Synthesizing A Phase Changing Bistable Electroactive Polymer
And Silver Nanoparticles Coated Fabric As A Resistive Heating Element

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ABSTRACT OF THE DISSERTATION

Synthesizing A Phase Changing Bistable Electroactive Polymer
And Silver Nanoparticles Coated Fabric As A Resistive Heating Element

by

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Transducer technologies that convert energy from one form to another (e.g. electrical energy to mechanical energy or thermal energy and vise versa) are considered as the basic building blocks of robots and wearable electronics, two of the rapidly emerging technologies that impact our daily life. With an emphasis on developing the essential smart materials, this dissertation focuses on two specific transducer technologies, bistable large-strain electro-mechanical actuation and resistive Joule heating, in pursuit of refreshable Braille electronic displays and wearable thermal management element, respectively.

Dielectric elastomers (DEs) have been intensively studied for their promising ability to mimic human muscles in providing efficient electro-mechanical actuation. They exhibit a
unique combination of properties, including large strain, fast response, high energy
density, mechanical compliancy, lightweight, and low cost. However, the softness of the
DE materials, which is a prerequisite for electrically induced large actuation strain, has
been hindering their application in adaptive structures. In these applications such as
braille displays, a certain amount of mechanical support is necessary in addition to large
strains for the device or system to function. Bistable electroactive polymers (BSEP) that
leverage the electrically induced large-strain actuation of DE actuators and the bi-stable
rigid-to-rigid deformation of shape memory polymers are innovated to provide large
electrical actuation strain in their rubbery state and fix the deformation by cooling down
to room temperature to incorporate mechanical rigidity.

BSEP materials that can suppress electromechanical instability and exhibit stable
mechanical properties in the rubbery state are desired. A bimodal BSEP material with a
glass transition temperature right above room temperature has been synthesized
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at room temperature that decreases to several MPa at above 70°C after a rigid-to-rubbery
transition via glass transition. The rubbery BSEP possesses a stable storage modulus
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performances under an electric field. The bimodal structure creates a framework
involving both long chain crosslinkers and small molecular crosslinkers. Due to the
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BSEP actuator with a braille dot size exhibits steadily increased actuation height with
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The preceding BSEP enters its rubbery state via glass transition at above 70 °C, where electrical actuation takes place. This actuation temperature has to be lowered in order to shorten the heating or cooling time for the reversible rigid-to-rubbery transition and to reduce thermal energy consumption. A phase changing bistable electroactive polymer based on stearyl acrylate (SA, or octadecyl acrylate) and urethane diacrylate oligomer (UDA, difunctional long chain crosslinker) has been synthesized to provide sharp rigid-to-rubbery transition (narrow temperature range of about 10 °C). At room temperature, the stearyl acrylate moieties are crystallized and harden the SA-UDA copolymers with a storage modulus of 10-100MPa. These aggregates melt at an elevated temperature (below 50 °C) with dangling octadecyl chains softening the polymer in its rubbery state. The difference of the storage modulus between the rigid state and the rubbery state ensures good shape memory properties of the SA-UDA polymers with both fixation and relaxation rate of 100%. The SA-UDA based BSEP exhibits steadily increased actuation strain with increasing electrical field. The SA-UDA films can be actuated at 50 °C up to 70% strain with the maximum actuation energy density comparable to the figure of merits of dielectric elastomers. No electromechanical instability was observed due to its self-stiffening property resulted from a similar bimodal structure as preceding bimodal BSEP.
Wearable thermal management strategy has presented itself recently as a new challenge to offer an optimal thermal experience for the occupant as well as to reduce building energy usage for heating, ventilation and air conditioning (HVAC). Joule heating based on a silver nanoparticles (AgNPs) coated non-woven fabric can provide a wearable localized heating element. Silver nanoparticles (AgNPs) can grow in situ onto non-woven fabrics and form a very uniform and conductive media performing as an efficient heating element. A multistep electroless deposition was employed to initially create heterogeneous nuclei on the surface of the fabrics, which subsequently grow into AgNPs in an electroless deposition solution. The electroless deposition was conducted at a low temperature (in a 4 °C refrigerator) in an Ag (I) containing deposition solution with selected metastable redox pairs such that homogeneous nucleation of silver nanoparticles is kinetically unfavorable. With an extended deposition time, AgNPs merge with each other on the surface of the polyester fabrics to form a conductive network. A sheet resistance of <0.3 ohm/square can be achieved for AgNPs-coated polyester fabrics upon thermal annealing. Multistep electroless deposition creates chemical bonding between oxygen groups on the fabrics’ surface and AgNPs. As a result, the bonding between the AgNPs layer and the polyester fabrics is strong enough to resist sonication damage. The resistance only increased slightly after an 80 minutes of sonication and therefore the AgNPs-polyester fabrics composite are regarded as washable. The AgNPs coated polyester fabrics was employed as a heating element. A voltage as low as 1volt is adequate to heat up the AgNPs-polyester fabrics to 60 °C in 2 seconds. The heat can be dissipated away fast after turning off the heating voltage, due to the mesh structure of the AgNPs-polyester fabrics. The strategy of the wearable heater can potentially play
influential roles in energy saving and consumer experience in a localized thermal management system.
The dissertation of Zhi Ren is approved

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PUBLICATIONS AND PRESENTATIONS


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Silver Nanowires, Carbon Nanotubes And An Elastomeric Dielectric. Nature
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And Special Resonance Of A Dielectric Elastomers Minimum Energy Structure

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• Oral Presentation: “A New Bistable Electroactive Polymer for Prolonged Cycle
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• Live Demonstration: The 17th annual EAP (electro-active polymers)-in-Action
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OUTLINE OF THE DISSERTATION

This dissertation is divided into 5 chapters.

Chapter 1 gives an overview of the dielectric elastomers and bistable electroactive polymers including the working mechanism and important applications.

Chapter 2 presents a background of braille application and describes a solution enabled by bistable electroactive polymer. A glass transition based BSEP having bimodal chain length distribution was developed exhibiting suppressed electromechanical instability and a prolonged actuation cycle lifetime in its rubbery state. A page size braille paper was fabricated, and the potential heating strategies were discussed.

Chapter 3 describes a new bistable electroactive polymer that utilizes phase transition involving reversible melting/crystallization of the stearyl acrylate moieties to obtain a narrow rubbery-to-rigid transition temperature range. This narrow rigid-to-rubbery transition range allows a lower operation temperature in pursuit of low thermal energy consumption and fast cycle response. The material shows good shape memory properties and actuation performance in its rubbery state.

Chapter 4 gives a brief overview of personal thermal management. A silver nanoparticles (AgNPs) coated non-woven fabric was developed via a multistep electroless deposition method to achieve a uniform coverage of AgNPs on the fabrics and low resistance, which allows low voltage joule heating. The bonding between AgNPs and the fabric is strong to endure extended bath sonication and therefore the AgNPs-fabric is considered to be washable as potential wearable heating element.

Chapter 5 concludes the dissertation.
Chapter 1. Overview Of Dielectric Elastomers

1.1 Background And Mechanisms Of Dielectric Elastomers

Scientist and engineers have long been seeking to develop transducer technologies with lightweight materials that can deform in size and shape when stimulated by an electric field, in mimicking human muscles for robotics and electromechanical transduction. Electromechanical transducers are devices that can transduce electrical energy into mechanical energy or vice versa. While traditional transducer technologies such as electromagnetic motors or pneumatic systems can produce large output force and strain by sophisticated mechanical design with gears or other mechanical coupling systems (e.g. Boston Dynamics, bigdog) \[1\], the bulky size required by these electromechanical transducer technologies has been hindering their small-scale applications. A few inorganic materials have been employed in transducer technologies in offering small-scale capabilities, including shape memory alloys \[2\] and piezoelectric ceramics \[3\]. However, they suffer from small strains during actuation. Electroactive polymers (EAP) \[4, 5\] are emerging as an electromechanical transducer technology that can provide many advantages including low cost, excellent compliancy, and simple form of factor. They present as promising alternatives to the conventional technologies. In general, electroactive polymers can be divided into ionic and electronic EAP \[6, 7\]. Ionic EAPs, including Ionic polymer–metal composites \[8\], ionic gels \[9\], carbon nanotubes \[10\], and
Conductive polymers \cite{11}, rely on ion migration under electric field and can typically offer large output forces with low driven voltages. However, they are relatively slow in response to electrical field due to their dependence on mass transport, and relatively energy inefficient due to their poor electro-mechanical coupling. In addition, ion migration often requires electrolyte or liquid media to facilitate. As a result, ionic EAPs (wet EAP) are essentially sensitive to temperature and moisture. In contrast, electronic EAPs, which include ferroelectric polymers \cite{12}, polymer electrets \cite{13}, electrostrictive polymers \cite{14,15}, and dielectric elastomers \cite{16}, can respond fast, be energy efficient, and are dry EAPs (requiring no electrolyte) that are relatively insensitive to temperature or humidity levels. Despite that most of electronic EAPs have to be operated with high voltage, they often require only a small current due to their innate insulating properties and capacitive characters. As a result, the energy required for each actuation is normally small which can reduce the size of power supply.

Among all the electronic EAP materials, dielectric elastomers (DEs) \cite{17} stand out for their large strain, large force output, simple form of factor, quietness, and high energy density. Their similar properties to that of natural muscle have earned them the moniker “artificial muscles”. DE transducers consist of a rubbery dielectric elastomer film sandwiched between two compliant electrodes on the surface, which are essentially compliant capacitors. Depending on whether the mechanical energy is converted from or to electrical energy, these DE transducers can be operated as either actuators or
generators. The operation mechanism of actuation mode of the DE transducers can be depicted in Figure 1-1.

When a voltage is applied across the dielectric elastomer film, the compliant capacitor draws positive charges and negative charges onto the surface of the film through the compliant electrodes. Due to Coulomb forces, the opposite charges attract, while the like charges on the same electrodes repel each other. As a result, the polymer shrinks in thickness and expands in area. The actuator converts electricity into mechanical energy resulting in deformation of the elastomer film. The electric field induced mechanical response can be represented by a popular term borrowed from capacitors, the Maxwell pressure, which is analyzed as following. The capacitance of the electrode-coated DE membrane is \( C = \varepsilon_r \varepsilon_0 A/z \). By applying voltage, the electrical energy \(^{[17]}\):

\[
U_e = 0.5Q^2/C = 0.5Q^2 z/\varepsilon_r \varepsilon_0 A = 0.5CV^2 = 0.5\varepsilon_r \varepsilon_0 \text{Vol} \cdot E^2,
\]

where \( \varepsilon_0 \) and \( \varepsilon_r \) are the permittivity of free space and the relative permittivity of the dielectric elastomer, respectively; \( A \) is the active area of the film coated with compliant electrode, and \( z \) is its thickness; \( E = V/z \) is the applied electric field; \( V \) is the applied voltage; \( \text{Vol} = Az \) is the volume of the active portion of the thin film.
Assuming a constant volume of the dielectric elastomer during actuation, the differential form of $U_e$ can be written as $^{[17]}$:

$$dU_e = (Q/C)dQ + 0.5(e_r\varepsilon_oA)^{-1}Q^2dz - 0.5z(e_r\varepsilon_oA)^{-2}Q^2dA$$

$$= (Q/C)dQ + U_e (dz/z - dA/A)$$

$$= (Q/C)dQ + 2U_e (dz/z).$$

The first part of the $dU_e$ $[(Q/C)dQ]$ indicates energy variation due to charging/discharging without deformation of the membrane, while the second part $[2U_e (dz/z)]$ represents the deformation induced electrical energy change under constant charge.

dW = $2U_e (dz/z)$ is denoted as the mechanical work to be done to deform the elastomer film with certain capacitive charge stored. On the other hand, dW can also be put as dW = -Apdz, where p is the pressure on the elastomer film to provide effective mechanical work equal to that by electrical actuation. Therefore, p as the effective pressure can be expressed as $2U_e/az$ or $e_r\varepsilon_oE^2$. The actuation strain ($S_z$ as thickness strain and $S_A$ as area strain) is thus calculated as $^{[17]}$:

$$S_z = -p/Y = -e_r\varepsilon_oE^2/Y,$$  while  $$S_A = 1/(1+S_z),$$

1.2 **Dielectric Elastomer: Materials Development**

Extensive research activities have been conducted on numerous DE materials including polyurethane, acrylics, silicones, etc. since the 1990s. A remarkable contribution from SRI was made by a work published in Science journal in 2000, which reported that DE materials including both acrylics and silicones were capable of large actuation strains in
excess of 100% \cite{16}. The enhancement of actuation strain was a synergistic result of the employment of a new dielectric elastomer (3M’s VHB 4910, an acrylic material) and the utilization of large prestrain of the membrane. The prestrain in one planar direction helped suppress electrical breakdown and led to major actuation in the low-prestrain planar direction. It had been well recognized that dielectric elastomers can fail prematurely at certain strain due to excess thinning down when stimulated by electric field, also known as pull-in effect or electromechanical instability (EMI) \cite{18a, 18b}. Due to the low mechanical stiffness of dielectric elastomer, the positive feedback loop between a sudden increase (‘snap-through’) of the strain and electric field can occur at a constant voltage at EMI and result in an electric field exceeding the breakdown field of the material. The film can easily break due to the ‘snap-through’. Therefore, the maximum stable actuation strain is severely constrained by EMI \cite{19}. By being prestrained to an extended state before actuation, the film stiffens substantially at relatively large actuation strain, thus suppressing the excessive thinning down during actuation to protect the film from pull-in effect. Further investigation also discovered that the electric breakdown field $E_B$ is positively related to prestrain \cite{20, 21}. Since the advent of large strain actuation of DEA, DE materials started to draw vast interest in the science community.

Although prestraining is an effective method to overcome EMI thus introducing large strain actuation of DE, it has its disadvantages. A rigid frame is necessary in order to hold the prestrain, thus increasing the complexity of the actuators. In addition, prestraining
may reduce the actuation strain for some DE materials that are not innately extremely stretchable to begin with. Ha et al. \cite{22,23} first introduced interpenetrating network (IPN) as freestanding (prestrain-free) DE materials, which exhibited electrically induced actuation strain up to 300%, comparable to highly prestrained VHB. The IPN was formed by curing a second network inside the highly prestrained primary network (400% x 400% prestrained acrylic film, VHB). When the primary network in tension was allowed to relax, the second network in compression can preserve a portion of the prestrain. This led to a freestanding dielectric elastomer with prestrain of the first network locked internally, performing equally well as highly prestrained DE materials. Alternatively, Niu \cite{24} et al. introduced a series of UV cured chemically crosslinked polymers as freestanding dielectric elastomers that can avoid EMI. The un-necessity of prestraining is due to the self-stiffening properties of such polymers at relatively large strain to resist excessive thinning down at large actuation strain.

In addition to EMI, one important factor that tends to impede the application of DE materials is the high voltage required to achieve large actuation strain. Judging from the equation $S_z = -p/Y = -\varepsilon_r\varepsilon_0E^2/Y$, where $E = V/z$, one obvious strategy to reduce the driving voltage while maintaining the effective electric field is to minimize the thickness of the DE film. However, the reduced film thickness may result in a low actuation force and small displacement in the thickness direction from a single layer device. Schlaak et al. developed an automatic fabrication process of multilayer actuators \cite{25}. The spinning
coating process can be controlled to allow the fabrication of homogeneous dielectric films with thickness from 100 microns down to 4 microns [26]. With a reduced voltage applied on a multiple-layer actuator, the overall deflection can be maintained.

Increasing the permittivity of the dielectric elastomers can also reduce the driving voltage while achieving sufficient actuation force or increase the actuation force under certain driving voltage. Heavily investigated strategies to increase the permittivity of the dielectric elastomers include adding high dielectric constant ceramic nanoparticles, e.g. TiO$_2$ [27, 28], blending or encapsulating conductive nanofillers [29-31], and chemically modifying the elastomers by grafted polarizable side chains [32, 33] or high dipole moieties [34]. Stoyanov [27] reported that by adding surface modified 300nm TiO$_2$ nanoparticles to an optimized volume ratio of 15% in SEBS matrix, effective reduction of the electric field by 27% can be achieved without compromising the actuation strain. Similarly, Nguyen et al. [28] also demonstrated the capability of tuning the modulus and dielectric properties to reduce the driving electric field by adding both dioctyl phthalate (DOP) and titanium dioxide (TiO$_2$) into Acrylonitrile butadiene rubber (NBR). In investigating the effect of blending or encapsulating of conductive nanofillers on the permittivity of the materials, Hu et al. [29] reported an Al-acrylate polymer system where Al nanoparticles were covalently bonded to the polymer chains. The dielectric constant was improved by 60% without sacrificing the electric breakdown field, indicating excellent dispersion of conductive fillers. Kofod et al. [30] synthesized silica encapsulated Cu nanoparticles that
can improve the dielectric constant of SEBS composites dramatically with only a tiny fraction of Cu content. Opris et al. \cite{31} used polymer shell encapsulated PANI fillers to improve the dielectric constant by 3 folds with increased actuation strain at breakdown. The addition of fillers has been proven to be effective to increase permittivity. However, in cases where special care was not taken on surface modification of the fillers, the increased mechanical modulus and decreased electrical breakdown field can result in small actuation strain. Chemical modification of elastomers by grafting polarizable side chains or high dipole moieties was considered as another good candidate due to their molecular-level distribution of polar group. Carpi et al. \cite{32} employed a method of blending small quantities of P3HT (as little as 1wt%), an undoped conjugated polymer, into silicone matrix before curing, which led to a compatible system that not only enhanced the permittivity of the elastomer, but also reduced the elastic modulus of the silicone. Those two factors both contributed to an improved electromechanical strain response of the elastomer and a reduction of the driving electrical field for a similar actuation strain. Stoyanov et al. \cite{33} introduced an alternative method of grafting a \( \pi \)-conjugated soft macromolecule onto SEBS via maleic anhydride moieties. A small quantity of 2wt\% grafted macromolecule resulted in a 470\% increase of permittivity over SEBS. However, an amount of larger than 2wt\% led to a sudden increase in the conductivity of the grafting composite, resulting in a drop of the breakdown field. Kussmaul et al. \cite{34} employed an innovative method to increase the electromechanical response in silicone elastomers by grafting N-allyl-N-methyl-p-nitroaniline molecules
with high push-pull dipole moment. An increase of the relative permittivity by nearly 100% and a decrease of the elastic modulus to 29% by grafting the dipole molecules synergistically contributed to a six times enhancement of the actuation strain under similar electric fields.

Aside from large actuation strain and reduced driving voltage, dielectric elastomer transducer often faces lifetime issues (actuation stability). Despite the fatigue and tear of dielectric elastomers, the performance of the electrodes located on the actuator’s surface is essential to the devices’ lifetime and reliability. The electrode of a DEA must be able to survive large deformations as the dielectric elastomers do (up to 100%) without losing conductivity. They should be mechanically compliant and place little mechanical impact on the overall stiffness of the dielectric elastomer actuators to avoid reducing the actuation strain. In addition, the compliant electrodes must be reliable for millions of cycles of actuation. Under such strict requirements, scientists and engineers have been seeking for an ideal solution to the compliant electrodes for DEAs. Early stage of the electrode development focused on the compliancy character. Carbon-based electrodes have been widely used in the DEA community, including loose carbon powder directly spray-coated on the elastomer (e.g. carbon powder, graphite powder), carbon particles dispersed in a viscous oil (carbon grease) and conductive elastomeric electrode \cite{35, 36}. Powder based electrodes often suffer from loss of conductivity due to their easy detachment from the surface. Carbon grease is commonly used to demonstrate large
actuation strain because of its excellent compliance. However, its performance may decay over time due to its viscosity nature (flowing-caused uneven distribution) or drying of the oil. Carbon grease is not compatible with multilayer structures or applications that require solid and smooth interfaces. The conductive rubber can provide good conductivity under large strain [37] and excellent adhesion to the dielectric elastomer by coating liquid conductive prepolymer mixture onto the elastomer and curing subsequently. However, the existence of the rubber materials on the surface of DEAs impacts the stiffness of the DEA, especially when the DEA itself is thin. As a consequence, the strain performance of the DEA is compromised. Other candidates also include thin film metallic electrodes in the forms of patterned metal electrodes [36], buckled [38] or corrugated metal electrodes [39]. Despite the good conductivity and self-healing properties of the metallic thin film based electrodes, they often suffer from their limited strain and their impact on the stiffness of the DEA.

In addition to compliancy, advanced electrode materials include fault tolerant electrode – single wall carbon nanotubes (SWNT) [40], and ion-implanted electrodes [41] are developed for prolonged lifetime. Similar to metallic thin films, SWNT possesses self-clearing property that can achieve fault-tolerant actuation and help survive local dielectric breakdown of dielectric elastomers through insulation of SWNTs from breakdown sites or defected area [40]. Stoyanov et al. [42] reported significantly improved reliability of DE actuation using SWNT. Cycling actuation tests on silicone coated with SWNT demonstrated that the actuators maintained highly functional and survived over
30 local electrical breakdown events by self-clearing of the electrodes. A long cycle lifetime of 85,000 cycles was demonstrated with the actuators performing at relatively high (25%) linear actuation strain without degradation. To increase the adhesion between the SWNT electrodes and DE membranes, Brochu et al. developed a silicone IPN based elastomer with the second network cured after SWNT was spray-coated \[43\]. With a mechanical load attached to the actuator, a stable DEA actuation performance of over 30,000 cycles at > 20% strain or over 500 cycles at 40% strain has been demonstrated as SWNT electrodes being bonded to the surface of IPN. On the other hand, the ion implantation technique proposed by Rosset et al. \[41\] created nm-scale metallic clusters with sizes up to 50 nm that are located right below the PDMS surface (PDMS thickness 15–40 µm). The ion-implanted electrode can remain conductive with up to 175% strain and introduce little mechanical impact to the elastomers. A cycling lifetime of over 4 million cycles has been shown without degradation of actuation strain at 1.5 kV.

With the advance of materials and electrodes, various applications by using dielectric elastomers as a potential transducer technology are considered.
1.3 Applications Of Dielectric Elastomers

Dielectric elastomers (DEs) exhibit a unique package of properties including mechanical compliancy, large actuation strain, fast response speed, high energy density, quiet operation, light weight, and low cost. They have stimulated envision of numerous applications, including robotics, adaptive structures, microelectromechanical systems, dielectric elastomer switches, haptic modules (vivitouch), and generators [44-51]. A walking robot [44] was developed following the debut of a large strain DE actuator reported in Science Journal. Multiple degree-of-freedom (DOF) spring-roll-actuators fabricated by rolling specifically electrode-patterned prestrained VHB elastomers onto a compressed spring (see Figure1-2a, b for fabrication process) were employed in the MERobot design. Six 2-DOF spring-roll-actuators capable of bending and extending were assembled into MERobot that can “walk” 13.4cm per second (Figure1-2c). The very same spring-roll-actuators were later assembled into a very large arm wrestling robot with 256 rolled actuators being arranged into two protagonist-antagonist groups (Figure 1-2d, e). It can provide a maximum force of 200N at the starting position for wrestling competition against a male human [45]. This first arm wrestling match of EAP robotic arm against human held on March 7, 2005 demonstrated the potential of the EAP technology for applications in the field of robotics, bioengineering, and similar technologies.
Figure 1-2 (a, b) Illustration of a spring roll actuator and (c) a walking robot MERobot consists of 6 spring roll actuators [44]. (d, e) An arm wrestling machine consists of 256 spring roll actuators and its competition against a male human [45].

Aside from applications in robotics, which is the original purpose of the EAP, DEs presented themselves to be capable of far beyond robotics. Carpi et al. [46] designed a tunable lens (Fig. 1-3a, a’) mimicking the human eye (Fig. 1-3b, b’) with an annular DE actuator as an artificial ciliary muscle to drive the fluid-filled elastomeric artificial lens in the center. Upon electrical stimulation, the annular dielectric elastomer actuator squeezes the lens resulting in a change of focal length (Figure 1-3c, c’). Murray and McCoul et al. [47] innovated PDMS microfluidic systems driven by dielectric elastomer (prestrained 3M™ VHB™ 4910) stack actuators. These electroactive microfluidic (EAM) devices were capable of active increase of PDMS microchannel width upon applying 3 or 4 kV voltages on the stack actuators (Figure 1-3d). The EAM can perform active de-clogging: when a clog occurs by introducing PDMS microbeads into the system, three actuation
attempts successfully cleared the blockage, as shown in Figure 1-3e. With sophisticated design, O’ Brien et al. was able to achieve a NAND gate with DE actuators functioning as switches [48] (Figure 1-4). The dielectric elastomer switches (DES) utilize the piezo-resistivity (change of resistivity with stretch) of resistor, R_var (Fig. 1-4a) to switch the output voltage on and off. Only when both DEA Input1 and Input2 are activated (Fig. 1-4b), the R_var is compressed and its value decreases by orders of magnitude, resulting in a low output voltage or an off state (Fig. 1-4c). The DES can be utilized to control the actuation of DEA in return. This two-way interaction between actuation and switching can be employed to manage the DE actuation toward a self-priming oscillating circuit.

Figure 1-3 (a, a’, b, b’, c, c’) Application of DE actuator in tunable lens [46] and electroactive
microfluidic devices capable of tuning the micro-channel width \(d\) and declogging \(e\) \[^{[47]}\].

![Image](image1)

Figure 1-4 Application of DE actuator in dielectric elastomer switches \[^{[48]}\]

Artificial Muscle Inc. (AMI) developed their first commercial haptic feedback module \[^{[49, 50]}\] that is thin and of high-fidelity for mobile handsets (Figure 1-5b). The mounting actuator module (Figure 1-5a) converts sound signal with certain frequency into vibration that can offer physical sensation to the surrounding skin of the ears for a 4D sound experience.

![Image](image2)

Figure 1-5 A mounting actuator module (a) in a headphone module (b) by AMI using DE \[^{[49, 50]}\]

1.4 Dielectric Elastomers As Generators
In the actuator mode, electrical energy is converted into mechanical energy as the Maxwell pressure exerting work on the polymer materials and the load attached to the polymers. In fact, the compliant capacitor (DE transducer) can also be operated in a reverse fashion, converting mechanical energy into electricity \cite{51} as a dielectric elastomer generator (DEG). The operating mechanism of the dielectric elastomer generator in a cycle is as follows (Figure 1-6). Mechanical energy is first input into the system by stretching the dielectric elastomer membrane (step 1). The charges are then transported to the surface of the membrane by applying a relatively low input voltage $V_{in}$ (charging, step 2) while the membrane is in its strained state. The amount of the charges is determined by the material itself, its area strain $\lambda$ and the $V_{in}$ as $Q = CV_{in} = C_o(1+\lambda)^2V_{in}$. The input electrical energy $e_{in} = 0.5QV_{in}$ ($C_o$ and $C$ represent the capacitance of the DEG in its original and strained state, respectively. $V_{in}$ is the input voltage). As the membrane being released from the mechanical stretch (step 3), it tends to recover its original configuration due to elasticity. The opposite charges are thus pulled apart and like charges are squeezed together. The stored mechanical energy conducts work against the electric field and is converted into electrical energy. In a constant charge mode, the discharging circuit is completely open/disabled during the recovery process, and the voltage exerted by the membrane increases to $V_{out} = Q/C_o = V_{in}(1+\lambda)^2$ in a fully recovered state. At this point, the charges are conducted away from the membrane to an electricity storage system (discharging, step 4) with a total electrical energy of $e_{out} = 0.5QV_{out} = 0.5QV_{in}(1+\lambda)^2 = e_{in}(1+\lambda)^2$. The mechanical energy is converted into electrical
energy in each cycle, resulting in an increase in electrical energy from $e_{\text{in}}$ to $e_{\text{out}} = e_{\text{in}}(1+\lambda)^2$.

Figure 1-6. Operating mechanism of dielectric elastomer generator

1.5 Bistable Electroactive Polymers

The development of DE materials and their various applications place vast potential to the field of electroactive polymers and transducer technologies. However, the softness of the DE materials, which is a prerequisite for electrically induced large actuation strain, has been hindering their application in adaptive structures. In these applications such as braille displays, certain amount of mechanical support is necessary in addition to large strains for the device or system to function. Bistable electroactive polymers (BSEP), which leverage the electrically induced large-strain actuation of DE actuators and the bi-stable rigid-to-rigid deformation of shape memory polymers, are innovated to solve the problem. A BSEP can provide large electrical actuation strain in its rubbery state and fix its deformation by cooling down to room temperature to incorporate mechanical rigidity
(rigid-to-rigid actuation). The refreshable rigid-to-rigid actuation of a typical BSEP with a glass transition is illustrated in Fig. 1-7. The active polymer sandwiched between two compliant electrodes has a rigid-to-rubbery transition temperature (e.g. glass transition temperature, $T_g$) separate from room temperature. At room temperature, it is a rigid polymer like polystyrene and poly (methyl methacrylate), which are widely used in our daily life. Above transition temperature, it behaves like a stretchable and elastic rubber having an elastic modulus smaller than 10 MPa. In its rubbery state, a voltage applied across the polymer film via a pair of compliant electrodes coated on opposite surfaces of the film can cause the rubbery polymer to expand in area and shrink in thickness (same as DE actuation, see Figure 1-1). The metastable deformation of the film can be preserved by cooling down the polymer toward room temperature until it regains its rigidity with an elastic modulus greater than 100 MPa. Recovery to its original shape can be achieved through reheating the BSEP to the rubbery state. Going through a full cycle, the BSEP can be deformed to any intermediate rigid shape between A and D reversibly and repeatedly. The BSEP with ‘rigid-to-rigid’ deformation is able to provide a large force support below transition temperature in addition to large deformation obtained by freezing the actuation strain produced in the rubbery state.
Figure 1-7 Schematic illustration of actuated deformation of BSEP \cite{52,53}. (A) A rigid polymer film is sandwiched between two compliant electrodes. (B) The structure is heated to above the glass transition temperature ($T_g$) of the polymer by an external heat source or Joule heating via the electrodes. (C) A high voltage is applied to induce Maxwell strain in the softened film. (D) The structure is allowed to cool to below $T_g$ to regain its stiffness. Shape (D) may be returned to (A) by a heating/cooling procedure similar to that in a shape memory polymer.

The performance of the BSEP actuator is determined by several key parameters including the shape memory property, dielectric breakdown strength, and mechanical fatigue strength of the BSEP polymer. The first experimentally proven high-performance BSEP polymer \cite{52} that has been developed is poly (t-butyl acrylate) (PTBA). The rigid thermoplastic at ambient temperature can be electrically actuated to strains up to 335% in its rubbery state (at 70°C). However, the actuation is not stable at strains larger than 100% due to the unstable mechanical modulus in the rubbery state of PTBA and electromechanical instability at relatively large actuation strains. PTBA is a thermoplastic polymer with physical crosslinks for the elasticity in its rubbery state above 60 °C. The physical crosslinks, which are nanocrystalline domains with a maximum melting...
temperature of around 190 °C, are unstable at relatively high temperature. As a consequence, temperature fluctuations and non-uniform temperature distribution will cause non-uniform modulus distribution, leading to local excessive actuation strains and dielectric breakdown. Meanwhile, similar to dielectric elastomers without self-stiffening mechanism at relatively large strain or prestrain, electromechanical instability \cite{22,54} (EMI, or the pull-in effect) causes premature electric breakdown of the PTBA in its rubbery state. PTBA-IPN was therefore developed to provide stable actuation in its rubbery state \cite{53}. To fabricate PTBA-IPN membrane, a first UV-cured PTBA network was swollen and ‘chemically prestrained’ in a monomer solution, which is subsequently cured as the second network to preserve the ‘prestrain’. The resulting PTBA–IPN membranes exhibit a stable modulus above the glass transition regardless of temperature fluctuation due to a chemically crosslinked network. EMI is effectively suppressed during actuation due to interpenetrating networks with a rapid increase of the polymers’ modulus at large strains. However, prestretching by chemical swelling, even not through mechanically stretching in the case of PTBA-IPN, complicates the device structure or fabrication process, limits the application, and impedes the scaling up into production.

1.6 Scope Of The Dissertation – Chapter 2 & 3

A BSEP material that can suppress electromechanical instability without the necessity of any form of prestraining and can exhibit stable mechanical properties in the rubbery state is desired. In Chapter 2, a bimodal BSEP material with a glass transition temperature
right above room temperature has been synthesized employing simple UV curing process. The BSEP has a large storage modulus $\sim 1$ GPa at room temperature that decreases to several MPa at above 70°C after a rigid-to-rubbery transition via glass transition. The rubbery BSEP possesses a stable storage modulus regardless of temperature fluctuations, which is beneficial to stable electrical actuation performances under electric field. The bimodal structure involves both long chain crosslinkers and small molecular crosslinkers and creates a framework that can self-stiffen the rubbery BSEP at modest strains to suppress electromechanical instability, which is responsible for premature electrical breakdown of the previous BSEP material (PTBA) in its rubbery states. A BSEP actuator with a braille dot size exhibits steadily increased actuation height with increasing electric field at 70 °C. A stable actuation with a cycle lifetime of over 2000 cycles at a raised dot height of 0.4 mm was demonstrated. A fabrication process for a page-size braille paper using the BSEP has been developed. Selective heating strategy has been investigated based on a 2-cell device to provide a selective actuation strategy of BSEP braille dots.

The preceding BSEP via glass transition enters its rubbery state at above 70 °C, where electrical actuation takes place. This actuation temperature has to be lowered down in order to shorten the heating and cooling time for the rigid-to-rubbery transition or the opposite and to reduce thermal energy consumption. In chapter 3, a phase changing bistable electroactive polymer based on stearyl acrylate (SA, or octadecyl acrylate) and urethane diacrylate oligomer (UDA) has been synthesized to provide sharp rigid-to-rubbery transition (narrow temperature range of about 10 °C). At room
temperature, the stearyl acrylate moieties are crystallized and harden the SA-UDA copolymers with a storage modulus of 10-100MPa. These aggregates melt at an elevated temperature (below 50 °C) with dangling octadecyl chains softening the polymer in its rubbery state. The difference of the storage modulus between the rigid state and the rubbery state ensures good shape memory properties of the SA-UDA polymers with both fixation and relaxation rate of 100%. The SA-UDA based BSEP exhibits steadily increased actuation strain with increasing electrical field. The SA-UDA films can be actuated at 50 °C up to 70% strain with the maximum actuation energy density comparable to the figure of merits of dielectric elastomers. No electromechanical instability was observed due to its self-stiffening property resulted from a similar bimodal structure as preceding BSEP in chapter 2.

1.6 Reference


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Chapter 2. A Bistable Electroactive Polymer With Bimodal Chain Distribution For Refreshable Braille Displays

2.1 Introduction

Vision impairment can place dramatic difficulties in a person’s livelihood, from the ability to communicate and learn, to travelling to new locations. There are 21 million vision-impaired individuals in the United States alone. Among those 1.3 million legally blind individuals, 55,000 are children [1, 2]. In recent years, audio devices have been widely used due to their facile use and low cost. Unfortunately, these audio devices cannot teach literacy or serve people who are both visually and hearing impaired. Braille has been the only media to educate blind children with literacy. However, due to a synergistic effect of both widely employed audio devices and less advanced/developed braille technologies, the literacy rate for blind children in the US has been decreasing: 50% of blind children read Braille in 1960 and only 10% in 2009 [3]. Braille paper manufactured by puncturing, embossing, or molding has been used for over 100 years and is still the primary communication media to teach blind children literacy. Braille paper, however, is inefficient, bulky, and resources consuming. Braille Lite [4], one widely used refreshable Braille electronic readers on the market, is based on braille cells made from piezoelectric ceramic bimorph actuator arrays [5]. Although they are capable of interfacing with computers, portable and lightweight, electronic readers can generally
include only a single line of Braille cells due to the difficulty to package a large number of piezoelectric cantilevers into a compact form. These single-line readers cannot display equations and graphics. The complicated mechanical structure also leads to a high price (a device with 36 cells in one line costs $5000, a device with 3 lines costs $15,000). The high price severely limits the distribution of these devices into the market. Besides braille display, it has been extremely difficult to convey graphics and math equations to blind children. Although a page size refreshable topographical tactile display could solve these problems, such product has been unavailable to date because of the lack of proper and low cost transducer technology.

There are a few alternative transducer technologies being proposed for Braille displays in early stage R&D, including shape memory alloys [6], thermopneumatic actuators [7], and electroactive polymers [8, 9, 10]. Despite the opportunities these technologies granted, they all present certain disadvantages. SMAs can be expensive due to the necessity of complicated thermal management strategies in order to maintain reasonable actuation rates. TPAs with slow response speed must be pulsed periodically to keep their actuated shape, which increases complexity and power consumption. Electroactive polymers such as DEs lack in long cycling lifetime, and are not bistable: they must be constantly electrically actuated to keep the deformation, which causes significant issues regarding limited reliability, high power consumption, and safety concerns.

Bi-stable electroactive polymer (BSEP) [11, 12] leverages the electrically induced
large-strain actuation of DE actuators in a rubbery state and the metastable rigid-to-rigid deformation of shape memory polymers (see chapter 1). It presents as an innovative transducer material that is uniquely positioned to meet all of the requirements for low-cost, reliable, page-size refreshable Braille displays. The BSEP coated with patterned conductive carbon-based material can create an array of pixels, or braille dots. An x-y addressable passive heater circuit can then scan through the array to turn each dot on or off selectively to reach a rubbery state capable of being actuated by the electric field, in order to display specific braille characters, images, etc. The contents can be fixed by cooling down the BSEP.

Aside from its shape memory properties, a BSEP must perform well in electrically induced actuation in the rubbery state. A BSEP that requires no prestrain and can suppress electromechanical instabilities during electrical actuation is desired. In synthesizing DE materials that produce similar or better actuation performance as highly prestretched DEAs but without the requirement of prestretching, Niu et al.\cite{13} developed a UV cured freestanding DE that is free of EMI. The incorporation of both long chain crosslinks and small molecular crosslinks introduces varying chain length in between crosslink sites, which is similar to a bimodal network\cite{14}. Upon stretch, the long chains will retard the rupture process and provide stretchability until the whole network is tightened up and the short chains stiffens the materials at relatively large strain. The stiffening mechanism from bimodal structure stops the elastomer’s premature electric
breaking down due to excessive thinning down, thus avoiding EMI. Inspired by this DE formulation with self-stiffening mechanism, a newly developed, easily fabricated BSEP was demonstrated in this chapter with its stable actuation for a prolonged lifetime of repeated actuation.

The BSEP has a bimodal network containing a long chain component that is typically associated with the rubber-like elasticity and a short chain component responsible to the stiffening mechanism at high elongations. A long-chain crosslinker (difunctional aliphatic urethane oligomer) was employed as an essential component responsible for the long-chain component and improved actuation stability. The amount of the difunctional long-chain oligomer employed was tailored to tune the transition temperature and mechanical properties in the rubbery state. A small molecular trifunctional crosslinker was employed to provide short-chain components and stiffening mechanism at high elongations. Isobornyl acrylate with a glass transition temperature of 94 °C in its poly (Isobornyl acrylate)$^{[17]}$ was employed to elevate the glass transition of the BSEP to above room temperature. Single Braille dots were fabricated and their actuation heights steadily increased with increasing electric field when tested at 70°C. Actuation of over 2000 cycles with an actuation height of 0.4mm was observed indicating the stability of the actuation. A facile fabrication process for a page-size Braille display prototype was demonstrated and selective heating strategy with a 2-cell heater concept was discussed.

2.2 Experimental
2.2.1 BSEP Material Preparation

Long-chain crosslinker (difunctional aliphatic urethane oligomer, oligomer-1), Isobornyl acrylate (monomer-a) and 2-(2-ethoxyethoxy) ethyl acrylate (monomer-b) were obtained from Sartomer Company and used as received. Trimethylolpropane triacrylate (TMPTA) and photo-initiators were purchased from Sigma Aldrich and used as received. The components were thoroughly mixed on a test tube rocker, and a doctor blade was used to coat the resulting solution on a page-size sheet of clean glass with corresponding thickness and good uniformity. The thin layer of liquid prepolymer was cured through a UV curing conveyor equipped with a Fusion 300S type ‘H’ UV curing bulb. After subsequent annealing at 60 °C for an hour to remove unreacted components, the resulting film was gently peeled from the glass.

2.2.2 Braille devices fabrication

Compliant electrodes were deposited by spray coating a solution of dispersed conductive material, such as carbon black in IPA (1 part carbon black per 1000 IPA in weight) and P3-SWNT in IPA/DI-water. Contact masks made from removable tape were created by a laser engraver, and were used to facilitate patterning of the electrodes, which were sprayed with an airbrush at a pressure of 20 psi. A constraint layer for the BSEP film, made from Kapton Green Tape, was laser engraved to match the pattern of the active dots.
and put onto each side of the electroded film. This constraining of the inactive area ensured vertical actuation of the active dots.

2.2.3 Actuation Tests

A Braille dot was fabricated having an active area of 1.3 mm in diameter. The device was placed on a hotplate to achieve a surface temperature of 70 °C. A J-type thermocouple was embedded near the active part of the device to estimate the actual temperature of the material. Lifetime tests were conducted by applying a square wave high voltage signal with a frequency of 0.2 Hz and duty cycle of 0.5. The vertical displacement was recorded in real time using an Acuity AR200-50 laser displacement sensor. An NI USB-9219 data acquisition module and a customized LabView code were used to output the driving voltage signal and collect the actuation height simultaneously.

2.2.4 Mechanical Tests

Mechanical properties were tested on a TA Instruments RSAIII dynamic mechanical analyzer (DMA). The samples used were 6 mm wide and 0.3 mm thick held by two grips separated by 10 mm. Dynamic temperature ramp tests were conducted at 7 °C/min, 1 Hz frequency and < 2% strain.

2.3 Results And Discussion

The majority of the results in this chapter have been published on SPIE. [Refer to “Ren Z,

2.3.1 Formulation Of The BSEP

In general, an oligomer, or a blend of oligomers, is selected as the framework responsible for the basic mechanical properties of the material system. Reactive diluents, including monofunctional and/or multifunctional acrylates, are used to adjust rheology, provide crosslinking, and finely tune the mechanical properties of the material. Photoinitiators are used to initialize the polymerization.

The homopolymer of oligomer-1 (difunctional aliphatic urethane oligomer) has high stretchability and a relatively high modulus. Therefore, oligomer-1 was selected as the framework oligomer to provide large tear strain. The difunctional long-chain crosslinker (oligomer-1) is also an essential component responsible for the long chain component in a bimodal network. Monomer-a having a glass transition temperature of 94 °C in its poly (Isobornyl acrylate)\(^{[17]}\) was employed to elevate the glass transition of the BSEP to above room temperature. Monomer-b was incorporated as reactive diluent to adjust the viscosity for improved coating qualities and as solvent for the viscous oligomer-1. TMPTA was used to increase crosslinking density as a tri-functional crosslinker and provide short
chain components and stiffening mechanism at high elongations. The ratio between oligomer-1 and monomer-a was the most crucial parameter in determining both the transition temperature and mechanical properties; samples with different amounts of oligomer-1 were tested to illustrate the effects. **Table 2-1** describes the content of the different formulas used.

**Table 2-1.** Formulas and nomenclature of different prepolymer solution with varying oligomer-1 (parts by weight)

<table>
<thead>
<tr>
<th>Formula</th>
<th>Oligomer-1</th>
<th>Monomer-a</th>
<th>Monomer-b</th>
<th>TMPTA</th>
<th>Photo-initiators</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 oligomer-1</td>
<td>40</td>
<td>63</td>
<td>15</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>20 oligomer-1</td>
<td>20</td>
<td>63</td>
<td>15</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>10 oligomer-1</td>
<td>10</td>
<td>63</td>
<td>15</td>
<td>1</td>
<td>1.5</td>
</tr>
</tbody>
</table>

2.3.2 Glass Transition And Mechanical Properties

Both the transition temperature and mechanical properties were investigated with the “temperature sweep” mode on the DMA (**Figure 2-1 a, b**). In particular, the modulus of the BSEP at room temperature was extracted, as that parameter is critical in providing large output force. It had been demonstrated using PTBA as a Braille prototype material [15], that a material with a modulus of 1 GPa can provide sufficient tactile support when the thickness is approximately 60 µm. As our current BSEP material has a modulus exceeding 1 GPa at room temperature, sufficient force support can be engineered. Upon
heating the samples, the BSEP material underwent a glass transition, evidenced by the appearance of a peak in loss tangent vs. temperature curve (Figure 2-1b) and a drop of the Young’s modulus to several MPa (Figure 2-1a). The modulus in the rubbery state remains constant regardless of temperature fluctuations, a behavior essential for stable actuation and prolonged cycle lifetime.

Samples with varying amounts of oligomer-1 were tested. Due to the low transition temperature of the homopolymer of oligomer-1, the transition temperature of the BSEP decreased with increasing amounts of oligomer-1 as shown by the peak value of the loss tangent moving towards lower temperature, and the completion of the transition from glassy to rubbery at lower temperature (Figure 2-1b). In samples with ‘40 oligomer-1’ formula, an earlier plateau is observed at 70 ˚C with a slightly narrower transition temperature range. This allows for stable mechanical properties and actuation performance at lower temperatures in contrast to samples with less oligomer-1. The amount of oligomer-1 also affects the stiffness of the BSEP in the rubbery state and its toughness at room temperature. Increasing the content of oligomer-1 increases the crosslinking density, thus increasing the stiffness in the rubbery state. On the other hand, ‘10 oligomer-1’ samples are more brittle and less tough at room temperature than samples with more oligomer-1. It is therefore concluded that increasing the amount of oligomer-1 toughens the BSEP at room temperature, increases the elasticity and stiffness at elevated temperature, and enhances the stability of mechanical properties at relatively
low temperatures (70 °C). However, excessive oligomer-1 can result in the decreased ratio between the modulus of the BSEP at room temperature and that in its rubbery state, affecting its shape memory properties.

![Figure 2-1. Revolution of storage modulus (a) and loss factor (b) with the temperature of Bimodal BSEP with three different oligomer-1 contents](image)

2.3.3 Actuation Performance

Actuation tests were performed with Braille dot actuators made with ‘40 oligomer-1’ formula. The diameter of the active area is around 1.3 mm, which is confined on both sides of the BSEP film by Kapton tape with a hole of 1.7 mm in diameter. Upon application of high voltage at 70 °C, the rubbery material buckles up to form a dome shape as a result of Maxwell pressure. The raised height of the dot steadily increases with voltage. For a film of 45µm thick (Figure 2-2a), the height of the raised dot is 0.2 mm at 3 kV (Figure 2-2b). At 4 kV, the height reaches 0.6 mm (Figure 2-2d), but the actuation is unstable with reaching dielectric breakdown field. A voltage of 3.5 kV (Figure 2-2c)
can result in stable actuation yielding a raised dot height of 0.4 mm. No apparent electromechanical instability (sudden increase of actuation strain) was observed thanks to a self-stiffening bimodal network.

![Figure 2-2. Actuation of dot actuator on the hotplate at elevated temperature with 0V (a), 3kV (b), 3.5kV (c) and 4kV (d).](image)

2.3.4 Cycle Lifetime

Single Braille dots were tested with a square wave voltage signal (0-3.5 kV at 0.2 Hz and 50% duty cycle) on a 45 µm thick film. SWCNTs were utilized as the electrodes for its self-clearing ability to enhance the lifetime of repeated actuation \[^{[16]}\]. A lifetime of 2000 cycles at a raised height of 0.4 mm was observed (Figure 2-3), indicating the stability of the actuation.
2.3.5 Page-Size Braille

A standard Braille cell consists of a 3x2 array of half-dome shaped dots. Each of the dots is 1.5 mm in diameter, with every two adjacent dots having a 2.5 mm center-to-center distance [8]. A page-size Braille device (Figure 2-5) with 18x18 Braille cells was made by spray-coating carbon black on both sides of a 7”x9” BSEP film, using the masks showed in Figure 2-4 a, b. Constraint layers (Figure 2-4 c) were stuck onto the electrode-patterned film for vertical actuation of all 18x18x6 dots. The capability of fabricating a page-size device speaks for the simpleness and potential to scale-up the process into manufacturing.
Figure 2-4. Top (a) and bottom (b) masks for spraying electrodes on page size BSEP film and pattern of constraints for page size braille device (c)

The prototype was then put into an environmental chamber to attain a uniform temperature of 70 °C. A voltage of 4 kV was applied to each dot by connecting the voltage source to conductive aluminum leads buried between the constraints and film, resulting in all dots being actuated simultaneously. Two lines (18x2 cells) were selectively actuated at 70 °C and frozen in place by cooling them down in air for a few seconds with the driving voltage being kept on during cooling and removed subsequently. Eight cells were zoomed in for good contrast between the original and actuated state as shown in Figure 2-5. The actuation height is slightly smaller than observed in devices using P3-SWNT as the electrodes. The uniformity of actuation could be improved simply by using high-quality electrode, such as finely uniformly spray-coated P3-SWNT. A clean fabrication environment would be beneficial to prolong the actuation lifetime as dust particles could cause dielectric breakdown.
Figure 2-5. Actuation of a page size braille device

Assuming the usage rate of each dot appeared in a character is 50% (3 dots being activated on average for one letter), each refreshable braille cell can then display 4000 characters before failure. A page of such braille cells can display \(4000 \times 18 \times 18 = 1296k\) characters or 259k words (5 characters in average for one word). That equals 4 medium novel books with one sheet of refreshable braille paper before in need of a new sheet.

2.3.6 Selective Heating Strategy

An array of heating elements made from commercial Nickel/Chrome alloy has been fabricated separate from the actuator array to provide an alternative controlling methodology (Figure 2-6a). The Nickel/Chrome alloy was sputtered onto a substrate
covered with patterned mask. Testing the device with a voltage source revealed that a temperature of 70 °C could be reached at a driving voltage of 5.5 V, with a current of 25 mA, within 8 seconds for a total power consumption of 0.1375 W per dot. Testing of the device has shown no significant degradation (higher voltages needed to achieve the same temperature) after tens of cycles.

Prior to deposition of the nickel/chrome metal film, laser drilled holes were patterned into the PI film for vertical connections. Silver paste was filled in the vertical holes and made contact with the heating materials of the heater array and with the conductive spring-loaded pins that are soldered to the wires of the external circuitry (Figure 2-6b). The heater was clamped against the pin-loaded plastic in order to make a tight electrical contact between the pins and silver paste (Figure 2-6c).

![Figures 2-6](image)

**Figure 2-6.** (a) Heating array for a two-cell device; (b) External circuitry with spring loaded pins
for connection to the heater array; (c) Heater array clamped/fixed on top of the spring loaded pins, connected through silver paste; and (d) Screenshot of the control circuitry for the Braille actuator device.

The circuitry can be connected via USB to a computer, where a software program (Figure 2-6d) is used to control which nickel/chrome dots are selectively heated. The actuator array can be laminated to the heater array with a high temperature adhesive. A good thermal conduction is needed for the heater to selectively heat the braille dots. With all the parts assembled, the selectively heating strategy for a 2-cell braille device can be implemented. X-y scanning of the 12-nickel/chrome heater elements on a 2-cell heater via predetermined software settings can determine which selected dots to be turned on joule heating in accordance to the braille contents to be displayed. With a high voltage on all 12 braille dots, only the heated ones can be actuated and fixed when cooled down with a rigid dome shape. The selective heating strategy provides a unique methodology for braille contents to be displayed on the braille device.

2.4 Conclusion

A BSEP material with bimodal chain length distribution has been synthesized to provide large force support in the rigid state and large out of plane deformation generated in the rubbery state. The amount of difunctional aliphatic urethane oligomer employed in the BSEP formulation can modify the transition temperature and mechanical properties,
providing a convenient method to optimize the polymer’s bistable actuation performance. Inspired by the formulation of a freestanding dielectric elastomer with suppressed electromechanical instability\cite{13}, a framework with both long chain difunctional oligomer and small molecular crosslinkers was constructed to provide stable actuation. A Braille dot actuator based on the BSEP material exhibited a cycle lifetime of over 2000 cycles tested at 70 °C and a raised dot height of 0.4 mm. A page-size Braille display prototype has also been successfully demonstrated. Further improvement in raised height and actuation stability could be obtained by fine control of the coating process in a clean environment. A 2-cell selective heating strategy was discussed. The work presented in this chapter represents one step forward in our effort on developing refreshable Braille displays. The simplicity of display architecture could lead to new Braille products that are compact, lightweight, and affordable.

2.5 Reference


2013-10-04

[4]. Freedom Scientific, Focus 40 Blue Braille Display
http://www.freedomscientific.com/Products/Blindness/Focus40BrailleDisplay


Chapter 3. A Phase-changing Bistable Electroactive Polymer Exhibiting

Sharp Rigid-to-Rubbery Transition

3.1 Introduction

The previous BSEP introduced, including poly (t-butyl acrylate) (PTBA), PTBA-IPN and bimodal BSEP, produced large rigid-to-rigid strains. The rigid-to-rubbery transition via glass transition spanned a rather broad temperature range from 45 to 80 °C \([1,2]\). Such a broad temperature range causes large thermal energy consumption and slows the response speed to complete a full cycle of rigid-to-rigid actuation. The electrical actuation of PTBA actuators was carried out at or above 70 °C, which is rather high for wearable and personal assistive devices such as Braille electronic readers \([2,3]\) and haptic touch pads. A BSEP with a sharp rigid-to-rubbery transition at a relatively low temperature is therefore desired for these applications. A sharp phase transition is promising in narrowing down the rigid-to-rubbery transition range.

Stearyl acrylate (octadecyl acrylate, SA) based polymers have been investigated as shape memory polymers due to their sharp phase transition between the crystalline and molten states of the stearyl moieties \([4-6]\). The transition is typically below 50 °C with a narrow phase change temperature range within 10 °C. Therefore, SA is an ideal component for imparting a sharp rigid-to-rubbery transition in the BSEP. Below the transition temperature, stearyl moieties can form crystalline aggregates to help stiffen the polymer
matrix. Above the transition temperature, the molten stearyl chains become plasticizers to soften the matrix. As a consequence, the phase change of stearyl moieties results in a rigid-to-rubbery transition of the copolymer comprising SA.

In addition to a sharp rigid-to-rubbery transition at a relatively low temperature, an ideal BSEP polymer must possess a high dielectric field strength, large elongation at break, and high tensile strength in the rubbery state in pursuit of large actuation strain and energy density. The reported SA-based shape memory polymers, however, are gel-like at elevated temperature and have low tear strength. Therefore, they are unsuitable for application as BSEP materials. This chapter presents a phase changing BSEP polymer comprising SA and a long-chain urethane diacrylate that retains the sharp phase transition characteristic of the SA homopolymer, exhibits high tensile strength both in the rigid and rubbery states, and possesses a modestly low modulus in the rubbery state allowing for large-strain electrical actuation. The sharp rigid-to-rubbery transition of the BSEP, which corresponds to the rapid and reversible crystallization/melting of the stearyl group within a narrow temperature range of about 10 °C, allows a low temperature for the BSEP entering a rubbery state to be electrically actuated. A maximum actuation strain of 70% can be achieved at an electrical field of 127 V/µm at 50 °C. No electromechanical instability (EMI) was observed due to a bimodal network similar to that in chapter 2, which helps stiffen the rubbery BSEP at modest strain to resist EMI. Reversible rigid-to-rigid actuation has been demonstrated with shape fixation and recovery rate close to 100%.
3.2 Experimental

3.2.1 Materials And SA-UDA Copolymer Thin Film Preparation

Urethane diacrylate (UDA) was obtained from Sartomer Company (catalog name: CN9021) and used as received. Stearyl acrylate (SA), Trimethylolpropane triacrylate (TMP-TA), 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and benzophenone were purchased from Sigma Aldrich and used as received. Single wall carbon nanotubes, P3-SWNT, were purchased from Carbon Solutions, Inc. Thin films of SA-UDA copolymers were prepared as following. A liquid prepolymer solution comprising UDA, SA, TMP-TA, DMPA and benzophenone was prepared by mixing above-mentioned compounds at the ratios defined in Table. 3-1 at an elevated temperature of 50 °C when SA is in a liquid state. The prepolymer solution was then injected between a pair of warm glass sheets spaced with Kapton tape. The thickness of the liquid layer was defined by the thickness of the Kapton tape spacer, typically 90 µm if not specified. The prepolymer was subsequently cured through a UV curing conveyor equipped with a Fusion 300S type ‘H’ UV curing bulb in ambient environment for around 3 minutes. Subsequent thermal annealing at 60 °C for two hours was applied to remove any unreacted small molecules. The film was then cooled to room temperature and gently peeled off the glass sheets.
3.2.2 Characterization And Actuation Test

Wide-angle XRD tests were performed on thin film SA-UDA samples using Cu Kα radiation with a 2θ step size of 0.05°. The separation of the amorphous diffractions and the crystalline peak was simulated using OriginPro 8. The phase transition of the aggregates of stearyl moieties within the SA-UDA copolymers was studied via a differential scanning calorimeter at a typical heating/cooling rate of 5 °C/min if not specified otherwise (PerkinElmer Instruments, Pyris Diamond DSC). Samples were pre-annealed at 60 °C and then cooled down naturally before DSC measurements if not specified. Mechanical properties were measured on a TA Instruments RSAIII dynamic mechanical analyzer (DMA). Dynamic temperature sweep tests were conducted at a temperature ramping rate of 2 °C/min and a frequency of 1 Hz from 25 °C to 55 °C. Samples of 6 mm wide and ~0.3 mm thick were loaded onto the DMA with a 10 mm gap between the thin film grips. The stress-strain curves of the rubbery copolymers were obtained at 50 °C at a stretching rate of 3.33 mm/s. The tested samples used were 6 mm wide and ~90 μm thick with a 6mm gap between the thin film grips of the DMA. A minimum of three samples were tested for each formula listed in Table. 3-1.

The BS60 actuators were fabricated by spray coating P3-SWNT (dispersed in IPA/DI-water) onto both surfaces of the BS60 film using an airbrush at an air pressure of 20 psi. Contact masks made from removable tape were applied to cover the polymer film during spray coating to define the active actuation area with the P3-SWNT electrodes.
(typically 7.6 mm in diameter). The resulting electrode-coated BS60 films were mounted on a diaphragm chamber to cover its circular opening with 9.5 mm in diameter. A small bias air pressure was applied in the chamber. The diaphragm actuators were placed in an environmental oven (Thermotron Instruments S1.2 model) set at 50 °C. A high-voltage power supply fabricated in-house was used to drive the actuators. Actuation strains were held for at least 5 seconds for each electric field applied. A digital video camcorder was used to record the actuation process. A Self Sensing Unit (SSU) developed in the Biomimetics Laboratory at the University of Auckland, New Zealand was employed to characterize its permittivity by measuring the capacitance of a BS60 actuator with known dimensions (45 mm diameter active area). The measurement was performed both at room temperature and at 50 °C. A base voltage of 400V was applied to conduct the measurement with oscillating voltage signal. This high voltage was selected to better represent the high voltage applied when the film is actuated, although it was far below the voltage that would induce observable actuation. The permittivity was not sensitive to temperature. The accuracy of the equipment according to the supplier is ±5%, while dimensional accuracy is higher than 5%.

3.3 Results And Discussion

The majority of the results in this chapter have been published on Macromolecules. [Refer to “Ren Z, Hu W, Liu C, Li S, Niu X, Pei Q. Phase-Changing Bistable Electroactive Polymer Exhibiting Sharp Rigid-to-Rubbery Transition. Macromolecules.]
3.3.1 Formulation And Microstructure Of SA-UDA Copolymers

Stearyl acrylate (see Figure 3-1) with a melting temperature of 32-34 °C was selected to provide a reversible and sharp rigid-to-rubbery transition around the ambient and wearable temperature range. A long chain urethane diacrylate (UDA, CN9021) compound was selected as the polymer framework due to the fact that UDA homopolymer has a large elongation at break of 1100%, a modestly low modulus (0.827 MPa) at room temperature, and low $T_g$ (−54 °C). The long urethane chain in UDA is made of a flexible polyether diol segment and a relatively flexible aliphatic diisocyanate and has a high molecular weight (UDA has a viscosity of 32,000 cps at 25°C)\[7\]. The UDA moieties in the resulting SA-UDA copolymers can help enhance the elongation strain at break and improve the toughness of the copolymers in the rubbery state. Our previous work \[7\] showed that a small molecule crosslinker can effectively stiffen the resulting elastomers at large strains, thus helping overcome electromechanical instability (EMI) that is often observed in soft dielectric elastomers which limits the maximum strain to about 26% \[8\]. Therefore, a tri-functional crosslinker of small molecular weight, trimethylolpropane triacrylate (TMP-TA), was also used in the SA-UDA copolymers. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and benzophenone (2:1 by weight) were synergistically employed as co-photoinitiators to obtain complete bulk and surface curing in thin films. \[7, 9\] The weight ratio of SA:UDA was the key parameter to adjust both the
transition temperature and mechanical properties. The ratio was varied between 80:20 and 40:60 as shown in Table 3-1. The resulting copolymers are assigned the acronyms BSxx, where xx refers to the parts of SA out of a total of 100 combined parts of SA and UDA.

Figure 3-1. Chemical structures of long-chain urethane diacrylate (UDA, where R₁ and R₂ are flexible units), TMP-TA, stearyl acrylate (SA), DMPA and benzophenone

Prepolymer solutions were obtained by mixing the aforementioned ingredients at specified ratios at 50 °C (at which SA is a liquid). The heated solutions were injected into a pair of glass slides separated by 90 µm, if not specified otherwise, and cured by exposure to an ultraviolet light source. The resulting SA-UDA thin films are ductile and flexible at ambient temperature due to the incorporation of UDA.

The crystallinity of the SA-UDA copolymers was examined by wide-angle X-ray diffraction (XRD) at room temperature. The long alkyl chains in poly (n-alkyl acrylates) were suggested by Plate and Shibaev to form inverse combs in the planar polymer chain structure (See Figure 3-2a inset for poly (n-octadecyl acrylates)), while the layered polymer chains stacked to give a 3D layer-by-layer ordered structure \(^{[4]}\). Similar crystalline ordering is expected in the SA-UDA copolymers. The XRD patterns (Figure
3-2a) reveal the presence of both amorphous chain segments (broad peaks) and crystalline packing (sharp peaks) of the SA moieties. The inter-planar spacing of the crystalline SA aggregates in the SA-UDA is calculated to be 0.416 - 0.42 nm (2\theta \approx 21^\circ), comparable with that of the crystalline aggregates observed in poly (n-octadecyl acrylate).[^4] The crystallinity of the SA-UDA copolymers decreases with lowering SA:UDA ratios, supported by the observation of a relative decrease of the intensity of crystalline peaks and an increase of the intensity of amorphous peaks from BS80 to BS40 (Figure 3-2b). The sharp peak centered at 21° at ambient temperature disappeared when the polymer was heated to 70°C (rubbery state), indicating the transition from crystalline aggregates to amorphous states of the stearyl moieties in the SA-UDA copolymer (Figure 3-2c). At room temperature, the XRD signal comprises both contributions from amorphous segments of UDA moieties and crystalline aggregates of stearyl moieties. At 70 °C, melting transition of crystalline aggregates of stearyl moieties is completed; therefore, the XRD pattern consists of only the contribution from amorphous segments (wide peak indicating short range order only).
Figure 3-2. XRD (a, b, c) & optical characterization (d, e) of the SA-UDA copolymers: Wide angle XRD patterns of SA-UDA films at room temperature (a), deconvoluted broad peak for the amorphous regime and shark peak for the spacing between the interplanar SA chains (b), XRD of BS60 at room temperature and at 70 °C (c), optical pictures of BS40, BS60, and BS80, from left to right (black paper with white UCLA logo printed on as background), at ambient temperature (d) and at 50 °C (e).

Optical photographs of SA-UDA thin films at ambient temperature (Figure 3-2d) show an increase of transparency while lowering SA:UDA ratios from BS80 to BS40, indicative of decreasing crystallinity. The opaque thin films all turned fully transparent upon heating at 50 °C (Figure 3-2e), suggesting crystalline-to-amorphous (melting) transition.

3.3.2 Thermodynamic Properties And Phase Transition

Differential scanning calorimetry (DSC) of SA-UDA copolymers at a heating/cooling rate of 5 °C min⁻¹ was carried out to monitor the phase transition property. The DSC diagrams displayed in Figure 3-3 show characteristic melting peaks during heating and a
recrystallization peak during cooling. During the first melting (Figure 3-3a), a narrow endothermic peak is observed with a full width at half maximum (FWHM) of 2.3-5.5°C. The melting transition temperature (T_m) as defined by the peak value is 46.2 °C for BS80, and 34.2 °C for BS40. Decreasing the SA contents in the SA-UDA copolymers can tune down the T_m. The T_m of SA-UDA copolymers are slightly higher than that of the SA monomer (32-34 °C), which should be caused by confined motion of the stearyl chains in the polymer network (The T_m of SA homopolymer is 50 °C[5]).

Figure 3-3. DSC diagrams of SA-UDA copolymers during the 1st heating (a), subsequent cooling (b), and 2nd heating (c). The baselines are subtracted using OriginPro 8. (Arrows indicate the temperature ramping direction.)

Upon cooling, the molten stearyl chains recrystallize with corresponding exothermic peaks shown in the DSC diagrams (Figure 3-3b). The enthalpy of crystallization (ΔH_c) was estimated by integrating the heat flow peak divided by the mass of the SA-UDA sample. The specific heat for the crystallization of the SA moieties was calculated by dividing ΔH_c by the weight fraction of SA in the copolymers (w_SA). The ΔH_c/w_SA value is 41.75 J g⁻¹ for BS80, and 30.75 J g⁻¹ SA for BS40. The decreasing ΔH_c/w_SA value may be
attributed to less complete crystallization of SA chains in copolymers with lower loading of the SA moiety. This observation is consistent with results for poly (n-octadecyl acrylate) comprising randomly interspersed lower acrylate homologs such as methyl acrylate. [10] The dilution of the n-octadecyl acrylate crystalline moiety, i.e., by the amorphous methyl acrylate moiety, leads to a decline in the heat of crystallization and the percentage of crystallinity. In the SA-UDA copolymers, incorporation of flexible UDA moieties leads to the suppression of crystallization of the stearyl moiety aggregates.

During the subsequent re-heating (second heating, Figure 3-3c), the melting temperatures of SA-UDA copolymers are quite comparable to those during the first heating. The difference is less than 1 °C for each specific copolymers, which indicates a highly repeatable phase transition with little impact by the thermal history of the sample.

The T_m of BS60 does not change despite of different cooling rates at 2, 5, and 10 °C min^{-1} during the crystallization of SA moiety aggregates (Figure 3-4). BS60 samples were synthesized and annealed at 60 °C for 2hrs before being characterized with DSC. An initial heating process (Fig. 3-4 Initial Heating) was conducted with a heating rate of 5 °C/min, showing an endothermic peak due to melting of stearyl acrylate moieties. Three consecutive cooling & heating cycles were conducted afterwards, with different cooling rate (2 °C/min for “Fig. 3-4 Cool-2-Heat-5”, 5 °C /min for “Fig. 3-4 Cool-5-Heat-5” and 10 °C/min for “Fig. 3-4 Cool-10-Heat-5”, respectively) but identical heating rates (5 °C/min). With the increasing cooling rate, the samples showed a decreasing crystallization temperature. The heat flow (mW) integrated with time showed similar
amount of heat (Joule) released during the crystallization process despite of different cooling rate. Furthermore, regardless of the different cooling rate or thermal history, the subsequent melting overlapped very well on the DSC diagrams. This result suggests that the phase transition (melting) temperature of BS60 is not affected by its thermal history, which is desirable in practical applications. The transition peak temperature, FWHM, and heat of phase transition are summarized in Table 3-1.

Figure 3-4. DSC characterization of BS60 with different cooling rate (2 °C/min, 5 °C/min, 10 °C/min) and identical heating rate (5 °C/min). Arrows indicate temperature ramping directions. Curves labeled as “Cool-x-Heat-5” with cooling rate of x °C/min and heating rate of 5 °C/min.

Table 3-1. Formulas and DSC results for SA-UDA copolymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formula ***</th>
<th>1st Heating</th>
<th>Cooling</th>
<th>2nd Heating</th>
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62
<table>
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<tr>
<th></th>
<th>SA</th>
<th>UDA</th>
<th>Peak °C (FWHM)</th>
<th>Peak °C (FWHM)</th>
<th>ΔH_{c/wSA} (J g⁻¹ SA)</th>
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<tr>
<td>BS80</td>
<td>80</td>
<td>20</td>
<td>46.2 (2.3)</td>
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<tr>
<td>BS70</td>
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<tr>
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<td>24.3 (1.8)</td>
<td>30.75</td>
<td>33.6 (5.9)</td>
</tr>
</tbody>
</table>

***Weight parts of SA and UDA out of a total of 100 SA and UDA combined parts. TMP-TA (1 part in weight in each formula), DMPA (1 part in weight) and Benzophenone (0.5 part in weight) are not listed.

3.3.3 Mechanical Properties And Shape Memory Effect

Dynamic mechanical analyses (DMA) of the SA-UDA copolymers were conducted at a temperature ramping rate of 2 °C min⁻¹ across the phase transition temperature range (Figure 3-5a, b). At room temperature, the storage moduli are on the order of 10-100 MPa due to the crystalline aggregates of SA moiety acting as hard segments in the copolymers. Melting of the crystalline aggregates with a rising temperature results in a drastic decline of the modulus. The molten stearyl chains become plasticizers to soften the matrix, and the copolymers in the rubbery state possess a storage modulus on the order of 100 KPa.
The rigid-to-rubbery transition is completed within a temperature range of 10 °C. This is in contrast to the glass transition of previously reported BSEP polymers in which the rigid-to-rubbery transition was completed over a temperature range of more than 50 °C.\[^3\] Once the transition is completed, the storage modulus of the SA-UDA copolymers remains constant with further increasing temperature, an important attribute for stable electrical actuation in the rubbery state. The SA:UDA ratio of the copolymers affects the storage modulus in both the rigid and rubbery states. In the rigid state, lower SA fraction leads to lower percentage of crystallinity, and thus smaller modulus. In the rubbery state, lower SA:UDA ratios results in higher fraction of the crosslinking UDA moieties. This leads to a higher crosslink density and therefore a higher storage modulus. Overall, the change of storage modulus during the rigid-to-rubbery transition of SA-UDA copolymers attenuates with decreasing SA fraction: being 1066 fold in BS80 (storage modulus $E_s$ is 160 MPa at RT and 0.15 MPa in the rubbery state), and only 15 fold in BS40 (7.8 MPa to 0.51 MPa). Meanwhile, the rigid-to-rubbery transition temperature decreases with SA content: BS60 completes the transition at a temperature 5 °C lower than BS80. This trend is consistent with the DSC results, which is also observed in the loss tangent charts in Figure 3-5b. The loss tangent of all SA-UDA copolymers are <0.1 in the rubbery state, which is desired for actuation, especially at high frequencies, since low loss tangent indicates faster response speed and less energy loss due to viscoelasticity.
Figure 3-5. Mechanical properties of SA-UDA polymers: Evolution of storage modulus (a) and tan δ (b) as a function of temperature determined by DMA with temperature ramping from 25 to 55 °C at 2 °C min⁻¹. Stress-strain curves of SA-UDA copolymers at 50 °C (c). Upturning strain $S_{upturn}$ is determined in the inset for BS60 at 188%. Stress-strain curve of 0SA/100UDA at 50 °C and at room temperature, and 0SA/100UDA-0TMP-TA at room temperature (d). Marker x at the end of each curve indicates rupture. See Table 3-2 for the specific formulations of the each polymer in (d).

The tensile stress-strain responses of the rubbery copolymers were measured at 50 °C at a stretching rate of 3.33 mm s⁻¹ (see Figure 3-5c). The tensile strength is 0.26 MPa for BS80 and 0.97 MPa for BS60, while the elongation at break is 191% and 252% for BS80.
and BS60, respectively. Further lowering the SA:UDA ratio can achieve higher tensile strength due to an increased crosslink density by increasing amount of UDA, while the elongation remains around 250%. These results indicate that lowering the SA:UDA ratio contributes to enhanced toughness of the resulting rubbery copolymers, which in turn helps prevent unwanted rupture before maximum strain is attained. The rubbery copolymers exhibit rapid upturns of modulus in the stress-strain curves at around 150%-200% strain. There are generally two suspicious causes for an upturn appearing in a stress-strain curve. One is strain-induced crystallization; the other is limited-chain extensibility. With lowering the SA content in the SA-UDA copolymers, the upturn appears at even earlier strain, indicative of little contribution from strain-induced crystallization of SA moieties to the upturns. As analyzed in Figure 3-5d, samples of 0SA/100UDA exhibit similar upturn of modulus at room temperature and at 50 °C. The independence of temperature on the upturning strain of 0SA/100UDA suggests that the crystallization of the UDA moieties during elongation can also be ruled out. Therefore, the upturning effect is mainly attributed to the limited-chain extensibility of the polymer chains \[^{[11]}\]. Copolymerization of small molecular monomer (SA) and trifunctional crosslinker (TMP-TA) with UDA having long flexible chains results in a network with varying chain length in between crosslinks, which is similar to a bimodal structure. The flexible long chains of UDA retard early rupture of the SA-UDA copolymer. The relatively short chains comprising SA and TMP-TA provide limited chain extensibility, which results in rapid upturns. The upturning strain defined in the Fig. 3-5c inset (BS60
as an example) is decreased as lowering SA:UDA ratio from BS70 to BS40. A plausible reason might be that by lowering the SA content, the short chains become shorter and the density of short chains also increases as the crosslink density increases, resulting in upturns in smaller strains. Samples of 0SA/100UDA-0TMP-TA (no TMP-TA content) exhibit upturn at a much larger strain than SA-UDA copolymers comprising small molecular components (TMP-TA) (Figure 3-5d), further proving the important role of short chains in upturning of modulus as the polymer is stretched. The steep stiffening at relatively large strains is important to overcoming electromechanical instabilities. [8]

Table 3-2. Formulas of prepolymer solutions employed in Figure 3-5d (parts by weight, 50SA/50UDA is identical to BS50)

<table>
<thead>
<tr>
<th>Sample</th>
<th>SA</th>
<th>UDA</th>
<th>TMP-TA</th>
<th>DMPA</th>
<th>BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>50SA/50UDA</td>
<td>50</td>
<td>50</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>0SA/100UDA</td>
<td>0</td>
<td>100</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>100SA/0UDA</td>
<td>100</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>0SA/100UDA-0TMP-TA</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The upturning strain, elongation at break, and tensile strength of SA-UDA copolymers at 50 °C as well as the storage moduli at RT ($E_{s-RT}$) and at 50 °C ($E_{s-n}$), are summarized in Table. 3-3. The effects of TMP-TA and photoinitiators (DMPA and benzophenone) on the mechanical properties of BS60 were also investigated (Supporting Information).

**Table 3-3.** Mechanical properties of SA-UDA copolymers
<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{s\text{-}RT}$</th>
<th>$E_{s\text{-}rub.}$</th>
<th>$E_{s\text{-}RT}/E_{s\text{-}rub.}$</th>
<th>$\Delta\text{urn}$</th>
<th>Elongation at break</th>
<th>Tensile strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS80</td>
<td>160MPa</td>
<td>0.15MPa</td>
<td>1066</td>
<td>--------------</td>
<td>191%</td>
<td>0.26MPa</td>
</tr>
<tr>
<td>BS70</td>
<td>93MPa</td>
<td>0.19MPa</td>
<td>489</td>
<td>195%</td>
<td>245%</td>
<td>0.67MPa</td>
</tr>
<tr>
<td>BS60</td>
<td>52MPa</td>
<td>0.27MPa</td>
<td>193</td>
<td>188%</td>
<td>252%</td>
<td>0.97MPa</td>
</tr>
<tr>
<td>BS50</td>
<td>28MPa</td>
<td>0.38MPa</td>
<td>74</td>
<td>173%</td>
<td>235%</td>
<td>2.6MPa</td>
</tr>
<tr>
<td>BS40</td>
<td>7.8MPa</td>
<td>0.51MPa</td>
<td>15</td>
<td>164%</td>
<td>230%</td>
<td>3.5MPa</td>
</tr>
</tbody>
</table>

The shape memory effect of SA-UDA was demonstrated in Figure 3-6a, b. A stripe made from BS60 was marked with two parallel blue lines separated by 10mm (Figure 3-6b-1). At 55 °C, the rubbery BS60 film was stretched (Figure 3-6a-I) to a strain of 96 % (Figure 3-6b-2). The film was then cooled down in air with the load on to maintain the deformation (Figure 3-6a-II). Crystalline aggregates of SA moieties can reform below the phase transition temperature. The extended conformation of the main polymer chains under stretch was locked by these newly formed crystalline aggregates. According with the large difference between the storage modulus of the stripe at RT and that in its rubbery state ($E_{s\text{-}RT}/E_{s\text{-}rub.} = 195$), the mechanical stretch can be easily fixed with load off (Figure 3-6a-III) with a fixation rate close to 100% (Figure 3-6b-3). The original shape can be recovered by heating the stripe again above the transition temperature (Figure 3-6a-IV) as the “strain locker” melts. The recovery proceeded within a narrow
temperature range and was completed at 42 °C, which coincided with both the DSC and DMA results. The recovery rate is 100%, owing to its high crosslink density (Figure 3-6b-4). A decrease of the stearyl acrylate content leads to a decrease of the fixation rate to 92% for BS50 and 6% for BS40, while the recovery rate of both BS50 and BS40 remains at 100%. The rather low percentages of shape fixation for BS50 and BS40 are a result of their small $E_{s-RT}/E_{s-rub}$ ratio, being 74 and 15, respectively.

Figure 3-6 Demonstration of the shape memory effect: Temperature-Strain-Stress diagram for a BS60 film (a) and photographs of the film (b) in demonstrating its shape memory effect: (I) the film is stretched uniaxially under stress to 96% strain at 55°C; (II) the stretched film was cooled down to room temperature under stress; (III) the mechanical stress on the film was removed at room temperature; (IV) the deformed film was heated up to 55°C under zero stress; (1) the original film; (2) deformed film with 96% strain at 55°C under external stress; (3) deformed film free of external stress at room temperature; (4) recovered film at 55°C.
3.3.4 The Effects Of TMP-TA And Photoinitiators On The Mechanical Properties Of BS60

In addition to the ratio of SA:UDA, the small molecular crosslinker, TMP-TA, and photoinitiator (mixture of DMPA and Benzophenone at a ratio of 2:1 in weight) are also important formulation parameters that can influence the mechanical properties, phase transition temperature, and shape memory properties of the SA-UDA polymers. To understand the roles of TMP-TA and photoinitiator, BS60 was selected as the baseline material. With an increase of TMP-TA content from 1 to 2 parts (BS60 to BS60-2TMP-TA), the rigid-to-rubbery transition temperature decreases slightly, as shown in Fig. 3-7a. The decrease of transition temperature is likely due to increased TMP-TA crosslink sites that suppress the aggregation of stearyl moieties by limiting the orientation of octadecyl chains. The storage modulus increases with the content of TMP-TA both in the rigid state and in the rubbery state (see Fig. 3-7b), due to higher crosslink density. The increasing TMP-TA content also lowers the elongation of the resulting copolymer, e.g., BS60 has an elongation of ~250% while it is only 150% for BS60-1.5TMP-TA. For sufficient tensile strain while providing effective self-stiffening of the rubbery SA-UDA at large strains, 1 part TMP-TA was used for much of the present work described in this chapter.
Figure 3-7. Evolution of storage modulus (a, c) as a function of temperature determined by DMA with temperature ramping from 25 to 55 °C at 2 °C min⁻¹. Stress-strain curves of the polymers at 50 °C (b, d). Marker x at the end of each curve indicates rupture. See Table 3-4 for the specific formulations of each polymer.

Mechanical properties of BS60 with varying amount of photoinitiators were also characterized (Fig. 3-7c, d). The temperature dependent moduli of BS60, ‘BS60-1/2 PI’ and ‘BS60-1/4 PI’ were shown in Fig. 3-7c. The modulus does not change with the varying amount of photoinitiator at room temperature. The transition temperature range becomes slightly narrower with lower photoinitiator content. The moduli of all three
materials plateau at temperatures above the transition, indicative of effective crosslinking
even when the photoinitiator content is reduced by 75%. The steady modulus at the
rubbery state increases with lower photoinitiator content. This could be explained by the
decreased number of dangling chain ends since, in principle, each photoinitiator
introduces two chain ends acting as plasticizers in the polymer network. The increasing
modulus is also shown in the normal stress-strain curves (Fig. 3-7d), obtained in the
rubbery state. Compared with BS60 that possessed a tear-strength of ~1MPa, the
‘BS60-1/4-PI’ had a tear strength of 2.6MPa indicating that it is a tougher material. On
the other hand, low photoinitiator content could lead to insufficient curing if the UV
curing conditions were not strictly controlled, and the resulting polymer film would be
difficult to peel off of the substrate. For convenience and reproducibility, we used 1part
DMPA and 0.5part benzophenone for much of the present work described in this chapter.

Table 3-4. Formulas of prepolymer solutions employed to investigate the effects of TMA-TA and
photoinitiators on the mechanical properties of BS60 (parts by weight)

<table>
<thead>
<tr>
<th>Sample</th>
<th>SA</th>
<th>UDA</th>
<th>TMP-TA</th>
<th>DMPA</th>
<th>BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>BS60</td>
<td>60</td>
<td>40</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>BS60-1.5TMP-TA</td>
<td>60</td>
<td>40</td>
<td>1.5</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>BS60-2TMP-TA</td>
<td>60</td>
<td>40</td>
<td>2</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>BS60-1/2 PI</td>
<td>60</td>
<td>40</td>
<td>1</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>BS60-1/4 PI</td>
<td>60</td>
<td>40</td>
<td>1</td>
<td>0.25</td>
<td>0.125</td>
</tr>
</tbody>
</table>
3.3.5 Actuation Performance And Refreshable Rigid-To-Rigid Actuation

Bistable dielectric elastomer actuation was carried out mainly using the BS60 films because of their good shape memory property, large elongation at rupture and a modestly low modulus while in the rubbery state. The rapid upturning of its modulus at ~190% strain could help suppress electromechanical instability during large-strain actuation. Single wall carbon nanotubes (SWCNT) were well dispersed and spray-coated as the compliant electrodes imparting fault-tolerance and enhancing actuation stability due to its self-clearing property. A SWCNT coated BS60 film with a 7.6mm diameter circular active area was mounted on a diaphragm chamber to cover a 9.5 mm circular opening. The diaphragm chamber was then placed inside an environmental oven at 50 °C. A small bias air pressure (0.025psi) in the diaphragm chamber was applied to prevent the polymer film from buckling, and thus an area expansion of the film upon actuation would form a raised dome shape. The active area of the polymer film covering the diaphragm opening was almost flat before actuation (Figure 3-8a). A high voltage was applied to actuate the polymer film. The actuation process was captured using a digital camcorder. Snapshots of the video are shown in Figure 3-8 (b-g).
Figure 3-8. Dielectric elastomer actuation of BS60. Snapshot images showing the actuation of BS60 at 50 °C at the specified applied electric field (a-g). The electric field (E) is calculated by dividing the applied voltage by the instantaneous thickness of the elastomer film \[13\]. Geometric change (height and diameter) of a BS60 film at 50 °C upon actuation at 127 V \(\mu\)m \(^{-1}\) (h) and calculated actuation strain (area increase) in response to applied electric field (i).

The geometric change (height and diameter, see Figure 3-8h) of the polymer film dome was used to calculate the actuation area strain \((S_A)\) by \[S_A = \left(\frac{h^2 + R^2}{h_0^2 + R_o^2}\right) - 1.\] [13]

The true electric field (E) applied was calculated by dividing the applied voltage by the instantaneous thickness of the elastomer film which was determined from \(S_A\) under the assumption that the volume of the rubbery polymer film remains constant during deformation. Figure 3-8i shows the actuation strain in response to the applied electric field. A steady increase of the strain is observed under an increasing field up to 70% strain. No electro-mechanical instability is observed which would otherwise results in a snap through or abrupt rise of strain before dielectric breakdown. The maximum strain of
70% is obtained at 127 V µm\(^{-1}\). Further increase of the electric field leads to a minor dielectric breakdown event and consequently a lower strain. The maximum energy density of the actuator was calculated\(^{[14]}\) by

\[
\frac{1}{2}e = -0.5\varepsilon_o\varepsilon_r E_B^2 \ln(1 + s_z)
\]

where \(s_z\) is the maximum thickness strain determined from the maximum area strain by \(s_z = 1/(1+S_A) - 1\), \(E_B\) is the breakdown field or 127 V µm\(^{-1}\), and the relative permittivity \(\varepsilon_r\) was determined to be 3.71. The calculated maximum energy density is 0.14 J cm\(^{-3}\), which is comparable to figure of merits for typical dielectric elastomers such as silicone elastomers with prestraining, e.g. HS III (280% prestrain, 0.16 J cm\(^{-3}\)) and CF19-2186 (100% prestrain, 0.2 J cm\(^{-3}\)).\(^{[15]}\)

A BSEP polymer with phase transition temperature \(T_m\) is typically operated through 4 states to obtain a rigid-to-rigid actuation (Figure 3-9a, A-D): the original stiff BSEP at room temperature (\(T < T_m\), state A), the softened BSEP film at any temperature above \(T_m\) (\(T > T_m\), voltage off, state B), electrically actuated BSEP in its rubbery state (\(T > T_m\), voltage on, state C), and rigid BSEP with fixed actuation strain after cooling down the actuated BSEP (\(T < T_m\), voltage off, state D). The fixed actuation strain can be recovered by heating up the BSEP at state D and cooling it down subsequently to achieve state A, thus the rigid-to-rigid actuation can be repeatable.
Figure 3-9. Working mechanism of BSEP (a, state A-D) and demonstration of refreshable rigid-to-rigid actuation of BS60 (b, picture 1-4): (A) the original stiff BSEP at room temperature; (B) the softened BSEP film at any temperature above $T_m$; (C) electrically actuated BSEP in its rubbery state; (D) rigid BSEP with fixed actuation strain after cooling down the actuated BSEP.

1. the film was mounted on a diaphragm chamber with a bias air pressure of 0.025 psi at 50 °C;
2. the film was actuated by an electric field of 53 V $\mu$m$^{-1}$;
3. the actuated shape was fixed and the voltage was turned off;
4. the actuated shape was recovered at 50 °C;

In a typical demonstration of refreshable rigid-to-rigid actuation (Figure 3-9b), a BS60 film was coated with single walled carbon nanotubes on both surfaces and mounted on a diaphragm chamber with a small positive bias air pressure in the chamber. The film was then heated to 50 °C (Figure 3-9b-1) into a rubbery state, and then a moderate electric field of 53 V $\mu$m$^{-1}$ was applied to actuate the film to a strain of 35.7% (Figure 3-9b-2). The voltage was kept on to maintain the strain while the film was cooled down to room
temperature to regain the rigidity. The voltage was then turned off with the actuated deformation fixed (Figure 3-9b-3). Finally, the deformation was reversed by heating the film to 50 °C (Figure 3-9b-4) to recover its original shape in the rubbery state and then cooling back to room temperature. This refreshable rigid-to-rigid deformation can be achieved at any intermediate strains as shown in Figure 3-8i, with all the deformed shapes able to be fixed as the active polymer film cools to room temperature.

3.4 Conclusion

A phase-changing polymer comprising SA and UDA has been synthesized and examined as a bistable electroactive polymer. The rigid-to-rubbery transition of the polymer is obtained via the rapid and reversible crystallization and melting of the stearyl group within a narrow temperature range of about 10 °C. The inflection temperature is tunable between 34-46 °C depending on the loading of the SA moiety, which could be further expanded by introducing n-alkyl acrylates with different lengths of alkyl chains. The SA-UDA films can be actuated at 50 °C up to 70% strain with the maximum actuation energy density comparable to the figure of merits of dielectric elastomers. The self-stiffening mechanism due to a bimodal structure helps avoid electromechanical instability during large strain actuation. The SA-UDA represents a new BSEP material whose rigid-to-rigid deformation could be performed at a temperature slightly above that of the human body but below the perceptible pain threshold temperature of 43.2 ± 0.4 °C [16], and should not cause any tissue damage.
3.5 Reference


[16]. Stoll AM, Greene LC. Relationship between pain and tissue damage due to thermal radiation. Journal of applied physiology. 1959 May 1;14(3):373-82.
Chapter 4. Non-Woven Fabrics Deposited With Silver Nanoparticles Via Multistep Electroless Deposition As A Wearable Heating Element

4.1 Overview Of Personal Thermal Management

The pursuit of human thermal comfort has been sought since the beginning of human history [1]. Thermal comfort is an impression of mind that reflects satisfaction with the thermal environment and is determined by subjective evaluation [2]. Satisfactory thermal comfort is heavily influenced by the difference between expectations of the ideal thermal environment in a particular situation and what exists at the moment [3]. As a consequence, human thermal comfort is strongly affected by one’s physiological expectations [4]. Buildings in our modern society can provide heating and cooling to maintain occupants’ comfort by creating a relatively uniform and satisfactory thermal environment. However, it is impossible to achieve thermal satisfaction for all occupants or the entire body of a single occupant with general building heating, ventilation and air conditioning (HVAC). Field studies reported a minimum dissatisfaction rate of 12% in a neutral thermal environment in air-conditioned buildings [5]. To achieve thermal comfort, emphasis should be placed on individual feedback and localized control over one’s body thermal profile [6]. Localized thermal management systems (LTMS) are thus desired to achieve optimal individual thermal sensation [7].

Meanwhile, the total energy consumption in the US is about 97 Quadrillion Btu, with 8.36 Quadrillion for spacing heating alone (8.6% of the total energy consumption) [8].
While HVAC is a conventional way to keep building occupants thermally comfortable, it is certainly not an efficient way, because human occupants do not occupy a lot of spaces in the building. By introducing LTMS as a complementary method to HVAC, a big portion of energy unnecessarily spent to heat up and cool down empty spaces can be saved \(^9\).

An LTMS can be defined as a local thermal envelope around the human occupant that is partially insulated or isolated from the surrounding air outside of the LTMS range \(^9\). It can range from wearable technologies to near range (<1m) and extended range (>1m) thermal management systems. Extended range LTMS often remotely heat or cool occupants uniformly, such as radiative heaters or overhead fans. In general, radiative overhead heaters \(^{10}\) are very efficient without transmission loss of heat energy in the air. However, the efficiency decreases dramatically with the increase of the distance between the heater and human occupants. The radiative heater warms up exposed skin more efficiently than clothing areas, resulting in uneven heating. In addition, a high power infrared heater often emits visible light, which is disturbing in a building environment.

Near range LTMS refers to systems that are in close contact with occupants such as chairs, desktop accessories, and floor mats. Electric blanket \(^{11}\) (near range) is a close range heating strategy that is commonly used in modern families. However, it limits human activity since the heating solution relies on heat conduction via contact between human bodies and the blanket. Wearable technologies should represent the most efficient LTMS due to its extreme proximity to the human body, and can include clothing, shoes,
shoe insoles, and wearable accessories. Wearable localized heating strategies are mostly based on Joule heating and are usually of low cost. Volt Resistance provides a variety of heated clothing products (e.g. working gloves) employing a patented technology called Zero Layer Heating System [12]. The heating system consists of ultra-thin panels that are constructed by weaving imperceptible stainless fibers into an insulated fabric. The heating elements are encapsulated and permanently protected from wear and tear with a special thermal bonding sealing tape. However, the comfort of wearing such heating elements is questionable. EXO² developed a heating technology called FabRoc® [13], which is a lightweight conductive polymeric layer that produces uniform resistive heating energy with a low voltage. The blended polymeric layer, however, is not breathable as regular clothing. Accessories like insoles [14] and bracelets [15] are also developed to provide localized heating. Despite the maturity of these heating strategies, the market is still open to innovative alternative solutions that can provide wearable technologies without much interruption to regular clothing or addition of extra weight/complexity. A desired LTMS should be wearable just like regular clothing. The wearable local thermal management device (LTMD) should also be washable and compliant without sacrificing its functionality.

4.2 Introduction To Fabric-Based Wearable Heating Elements

There are a couple of heating elements based on fabrics that are under investigation, including silver nanowire (AgNW) clothing [16] and CNT-based heater [17]. A metal
nanowire textile (AgNW clothing) proposed by Hsu et al. [16] presented as an effective LTMD that can not only reduce radiation heat loss due to high infrared reflectance, but also act as a resistive heating element when necessary. However, the dip-coating method they adopted is expected to be vulnerable to washing as will be proved in the current work. Ilanchezhiyan et al. [17] demonstrated a flexible electro-thermal heater by dip coating highly conductive carbon nanotubes (CNT) onto cotton fabrics. The CNT-based heater required high voltage (10x volts) in order to achieve adequate heating capability due to its relatively high resistance, which is not desirable in LTMDs. Immobilization of nanoparticles (AgNPs in particular) on textile has received growing interest in pursuit of functionalized textile materials for its antimicrobial properties, electromagnetic interference shielding, etc. Silver coating with good conductivity and stability has gain vast popularity in creating conductive textile. Among diverse metal coating processes, including sputtering [18], chemical vapor deposition [19], electric plating [20] and chemical electroless deposition [21], chemical electroless deposition provides advantages such as uniformity, low cost (performed at low temperature in an ambient environment), and applicability to a variety of surfaces [22]. In particular, a multi-step electroless deposition process was developed in synthesizing metal nanotubes with track-etched polycarbonate or mica as templates [23, 24]. This versatile and well-controlled process resulted in nanoparticles growing and merging on the templates with high coverage and uniformity.
This chapter demonstrates that silver nanoparticles (AgNPs) can grow in situ onto non-woven fabrics and form a very uniform and conductive media to perform as an efficient heating element. A multistep electroless deposition was employed to initially create heterogeneous nuclei on the surface of the fabrics, which subsequently grow into AgNPs in an electroless deposition solution. The electroless deposition was conducted at a low temperature (in a 4 °C refrigerator) in an Ag (I) containing deposition solution with selected metastable redox pairs \(^{[23]}\) such that homogeneous nucleation of silver nanoparticles is kinetically unfavorable. With an extended deposition time, AgNPs merge with each other on the surface of the polyester fabrics to form a conductive network. A sheet resistance of <0.3 ohm/square can be achieved on an AgNPs coated polyester fabric upon thermal annealing. In contrast to a dipping method that relies on physical attachment of conductive fillers to the fabrics’ surface to form a conductive network \(^{[16, 17]}\), multistep electroless deposition creates chemical bonding between oxygen groups on the fabrics’ surface and AgNPs. As a result, the bonding between the AgNPs layer and the polyester fabric is strong enough to resist sonication damage. The resistance only increased slightly after an 80min sonication, and therefore the AgNPs-polyester fabric composites are regarded as washable. The AgNPs coated polyester fabric was employed as a heating element. A voltage as low as 1volt is adequate to heat up the AgNPs-polyester fabric to 60 °C in 2 seconds. The heat can be dissipated away fast after turning off the heating voltage, due to the mesh structure of the AgNPs-polyester fabric.
The resistance of AgNPs-polyester fabric remains unchanged after bending and even after folding several times, thus rendering it a functioning and compliant heater.

4.3 Experimental

4.3.1 Sample Preparation

All glassware were cleaned with detergent and DI water and rinsed with ultrapure water (resistance > 18Mohm). Fabric samples including polyester/cellulose, polyester, and polyester/polyethylene fabrics were requested from Midwest Filtration LLC. Tin chloride (SnCl₂), silver nitrate (AgNO₃), sodium L-tartrate dihydrate, and ethylenediamine are purchased from Sigma-Aldrich and used as received. Poly(acrylic acid) (PAA) and sodium hydroxide purchased from Sigma-Aldrich were reacted to prepare PAA-Na solution. Trifluoroacetic acid (CF₃COOH) is purchased from EMD and ammonium hydroxide (28-30%) is purchased from BDH.

Procedure of electroless deposition of AgNPs on the fabrics:

1. Sensitization: A sensitization solution was prepared by adding 160mg SnCl₂, 108µL CF₃COOH into a mixture of 10ml methanol and 10ml ultrapure water in a jar. The fabrics were immersed in the solution for 45min at room temperature. Tin (II) ions were attached/absorbed onto the template surface. The fabrics were then washed with MeOH and pure water to remove excessive SnCl₂.

2. Activation: The tin (II) impregnated fabrics were immersed in a Ag (I) containing
solution (200mg AgNO$_3$, 326µL ammonium hydroxide in 20ml ultrapure water in a jar) for 3min at room temperature. Small nuclei of Ag were formed in situ. Similar washing steps were carried out as in the sensitization step to remove excessive AgNO$_3$.

3. Electroless deposition: The deposition solution included AgNO$_3$ (57.7mg), sodium L-tartrate dihydrate (0.55g) and complexing agents (134µL ethylenediamine and 200µL 0.51g/ml PAA-Na solution) in 20ml ultrapure water in a jar. The solution was kept in the refrigerator at around 4°C. The fabrics were placed in the deposition solution for an extended time (12hrs, 1day or 2days). The Ag nuclei (heterogeneous sites) would grow and merge with neighboring silver nanoparticles. The silver nanoparticles coated fabrics were then washed with water and dried by pressured air at ambient temperature.

Procedure of Dip-coating AgNWs on the fabrics:

A dispersion of AgNWs in methanol and isopropanol was prepared by short pulse bath sonication and shaking (0.14wt%). Nonwoven fabrics (polyester/cellulose, polyester, polyester/polyethylene fabrics) were soaked in the AgNWs solution and then dried, with this 2-step process being repeated for several cycles. The sheet resistance of the AgNWs-cloth reached 1-4 ohm/square after annealing on a hotplate (set at 170 °C) for 5min.

4.3.2 Characterization

SEM images were taken with FEI Nova NanoSEM 230 and the operation voltage is 10kV.
The thermal annealing process was conducted on a hotplate with a set point of 170 °C. The samples were placed in between two glass slides on the hotplate for 5 – 7 min.

In the sonication process, the AgNPs coated fabrics samples were immersed in DI water in a 20ml glass vial, which was then placed in a 400 W bath sonication. The samples were sonicated for some period of time and taken out (at 2\textsuperscript{nd}, 10\textsuperscript{th}, 20\textsuperscript{th}, 40\textsuperscript{th}, 80\textsuperscript{th} min) for resistance tests to examine the bonding between AgNPs and the fabrics.

Heater characterization was conducted on a 19mm x 8mm AgNPs-polyester fabrics stripe. A copper clip on each end of the sample fixed the sample to a stage and connected the sample to the power source – a Keithley 2400 SourceMeter. An IR camera was employed to record the thermal profile of the sample in real time (data and thermal images) when varying voltage was applied to the heater sample.

Bending tests were carried out on a 19mm x 8mm AgNPs-polyester fabrics stripe. A copper clip on each end of the sample fixed the sample to a motorized stage and connected the sample to the meter in a resistance mode – a Keithley 2000 multimeter. The active length of the sample was 15mm, and it was gradually bent to a shorter and shorter end-to-end distance, driven by the motorized stage. The multimeter recorded the resistance of the sample during bending.

**4.4 Results And Discussion**

The majority of the results in this chapter are utilized in preparation for journal publication.
4.4.1 Multistep Electroless Deposition Of AgNPs On Fabrics

In order to uniformly coat AgNPs onto non-woven fabrics, the deposition process has to be kinetically suppressed in the bulk solution or the surface of the reaction container (glass wall) and favor the fabrics’ surface. A multi-step electroless deposition process of AgNPs onto non-woven fabrics via electroless deposition was adapted as illustrated in Figure 4-1. The electroless deposition consists of three steps in sequence, to favor AgNPs growth on non-woven fabric that acts as a template. To initiate, the non-woven fabrics were soaked in a tin (II) chloride containing solution for 45 minutes at room temperature (sensitization step). The tin ions were absorbed on the surface of the fabrics and attached to polar oxygen atoms. After washing away excessive tin (II) solution, the impregnated fabrics bonded with tin (II) were then transferred into a Ag (I) containing solution for 3 minutes, where silver was reduced by tin (II) on the tin-absorbed site to form nuclei of Ag (activation step). The sensitization and activation step can be repeated if more nuclei are needed for an oxygen deficit surface (in the current work, no repeated steps were taken). The fabrics turned to a light yellow color indicating successful attachment of AgNPs nuclei. In the final step, the AgNPs-nuclei covered fabrics were immersed in the Ag deposition solution for an extended time until AgNPs grow into each other and merge together to form a conductive AgNPs layer on the surface of the fabrics (deposition step). The deposition process is autocatalytic and proceeds on the nuclei surface. The electroless deposition was conducted at a low temperature (in a 4 °C
refrigerator) in an Ag (I) containing deposition solution with selected metastable redox pairs [23] such that homogeneous nucleation of silver nanoparticles is kinetically unfavorable. After deposition, the fabrics turned into a brown color with high uniformity as a sign of large AgNPs covering on the surface of the fabrics.

Figure 4-1. Schematic of multistep electroless deposition of AgNPs onto non-woven fabrics

4.4.2 Deposition Time Split

The deposition step can play an important role in determining the morphology of the AgNPs on the surface of the fabrics. AgNPs-polyester fabrics with different deposition times (12hrs, 24hrs, and 48hrs) were investigated. The average size of the AgNPs increases with increasing deposition time judging from the SEM images (Figure 4-2a, b, c). With a deposition time of 12hrs, a dense layer of AgNPs was already formed, with small nanoparticles covering the whole surface of the fabrics and contacting each other (Fig. 4-2a). The resistance is around 500 ohm/square for an as-prepared sample.
(1000ohm for a sample with a dimension of 19mm long and 8mm wide, as tested by multimeter). As the deposition time increased, the AgNPs grew in size with similar surface coverage. In addition to increased Ag (I) being reduced on the AgNPs surface that resulted in the growth of AgNPs to large sizes, the number of AgNPs decreased with increasing deposition time indicating a contribution from coarsening process where small nanoparticles coalesce into large ones. Large nanoparticles (Fig. 4-2c) made better contact with neighboring ones than small nanoparticles (Fig. 4-2a) to form a well-merged conductive path. As a consequence, the sheet resistance decreases with increasing deposition time. A 24hrs deposition of AgNPs can achieve a sheet resistance below 10ohm/square for an as-prepared sample. A 5 min annealing can further decrease the sheet resistance (Fig. 4-2d) of 24hr-sample to 0.8ohm/square. The AgNPs-polyester fabrics with 48hr deposition time can achieve a sheet resistance of 0.3ohm/square after annealing, which demonstrates a very conductive composite with AgNPs layer covering the fabrics’ surface uniformly.
Figure 4-2. SEM images of AgNPs-polyester with a deposition time of 12hrs (a), 24hrs (b) and 48hrs (c) respectively, and the evolution of resistance with deposition time before and after annealing (d). Samples in the resistance test were of 19mm long and 8mm wide.

4.4.3 Fabrics Selection – Uniform Morphology And Sonication Contested AgNPs Layer Bonding Strength

The chemical condition of the fabrics’ surface can affect the sensitization step in determining tin (II) absorption and the subsequent nucleation and deposition process.
Three different fabrics were used to study the deposition of AgNPs on the fabrics, including polyester/cellulose, polyester, and polyester/polyethylene, with decreasing oxygen content on the surface and increasing hydrophobicity. The SEM images of AgNPs-fabrics were shown in Figure 4-3a, b, and c with each inset on the left corner showing the pristine fabrics and the right corner inset showing a magnified image after AgNPs coating. With deposition/growth time of 2days for each fabric, AgNPs were coated onto all three fabrics successfully. Polyester/cellulose fabrics increased by 131% in weight, while polyester fabrics and polyester/polyethylene fabrics increased by 106% and 69%, respectively. It is clear that polyester/cellulose fabrics are covered with abundant AgNPs of relatively small size comparing with those on polyester or polyester/polyethylene fabrics. This may be due to the hydrophilic nature of polyester/cellulose fabrics, with cellulose carrying dense polar oxygen atoms that act as tin (II) absorption sites and subsequent Ag nucleation sites. The relatively dense AgNPs nuclei limit the size of each AgNPs can grow into. The polyester/cellulose fabrics also have a non-uniform AgNPs distribution. In contrast, polyester and polyester/polyethylene fabrics are covered with uniform layers of AgNPs of relatively large sizes.
Figure 4-3. SEM images of AgNPs coated polyester/cellulose (a), polyester (b) and polyester/polyethylene (c) nonwoven fabrics. Insets: pristine fabrics (left) and magnified SEM images of AgNPs coated nonwoven fabrics (right).

As a consequence, AgNPs-polyester/cellulose has an inferior conductivity comparing to that of the other two fabrics, with as-prepared AgNPs-polyester/cellulose having a sheet resistance of 3.7 ohm/square while AgNPs-polyester and AgNPs-polyester/polyethylene having a sheet resistance of 1.3 and 0.35 ohm/square, respectively. A thermal treatment of 5 to 7 minutes at around 170 °C can further increase the electrical conductivity of all three fabrics with AgNPs-polyester and AgNPs-polyester/polyethylene fabrics achieving a sheet resistance of < 0.3ohm/square and that of AgNPs-polyester/cellulose fabrics 2.1 ohm/square. This may be due to a ripening process of AgNPs that eliminates relatively small nanoparticles, grows relatively large nanoparticles and partially eliminates grain boundaries, resulting in a more conductive thin layer of AgNPs. The ripening process is confirmed by the observation of a smoother surface of AgNPs layers and disappearance of “hills” of loose AgNPs under SEM after annealing (Figure 4-4). SEM images of AgNPs coated polyester/cellulose fabrics did not show any observable change by thermal
annealing process due to its non-uniform microstructure.

Figure 4-4. AgNPs coated polyester and polyester/polyethylene fabrics before (a, c) and after (b, d) annealing. Small protrusions of AgNPs disappeared after annealing.

4.4.4 Adhesion Between AgNPs Layer And Fabrics

The adhesion between AgNPs layer and fabrics was contested by bath sonication in order to determine if the AgNPs-fabrics are washable or not. As shown in Figure 4-5, AgNPs-polyester shows only a slight increase in resistance with increasing sonication time up to 80 minutes and remains to be very conductive. In contrast, AgNPs-polyester/polyethylene displays a drastic loss of conductivity after sonication for 40 minutes. SEM images of AgNPs-polyester and AgNPs-polyester/polyethylene in Figure 4-6b, c can prove the observation in Figure 4-5. A great portion of AgNPs was detached from the polyester/polyethylene fabrics after sonication (Fig 4-6c), indicating a
weak bonding between AgNPs and polyester/polyethylene fabrics’ surface. In contrast, the AgNPs-polyester fabrics remain nearly intact by sonication despite several sparsely distributed defected spots under SEM image (Fig. 4-6b). The vulnerability of AgNPs-polyester/polyethylene is likely due to a deficit of surface oxygen atoms in the sensitization stage to introduce enough nuclei sites, which later act as bonding sites between AgNPs layer and the template fabrics. Due to the low uniformity of AgNPs on polyester/cellulose fabrics, it is difficult to tell solely from the SEM image if AgNPs-polyester/cellulose was severely damaged or not by the bath sonication (Fig. 4-6a), however, a slight increase of resistance as shown in Fig. 4-5 indicates a partial interruption of its conductive path by the sonication process.

Figure 4-5. Evolution of resistance of AgNPs coated fabrics with bath sonication time. Samples in resistance tests were of 19mm long and 8mm wide.
4.4.5 Bonding Between AgNWs And Fabrics In The AgNWs Cloth Made Via Dipping Method – A Comparison

As mentioned earlier, Hsu et al. \[^{[16]}\] developed a dip-coated AgNWs-cloth as an effective LTMD. A 0.9V voltage was able to heat up the AgNWs-cloth to 38 °C in 300 seconds. The cloth also survived for 5 washing cycles in the demonstration of its durability (600 rpm swirling distilled water). However, a much stricter test should be carried out to testify the long-term durability of the AgNWs-cloth. Here, we compared the bonding of AgNWs to the clothing materials with that of our AgNPs coating to the fabrics. A dip-coating method was adapted to coat the nonwoven fabrics (polyester/cellulose, polyester, polyester/polyethylene fabrics) with a thin layer of silver nanowires. SEM images (Fig. 4-7) show that all three fabrics are covered by the dense AgNWs after several dipping-dry cycles. However, the uniformity is not as high as the AgNPs-fabrics (Fig. 4-3), representing one of the disadvantages of dipping method. The optical images
show that the fabrics turn to a darker color after dip coating. The three AgNWs-fabrics show good electrical conductivity after 5min annealing at 170 °C, with a sheet resistance of 2.2 ohm/square for polyester/cellulose-AgNWs, 1.1 ohm/square for polyester-AgNWs, and 4.2 ohm/square for polyester/polyethylene-AgNWs, respectively.

The AgNWs-fabrics were then immersed into DI water and sonicated in a bath sonicator for around 10 seconds. The AgNWs soon came off the fabrics during sonication as indicated by a color change of the fabrics (Fig. 4-8 a”, b” and c”). SEM images (Fig. 4-8) also show that most of the AgNWs were detached from the fabrics after sonication. Electrical tests revealed that the conductivity was lost entirely as a consequence of sonication. It is thus concluded that dipping method is not comparable to the electroless
deposition method of AgNPs in the aspect of providing strong bonding between the conductive silver layer and the fabrics.

Figure 4-8. SEM images of dip-coated AgNWs cloth with polyester/cellulose (a), polyester (b), polyester/polyethylene fabrics (c) after sonication, and optical images showing the fabrics before and after sonication (a” for polyester/cellulose fabrics, b” for polyester fabrics, c” for polyester/polyethylene fabrics).

4.4.6 Mechanical Properties Of AgNPs-Polyester

Dynamic mechanical analyses (DMA) of the AgNPs-polyester fabrics were conducted at a temperature ramping rate of 3 °C min⁻¹ from room temperature to 120 °C (Figure 4-9a). Polyester goes through a glass transition starting at 80 °C. A thin layer of AgNPs does not affect the glass transition of polyester itself. The stability of the mechanical properties of AgNPs-polyester at temperatures lower than 80 °C regardless of different deposition time is beneficial for a heating element, as wearable heaters will not be heated to a temperature
that is higher than 80 °C. The storage modulus of the pristine polyester fabrics is around 100MPa at room temperature. With 1/2 day deposition time of AgNPs, it increases to 166MPa. A further increase of the deposition reaction time decreases the modulus at room temperature of the resulted fabrics to 115MPa for a 2 days deposited fabrics. The mechanism of this trend (Fig. 4-9b) is still not clear. A reasonable suspect is that the deposition solution affects the mechanical properties of the polyester fabrics being immersed over time. At 120 °C, the AgNPs-polyester fabrics with longer deposition time show a larger modulus when the polyester is softened. This indicates a thicker and stronger layer of AgNPs on the fabrics with longer deposition time.

Figure 4-9. (a) Evolution of storage modulus of polyester fabrics and AgNPs-polyester as a function of temperature determined by DMA with temperature ramping from 25 to 120 °C at 3 °C min⁻¹. (b) Storage modulus at room temperature of polyester fabrics and AgNPs-polyester with 1/2 day, 1 day and 2 days as deposition time, respectively.
4.4.7 Heating Performance And Compliancy

Since AgNPs-polyester has been demonstrated to be a washable conductive fabric with AgNPs uniformly coated on the surface, its heating capability was also investigated in pursuit of a washable and wearable heating element. The active heating capabilities were demonstrated in the ambient with IR camera recording the temperature profile (Figure 4-10b). Upon applying a constant voltage, the AgNPs-polyester started to heat up spontaneously (Figure 4-10a). In 2 seconds, the temperature reached a steady state with voltage on. The steady state temperature increases with increasing voltage; a 1volt voltage can heat up the materials to around 60 °C. The low voltage requirement is beneficial to such a wearable technology as a portable battery can serve as the power source. Since the resistance of human skin is on the order of 10k ohms, such low voltage power source would not pose any safety threat to the human body. Due to a mesh structure of the heater, the heat can be dissipated away to the ambient once the heating voltage is turned off. The fast dissipation of heat can be advantageous for the AgNPs-polyester being a heater to ensure an efficient local heat transfer to human body. The IR images of one heating cycle are displayed (Figure 4-10c). As soon as the voltage is applied, the heater started to heat up (the IR image starts to turn red from a cold blue). The heat dissipated away when the voltage is off, and the heater returned to its cold blue state under IR camera. Despite the porous structure of the fabric itself, the heating is overall uniform indicating an even coverage of conductive AgNPs on the fabric surface.
Figure 4-10. (a) The temperature profile of AgNPs-polyester heater in response to a constant voltage. (b) A setup with IR camera to detect the temperature of fabrics as a heater. (c) IR images of one heating cycle of AgNPs-polyester as a heater. Red arrows indicating heating upon applying voltage; blue arrows indicating cooling down once turning off the heating voltage.

As a promising heating element, the AgNPs-polyester composite demonstrated its compliance. A 15mm long stripe was attached to the stage and was bent by decreasing the end-to-end distance. The resistance does not change even when the stripe is close to folded or actually folded (Figure 4-11a). The AgNPs-polyester fabric can be cut into any shape that it still functions well as a heater. A sample cut to display “SMRL” (short for soft materials research laboratory) was connected to a 0.8volt power supply. The sample starts to heat up instantly after the power is on, indicated by its color change to display SMRL under IR camera (Fig. 4-11b). In only 2seconds, the heater was able to reach a temperature right above human body temperature (38 °C). The bent AgNPs-polyester functions equally well as flat sample, indicating its excellent compliance as a heater (Fig.
Figure 4-11. (a). The resistance change $R/R_o$ of AgNPs-polyester stripe related to the bending states indicated by the end-to-end distance on a stage. A heater cut with laser engraver to SMRL letters and stuck on a tape functions in it flat (b) and bent state (c).

It has also been demonstrated that the heater can evaporate water drops absorbed in the AgNPs-polyester fabrics. A drop of water can cool down the heating AgNPs-polyester fabrics upon being absorbed by the heater. With the heating voltage kept on, the water was evaporated gradually accompanied with a sudden increase of temperature of the heater at the finish point of evaporation. The ability of the heater to dry itself speaks highly for its potential as a wearable heater, where moisture control is also vitally important to personal thermal comfort.

**4.5 Conclusion**

In conclusion, silver nanoparticles (AgNPs) can grow in situ onto non-woven fabrics and form a very uniform and conductive media, allowing it to perform as an efficient heating
element. A multistep electroless deposition was employed to initially create heterogeneous nuclei on the surface of the fabrics, which subsequently grow into AgNPs in an electroless deposition solution. The electroless deposition was conducted at a low temperature (in a 4 °C refrigerator) in an Ag (I) containing deposition solution with selected metastable redox pairs \cite{23} such that homogeneous nucleation of silver nanoparticles is kinetically unfavorable. With an extended deposition time, AgNPs merge with each other on the surface of the polyester fabrics to form a conductive network. A sheet resistance of <0.3 ohm/square can be achieved on AgNPs-coated polyester fabrics upon thermal annealing. In contrast to a dipping method that relies on physical attachment of conductive fillers to the fabrics’ surface to form a conductive network \cite{16,17}, multistep electroless deposition creates chemical bonding between oxygen groups on the fabrics’ surface and AgNPs. As a result, the bonding between the AgNPs layer and the polyester fabrics is strong enough to resist sonication damage. The resistance only increased slightly after an 80min sonication and therefore the AgNPs-polyester fabrics composite are regarded as washable. The AgNPs coated polyester fabrics was employed as a heating element. A voltage as low as 1volt is adequate to heat up the AgNPs-polyester fabrics to 60 °C in 2 seconds and the heating capability is well maintained in a bent state. The capability of the AgNPs-polyester heater to dry itself by evaporating any water absorbed on it suggests its function to control moisture as well. The AgNPs-polyester heater presents a promising heating element in a future localized thermal management system.
4.6 Reference


Chapter 5 Conclusion And Future Work

This dissertation investigates several fundamental issues concerning transducer technologies, including bistable electro-mechanical actuation and Joule heating, in pursuit of refreshable Braille displays and a wearable heater for personal thermal management.

Bistable electroactive polymers (BSEP) that leverage the electrically induced large-strain actuation of dielectric elastomer actuators and the bi-stable rigid-to-rigid deformation of shape memory polymers have been developed. This innovative material has positioned itself to uniquely meet the requirements for low-cost, reliable, page-size refreshable Braille displays. In chapter 2, a bimodal BSEP material with a glass transition temperature right above room temperature has been synthesized employing simple UV curing process. The bimodal structure by incorporating both long chain crosslinkers and small molecular crosslinkers creates a framework that can self-stiffen the rubbery BSEP at modest strains to suppress electromechanical instability. A braille dot size actuator with a cycle lifetime of over 2000 cycles at a raised dot height of 0.4 mm was demonstrated at 70 °C, indicating the stability of electrical actuation. The fabrication process for a page-size braille paper was demonstrated and selective heating strategy has been investigated based on a 2-cell device. The simplicity of envisioned Braille display architecture could lead to new Braille products that are compact, lightweight, and affordable. In the future work, the actuation temperature has to be lowered in order to
shorten the heating and cooling time for the reversible rigid-to-rubbery transition and to reduce thermal energy consumption. Therefore, emphasis should be on formulating a bimodal BSEP with a lower glass transition temperature. Increasing the amount of difunctional aliphatic urethane oligomer employed in the current BSEP formulation can tune down the transition temperature due to the low T\textsubscript{g} in its homopolymer. Alternatively, it is well known that by adding plasticizer component or low T\textsubscript{g} component in the formula, the glass transition temperature can be lowered. However, it is inevitable that strategies to reduce the glass transition temperature will collateral affect the mechanical properties both in the rigid and rubbery state of the BSEP materials. The crosslink density can play a role in adjusting the stiffness and involving nanoparticles in the BSEP matrix can be a secondary strategy to stiffen the BSEP. Transition temperature and mechanical properties of the BSEP must be synergistically modified according to specific applications.

Via glass transition, BSEPs go through a wide rigid-to-rubbery transition in order to enter the rubbery state for actuation, resulting in a high actuation temperature. An alternative strategy of lowering down the transition temperature is presented in chapter 3. A phase changing bistable electroactive polymer based on stearyl acrylate and urethane diacrylate oligomer has been synthesized to provide sharp rigid-to-rubbery transition (narrow temperature range of about 10 °C). At room temperature, the stearyl acrylate moieties are crystallized and harden the SA-UDA copolymers with a storage modulus of 10-100MPa. These aggregates melt at an elevated temperature (below 50 °C) with dangling octadecyl
chains softening the polymer in its rubbery state. The difference of the storage modulus between the rigid state and the rubbery state ensures good shape memory properties of the SA-UDA polymers with both fixation and relaxation rate of 100%. The SA-UDA based BSEP exhibits steadily increased actuation strain with increasing electrical field. The SA-UDA films can be actuated at 50 °C up to 70% strain with the maximum actuation energy density comparable to the figure of merits of dielectric elastomers. No electromechanical instability was observed thanks to its self-stiffening property arising from a similar bimodal structure as preceding BSEP via glass transition. The inflection temperature is tunable between 34-46 °C depending on the loading of the SA moiety, which could be further expanded in the future work by introducing n-alkyl acrylates with different lengths of alkyl chains. Alternatively, incorporating plasticizer can tune down the transition temperature by interrupting the aggregation of SA moieties. To expand the application of the SA-UDA copolymers as BSEP, the stiffness both in the rigid state and rubbery state should be further increased with a larger toughness in addition to tuning the inflection temperature. It has been shown that by decreasing the photoinitiator employed in the UV curable polymer formula, the stiffness in the rubbery state of the SA-UDA copolymers can be increased due to a decrease of dangling free chain ends from the photoinitiators. The amount of small molecular crosslink and photoinitiators should be optimized for the BSEP to have improved elongation strain at break and stiffness to enhance the toughness while adequate actuation strain can be achieved as well. The addition of nanofillers such as boron nitride can potentially stiffen the SA-UDA without
much sacrifice on the dielectric properties, which is interesting to be investigated. The phase changing SA-UDA polymers can potentially be useful as materials capable of thermal energy storage or management.

A wearable heater based on AgNP coated non-woven fabric is described for personal thermal management. Silver nanoparticles (AgNPs) can grow in situ onto non-woven fabrics and form a very uniform and conductive media performing as an efficient heating element. In chapter 4, a multistep electroless deposition was employed to initially create heterogeneous nuclei on the surface of the fabrics (sensitization and activation step), which subsequently grow into AgNPs in an electroless deposition solution (deposition step). The electroless deposition was conducted at a low temperature (in a 4 °C refrigerator) in an Ag (I) containing deposition solution with selected metastable redox pairs such that homogeneous nucleation of silver nanoparticles is kinetically unfavorable. With an extended deposition time, AgNPs merge with each other on the surface of the polyester fabrics to form a conductive network. A sheet resistance of <0.3 ohm/square can be achieved on an AgNPs coated polyester fabrics upon thermal annealing. Multistep electroless deposition creates chemical bonding between oxygen groups on the fabrics’ surface and AgNPs. As a result, the bonding between the AgNPs layer and the polyester fabrics is strong enough to resist 80min bath sonication with minimal increase of the resistance. The AgNPs coated polyester fabrics was employed as a heating element. A voltage as low as 1volt is adequate to heat up the AgNPs-polyester fabrics to 60 °C in 2 seconds. The low voltage requirement is greatly beneficial to such a wearable technology
as a portable battery can serve as the power source. The strategy of wearable heater can potentially contribute in energy saving and consumer experience to a localized thermal management system. To better control the deposition process of the AgNPs, a few studies can be carried out in the future. Firstly, time split studies on each of the three steps (sensitization, activation and deposition) should optimize the uniformity and particle size of the AgNPs being coated on the polyester fabrics’ surface. Polyester/cellulose, polyester, and polyester/polyethylene fabrics may require different optimal deposition conditions. The exact mechanism of tin ions absorption and AgNPs nucleation can help select the optimal multistep electroless deposition for any known surface to just broaden the range of fabrics that can be employed. Secondly, the effect of the deposition solution on the mechanical properties of the fabrics still remains unknown and should be investigated as well. Thirdly, thermal annealing of the AgNPs-fabrics can help reduce the resistance possibly due to a ripening process; however, microscopic study is still not available in this work to justify the exact causes. With the combination of characterization techniques on the change of AgNPs (e.g. XRD), varying thermal annealing conditions could be used to hopefully help understand how thermal annealing affects the morphology of the AgNPs on the fabrics’ surface.