovery stress values are lower than expected. The lower recovery stress values are most likely occurring because this is a microstructure that relies upon physical entanglements instead of chemical crosslinks, and microCT showed a decreased connectivity density during programming.

To the authors' knowledge, this is the first study that uses high resolution 3D microCT imaging and morphometric analysis to evaluate how the microfiber structure changes during the shape-memory cycle for unconstrained recovery. The inherent advantage of this technique is the quantitative information that is possible to collect. During programming, the overall nonwoven microstructure becomes aligned as seen by changes in degree of anisotropy, and returns to a more unaligned state during recovery. The significant increase of SMI due to programming indicates a shift toward more rod-like structures throughout the nonwoven structure [35], which supports the idea of longer aligned fibers compared to more randomly entangled fibers and intersection points. Changes in the nonwoven microstructure seen through microCT quantifications provide an explanation for the partial (less than ideal) macroscopic recovery observed for the shape-memory nonwovens. The porosity increases during the shape-memory cycle likely because of an increase in the interfiber spacing (i.e. pore diameter), and not a full return of the connectivity density, suggesting fewer entanglements than in the original state and a more open microstructure. Most of the fiber's diameters are recovering, but the fiber diameter distribution has shifted towards small fibers, thus increasing the interfiber spacing because there are fewer thick fibers. In comparison, two studies examined the change in microstructure during the shape-memory cycle using capillary flow porometry for electrospun shape-memory nonwovens. The average pore diameter increased 1.2 to 2.3 times the original average pore diameter during programming into the temporary shape with 50% strain, but complete recovery back to the original average pore diameter did not occur [50, 51]. However, a direct comparison cannot be made because changes in porosity and fiber diameter were not measured during the shape-memory cycle for these studies.

5. Conclusion

The results of this study demonstrate the feasibility of producing a melt blown nonwoven with shape memory capabilities. The shape-memory recovery is dictated by a combination of the melt blow processing parameters (by changing the fiber microstructure) and the shape-memory programming parameters. MicroCT allowed for a greater understanding of the changes in the fiber microstructure during programming and recovery. Future studies will include performance under simulated physiological conditions, cellular response, cyclical behavior, and the effect of post-processing, such as calendaring.

6. Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. 1315011. This work was performed in part at the Georgia Tech Institute for Electronics and Nanotechnology, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542174). The authors would like to acknowledge Dr. Bhat and Mr. Sheriff at UTNRL for their assistance in processing the melt blown nonwoven.

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8. Tables and Figures

Table 1. Porosity of Shape-Memory Nonwovens (g/cm³/g/cm³)

Collector Speed (m/min)	Air Pressure (psi)		
	10	20	30
0.3	0.663 ± 0.031	0.587 ± 0.021	0.57 ± 0.030
0.6	0.741 ± 0.014	0.691 ± 0.012	0.708 ± 0.025
1.0	0.754 ± 0.011	0.728 ± 0.013	0.75 ± 0.026

Table 2. Shape recovery ratio (%) for nonwovens under various conditions with all other factors held constant.
Collector speed = 0.6 m/min (CS). Air Pressure = 20 psi (AP). Programming temperature = 55°C (PT).
Programming Strain = 200% (PS). *PS=50%.

Constant	Shape recovery ratio (%)	
	Air Pressure (psi)	
CS,PT,PS	10	65.3 ± 5.5
	20	72.3 ± 5.7
	30	92.1 ± 3.5*
Constant	Collector Speed (m/min)	
	AP,PT,PS	
AP,PT,PS	0.3	70.6 ± 3.8
	0.6	72.3 ± 5.7
	1.0	66.6 ± 0.4
Constant	Programming Temperature (°C)	
	CS,AP,PS	
CS,AP,PS	55	72.3 ± 5.7
	75	57.5 ± 2.0
	95	39.5 ± 4.1
Constant	Programming Strain (%)	
	CS,AP,PT	
CS,AP,PT	50	83.3 ± 4.7
	100	77.5 ± 2.0
	200	72.3 ± 5.7

Table 3. Recovery Stress (MPa) for nonwovens under various conditions with all other factors held constant.
Collector speed = 0.6 m/min (CS). Air Pressure = 20 psi (AP). Programming temperature = 55°C (PT).
Programming Strain = 200% (PS). *PS=50%.

		Max Recovery Stress (MPa)	Final Recovery Stress (MPa)
Constant	Air Pressure (psi)		
CS,PT,PS	10	0.64 ± 0.09	0.33 ± 0.04
	20	0.65 ± 0.12	0.32 ± 0.12
	30	0.76 ± 0.12*	0.64 ± 0.08*
	Collector Speed (m/min)		
AP,PT,PS	0.3	1.51 ± 0.05	0.76 ± 0.05
	0.6	0.65 ± 0.12	0.32 ± 0.12
	1.0	0.74 ± 0.06	0.42 ± 0.09
	Programming Temperature (°C)		
CS,AP,PS	55	0.65 ± 0.12	0.32 ± 0.12
	75	0.32 ± 0.04	0.31 ± 0.04
	95	0.16 ± 0.04	0.15 ± 0.04
	Programming Strain (%)		
CS,AP,PT	50	0.38 ± 0.24	0.22 ± 0.11
	100	0.46 ± 0.10	0.20 ± 0.05
	200	0.65 ± 0.12	0.32 ± 0.12

1 Table 4. Structural properties of 20 psi 0.6m/min nonwoven determined by microCT given as average $\pm$ st.dev.
2 $\#^*$, $p < 0.05$ between groups.
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	Pre-programmed	Programmed	Recovered
Average Fiber Diameter (μm)	$11 \pm 0.12\#$	$9.75 \pm 0.34\#^*$	$10.63 \pm 0.13^*$
Porosity (mm^3/mm^3)	$0.73 \pm 0.003\#^*$	$0.8 \pm 0.017\#^*$	$0.767 \pm 0.008\#^*$
Average Interfiber Spacing (μm)	$25.78 \pm 0.38\#^*$	$27.95 \pm 1.14\#$	$28.9 \pm 1.26^*$
Connectivity Density ($1/\text{mm}^3$)	$48099 \pm 1578\#^*$	$35271 \pm 2895\#^*$	$40860 \pm 1920\#^*$
Structural Model Index	$1.889 \pm 0.04\#$	$2.485 \pm 0.173\#^*$	$2.095 \pm 0.042^*$
Degree of Anisotropy	$1.271 \pm 0.018\#$	$1.664 \pm 0.048\#^*$	$1.303 \pm 0.0264^*$

Figure 1. Scanning electron microscope images of shape memory nonwovens produced at 0.6m/min at (A) 10 psi, (B) 20 psi, (C) 30 psi.

Figure 2. (A) Fiber diameter as a function of air pressure for each collector speed. For 0.3 m/min, * $p < 0.05$ for 10 psi vs 20 psi, 10 psi vs 30 psi. For 0.6 m/min, ^ $p < 0.05$ for 10 psi vs 20 psi, 10 psi vs 30 psi. For 1.0 m/min, # $p < 0.05$ for 10 psi vs 20 psi, 10 psi vs 30 psi, † $p < 0.05$ for 20 psi vs 30 psi. (B) Fiber diameter distribution for 0.6 m/min nonwoven. Step size is 1 micron.

Figure 3. Dynamic mechanical analysis of 20 psi nonwovens at varying collector speed.

Figure 4. Unconstrained recovery at 90°C of 20 psi, 0.6m/min nonwovens (A) programmed at varying strain and (B) programmed at varying temperatures.

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Figure 5. Recovery stress at 90°C of 20 psi, 0.6m/min nonwovens (A) programmed at varying strain and (B) programmed at varying temperatures.

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100 μ m

1
2 AL - DS - progr 2x6x1 fabrics

100 μ m

AL - DS recov 2x6x1 fabrics

100 μ m

Figure 6. MicroCT images showing fiber thickness in color scale at (A) pre-programmed, (B) programmed 200% strain, (C) and after recovery. Scale is 100 microns. Color scale is 5 to 15 microns.

Figure 7. (A) Fiber diameter distribution as determined by μ CT at each stage of shape-memory cycle. (B) Percent change of fiber diameter as determined by μ CT. Solid line represents ideal 100% recovery.