Shape Memorization and Reconfiguration of Polymer Particles

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SHAPE MEMORIZATION AND RECONFIGURATION OF POLYMER PARTICLES

by

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B.S., Virginia Tech, 2009

M.S., Virginia Tech, 2011

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Shape Memorization and Reconfiguration of Polymer Particles
written by Lewis Michael Cox
has been approved for the Department of Mechanical Engineering

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Professor Yifu Ding

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Professor Rong Long

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Abstract

Cox, Lewis M (Ph.D., Mechanical Engineering)

Shape Memorization and Reconfiguration of Polymer Particles
Thesis directed by Professor Yifu Ding

Polymer particle systems have been experienced tremendous research efforts in recent years owing to their rapidly expanding applications. Improvements in synthesis methodologies have resulted in unprecedented control over the structure and chemistry of particles. In contrast to these advancements, knowledge of the experimental studies of the mechanical properties of particles remains scarce. Smart particles, specimens capable of changing shape in response to external stimuli, have specifically begun to attract attention. In this thesis two different smart particle systems capable of conforming to an infinite spectrum of user-controlled geometries are investigated: shape memory and shape reconfiguring particles.

Shape memory polymers have the unique ability to memorize and recover their permanent shapes after being programmed to hold high strain levels up to a few hundred percent. By heating the material above its glass transition temperature ($T_g$), applying a deformation, then cooling the material back
below \( T_g \), entropically unfavorable network topologies can be fixed and later recovered. Utilizing nanoimprint lithography, this thesis first investigates the ability of micro- and nano-scale shape memory particles to fix and then recover from user-controlled, highly strained geometries. It then examines how elastic and surface energies influence the shape memory cycle at different length scales.

Shape reconfiguration in polymeric materials is a more recent phenomenon. Covalent adaptive networks (CANs) that can reversibly break and reform covalent bonds through their molecular network have been shown to successfully relax internal stresses upon stimuli by either heat or light. In contrast to shape memory polymers, where higher energy geometries are temporarily fixed, plasticity in CANs results in new, permanent, thermally stable geometries. In this thesis we present the first instance of micro-particles synthesized with a CAN and explore the ability of the particle system to permanently fix new network topologies.
I dedicate this dissertation to my family, friends, Otis, and coffee.
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Chapter 1: Motivation and Background

Polymeric micro- and nano-particles, ranging from structurally homogeneous, to core-shell, to Janus particles, have enjoyed growing interest over the past several decades in industrial and academic settings due to their uses in drug delivery, electronic packaging, optical bio-sensors, and test-beds for the mechanosensitivity of cells.\(^{(1–8)}\) In many of these applications the ability of these particles to change structure or properties in response to an external stimulus is greatly desired. Smart polymeric materials capable of exhibiting these controllable behaviors include hydrogels, liquid crystal polymers, and shape memory polymers.

Hydrogels are one of the most common stimuli-responsive materials, including widely used materials as poly(N-isopropylacrylamide), which displays a volume-phase transition (VPT) in water, Figure 1.\(^{(9–12)}\) This phenomenon is driven by the temperature-dependent miscibility between the material and the water. Incorporation of this behavior into particle systems has generated a wide range of microgel spheres which, by varying temperature, can be made to swell with or expel water, exhibiting a shape-changing behavior.\(^{(13–22)}\) The system requires an aqueous media, and the shape change iso-geometric, where only spheres are obtained. Accordingly, this system enables only a minor degree of control over the particle shape.
Figure 1: Shape change in a particle as it undergoes a volume-phase transition.

Thermally responsive, main-chain liquid crystalline polymers are also known to exhibit shape memorizing abilities that are not reliant upon the presence of a solvent.\textsuperscript{(23–34)} Recently, particles based upon these materials have also been synthesized and studied. In these systems particles exhibit intrinsic ellipsoidal shapes associated with the alignment of mesogens. Such particles can reversibly evolve into spherical shapes when heated above the nematic transition temperature, as shown in Figure 2.\textsuperscript{(35)} However, these particles are highly chemistry specific and the shape change is both minor and limited to two geometries.
Figure 2: Main chain liquid crystalline particles exhibit an inherently elliptical state due to mesogen alignment. When annealed above the nematic transition temperature this alignment is lost and a spherical shape is assumed. By quenching annealed particles this spherical shape is preserved whereas a slower cooling allows for realignment of mesogens.(35)

Shape memory polymers (SMPs) on the other hand offer a very appealing material for use in smart particle systems, and will be one area of focus in this thesis.
SMPs have the unique ability to memorize and recover their permanent shapes after being programmed to hold high strain levels up to a few hundred percent.\((36–45)\) This ability to switch between a programmed and permanent shape has found these materials applications as surgical stents and catheters,\((36, 46–48)\) temperature sensors,\((38)\) pattern memorizing surfaces,\((49–51)\) flexible electronics,\((52, 53)\) and platforms for cell growth.\((54, 55)\) The permanent shape of an SMP is the state in which the polymer chains in between crosslinking points are at an equilibrium, or lowest energy state. During a typical shape memory cycle the permanent shape is deformed under a mechanical load at a temperature higher than its glass transition temperature \((T_g)\), which deforms the chains in between crosslinking points into a higher energy state with lower entropic freedom. In order to minimize system energy, this deformed, temporary shape, will return to its permanent shape in the absence of mechanical loading unless it is fixed by decreasing the temperature below \(T_g\) prior to removal of the mechanical loads. Once fixed, this temporary shape remains stable indefinitely or until exposure to a sufficient environmental stimulus such as heat, UV light, or solvent vapor. Upon application of a stimulus, strain energy release occurs in the polymer network and either the permanent shape will be recovered or energy is captured via mechanical constraints. This process is illustrated in Figure 3.
Recently, micro-scale particles made from shape-memory polymers (SMPs) contained in a composite material were shown to deform when the surrounding matrix was strained, then recover their original shape after dissolving the matrix and then annealing the particles, exhibiting shape memory characteristics, Figure 4. (57)
Figure 4: Particles are embedded in a matrix and heated $T_g$. The matrix is then deformed and then cooled down, fixing temporary particle shapes. When the matrix is dissolved and particles are reheated they recover the initial spherical shapes. (57)

This methodology however, still requires the use of solvents and the achievable particle deformation is limited by the stress fields imposed on the matrix. The ability to directly impose controlled, non-uniform deformations on particles could potentially lead to a host of new engineering applications, and inform the field of contact mechanics. Numerous questions await exploration. To what degree are particles able to fix a highly deformed shape? Directly deforming particles requires the use of substrates and superstrates and it is unknown how these constraints will influence the shape memory characteristics of particles. Can confining superstrates be used to generate novel particle surface topologies? Metal-polymer bilayer wrinkling has recently been investigated on curved surfaces, but has not been achieved on small particle systems. Johnson, Kendal, and Roberts (JKR), Derjaguin, Muller, and Toporov (DMT), and nanoparticle adhesion models have been used to investigate the contact
mechanics between soft particles and rigid substrates, and results emphasize the importance of both surface energies and particle size in these systems.\(^\text{58–61}\) No studies investigating the effects of particle size and substrate adhesion on shape memory particles have been performed. Furthermore, experimental work investigating the contact mechanics of soft particles in general is scarce. To the best of our knowledge, only a single study measuring the contact mechanics between a soft particle and rigid substrate has been performed, and this work investigates small strains of just a few percent.\(^\text{62}\) How will the effects of elastic energy and substrate adhesion depend on the length scale of the particles being deformed? Neither the degree nor the kinetics of particle recovery after deformation have ever been studied. These questions motivate the first aim in this research proposal.
Aim 1: Investigate the shape memory effect in conventional, cross-linked polymer micro- and nano-particles

We aim to first demonstrate the ability of micro- and nano-scale particles to be directly compressed to fix highly deformed geometries via Nanoimprinting and recover their original shape upon thermal stimulus. Furthermore, we explore the potential uses of this system in engineering applications by coating compressed particles with thin metal superstrates and harnessing the elastic energy during recovery to generate controllable, wrinkling patterns on the particle surfaces in an attempt to fabricate dielectric, topographical Janus particles. Building off this work we aim to investigate how elastic energy and work of adhesion compete in the recovery process of deformed particles at different particle length scales. We measure shape recovery of differently sized particles on substrates with modified surfaces to controllably vary work of adhesion and investigate final particle geometries via scanning electron microscopy. The recovery kinetics of particles on different surfaces is measured using an in situ atomic force microscopy technique.

Our interests do not stop here. The major limitation of these shape memory particles is that they always store a fixed, un-tunable amount of elastic energy for any given deformation and upon release of this energy, particles always attempt to recover their original shape. Upon exposure to a favorable solvent or when heated above their $T_g$, the temporary shape is lost. Since only spherical particle geometries
are obtained during emulsion polymerization procedures, shape memory particle systems currently lack the ability to fix thermally stable non-spherical shapes. However, if some of this elastic energy stored in deformed particles could be dissipated via highly controlled plastic deformation, without compromising mechanical properties of the particles, then an unprecedented degree of control in the shape-changing abilities of these smart particles could be achieved.

Recent work has demonstrated the ability of certain cross-linked polymers, known as covalent adaptive networks (CANs) to achieve plastic deformation (or stress relaxation) by altering their covalently bonded network topology in response to an applied external stimuli such as light exposure or heat.(63–67) This smart material behavior has generated substantial interest in utilizing the photoplasticity,(68, 69) stress relaxation,(70–72) and self-healing(73, 74) capabilities of such materials.(75–80) Recently, photoinduced plasticity has been exploited to generate unique topological features on strained polymer films, Figure 5.(81)
Figure 5: a) The material is stretched to 10% strain two perpendicular axes and irradiated through a concentric ring mask. Stylus profilometry shows concentric ring patterns similar in size to the mask. b) The sample under the same biaxial strain is irradiated twice, once through a line grating mask, and then a second time through the same mask after rotating it 30°. c) Using the same protocols as (a) and (b), except that the samples are subsequently irradiated again across the entire patterned area, resulting in warping of the macroscopic structure. (81)

One such mechanism by which covalent bonds can be transferred is reversible addition-fragmentation chain transfer (RAFT). (82) During the RAFT process, a covalent bond is exchanged, as illustrated in Figure 6, and the polymer chain whose bond
is broken is able to relax to an entropically more favorable conformation. This network reconfiguration process has been shown to relieve internal stresses, and thus enables permanent shape changes in these types of network polymers. The fractured chain retains a free radical at its terminus and will proceed to attack another covalent bond. The RAFT process therefore propagates throughout the polymer network, as shown in Figure 7.(70, 82)

![Diagram of RAFT mechanism](image)

Figure 6: Connectivity transition of covalent bonds in the RAFT mechanism.(67)
To date, work has focused on quantifying and controlling stress relaxation in uniformly deformed bulk samples\(^{(68–70, 78)}\). To my knowledge, no covalent adaptive networks have been incorporated into particle systems. Achieving this sort of a system would allow for the controlled programming of particles with permanent, non-spherical shapes.

Prior to this work, investigations of stress-relaxation in RAFT materials have been limited to macroscopic deformations, leaving many unexplored questions. How does the stress-relaxation behavior change at smaller length scales? Can deformations on the nanometer length scale be permanently fixed? In the presence of a directional UV source how heterogeneous is the network reconfiguration and can this be exploited for engineering purposes? In the specific case of RAFT-based particles,
can photoplastic dissipation be harnessed to generate thermally stable, non-spherical geometries? These questions motivate our second aim.
Aim 2: Investigate controllable shape reconfiguration in RAFT-based particles

We wish to investigate the shape reconfiguration of RAFT-based particles by coupling a UV source in the imprinting process. We wish to see if particles exposed to a constant UV source during a typical imprinting cycle can exhibit the reprogramming of the permanent particle shape from that of a sphere to a flat plate. We also wish to investigate whether controlling the intensity and duration of a UV source can achieve a partial and non-uniform stress relaxation across particles. As an initial study leading up to the particle-based aims, we investigate the length scale dependency of stress relaxation in RAFT-based materials by lithographically patterning the surfaces of bulk materials. After completion of this study, RAFT-based particles are then synthesized. We lithographically compress particles into high aspect ratio geometries and investigate the degree and kinetics of shape reconfiguration as a function of the elastic strain level imposed on particles.
Chapter 2: Investigations of Shape Memorization in Polymer Particles

2.1 Free and Constrained Recovery of Model Microspheres

2.1.1 Overview

As previously mentioned, existing smart particle systems capable of changing shape in response to external stimuli include hydrogels and main-chain liquid crystalline particles. Hydrogels are the most common, exhibiting a volume-phase transition in water driven by the temperature-dependent miscibility between polymer network and the water. By varying temperature, particles can be made to swell with or expel water, exhibiting a shape-changing behavior. The system requires an aqueous media, and the geometry and strain cannot be directly controlled. Similarly, thermally responsive, main-chain liquid crystalline particles, which do not require the presence of a solvent, exhibit intrinsic ellipsoidal shapes associated with the alignment of mesogens. Such particles can reversibly evolve into spherical shapes when heated above the nematic transition temperature. However, these particles are highly chemistry specific and the shape change is both minor and limited to only two geometries. As per Aim 1, we therefore explore the ability to use shape memory particles to overcome the limitations of these other particle systems to fix and recover large user-controlled strains.

The direct deformation and shape recovery of micron-sized polystyrene particles via nanoimprint lithography is reported here. The recovery of these particles is shown to
depend strongly on the constraints of substrates and superstrates. Finite Element Analysis is used to map strain levels in compressed particles. It is shown that the recovery of the programmed PS particles can be utilized to create a range of smart Janus particles with contrasting properties in conductivity and topography, by use of metal-layer superstrate-constrained recovery.

2.1.2 Methods

2.1.2.1 Programming of Particles

PS particles with 4.25-µm diameter and 2 % divinylbenzene cross-linker (PS05N/5689, Bangs Laboratory Inc.) were deposited on a flat silicon wafer by dipping the wafer into an aqueous solution containing particles and then drawing it out at 1 mm/s. Prior to the NIL process, the silicon mold used for compression was first cleaned using piranha solution and coated with a low-surface-energy, self-assembled monolayer of \( \text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SiCl}_3 \) (tridecafluoro-1,1,2,2-tetrahydrooctyltrichlorosilane, Sigma-Aldrich) by vapor deposition to facilitate mold release from the particles after imprinting. All NIL processes were performed on a nanoimprinter (Eitre 3, Obducat) at 120 °C under a pressure of 1.5 MPa for 5 minutes. After this time period, the compressive force was maintained while the particles were cooled back to room temperature, at which point the pressure was relieved and the silicon mold was removed from the flattened particles. A thermal evaporator (SC-3000, CVC Products Inc.) was used to deposit metal films onto the surface of flattened particles.
2.1.2.2 Predicting Wrinkling Patterns

Material systems where a soft substrate, such as SMPs, has been capped with a stiff film have been utilized to study the spontaneous generation of complex wrinkling patterns.\(^{(83)}\) Incorporating such structures into a shape memory particle system opens up the possibility of fabricating a wide range of surface morphologies on topographic janus particles. In the simplified case of a uniaxial strain field wrinkling occurs when the uniaxial compressive strain exceeds a critical strain in the bilayer system,\(^{(84)}\)

\[
\varepsilon_c = \frac{1}{4} \left( \frac{E_f}{E_s} \right)^{1/3}
\]

where \( \overline{E} \) represents the plane strain modulus \( E/(1 - \nu)^2 \) that depends on Poisson’s ratio \( \nu \) and Young’s modulus \( E \) of the materials, and the subscripts \( f \) and \( s \) refer to the film and substrate, respectively. Furthermore, the characteristic periodicity of the wrinkles is,\(^{(85)}\)

\[
\lambda = 2\pi \left( \frac{E_f}{3E_s} \right)^{1/3}
\]

where \( t \) is the thickness of the film. Such strains can be imposed via direct mechanical loading of the bilayer, mismatches in thermal expansion (contraction, specifically), or, of particular interest to this study, by the release of strain energy of an
SMP substrate. This simplified wrinkling model is applied to our system in order to analyze and help predict surface morphologies of particles capped by a thin, stiff superstrate.

2.1.2.3 Determination of Labyrinthine Areal Coverage

Images of wrinkled particles captured via SEM were divided into eighths by four axes drawn across the diameter of the particle surface (acute central angles of 45°). The domain along each given axis where wrinkles are observed to intersect at angles greater than 45° was measured, and the domain sizes across all 4 axes were averaged to obtain the effective diameter of labyrinthine area covering a given particle surface.

2.1.2.4 Particle-Substrate Contact Calculations

For contact between an elastic sphere and a flat substrate, JKR theory predicts the contact radius to be:

\[
a = \left( \frac{3RP_1}{4E^*} \right)^{1/3}
\]

(2.1-3)

where \( R \) is the particle radius of 2.125 um, while \( E^* \) and \( P_1 \) are the contact modulus and apparent Hertz load given by the equations

\[
\frac{1}{E^*} = \frac{1 - \nu_{SO}^2}{E_{SO}} + \frac{1 - \nu_{PS}^2}{E_{PS}}
\]

(2.1-4)
and

\[ P_1 = P + 3\pi \Delta \gamma R + \sqrt{6\pi \Delta \gamma RP + (3\pi \Delta \gamma R)^2} \]  \hspace{1cm} (2.1-5)

where \( E \) and \( \nu \) are the Young’s modulus and Poisson’s ratio of the two materials, \( P \) is the load applied to the sphere, and \( \Delta \gamma \) is the thermodynamic work of adhesion expressed by

\[ \Delta \gamma = \gamma_1 + \gamma_2 - \gamma_{12} \]  \hspace{1cm} (2.1-6)

where \( \gamma \) is the excess surface or interface free energy; the subscripts denote surfaces 1 and 2 and the interface 12. In our experiments the applied load is zero yielding the simplified equation

\[ P_1 = 6\pi \Delta \gamma R \]  \hspace{1cm} (2.1-7)

From Seemann et al the work of adhesion is approximated to be 61 mN/m.\(^{(86)}\) Using this value, the Hertz load is calculated to be 2.5 \( \mu \)N, and the equilibrium contact radius is 0.66 \( \mu \)m.
2.1.3 Results and Discussion

NIL is a reliable, high-throughput fabrication technique, capable of compressing two parallel rigid substrates by use of high pressures.\(^{87, 88}\) The programming and recovery of polystyrene (PS) particles with NIL are illustrated in Figure 8. The model PS spheres used were lightly crosslinked with 2% divinylbenzene (4.25 µm diameter) and were first deposited on a silicon (Si) wafer with a native silicon oxide (SiO\(_x\)) surface layer via dip-coating. The particles were then “imprinted” with a flat mold (Si wafer) at 120 °C (glass transition temperature, \(T_g\), of PS \(\sim\)100 °C) under a relatively high pressure (1.5 MPa). The deformed PS particles were cooled to room temperature, well below their \(T_g\), to fix the temporary disc-like shape after pressure release.

![Figure 8: Illustration of the programming of polymer particles with NIL and their recovery.](image)

SEM images show that following this procedure, deposited particles (Figure 9A) are successfully programmed to hold highly strained temporary shapes (Figure 9B), with compressive ratios (defined as the ratio of the difference between the original height and the compressed height to the original height of the particle) as large
as 0.931. When these deformed particles are annealed at 120 °C for a period of 1 hour they exhibit significant recoveries of their permanent shapes (Figure 9C).

Figure 9: SEM images showing the PS particles after deposition (A), compression (B), and recovery (C). The insets are the corresponding cross-sectional view of the particles. The scale bar applies to all the images.
Depending on the initial compression ratio, the height of the recovered particles ranged from 72% to 90% of its original value, Figure 10. Based on the low (< 40°) contact angle between similar PS microspheres and SiO₅ surfaces,(86) the shape recovery (Figure 9B to 9C) is driven by elastic strain energy release rather than surface energy minimization between the particles and the substrate. The side-view profiles of these particles (Figure 9C inset) revealed that a relatively large contact radius of (2.1 ± 0.8) μm (standard deviation, N = 7), still exists between the PS and SiO₅ interface after resulting in the incomplete recovery of the PS particles (Figure 10). This residual contact radius is much larger than the equilibrium contact radius (= 0.66 μm) between the rubbery PS particle and the Si wafer, as estimated from the traditional JKR model detailed in the previous methods section.(58) The residual contact radii are results of either viscous or plastic deformation during the compressions and/or the work of adhesion between the PS and Si substrate. Both factors could increase with the larger compression ratios, leading to the lower degrees of recovery shown in Figure 10. This adhesive contact effect can be alleviated by sonicating to release the compressed PS particles off the Si wafer and then re-depositing them onto a freshly prepared Si wafer. After annealing at 120 °C for 1 h, re-deposited PS particles recovered (96.1 ± 0.8)% (N = 9) of the initial height, since these particles do not form as intimate a contact with the wafers as those in Figure 10.
Previous studies have reported both strain-hardening effects during the compression of micro-particles and the presence of non-homogeneous cross-linking densities that structurally form a stiffer shell with a softer particle core. To assess
whether or not these characteristics affect the PS particle deformations during compression, the geometries of programmed PS particles (Figure 9 – SEM images) were analyzed. In particular, Figure 11 plots the lateral deformation ratio (the ratio of the overall lateral extension of the compressed particle to the diameter of the uncompressed particle) as a function of compression ratio. Compared to the theoretical and experimental deformation geometries of centimeter-scale rubber balls, which are accurately modeled as incompressible solids,\(^{(90)}\) the compressed PS micro-particles exhibit no obvious deviation. In order to capture the particle geometries during recovery, we annealed the compressed particles at 110 °C. At this temperature, shape recovery rate is slower compared to that at 120 °C,\(^{(91)}\) which allows \textit{in situ} heated-stage atomic force microscope (AFM) imaging of the particle shapes. From the measurements, the lateral deformation and compression ratios of the recovering particles exhibit relationships similar to those in compressed particles (Figure 11). This relationship is crucial for the morphological development of metal-film-capped recovery described below.
Figure 11: The lateral dimensions of the compressed PS micro-particles as a function of compression ratio compared to the dimensions of centimeter-scale rubber balls (90), as well as recovering PS particles and recovering particles with a 10.2 nm Au capping layer (the latter two recovered at 110 °C).

The NIL process is not limited to compressions using plates with smooth surfaces. Figure 11 shows that novel deformation strains can be achieved simply by using silicon molds patterned via e-beam lithography during the NIL process. Here, we pattern the particles with an optically diffractive line-space grating that fully dissapears after annealing above $T_g$ for one hour.
In addition to the SiO$_x$ substrate, a thin metal layer deposited on top of the programmed PS particles can also constrain their shape recovery. For bulk shape-memory polymers, such metal-film-constrained recoveries give rise to a range of wrinkling patterns, which has recently attracted much attention.$^{(92–105)}$ In the following, we show that metal-layer constrained recovery in the above programmed PS particles creates a series of intricate and controllable wrinkle patterns, which have never before been observed. Au films with varying thicknesses were deposited on top of the compressed PS particles by use of a thermal evaporator. The Au film thickness (which varied less than 2 % across the sample) was subsequently determined via AFM by scanning across the edges of the ring left after the compressed particles had recovered, thus exposing bare silicon substrate (as marked by the dotted line in Figure 13A). The sizes of the rings also mark lateral expansion of the compressed PS before

Figure 12: A) SEM image of PS particles programmed using a patterned mold during the imprinting process. B) The unique strain fields are completely reversible when annealed above $T_g$. 
metal deposition. During the metal deposition, no particle recovery due to heating from thermal evaporation was observed.

Figure 13: A)-(C) are SEM images of wrinkling patterns on the surface of Au coated particles after being annealed at 110 °C for given durations as marked in each figure. The top and bottom insets are magnified views of the azimuthal wrinkles near the edge and labyrinthine wrinkles at the central region of annealed particles, respectively. The scale bars in (A) and in the inset of (A) apply to all primary images and insets, correspondingly.
Figure 14 shows the evolution of wrinkle patterns during the recovery of a compressed PS particle capped with a 10.2 nm Au film. In order to slow down recovery and capture the early-stage morphologies, we once again annealed the Au-coated particles at 110 °C. After 45 s of annealing particles with compressive ratios of ≈ 0.88, a hierarchical wrinkle pattern emerged, consisting of azimuthally-oriented wrinkles along the particle edges (Figure 13A, top inset) and labyrinthine wrinkles in the central regions (Figure 13A, bottom inset). Note that in this study, wrinkling refers to any observable change in surface morphology and does not distinguish between elastic deformation and plastic buckling of the thin metal films. With annealing time increased to 5 min (Figure 13B) or 60 min (Figure 13C), no significant changes were observed in the overall features of the hierarchical wrinkles. Specifically, the period or correlation length of the azimuthal wrinkles grows only slightly with the increase of annealing time (Figure 14).
Figure 14: The azimuthal wrinkling periodicity as a function of annealing period at 110 °C. The two solid lines correspond to the upper and lower bound assuming the rubbery modulus and glassy modulus of PS.

The hierarchical wrinkling patterns originate from the unique strain loading on the metal films during the particle recovery. From finite element analysis (FEA), the strain fields in the highly compressed particles consist of both strong circumferential and radial strains (Figure 15).
Figure 15: Circumferential and radial strains across the centerline of compressed particles.

At the central region of the particles, the magnitude of these two perpendicular strains is comparable, effectively causing an equibiaxial-type (in cylindrical coordinates) compressive strain on the metal/polymer bilayer. This results in the labyrinthine type wrinkle patterns, similar to those observed in planar bilayer system under biaxial compressive loading. In contrast, near the edges of the compressed particles, the circumferential strains dominate, primarily creating uniaxial compressive strain loading during recovery. Note that (a) the particles presented here exhibit compression ratios larger than 0.6, a deformation regime where changes in lateral strain are significantly greater than associated changes in vertical strain (Figure 11),
and that (b) the wrinkling periodicity is significantly smaller than the bilayer radius of curvature, indicating that film curvature plays no significant role in the formation of wrinkling patterns. Accordingly, we compare the azimuthal wrinkling patterns to the sinusoidal wrinkling patterns observed in uniaxially compressed flat bilayers.\(^{(96, 106)}\) Specifically, surface wrinkling occurs when the uniaxial compressive strain exceeds a critical strain in the bilayer system.\(^{(84)}\)

\[
\varepsilon_c = \frac{1}{4} \left( \frac{3\bar{E}}{E} \right)^{2/3}
\]  

(2.1-8)

where \(\bar{E}\) represents the plane strain modulus, \(E/(1-\nu)^2\), that depends on Poisson’s ratio \(\nu\) and Young’s modulus \(E\) of the materials, and the subscripts \(f\) and \(s\) refer to the film and substrate, respectively. Furthermore, the characteristic periodicity of the wrinkles is,\(^{(85)}\)

\[
\lambda = 2\pi t \left( \frac{E_s}{3\bar{E}} \right)^{1/3}
\]  

(2.1-9)

where \(t\) is the thickness of the film. During the recovery of the Au-capped PS particles, the PS modulus is typically assumed to drop three orders of magnitude, from 3.2 GPa to 10 MPa\(^{(107)}\) (while the \(\nu\) increases from 0.33 to \(\approx 0.49\)), as the annealing temperature rises above the \(T_g\) of PS. Using plane strain modulus values of 98 GPa for the Au film,\(^{(108)}\) the characteristic periodicities for the classical 10.2 nm thick
Au-PS bilayer are 0.129 µm and 0.864 µm, assuming glassy and rubbery modulus of PS, respectively, as marked in Figure 14.

As compressed PS micro-discs were heated, the modulus started to decrease, triggering the shape-recovery. The estimated critical strain needed to cause buckling in the Au film on a glassy PS substrate is 6 %, a strain level not achievable by the glassy polymer without fracturing.\(^{(109)}\) However, as the PS modulus drops during annealing, this critical strain decreases (to as low as 0.14 % for a rubbery PS substrate), and wrinkling occurs when the recovered strain exceeds the critical value. After the wrinkles form (Figure 13A), increasing strain due to the continuous recovery leads to the growth in amplitude of the wrinkles, observed in Figure 13B and Figure 13C, consistent with the wrinkling of classical bilayer systems.\(^{(85)}\) For the Au-coated PS particle the measured periodicity slightly increased with annealing time, but remained close to the lower bound (associated with a more glassy PS substrate). This result is not altogether unexpected. The predicted bound for a rubbery modulus in Figure 14, does not consider any effects of strain hardening. Previous work by Tatara has applied the theory of large elastic deformation to the case of sphere under compression and concludes the following relationship.\(^{(110–116)}\)

\[
E = E_0 \frac{1 - \varepsilon + \varepsilon^2 / 3}{(1 - \varepsilon)^2}
\]  

(2.1-10)
Where $E_0$ is the initial Young's Modulus at zero compressive strain $\varepsilon = 0$. Applying this updated modulus at a compression ratio of 0.88 the modulus is calculated to be 260 MPa and the expected wrinkling wavelength is 0.32 µm, which is in excellent agreement with the measured wavelength in Figure 14.

Figure 16: Wrinkling morphologies on the surface of Au coated particles after 1 hour of annealing at 110 °C, with varying Au film thicknesses and degrees of pre-strain (increasing left to right). The scale bar applies to all 12 images.
Figure 16 summarizes the morphologies of the Au-coated PS particles obtained after annealing at 110 °C for one hour, varying the compression ratio of the programmed PS particles as well as the thicknesses of the Au film. Along the edges of all annealed particles, azimuthal wrinkles dominate the surface topography. Varying compression ratios within the range shown in Figure 16 had no significant effect on the wrinkling periodicity observed for a given thickness of Au film. This type of strain-independence is expected when particle curvature effects do not dominate wrinkling morphologies, and the system behaves similar to the classical case of bilayer buckling. On the other hand, the periodicity of the azimuthal wrinkles increases with the Au film thickness, and the periodicity shifts from being close to the lower bound (glassy PS) to the upper bound (rubbery PS) (Figure 17). This increase in periodicity is most likely due to confinement effects. As the periodicity approaches the length scale of the particles, the assumption of an infinitely large surface implicit in the bilayer wrinkling equations becomes violated.
Figure 17: The periodicity of azimuthal wrinkles at the outermost edges of the particles as a function of Au film thickness, compared to the theoretical wrinkling periodicity for glassy and rubbery PS.

For Au films of 19.8 nm and thinner, labyrinthine wrinkling pattern forms in the center of the PS particles and its areal coverage decreases with the increase of Au film thickness (Figure 18). For Au films thicker than 19.8 nm, this type of labyrinthine wrinkling was not observed.
Figure 18: The areal coverage of the labyrinthine wrinkling patterns on the annealed particles as a function of Au film thickness.

Limited by our current NIL setup, i.e., a pressure-controlled compression, low compression ratios (below 0.5) are difficult to achieve. To examine the morphology of metal-constrained recovery on particles with low compression ratios, FEA simulations were carried out (Figure 19D and E). For a compression ratio of 0.4, the azimuthal wrinkles along the edges of the particles are still observed, but no labyrinthine wrinkles were present in the central region. As expected, the azimuthal wrinkle periodicity increased with metal film thickness. In comparison, the absence of labyrinthine wrinkling is due to the larger changes in out-of-plane strain relative to
the accompanying lateral strains during the recovery of particles with lower compression ratios (Figure 11). In other words, recovery in the vertical dimension is larger than the lateral dimensions, and the compressive forces inducing wrinkling morphologies are primarily driven by an increase of curvature. Such morphology has been observed in stiff films experiencing large out of plane strains.\textsuperscript{(117, 118)}

Figure 19: (A) and (B) are FEA simulations showing the azimuthal wrinkling patterns in particles deformed to compression ratios of 0.4 with Au capping layers of 5 nm and 10 nm, respectively.
The morphologies shown in Figure 16 can further evolve, given longer annealing time or higher annealing temperatures. Figure 20 shows the Au-coated PS particles after being annealed at 120 °C for one hour, which leads to higher degree of recovery and thus higher compressive strain on the system. The PS particles coated with 11.6 nm thick Au layers recovered into a rosette-type shape, where the azimuthal wrinkles become rougher, and the labyrinthine wrinkles have evolved into a highly folded shape. Such unique morphology has never before been demonstrated. It is known that hierarchical wrinkling can occur in the presence of larger compressive stresses when the amplitudes of the smaller, first generation wrinkles saturate and effectively form a new, stiffer skin.\(^{119}\) Similarly, the earlier-formed labyrinthine wrinkles are still discernible, and superimposed on the surfaces of these new protrusions (Figure 20). As the compression ratio increases, the central protrusion is seen to grow from an elegant, circular ridge to a larger, bowl-like shape.
Figure 20: The wrinkling morphologies of particles with an 11.6 nm Au film after annealing for 1 h at 120 °C exhibit a rosette structure with a cup-like pocket in the center (A). Particles capped with an 11.9 nm Cr film and annealed result in similar rosette morphologies (B).

To examine the generality of the wrinkled morphology generated during the constrained shape recovery, we also coated programmed PS particles with an 11.9 nm
thick chromium (Cr) film. As shown in Figure 20B, the rosette structures are again observed, with a similar dependence on the compression ratio. According to the bilayer buckling analysis mentioned above, due to its larger modulus the azimuthal wrinkling periodicity of the stiffer Cr film should be 47.6 % larger than that of the Au. This is indeed observed experimentally: the average azimuthal periodicity along the edges of the Cr coated systems [(0.36 ± 0.07) µm, N=6] is 44.0 % larger than those associated with the Au coated system [(0.25 ± 0.03) µm, N=6]. Such results suggest a significant predictability and reproducibility of these complex wrinkling structures applicable to generalized material systems not investigated here.

The opportunity to study more complex systems of confined recovery remains. Aggregated particles can be compressed and recovered to generate guided wrinkling patterns (Figure 21A), while particles compressed using a mold with a line-space grating will generate wrinkles perpendicular to the mold geometry (Figure 22B). Furthermore, annealing above $T_g$ is not the only method by which compressed particle-bilayer systems can be recovered. Exposure to solvent vapor can be used to lower the $T_g$ of the particle below ambient temperature to initiate recovery. Figure 21C and D show the resulting morphology when compressed particles coated with 11.6 and 5.5 nm Au films, respectively, are exposed to acetone vapor. These systems are not expected to follow the same geometric pathways articulated in Figure 11. Bilayer wrinkling will occur as the polymer network releases the programmed strains, swells to an unknown extent as solvent molecules diffuse into the polymer network, then
shrinks as solvent is evaporated out. The intricacies of this system remain an open area for exploration.

Figure 21: Aggregated particles that were compressed, coated with a 5.5 nm Au film, then annealed exhibit guided wrinkling geometries (A). Particles compressed using a patterned mold, then coated 5.5 nm Au film develop wrinkles normal to the mold grating pattern when annealed (B). A compressed particle with an 5.5 nm Au film deposited on its surface is exposed to acetone vapor. The resulting geometry is highly complex and hierarchical (C). A compressed particle with an 11.6 nm Au film deposited on its surface is exposed to acetone generating complex, yet not hierarchical structures.
To summarize, we demonstrate that lightly cross-linked PS micro-particles exhibit the ability to undergo shape-recovery after fixing large degrees of compression. This recovery behavior is shown to be highly dependent on the substrate confinement. Furthermore, these programmed particles can be used as the foundation for creating unprecedented, highly hierarchical surface features in the presence of metal coatings, which can be tuned by the degree of particle compression, thickness and stiffness of the capping layer, and annealing conditions. Small-scale wrinkling structures on Au-coated polymer sheets demonstrate plasmonic characteristics which yield ultrahigh surface enhanced Ramen scattering for molecule detection, and these particles offer similar potential, but on smaller-scale platforms that can be easily deployed into solutions.\(^{(120)}\)

The incorporation of shape-changing capability into polymer-based micro- and nano-particles opens a new avenue for creating deployable smart particles. Compared with current, chemically activated smart particle technologies such as hydrogel particles\(^{(121)}\) and liquid crystal particles\(^{(35)}\), the approach presented here is dramatically simplified and requires only a cross-linked particle capable of being physically strained to large degrees. Such smart particles can have exciting potential in applications of thermo-responsive composites and smart fluids with tunable rheological properties. Further, the constrained recovery with metal films offer a new approach to create smart, multifunctional Janus particles, with unique combinations of
contrasting properties including both topography and physical and chemical properties, which are promising for applications in catalysis, drug delivery, and magnetic biomarkers.\((122-124)\)

This work opens the door for several possible avenues of exploration. As mentioned above, solvent induced recovery has not been systematically investigated. Similar to the work here, an investigation of solvent based recovery would benefit from varying particle compression, film thickness during, and the duration that particles are exposed to solvent vapor. Recovery in a purge-able chamber would be necessary for this. Finally, the use of metal coatings on particles is also of future interest. Rather than using gold, magnetically responsive metals could be sputter-coated onto particles. It is possible then that magnetic fields could be applied to particles deployed in an aqueous solution to induce assembly, this would be particularly interesting in the case of the optically diffractive particles. Finally, how deployed shape memory particles could be used to alter the properties of solids and liquids is a very interesting question. Preliminary experiments examining how the viscosity of dimethyl sulfoxide/PS particle solution could be tuned by changing particle shapes from a disc to a sphere were unsuccessful. The particle concentration required to detect a difference in viscosity proved too large for us to achieve experimentally. If the nanoimprinting process could be scaled up significantly such experiments would become possible. In regards to modification of solids, however, what would happen if shape change was
induced in particles embedded in a matrix? Perhaps, if randomly distributed throughout the matrix they could produce a tunable surface roughness. If somehow oriented uniformly throughout the matrix, perhaps they could induce large-scale deformation. To run such experiments, a matrix with a modulus significantly below that of rubber PS particles would be needed. Given a low enough cross-linking density, PDMS films can be synthesized with a modulus on the order of 10’s of kPa, which might suffice.
2.2 Influences of Substrate Adhesion and Particle Size on the Shape Memory Effect of Model Microspheres

2.2.1 Overview

We have now demonstrated the ability of shape memory polymer particles to memorize and recover their permanent shapes after being deformed to high strain levels up to 90% via nanoimprint lithography. However, upon strain release only 70-90% of the pre-compression height was recovered in particles and the possible reasons for this beg for explanation. During NIL, both compression and recovery occur while particles are in a rubbery state above their $T_g$, and Johnson, Kendal, and Roberts (JKR), Derjaguin, Muller, and Toporov (DMT), as well as nanoparticle adhesion models have been used to investigate the contact mechanics between soft particles and rigid substrates, and results all emphasize the importance of both surface energies and particle size in these systems.(58–61) Since no experimental studies investigating the effects of particle size and substrate adhesion on shape memory particles have been performed, this section aims to address this gap in knowledge.

Provided here are the first experimental insights into the thermomechanical behavior of shape memory particles at different length scales, with varying work of adhesion, across large compressive strains. Specifically, we characterize how the size and strain levels of nano-imprinted particles affect their ability to recover permanent shapes after being programmed into flattened discs on different substrates. In situ
AFM measurements are performed to give time-sensitive insights into recovery kinetics and finite element models of elastic energy stored in particle networks are compared to adhesive energies between the particles and substrates to analyze experimental findings.

2.2.2 Methods

2.2.2.1 Particles

Two different cross-linked polystyrene (PS) particle solutions are used in this study all of which were dispersed in aqueous solutions upon acquisition. The larger PS particles have a 4.25 µm diameter and a 2% divinylbenzene (DVB) cross-linker (PS05N/5689, Bangs Laboratory Inc.). The smaller particles have a diameter of 200 nm and 3% DVB cross-linker (S37392, Life Technologies).

2.2.2.2 Programming Particles

PS particles were deposited onto flat silicon wafers by dipping the wafer into the respective aqueous solution and then drawing it out at 1 mm s\(^{-1}\). After deposition of particles some of substrates were then modified with a low-surface-energy, self-assembled monolayer (SAM) of CF\(_3\)(CF\(_2\))\(_5\)(CH\(_2\))\(_2\)SiCl\(_3\) (tridecafluoro-1,1,2,2-tetrahydroxydrolorosilane, Sigma-Aldrich) to modify adhesion between particles and substrate. Henceforth these modified surfaces will simply be referred to as SAMs surfaces. Particles were then compressed via nanoimprint lithography (NIL). In this case one of the two plates is the substrate upon which particles were deposited and the other plate is a silicon mold, which was first cleaned using piranha solution and then
coated with the same SAM previously mentioned. All NIL process were performed on a nanoimprinter (Eitre 3, Obducat) at 120 °C under a pressure of 1.5 MPa for 5 minutes. The NIL procedure used here is similar to that detailed in the previous section.(125) After this time period, the compressive force was maintained while the particles were cooled back to room temperature, at which point the pressure was relieved and the silicon mold was removed from the flattened particles. Annealing particles was also performed at 120 °C, for a period of one hour.

2.2.2.3 Finite Element Model of Compressed Sphere

An axisymmetric finite element model is established using ABAQUS to obtain the total elastic energy stored in different sized particles under different compressive strains. For simulation, four-node bilinear axisymmetric quadrilateral (CAX4) elements are used to discretize the geometry of polymer particle, and refined meshes were adopted to ensure the accuracy. The Young’s modulus and Poisson’s ratio are $E = 1.8$ MPa and $\nu = 0.49$ for the polymer particle. The silicon mold is considered to be rigid, since it’s much stiffer than the polymer particle and the deformation is negligible. “Hard contact” is implemented to simulate the interface between the silicon superstrate and the polymer particle. Finally, displacement boundary conditions are assigned to the rigid plate to apply different levels of compression.

2.2.2.4 Adhesive Energy Between Compressed Sphere and Substrates

Adhesive energy between particles and SiO$_x$ substrates was calculated by multiplying the work of adhesion, taken to be 21 mN/m as measured by Raegen et al,(126) by the contact area between the particle and the surface after programming. Work of
adhesion between polystyrene and the SAMs surface, however is not known. We approximate this value to be 2.1 mN/m since previous work has demonstrated that the surface energy of the SAM is known to be an order of magnitude lower than that of SiO$_x$.\textsuperscript{(127)} The adhesive contact area as a function of compressive strain is derived from work investigating the geometries of macroscopic, incompressible rubber spheres under compression.\textsuperscript{(90)} The macroscopic geometries are in good agreement with a subsequent, but less thorough, micro-scale particle compression study.\textsuperscript{(125)}

\textbf{2.2.3 Results and Discussion}

As we reported above, PS micro-particles an be highly compressed, yet recover their permanent shapes.\textsuperscript{(125)} A typical shape memory cycle consists of two primary stages: Programming a deformed (temporary) shape and recovering the original (permanent) shape. The two different sized PS particles studied here were lightly cross-linked with a DVB concentration of either 2 \% or 3 \%. With such a low concentration of crosslinker, the $T_g$ of the PS particles will be only slightly higher than that of the bulk PS, which is $\approx 100$ °C. Recent studies by Lu et al. showed that the $T_g$ of PS particles containing a larger, 10 \% DVB concentration was still less than 120 °C.\textsuperscript{(128)} For the smaller 0.2 μm particles free-surface chain mobility and substrate confinement effects may also have some effect on $T_g$, that is otherwise negligible in the larger particles.\textsuperscript{(129)} Nonetheless, both factors (low degree of crosslinking and the confinement effect) did not inhibit thermomechanical programming of the PS particles. Specifically, both particle sizes displayed rubbery-like behaviors and were easily deformed during the programming process at 120 °C. After removal of the superstrates
at room temperature both particles exhibited flattened programmed shapes. In the following, we describe the detailed analysis of the shape memory behaviors of both sizes of PS particles on both SiO$_x$ and F-SAM surfaces.

Figure 22 shows the temperature-dependent particle heights from in situ AFM scans as the programmed particles were heated from 90 °C to 130 °C at a slow temperature ramp of 0.5 °C/min. Before annealing, the 4.25 µm particles were programmed into flattened discs with a compressive strain $\varepsilon_p = \text{abs}(h - h_0)/h_0 \approx 0.77$, where $h$ and $h_0$ were the height of the programmed and undeformed PS particles (Fig. 22a), respectively. Detailed analysis of the shapes of the compressed PS particles confirmed that they behave similar to incompressible bulk elastomeric particles.(90) Therefore, in this report, we only use the heights of the particles as a sole quantitative measure of particle shape at different stages of the shape memory cycle.
Figure 22: Heights $h$ of the PS particles, normalized by the undeformed heights, $h_0$, as a function of temperature when annealed at a heating rate of 0.5 °C/min. A) and B) are data for the 4.25 µm and 0.2 µm PS particles, respectively. Filled and empty symbols correspond to the recovery of the PS particles on SiO$_x$ and F-SAM substrates, respectively.

No particle fracture or crazing was observed during the programming even for $\varepsilon_p > 0.90$, and PS particles were able to retain the programmed shape at temperatures
below 100 °C. Such high ductility of the PS particles was attributed to both the nature of compressive deformation and the low degree of crosslinking of the particles. He et al. reported that even at room temperature, 5 µm PS particles crosslinked with 2 % and 3 % DVB were able to plastically deform with compressive strains up to $\varepsilon_p = 0.8$. No fractures were observed for their particles, albeit some crazes were observed near the circumferences of the compressed particles.

As shown in Fig. 22a, the degree of recovery $h/h_0$ of the PS particles started to increase as temperature increased above 100 °C, driven by the entropic elastic energy stored in the deformed PS network. Between the SiO$_x$ and F-SAM substrates, the recovery of the larger PS particles was similar at the early stage. On both substrates, the temperature at the onset of recovery was between 102 °C and 104 °C, which coincides with the bulk $T_g$ of high molecular weight PS. The later stage of the particle recovery was distinctively different between the two substrates. On the F-SAM substrates, the 4.25 µm PS particle had recovered $h/h_0 \approx 0.7$ at 115 °C whereas $h/h_0 \approx 0.7$ was not achieved on the SiO$_x$ substrate until 130 °C. Furthermore, recovery on the F-SAM achieves a constant a value of $h/h_0 \approx 0.82$ at a temperature of 126 °C while the particle on the SiO$_x$ surface exhibited a gradual slowing of recovery, resulting in $h/h_0 \approx 0.70$ at the end of the experimental time window.
Figure 22b presents the recovery kinetics for the 0.2 µm PS particles on both substrates. Similar to the larger PS particle systems, the programmed particles were able to fix and retain their temporary shape (with $\varepsilon_p \approx 0.5$ at temperatures below 100 °C. However, the onset recovery temperature of the PS particles on the F-SAM substrate was ~3 °C lower than that on the SiO$_x$ surface. Note that the programmed 0.2 µm particles exhibit $h \approx 100$ nm, which is in the height-regime where a thickness-dependence of $T_g$ for PS films has been observed (132–136). Both the free surface of the PS and the repulsive interface between the F-SAM layer and the PS particle should cause reduction in the $T_g$ of PS. In comparison, on the SiO$_x$ surface, the free surface effect could be counter-balanced by the attractive interactions at the particle-substrate interface, which are known to increase $T_g$. As a result, the onset recovery temperature of the 0.2 µm particles on the SiO$_x$ surface appeared similar to that of the 4.25 µm particles (Fig. 22a). For the larger particles, the volume of near surface material expected to exhibit free-surface or confinement effects would be negligible resulting in no difference in onset temperature between substrates.

The recoveries of the 0.2 µm particles on both substrates quickly plateaued after reaching 110 °C. In comparison, the 4.25 µm particles on SiO$_x$ continued to recover even above 120 °C. The 0.2 µm particle on the F-SAM exhibited $h/h_0 \approx 0.75$, in comparison to $h/h_0 \approx 0.60$ on the SiO$_x$ surface. Based on these in situ recovery experiments, the particles initiated recovery at $\approx 100$ °C and reached steady state (or close
to) at 120 °C, a period of time that spanned 40 min. Accordingly, for the following experiment, we chose to examine particle recovery after annealing at 120 °C for 1 hr.

Figure 23 summarizes the experimental findings for degree of recovery in PS particles as a function of the compressive strain achieved after the thermomechanical programming process. During the programming process a 1.5 MPa pressure is applied to the superstrate and not to individual particles. Since the areal density of deposited particles varies after dip coating, a wide range of compressive strains is achieved in a single iteration. Each of the PS particles shown in Fig. 23 was characterized individually with the AFM.
Figure 23: Recovered PS particle heights, normalized by the heights of the undeformed particles, as a function of compressive strain exerted after thermomechanical programming, for a) 4.25 µm and b) 0.2 µm particle systems. Different symbols represent substrate surface chemistry (native oxide or F-SAM surface), as well as different annealing time (1 and 16 hr) used. The dotted line represents the expected trend if no particle recovery occurred after annealing.
On the SiO$_x$ substrates, the 4.25 µm particles with small compressive strains ($\varepsilon_p < 0.4$) recovered $\sim h/h_0 = 0.90$ of the original particle height after annealing (Fig. 23a). For particles with compressive strains $\varepsilon_p > 0.4$, a slight decrease of particle recovery with increase of compressive strain is observed ($m = -0.17$, the slope of a linear fit, $N = 17$). While the difference is slight, at larger compression ratios ($\varepsilon_p > 0.6$) the recovery of 4.25 µm on SiO$_x$ ceases to exhibit a clear dependency on compressive strain. Specifically, the PS particle with a compressive strain of $\varepsilon_p = 0.9$ recovered $h/h_0 = 0.74$ of the original particle height. In comparison, the recovered particle height on the F-SAM substrate ($h/h_0 = 0.86 \pm 0.02$, average ± standard deviation, $N = 13$) appeared independent of the compressive strain of the programmed particles. Increasing the annealing time from 1 hr to 16 hr indeed caused more recovery for the particles on the SiO$_x$ surface, consistent with observations in Fig. 22a. However, the recovered heights were still below that achieved on the F-SAM substrate. Additional annealing time for particles on the F-SAM substrate resulted in no change in recovery and therefore such data are not shown.

Figure 23b presents the results obtained for the 0.2 µm particles. On the F-SAM substrates, the recovered particle heights ($h/h_0 = 0.81 \pm 0.02$, $N = 16$) appeared independent of the compressive strain of the programmed particles, which is similar to that observed for the 4.25 µm particles, although the total recovery is slightly less. In stark contrast, the recovered particle heights on the SiO$_x$ surface dramatically decreased with increase of compressive strain, with $m = -1.36$ (the slope of a linear fit,
N = 19), which is 8 times greater compression-dependence than that observed for the 4.25 µm particles on the SiO\textsubscript{x} substrate.

Figure 24 presents side-view images of the recovered 4.25 µm and 0.2 µm PS particles on both SiO\textsubscript{x} and F-SAM substrates. In the 4.25 µm particle systems, a very small, yet highly deformed necking shape appears at the point where the particle edge contacts the substrate (marked by the arrows in Fig. 24). Using the mid-points of the neck in the SEM images, the local contact angles between the PS particle and the SiO\textsubscript{x} substrate were approximately 29° ± 6° (N = 5) for the 4.25 µm particles. The residual contact, represented by the ratio between the contact radius \(a\) and the particle diameter (2\(R\)), \(a/2R \approx 1.10\) for the 4.25 µm particles. In comparison, no neck formation was observed for the 4.25 µm particles on the F-SAM surfaces. The contact angle was measured to be 130° ± 7° (N = 5), which is significantly larger than that on the SiO\textsubscript{x} surface. The residual contact of the recovered particle was \(a/2R \approx 0.54\), much smaller than that on the SiO\textsubscript{x} surface. However, since the neck accounts for only a very small portion of the particles’ volume, the recovered particle heights on both substrates do not differ significantly. For the 0.2 µm particles, no clear neck was observed on either SiO\textsubscript{x} or F-SAM surfaces. Quantitatively, the contact angles were measured to be 58 ± 3° (N=5) on the SiO\textsubscript{x} surface and 87 ± 1° (N = 5) on the F-SAM surface, with corresponding residual contact of \(a/2R \approx 1.54\) and \(a/2R \approx 1.13\), respectively.
Figure 24: Side-view SEM images of recovered 4.25 and 0.2 µm particles, taken at 90° and 80° angles, respectively. The inset shows the magnified view of the necking area including the profile of the 0.2 µm particles.

The above experimental findings indicate that the size of the particles and the contact adhesion between the substrate and the PS particles significantly affect the recovered particle heights and shapes. Understanding this behavior requires analysis of the interplay between adhesion and elastic energy. Adhesion energy will be predicted using the Johnson-Kendall-Roberts (JKR) theory. The JKR theory was derived for infinitesimal deformations (δ<<R), but has been experimentally shown to be
quite accurate for moderate deformations as well.\(^{(137, 138)}\) Elastic energy will then be estimated from finite element analysis of the deforming particles.

According to JKR, even if the particle is not under any compressive loading, adhesive interaction can still deform the particle and establish an equilibrium contact area. The relation between compressive force \(P\), contact area \(a\), and work of adhesion \(\gamma\) is:\(^{(58)}\)

\[
\left( P - \frac{4E^*a^3}{3R} \right)^2 = 16\pi\gamma E^*a^3 \tag{2.2-1}
\]

where \(E^* = E/(1 - \nu^2)\), \(E\) is the Young’s modulus and \(\nu\) is the Poisson’s ratio. When the compressive force \(P\) is zero, we have

\[
a^3 = \frac{9\pi R^2}{E^*} \tag{2.2-2}
\]

The indentation depth of the particle \(\delta\) (reduction in particle height due to adhesion) is given by

\[
\delta = \frac{a^2}{R} - \sqrt{\frac{4\gamma a}{E^*}} \tag{2.2-3}
\]

In terms of \(\delta\), the recovery ratio may be defined as

\[
\frac{h}{h_0} = 1 - \frac{\delta}{2R} \tag{2.2-4}
\]

By substituting Eq 2 into Eq 3, and rearranging, Eq 4 becomes
\[
\frac{h}{h_0} = 1 - \left(\frac{1}{2}\right) \left(\frac{3\pi \gamma^2}{E\nu^2 R^2}\right)^{1/3}
\]  

Eq (5) shows that the equilibrium recovered particle height decreases with decreasing particle size. Furthermore, Eq (5) allows us to estimate the particle height recovery. The work of adhesion \(\gamma\) depends strongly on the temperature, separation rate, and material properties, and ranges over 3-4 orders of magnitude.\((139, 140)\) The lowest bound for the value of \(\gamma\) is the thermodynamic work of adhesion \(\gamma_0\). The value of \(\gamma_0\) does not account for viscoelastic dissipation during the separation and is often directly estimated from the Young’s equation. Using the known value of \(\gamma_0 = 21 \text{ mJ/m}^2\) for the PS on SiO\(_x\) contact \((126)\), \(E = 1.8 \text{ MPa}\) for lightly crosslinked PS and \(\nu = 0.49\), we calculate \(h/h_0 = 0.97\) for the 4.25 µm PS particles, which is significantly higher than that observed experimentally (average: \(h/h_0 = 0.82\) for all the particles shown in Fig. 23a). This suggests that thermodynamic adhesion alone is not able to explain the observed recovery ratios.

In addition, Eq. (5) implies that the recovery ratio is independent of the initial compression, which is inconsistent with our experimental data in Fig. 23. To explain this discrepancy, we first introduce the phenomenon of adhesion hysteresis existing in a wide range of adhesion systems.\((141–143)\) This means that the work required to separate two contacting surfaces is larger than the work gained by bringing them into contact. As a result, the work of adhesion during recovery can be significantly
larger than that during initial compression. This leads to two possible regimes for adhesion during recovery. First, if the initial compressive strain is small, the elastic energy is not sufficient to drive detachment and thus contact area is “locked” in place by adhesion. This situation can be described by an inequality that $G < \gamma_{e}$, where $G$ is the energetic driving force for contact detachment due to elasticity, also known as the energy release rate in the literature. In this regime, larger initial compressive strain leads to a larger final contact area and thus smaller recovery ratio. Second, if the initial compressive strain is sufficiently large, elasticity is able to drive detachment at the beginning of the recovery stage. As the contacting surface is being detached, the driving force $G$ decreases. Eventually the detachment stops when $G = \gamma_{e}$. In this regime, the final contact area, and hence the recovery ratio, is independent of the initial compressive strain. Transition between the two regimes depends the competition between elasticity and adhesion. For the F-SAM substrate, the second regime is observed for both particle sizes due to the relatively small adhesion. For the SiO$_x$ substrate, the first regime is observed for the 0.2 m particles, while for the 4.25 m particles, the first regime transitions to the second one at compressive strain $\sim$ 60% which is also evidenced by the data with 16 hours of annealing time. Eq. (5) is based on the implicit assumption of $G = \gamma_{e}$, or the second regime.

Accordingly, using the experimentally observed recovery ratio, the effective work of adhesion, $\gamma_{e}$, during the recovery of PS from the substrate can be extracted using Eq. (5) and is listed in Table 1. For the F-SAM substrate, the recovered heights were independent of the compressive strain for both sized particles, and the $\gamma_{e}$ were
estimated to be ~15 mJ/m² for the 0.2 µm PS particles in comparison to ~200 mJ/m² for the 4.25 µm PS particles. For particles on the SiOₓ surface, the recovery ratio depends on the compressive strain as discussed above. The γₑ calculated using Eq. (5) should be interpreted as the lower bound of the actual work of adhesion. For the 0.2 µm particles, γₑ increased with increasing compressive strain from 3 mJ/m² to 57 mJ/m², and we therefore conclude that the actual work of adhesion is greater than or equal to 57 mJ/m². For 4.25 µm particles, since the second regime, discussed above, is reached for compressive strains εₓ > 0.6, the work of adhesion is found to be 500 mJ/m² and is interpreted as the true value rather than a lower bound. The comparisons show that the γₑ for “peeling” the PS particles from both SiOₓ and F-SAM surface increases with increase of particle size, which can be attributed to the viscoelastic dissipation within the PS particle volume near the moving contact region during recovery. Larger particle volumes are expected to dissipate more energy.

<table>
<thead>
<tr>
<th>Particle size (nm)</th>
<th>SiOₓ surface (mJ/m²)</th>
<th>F-SAM surface (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.25 µm</td>
<td>500</td>
<td>200</td>
</tr>
<tr>
<td>0.2 µm</td>
<td>≥ 57</td>
<td>15</td>
</tr>
</tbody>
</table>

Table 1: Effective adhesion energy, γₑ, on different substrates
Even though $\gamma_e$ is greater in larger particles, a steeper compression-dependence was observed in the smaller particles (Fig. 23b) relative to their larger counterparts (Fig. 23a) on SiO$_x$. While adhesion serves to inhibit separation of the particle and substrate, it is the entropic elasticity stored in the compressed particles, which drives particle recovery. Figure 25 presents the total elastic energy stored in the deformed PS particles, in comparison to the total adhesion energy for both PS particles on the two different substrates. The elastic energy was obtained from finite element analysis (FEA), assuming linear elasticity. The modeled elastic energy density was $\sim 0.35$ MJ/m$^3$ for both particles at $\varepsilon = 0.60$. For comparison, it was reported elsewhere that the elastic energy density stored in a lightly-crosslinked, cylindrical PS sample was $\sim 0.3$ MJ/m$^3$ at $\varepsilon = 0.72$.(144)

For comparison, the total adhesion energy was estimated according to $W_0 = \gamma A$, where $A$ is the contact area. Using $\gamma_0$, the lower bound value of $W_0$ can be estimated. As mentioned, $\gamma_0 \approx 21$ mN/m$^2$ for the PS on SiO$_x$ contact (126), but is unknown for PS on F-SAM. Probe-based measurements showed that $\gamma_0$ between Si and fluorinated SAM was measured to be $\sim 3.2$ mN/m$^2$.(145) Here, based on the order-of-magnitude difference in free energies of SiO$_x$ and F-SAM surfaces(127), we assumed $\gamma_0 = 2.1$ mN/m$^2$ for the PS/F-SAM contact. The contact areas were calculated according to the relationship between the lateral extension and compressive strain for a typical incompressible rubber particles.(90)
Figure 25: Elastic energy, and total adhesion energy for the A) 4.25 µm and B) 0.2 µm PS particles at different compressive strain magnitude on both the SiOx and F-SAM substrates.

Figure 25a shows that for the 4.25 µm particles with varying compressive strains, the total elastic energy stored in the deformed particles was dramatically larger than total adhesion energy. As a result, the deformed particles were able to
“peel” themselves by overcoming the adhesive contact with the SiOₓ or F-SAM surfaces. During such a particle recovery process, dissipation of energy within the vicinity of the moving contact lines was expected to occur, giving rise to the observed γₑ for both substrates, which is an order of magnitude higher than γ₀.

In contrast to the 4.25 µm particles, for the 0.2 µm particles on the SiOₓ surface, W₀ becomes larger than the elastic energy stored in the deformed particles (Fig. 25b) across the different compressive strains studied. This suggests that on SiOₓ surfaces, the stored energy is insufficient to overcome the adhesive contact between the compressed PS particles and the substrate. As a result, the degree of recovery dramatically reduces with the increase of compressive strain. Only a small recovery of the particle height was observed due to the shape relaxation at the top surface of the particles (Fig. 24b). In comparison, W₀ of the PS on F-SAM contact remained lower than the stored elastic energy, allowing particle recovery.

Note that both the elastic energy and W₀ presented in Fig. 25 are underestimated. For example, according to Tatara’s estimate, the secant Young’s modulus would increase 7 times, as the compressive strain increases to 0.7.(110) Table 1 also indicates that effective work of adhesion, γₑ, would be ~ 10 times higher than that of γ₀ used in Fig. 25. Nevertheless, Fig. 25 unambiguously shows that there are size-dependent regimes governing the recovery of particles. At even smaller length-scales surface tension could begin to affect recovery and would need to be included in the
model. However, surface tension is not expected to affect recovery in these systems as the particle sizes investigated are much larger than the elasto-capillary length (\(\gamma/E \approx 10 \text{ nm for PS}\)).(146)

In conclusion, the influence of compressive strain, substrate surface energy, and particle size on the shape memory cycle of polystyrene particles has been investigated here. Results reveal that the influence of substrate adhesion on particle recovery is size-dependent, and can become dominant at sub-micron length scales. Shape recovery on high-energy surfaces exhibits a dependence on compressive strain and this effect is more pronounced as particle size is reduced from 4.25 \(\mu\text{m}\) to 0.2 \(\mu\text{m}\). FEA models corroborate a size-dependent effect, suggesting that while elastic energy tends to dominate in the presence of high strain levels in the larger particles, the difference between elastic and total adhesion energy becomes negligible at smaller length scales across the compressive strains investigated here. Particles recovering on fluorinated self-assembled monolayer surfaces quickly reach a plateau in height and exhibit no dependency on pre strain. In situ AFM scans of the 0.2 \(\mu\text{m}\) particles further suggest that confinement effects may influence the \(T_g\) of compressed particles at this length scale. Small particles on the F-SAM substrate exhibit a slight depression in the temperature at which recovery initiates compared to the SiO\textsubscript{x} surface. Side profile images of recovered particles were also obtained via SEM, allowing for contact angles and contact areas to be measured. We find systematically larger con-
tact angles in particles recovered on F-SAM surfaces. From the contact areas, effective work of adhesion is calculated and compared to predicted thermodynamic work of adhesion. Experimentally measured work of adhesion is consistently larger than predicted adhesion, indicating that a significant amount of energy dissipation occurs during the peeling process.

Many questions remain about the adhesive interactions between polymer particles and substrates. In this study, two very different surface energies were examined here, but measuring recovery on a set of surfaces with incrementally varied surface energies would be interesting. Carboxylic acid – capped silanes with different chain lengths are commercially available, which could be used to fabricate SAM-coated substrates with very small changes in surface energies. Furthermore, these SAMs could further be coupled with colloidal probe AFM measurements, providing direct measurements of particle – substrate adhesion. This would be very interesting since not only have the adhesive forces not been directly measured for these systems, but the effects of strain rate on particle-substrate interactions remains unknown.
Chapter 3: Investigations of Shape Reconfiguration in Polymer Particles

3.1 Reconfiguration of Film Surface Topologies

3.1.1 Overview

The major limitation of shape memory systems is that they always store a fixed, un-tunable amount of elastic energy for any given deformation and upon release of this energy, particles always attempt to recover their original shape. Upon exposure to a favorable solvent or when heated above their $T_g$, the temporary shape is lost. While shape memory polymers are able to undergo large deformations in their rubbery state and small deformations on the order of a few percent in their glassy, in both cases the deformation is elastic and plastic deformation is typically not achieved without fracturing the polymer. Recent advances in polymer chemistry have led to a class of novel polymer networks that are capable of relaxing internal stress by breaking and reforming network bonding, which allows them to reconfigure their permanent shapes while remaining crosslinked.\(^{(82, 147, 148)}\) These so-called covalent adaptive network (CAN) polymers possess the properties of malleability,\(^{(68)}\) recyclability,\(^{(80)}\) and self-healing capability,\(^{(73, 76, 77)}\) all of which were impossible for the conventional crosslinked polymers. The corresponding chemical reaction mechanisms enabling these CANs include Diels-Alder,\(^{(149, 150)}\) transesterification,\(^{(64)}\) reversible addition-fragmentation chain transfer (RAFT) reactions,\(^{(68, 69, 72, 151)}\) and very recently a one-step nitroxide-mediated polymerization.\(^{(152)}\) The RAFT-based
CANs are especially attractive because the network rearrangement process can be initiated with UV light, which allows precise spatial and temporal control of the stress relaxation in the polymer network.\(^{(82)}\)

Prior to this work, investigations of stress-relaxation in RAFT materials have been limited to macroscopic deformations, leaving many unexplored questions about how stress-relaxation behavior changes with length scale. At the time of this study we had not yet incorporated RAFT networks into particle systems and, as per Aim 2, we begin our investigation here by characterizing the ability of bulk, RAFT networks to conform to sub-micron scale surface topologies via nanoimprint lithography. The effects that different imprinting parameters and material properties have on the achievable surface pattern geometries are investigated, and we provide the first demonstration of permanent sub-micron surface reconfiguration on crosslinked polymers, which exhibit features orders of magnitude smaller in size than any previously published.

### 3.1.2 Methods

#### 3.1.2.1 Material System

Polymer networks were formed using a base catalyzed thiol-Michael “click” reaction using a 1:1 stoichiometric ratio of thiol to acrylate functional groups. The thiol used was trimethylolpropane tris(3-mercaptopropionate) (TMPTMP) and the two different acrylates used were tetra(ethylene glycol) diacrylate (TEGDA). The RAFT di-
acrylate used (2-methylene-propane-1,3-bis(thioethyl acrylate)) (MBTA) was synthesized according to previous work.\textsuperscript{(81)} Chemical structures of the three monomers used are shown in Figure 26. The two acrylates were combined with the RAFT monomer (i.e., MBTA) comprising 100%, 75%, 50%, or 0% of the acrylate mixture in four separate samples referred to as RAFT 100, RAFT 75, RAFT 50, and RAFT 0, respectively. The thiol-Michael addition polymerization was catalyzed using 0.6 wt% triethylamine while the subsequent network rearrangement mediated by the RAFT moiety was catalyzed using 2 wt% 2,2-dimethoxy-2-phenylacetophenone (DMPA, Irgacure 651). In order to reintroduce the DMPA initiator into the network after its exhaustion during imprinting, a sample was soaked in a 3% DMPA/acetone solution for 12 h and then placed in a vacuum oven for 2 h at 50 °C to dry.
**Figure 26:** Monomers and the initiator used to create the polymer networks.

### 3.1.2.2 Dynamic Mechanical Analysis

The elastic modulus of each material was obtained via dynamic mechanical analysis (DMA, DMA Q800, TA Instruments) with a film-tension clamping geometry, and the values are summarized in Table 2. Specimens were cut into rectangular shapes with dimensions of approximately 0.2 mm thick, 2 mm wide, and 12–15 mm
long, then subjected to controlled strain amplitudes of 0.1% at a frequency of 10 Hz and a temperature of 50 °C, which is the temperature adopted during the network reconfiguration under NIL conditions as described below. These measurements were performed five times for each material and the average moduli with associated standard deviation of these measurements are reported. Previous work has shown that the network modulus remained similar before and after the RAFT-induced network re-arrangement. The RAFT 100 material was then subjected to the same strain amplitude and frequency while the temperature was ramped from −50 °C to 50 °C at a rate of 3 °C per minute. The temperature corresponding to the maximum of the tan(δ) peak is used to identify the $T_g$ of the samples.

Table 2 Modulus dependency on RAFT agent, determined from DMA measurements at 50 °C.

<table>
<thead>
<tr>
<th>RAFT agent</th>
<th>100%</th>
<th>75%</th>
<th>50%</th>
<th>0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus, MPa</td>
<td>3.0 ± 0.9</td>
<td>3.3 ± 1.8</td>
<td>6.5 ± 1.3</td>
<td>5.0 ± 3.8</td>
</tr>
</tbody>
</table>

### 3.1.2.3 Finite Element Analysis

Finite element analysis (FEA) was performed using ABAQUS to study the deformation of the CANs with different Young’s modulus under constant external pressures. Due to the periodic nature of the surface patterns, a unit cell with periodic boundary conditions is adopted for the simulation. At the silicon mold–polymer in-
terface, a “hard contact” condition is defined, and a constant external pressure is applied at the bottom surface of the polymer substrate. The polymer substrate \( E \) (Young’s modulus) = 3.0, 3.3, 6.5 MPa, Poisson’s ratio = 0.48) and the top silicon mold \( E = 130 \) GPa, Poisson’s ratio = 0.27) are discretized by 4-node plane strain elements (CPE4).

### 3.1.3 Results and Discussion

The NIL process used in this study to pattern the CAN polymers is schematically illustrated in Fig. 27. While in their rubbery state, the polymers were brought into contact with a patterned Si mold (the cross-sectional profile of the pattern is shown in Fig. 28), a normal pressure was then applied to the samples, and a UV lamp was turned on for controlled durations, after which the samples were separated from the mold upon pressure release. As shown in Figure 27, the CANs were exposed to UV light through the PET substrate side, as the Si mold is non-transparent for the UV light.

![Figure 27: Schematic illustration of the imprinting process where a CAN polymer is compressed and exposed to UV irradiation.](image)

Figure 27: Schematic illustration of the imprinting process where a CAN polymer is compressed and exposed to UV irradiation.
Traditionally, fixing a pattern on the surface of a cross-linked polymer necessitates heating the material above its $T_g$, deforming the material, and then cooling it below $T_g$ to freeze the elastically deformed network. As a result, a surface pattern is formed but it is only a temporary structure and the deformation is reversed when the material is heated above $T_g$ or exposed to a favorable solvent, thereby recovering its permanent shape.\(^{(49,125)}\)

The $T_g$ of the RAFT 100 polymer used in this study is -19 °C, determined from DMA measurements. Accordingly, when the pressure was first applied during NIL, the rubbery polymers underwent a large elastic deformation. Since the elastic deformations could not be observed \textit{in situ}, we developed an FEA model to illustrate them instead. For example, the deformation of the RAFT 100, with a 3 MPa Young’s modulus, under a 2 MPa imprinting pressure is shown in Figure 28.
Figure 28: FEA simulation of the elastic deformation of the RAFT 100 material, occurring under a 2 MPa pressure without UV exposure. $S_{22}$ is the normal stress in the vertical direction, and the unit of stress is MPa.

The elastic deformation of this polymer filled over half of the mold cavity, reaching a pattern height of 115 nm at its highest point but did not contact the top of the mold cavity. The elastically deformed polymer indeed contacted both sidewalls near the bottom of the mold cavity, leading to a highly non-uniform stress field. If UV radiation was not applied during the NIL process, all the elastic deformation of the RAFT 100 shown in Figure 28 would be completely recovered upon pressure release. As a result, no surface patterns would be achieved after the NIL process, which was indeed observed experimentally for the RAFT 100 sample with complete recovery of the initial shape in the absence of light exposure (image not shown).
Though reversible, this initial elastic deformation is important for the subsequent photoplasticity, since it governs the initial stress state in the deformed CANs and thus directly affects the final pattern formed. More specifically, upon UV radiation, the radical-mediated RAFT reaction occurs throughout the polymer and leads to bond exchange, stress relaxation and photo-plastic flow.\textsuperscript{(153, 154)} Figure 29 shows the cross-sectional profiles of the obtained surface patterns, from AFM measurements, on RAFT 100 samples that were subjected to UV exposure for varying durations during the NIL process.

![Cross-sectional profiles](image)

**Figure 29**: Cross-sectional profiles (from AFM measurements) of the surface patterns obtained on the RAFT 100 polymer, after UV exposure with varying duration as marked on the graph, under a pressure of 2 MPa.
Permanent patterns were clearly achieved on the surface of the rubbery RAFT 100 samples even after UV exposures of as short as 20 s. The pattern heights increased with increase of UV exposure times. Evidently, with increasing UV exposure, a greater degree of permanent deformation was achieved via the RAFT-mediated photoplasticity. Interestingly, the final pattern height achieved after 15 min of UV radiation was \(~ 120\) nm, which is slightly larger than the bulging height of the elastic deformation occurring prior to UV exposure (Figure 28). This indicates that during imprinting and exposure the material perhaps crept further into the mold cavity. The final pattern height, extracted from Figure 29, as a function of the UV radiation time is summarized in Figure 30C.
Figure 30: (A, B) The stress profiles of elastically deformed RAFT 100 material under imprinting pressures of 0.8 MPa and 7 MPa, respectively. In both figures, $S_{22}$ is the normal stress in the vertical direction, and the unit of stress in the legends is MPa. (C) The final pattern heights after the NIL process, from AFM measurements, as a function of UV exposure time under varying imprinting pressures.
Clearly, the initial deformation of the polymer being imprinted is controlled by both material properties and the imprinting pressure. Fig. 30A–B shows that the elastic deformation within the mold cavity of the RAFT 100 samples at 0.8 MPa and 7 MPa, which represent the lower and upper bounds of the pressure range of our nanoimprinter. Under a pressure of 0.8 MPa, the height of the elastically deformed polymer bulged less than halfway into the mold cavity (Figure 30A), noticeably smaller than that observed under a 2 MPa pressure (Figure 28). As the pressure increased to 7 MPa, the RAFT 100 polymer completely filled the mold cavity, even at the two upper sharp corners, where the polymer displayed the highest stress with non-uniform stress fields.

Figure 30C summarizes the heights of the final imprinted patterns on RAFT 100 as a function of UV exposure time under imprinting pressure of 0.8 MPa and 7 MPa. Similar to that observed under a 2 MPa pressure, the final pattern height obtained under both 0.8 MPa and 7 MPa increased with an increase of the UV exposure time (Figure 29C). For all three pressures, the pattern heights approached asymptotic values after 5–15 min of UV exposure, likely due to consumption of the initiator. After 15 min of imprinting and UV exposure at 2 MPa and 7 MPa, the final pattern heights reached over 90% of the depth of the mold cavity, exhibiting an excellent degree of photo-induced plasticity at this small length scale. Such a time-dependence of pattern reconfiguration is qualitatively similar to that observed in bulk samples.(68)
The difference between the final pattern heights obtained under the varying pressures, however, were not as large as that of the bulging heights during initial elastic deformation (Figures 28 and 30A–B). This discrepancy is mostly attributed to the fact that the photo-induced plasticity of the RAFT 100 under a pressure was a combination of stress relaxation and creep. When the elastically deformed RAFT 100 completely filled the mold cavity, no creep could occur due to the confinement of the cavity walls. Upon UV-initiated RAFT process, stress relaxation occurred within the network resulting in permanent deformations, which increased with UV exposure time but never achieved 100%.(68) The pattern reconfiguration of the RAFT 100 under a 7 MPa pressure clearly falls into this scenario. In stark contrast, when there was not a large degree of cavity confinement, such as in the case of the RAFT 100 under smaller pressures (Figures 30A and 28), appreciable creep could occur during the UV-initiated network reconfigurations, which resulted in pattern heights that were taller than the initial elastic deformation.

Previous work, however, has shown that at the macro-scale the degree of stress relaxation achievable in RAFT-materials is highly dependent on the amount of the RAFT agent present in the polymer network.(68) Accordingly, we synthesized materials with various degrees of the RAFT agent present and compared their capabilities in terms of pattern reconfiguration during similar NIL process. Figure 31 summarizes the cross-sectional profiles of the final patterns obtained for all 4 samples after
15 min of UV exposure under a 2 MPa pressure. When no RAFT agent was present in the polymer (RAFT 0, images not shown), no surface patterns were observed after NIL, again confirming that the RAFT process was exclusively responsible for the plasticity/permanent deformation in these network polymers.

Under the same NIL process conditions, the final pattern heights increased with the concentration of RAFT agents present in the materials. Specifically, the RAFT 75 and RAFT 50 samples displayed pattern heights that were 81 and 68% of that achieved by the RAFT 100 sample, respectively. These differences in patterns

Figure 31: Cross-sectional profiles (from AFM measurements) of the final patterns obtained after NIL process for 15 min for samples containing different RAFT concentrations. The pressure used was 2 MPa.

Under the same NIL process conditions, the final pattern heights increased with the concentration of RAFT agents present in the materials. Specifically, the RAFT 75 and RAFT 50 samples displayed pattern heights that were 81 and 68% of that achieved by the RAFT 100 sample, respectively. These differences in patterns
can be attributed to changes in both differing moduli and the degree of photoplasticity with changes in RAFT contents. Further interpretation of the differences observed in Figure 31 requires better knowledge of the nature of the transient, coupling responses between chemical reaction and mechanical deformation.

While some CANs, such as those incorporating thermoreversible Diels–Alder bonds in the network, do not rely on free radicals to initiate bond exchange, RAFT-based systems do and can reconfigure their network only when and where free radicals are present in the network. Accordingly, the surface patterns on these materials can be reconfigured multiple times as long as the photoinitiators remain present in the sample. For example, a RAFT 100 sample, exhibiting a large surface pattern (~120 nm, created after 15 min of imprinting/UV exposure, Figure 32) was soaked in an acetone solution containing 3 wt% DMPA to replenish some of the photoinitiator consumed during the initial exposure. This is a diffusion-controlled process and the DMPA concentration in the center of the 0.2 mm thick sample after 12 h of soaking reaches 2.74 wt%, assuming a diffusion coefficient ~10⁻⁷ cm²/s. (155) Furthermore, nanoimprinting primarily deforms the materials' surface and the DMPA concentration at a depth of 200 nm from the surface reaches 2.99 wt% after 12 h of soaking. Accordingly, the RAFT process during the second network rearrangement should be able to achieve similar degrees of stress-relaxation as the first time.
After completely drying, the sample was then subjected to a second round of NIL with UV exposure under a pressure of 2 MPa, using a flat Si wafer as the mold. As shown in Figure 32, after a second 15 min imprinting, the surface patterns were reduced from ∼120 nm to ∼5 nm, showing the ability of the RAFT 100 to reconfigure the surface pattern for the 2nd time with the initiators replenished. Once again, this residual, small-scale surface pattern was a result of the material's inability to completely relieve 100% of all internal stresses, as discussed earlier. It is worth emphasizing that the flat and patterned surfaces achieved throughout the two consecutive NIL/UV exposure processes are both permanent shapes, achieved in rubbery polymers.
Figure 32: Cross-sectional profiles of the surface pattern of the RAFT 100 sample obtained after 15 min under 2 MPa, imprinted with a Si mold; and that obtained after a 2nd NIL process under 2 MPa with a flat wafer. Prior to the second imprint, initiators in the RAFT 100 were replenished (see experimental for details).

In summary, we demonstrate that permanent reconfiguration of surface patterns on CANs can be achieved using a UV-assisted NIL process. Upon initial contact, the polymers elastically deform into the mold cavities, which can be transformed into permanent deformation during the UV-initiated RAFT process. Depending on whether or not complete cavity filling is achieved during the initial deformation, photoplasticity occurs via stress relaxation or creep during the network reconfiguration. By controlling the imprinting pressure, material properties of the CANs (e.g., the concentration of RAFT agents and the modulus), and UV exposure time, the geometry
of the permanent pattern can thus be controlled. The features generated by NIL are three orders of magnitude smaller than previous work utilizing a photomask.\(^{(81)}\) The combination of NIL and CANs can thus reconfigure surface patterns at length scales that are principally not limited by the diffraction of light. Accordingly, RAFT-based micro- and nano-particles should be able to exploit this network reconfiguration to selectively relieve stress in programmed particles for very fine control over the degree of achievable recovery.

The results presented in this section were done using commercial silicon molds. Given greater time as well as resources, the pattern shape used to imprint the films could be varied to create a wide spectrum of interesting topographies. Particularly interesting would be a project investigating the degree to which the mold height is fixed as a function of length scale. If imprinting was done using molds etched with line-space grating patterns whose geometries were on the order of 10's of nanometers, rather than 100's, changes in surface reconfiguration could be investigated at feature sizes nearing the elasto-capillary length scale of the film material (\(~ 10 \text{ nm}\)).
3.2 Permanent Shape Reconfiguration of Polymer Microparticles

3.2.1 Overview

As previously mentioned, shape memory particles are but one example of the broader class of ‘smart’ particles, also including volume-phase transition hydrogels and liquid crystal particles, which can temporarily alter their geometry given certain environmental stimulus. Since only spherical particle geometries are obtained in emulsion polymerization procedures, shape memory and liquid crystal particles are uniquely interesting since they present particle systems that may conform to non-spherical geometries. These geometries are not stable, however, when heated above their respective glass and nematic transition temperatures both particle systems revert back to their permanent spherical shape. In the previous report we demonstrated the ability of a CAN film using the RAFT mechanism to dissipate elastic energy via photoplastic deformation to permanently fix nano-scale surface patterns. Encouraged by this ability to fix such small deformations we now synthesize and characterize particles capable of this RAFT process. Here we demonstrate the large-degree, permanent shape reconfigurations of crosslinked polymer microspheres. By combining a novel CAN chemistry with UV-based nanoimprint lithography (UV-NIL), as-synthesized CAN microspheres were reconfigured into a series of oblate-ellipsoidal particles. These reconfigured, non-spherical particles were at their rubbery states, i.e. at their minimum energy state without any memory effect. Specifically, we use spac-
ers to impose controlled elastic strains on particles during NIL and measure the
degree to which the imposed elastic strain is fixed. Spacer size and imprinting duration
are both varied to investigate the rates and degree of photoplasticity achieved in these
systems.

3.2.2 Methods

3.2.2.1 Particle Synthesis

Figure 33 describes the chemical compositions of the network and correspond-
ing RAFT-based bond-exchange mechanism. The RAFT-based microspheres (Fig.
33a) were synthesized using a solution-based polymerization process. We used a base
catalyzed thiol-Michael “click” reaction with a 1:1 stoichiometric ratio of thiol to acry-
late functional groups. The thiol used was pentaerythritol tetrakis(3-mercaptopropi-
onate) (PETMP) and the two different acrylates used were tetra(ethylene glycol) di-
acrylate (TEGDA) and diacrylate (2-methylene-propane-1,3-bis(thioethyl acrylate)
(MBTA) (Fig. 33c). MBTA was the RAFT-agent and was synthesized according to
literature.(81) The molar ratio of the acrylate groups between TEGDA and MBTA is
1:1, i.e. 50% of the network points contain an active site for the RAFT process, while
50% of network points are permanent. The thiol-Michael addition polymerization
was catalyzed using 0.6 wt% triethylamine while the subsequent network rearrange-
ment mediated by the RAFT moiety was initiated using Irgacure 651. Infrared spec-
troscopy (IR, Thermo Scientific, Nicolet 6700) measurements were performed on the
CAN particles. From the spectrum, no monomers remained in the particles and that
the bond-exchanging allyl sulfide compound contained in the MBTA monomer had
been successfully integrated into the network. This confirms that particle networks are fully polymerized and able to undergo the RAFT process. The diameter of as-synthesized, dry CAN particles was 3.1 ± 0.3 μm (N = 30), according to the AFM measurements.
Figure 33: a) SEM image of an as-prepared CAN microsphere and an illustration of different components in the network structure. b) Illustration of the RAFT-based bond exchange process. c) Chemical formula of the monomers, crosslinkers including RAFT-agent containing monomer, and photoinitiator used in the synthesis of the CAN particles.
Fig. 33b illustrates the photo-induced network rearrangement process used in our CAN particles. Upon irradiation with UV light, the initiators dispersed in the network dissociate into free radicals. The radicals then react with a RAFT agent (e.g. the allyl sulfide groups in MBTA, Fig. 33c) on the polymer backbone, which breaks a network connection and generate radicals that are attached to the chains. The chain radicals can react with the remaining allyl sulfide groups on the network through the RAFT process. Through such repeated cleavage and reformation of the polymer backbones, the network topology is rearranged, during which the internal stress is relaxed. At the macroscopic level, the sample is permanently deformed, but the overall network crosslinking density remains unchanged.

3.2.2.2 Nanoimprint Lithography

The particle shape reconfiguration process was carried out using a UV-NIL process, as schematically illustrated in Fig. 34. The CAN microspheres were deposited onto a Si wafer (containing a native oxide layer) using a dip-coating process. Different-sized silica particles were co-deposited and functioned as spacers during the UV-NIL process. A transparent, untreated glass slide with a surface roughness of approximately 5 nm was used as superstrate to apply a compressive loading on the particles while allowing UV (300-400 nm at an intensity of 20 mW/cm²) penetration. In this work, the applied pressure was fixed at 3 MPa, but the true pressure on each particle should be significantly higher because the surface coverage of the particles was less than 10%. For this reason, silica spacers were used to precisely control the
degree of deformation, i.e. a true stress relaxation experiment under compressive loading. After certain amount of UV-irradiation time, the pressure was released and the resultant particle shapes were characterized.

![Figure 34: Schematic illustration of the particle shape reconfiguration using UV-NIL process.](image)

### 3.2.3 Results and Discussion

We first characterized the thermo-mechanical properties of individual CAN particles with an AFM-indentation measurement. As shown in Fig. 35a, from the force-displacement curve, the elastic modulus of the CAN particles at room temperature was estimated to be 10 MPa, suggesting that $T_g$ of the particles is well below room temperature. To obtain reliable probe measurements, a specialized tip (Team Nanotech HSC60 225C3/MC/R) with a highly uniform, 60 nm radius of curvature tip was used for the indentation curves. To further verify these findings, we prepared bulk polymer films using a similar chemical composition as that of the CAN particles. From DMA measurements shown in Fig. 35c, the $T_g$ of the as-prepared CAN film was -15 °C and the room-temperature modulus was 5 MPa, which agrees well with that
of the probe-based measurements on the CAN particles. These measurements confirm that the CAN particles are rubbery throughout the shape-reconfiguring process in this study. No shape memory effect was present and any changes in particle geometry are permanent.
Figure 35: a) AFM indentation measurements of the mechanical properties of a single CAN particle at room temperature. The data points are the experimental results, and the three lines represent different model fitting of the data. b) SEM image of the specialized probe tip with a uniform 60 nm radius of curvature tip, used to for the indentation measurements in a). c) DMA temperature scan of the film synthesized with a similar chemistry as the particles. The $T_g$ is taken at the peak of the Tan δ.
We then imprinted the particles as detailed above. Figure 36 presents the side-view SEM images of the CAN particles before and after 15 min of UV irradiation with 0.73 µm silica spacers applied. Evidently, the microspheres were successfully reconfigured into a permanent, non-spherical shape.

Figure 36: Side-view SEM images of CAN particles before (top) and after (bottom) the UV-NIL process (15 min of UV irradiation with 0.73 µm silica spacers).
The particles in both images exhibited distinctive surface wrinkles, which was induced by extended focusing times with the electron beam that could not be avoided during side-view imaging. This e-beam induced surface-wrinkling represents a chemical-specific and a unique way to selectively modify the particle surface morphology. By focusing on certain areas of the particle, surface wrinkling can be induced with spatial control, Fig. 37. However, it prevents reliable characterization of the particle geometry. Instead, we applied AFM to quantify the particle shapes for all subsequent studies. Specifically, the shape of the oblate ellipsoidal particles can be represented by the width ($w$) and height ($h$), which are determined from AFM measurements.
We first examined the influence of UV-irradiation time on the degree of particle shape reconfiguration. Under a fixed pre-strain, $\varepsilon_E = 0.76$ (using the 0.73 $\mu$m silica
spacer), the compressed particles were exposed to UV irradiation (with an intensity of 20 mW/cm²) for different durations. As summarized in Fig. 38, the aspect ratio of the resultant CAN particles increased from ~1.2 to ~3.4 as the UV irradiation time increase from 1 min to 15 min, indicating higher degree of permanent shape changes at longer UV exposure time. Before further interpreting the shape changes, two phenomena must be noted here. First, the electrocapillary length, i.e. ratio between surface tension and elasticity, for the CAN particle is on the order of 10 nm, which suggests that the effect of particle surface energy on its geometry is negligible. On the other hand, particle-substrate adhesion does play a role in determining the final particle shape, but the effect is insignificant when compared with the effect of photoplasticity, as discussed below.

![Figure 38: Aspect ratio (line) between particle width ($w$) and height ($h$) of the CAN particles after UV-NIL as a function of UV exposure time, under 3 MPa pressure and 0.73 μm silica spacers. Correspondingly, the symbols show the the shape fixity of the vertical (circles) and lateral (squares) dimensions.](image)
As shown in our recent study,\cite{156} the height \((h)\) of a rubbery microsphere in contact with rigid substrate is affected by the work of adhesion \((W)\) between the particle and substrate,

\[
h = 2R \left(1 - \frac{1}{2} \left(\frac{3\pi^2 W^2}{E^* R^2}\right)^{1/3}\right)
\]

where \(R\) is the particle radius, \(E^* = \frac{E}{(1 - \nu^2)}\), \(E\) is the Young’s modulus and \(\nu\) is the Poisson’s ratio of the particle.

Extensive measurements of a model rubbery polystyrene (PS) microsphere - Si system show that \(W\) is dominated by the viscoelastic dissipation (rather than thermodynamic interfacial energy) during the particle recovery or detaching from the substrate. Assuming a similar value of \(W\) for the CAN-Si system as the PS-Si system (~500 mJ/m\(^2\) at a compressive of strain of 0.8), the CAN particle would recover to an aspect ratio of 1.34 at \(\varepsilon_E = 0.76\), when no stress relaxation has occurred. This value is in close agreement with that observed experimentally when limited stress relaxation occurred (1 min UV irradiation). However, the particle aspect ratio increased to 2.1, 2.8, and 3.3, when UV irradiation increased to 5, 10, and 15 min, correspondingly. This confirms that the final particle shapes were dominated by the permanent deformation due to UV-induced stress relaxation within the particles, rather than particle-substrate adhesion.

To better quantify the degree of shape configuration for the CAN particles, we define,
\[ fixity = \frac{\varepsilon_F}{\varepsilon_E} \times 100\% \]  \hfill (3.2-2)

where \(\varepsilon_E\) is the initial strain of the compressed particle (defined by the size of the silica spacer), and \(\varepsilon_F\) is the final (or permanent) strain achieved after the UV-NIL process. The fixity describes the percentage of the initial elastic strain that was converted into permanent strain due to the network rearrangement. Accordingly, fixity for vertical and lateral dimension increases with the UV irradiation time (Fig. 38). However, the fixity was larger for particle height than width, which is an inherent feature for compressive deformation of spheres. For a rubbery sphere, at large compressive strain, small changes in particle height is accompanied by larger changes in particle width. For example, when particle height changes from compressive strain of \(\varepsilon_E = 0.76\) to \(\varepsilon_F = 0.55\), i.e. a 72% height fixity, the corresponding width fixity is 50%.

Without question, the degree of particle shape reconfiguration is directly attributed to the degree of stress relaxation of the polymer network. Directly measuring degree of stress relaxation during UV-NIL within a compressed CAN microparticle is challenging. Instead, we developed a finite element model (FEM) to simulate the recovered particle shape after the UV-NIL process, which allows us to estimate the degree of stress relaxation. Most significantly, degree of stress relaxation is quantified as, \(\sigma_t = f\sigma_0\), where \(\sigma_0\) is the Cauchy stress in the compressed particle before UV irradiation, and \(f\) denotes the stress relaxation ratio and is set to be uniform within the particle. By fitting the experimentally measured particle aspect ratio, the degree of stress relaxation \(f\) was extracted. As summarized in Fig. 39, degree of
stress relaxation increases with increase of UV irradiation time, approaching steady state of ~ 50% after 15 min.

Figure 39: Percentage of the stress relaxation obtained from the FEM analysis, based on the experimentally determined particle aspect ratio. Inset shows FEM-simulated full particle shape and the residual stress distribution within the reconfigured particles.

Fig. 39 also displays the shape as well as the residual stress state of the reconfigured particles, obtained from the FEM. As mentioned, full-shape imaging with SEM and AFM was challenged by the chemical stability and tip-particle convolution, correspondingly. The simulated shape provides a full view of the particle, in the absence of substrate adhesion. In addition, the residual stress within the reconfigured particles is evident, particularly for the longer UV-exposure time. From FEM, this stress is inherent for CANs with partial stress relaxation: the unrelaxed network
strands (chains) drive the partial recovery of the particles, during which the already relaxed network strands (chains) will be re-deformed. The recovered particle shape is therefore a result of the energy balance between the conformational energy of the two types of network strands. Clearly, FEM suggests that reconfigured particles with partial stress relaxation (our 50% MBTA system) can contain relatively substantial amount of residual stress. Of course, when 100% fixity was achieved, the residual stress should be negligible.

We further compared the rate of stress relaxation in the CAN particles with that of a bulk film that can be directly measured. Using a DMA setup under a 10% tensile strain, the stress relaxation of the CAN film at room temperature as a function of UV irradiation with an intensity of 20 mW/cm² was measured (Fig. 40). Thus the stress relaxation in the case of a film mounted in a DMA, while quite close, appears to occur more rapidly than that observed in the particle system. This difference in relaxation rate may be due to the differing amounts of photoinitiator present in the particles and film. While the same formulation was used to make both film and particle, it is unknown how much of the photoinitiator actually ends up contained in the particle networks after dispersion polymerization and subsequent washing. A higher concentration of photoinitiator in the film during DMA testing would result in faster production of free radicals, which drive covalent bond exchange, thereby increasing the kinetics of stress relaxation.\(^{(157)}\) After 15 minutes of UV exposure, however, the
DMA test exhibits 42% stress relaxation, a value that is in very good agreement with the calculated stress relaxation in the particles.

![Graph showing stress relaxation over time](image)

Figure 40: Stress relaxation of a thin film consisting of similar chemistry as the CAN particles, under 20 mW/cm² UV irradiation at a tensile strain of $\varepsilon = 0.1$ using DMA.

Next, we examined the influence of $\varepsilon_E$ on the degree of shape reconfiguration (Fig. 41a) and the corresponding degree of stress relaxation (Fig. 41b). The CAN particles were compressed into varying $\varepsilon_E$ using different sized silica spacers, and then was irradiated with UV light for 15 min. As summarized in Fig. 41a, the aspect ratios of the reconfigured particles were 1.3, 2.3 and 3.4, when the $\varepsilon_E = 0.37$, 0.69, and 0.76, correspondingly. Clearly, larger degree of shape reconfiguration in CAN particles was achieved with larger $\varepsilon_E$. Interestingly, the fixity in particle height appear to be lower than that in particle width for $\varepsilon_E = 0.37$, while the opposite was observed for $\varepsilon_E = 0.69$, and 0.76. This behavior is attributed to the unique geometric constrains
for compressed spheres: at low degree of compression ($\varepsilon_E < \sim 0.5$), the vertical deformation ratio is larger than that of the lateral expansion; at higher degree of compression ($\varepsilon_E > \sim 0.7$) the opposite is true. For example, using the geometric relationship for the dependence of lateral extension on vertical compression, given a height fixity of 72% (for $\varepsilon_E = 0.69$) the corresponding fixity in width should be 41 %, a value reasonably close to (and well within one standard deviation of) the 50 % fixity measured by AFM.
Figure 41: a) Aspect ratio (dash-dot line) of the reconfigured particles as a function of the compressive pre-strain, after UV-NIL for 15 min. Correspondingly, the shape fixity in particle height (circles) and width (squares) are plotted. b). Degree of stress relaxation of the particles measured in a), obtained from the FEM simulation. Insets are the simulated oblate ellipsoidal CAN particles with residual stress distributions at corresponding degrees of stress relaxation.
Using FEM, the degree of stress relaxation in the CAN particles was estimated to be 42% for $\varepsilon_E = 0.37$ and 0.69, and 49% for $\varepsilon_E = 0.76$, correspondingly (Fig. 41b). The higher degree of stress relaxation at $\varepsilon_E = 0.76$ is intriguing, which might suggest the degree of stress relaxation is strain-dependent, especially at high strain levels. Nonetheless, the degree of stress relaxation in all samples agrees well with the percentage of the RAFT-agent (50%), suggesting that the majority of the active bonds participated in the network rearrangement process. The full shapes of the corresponding reconfigured particles were simulated from the FEM (inset of Fig. 41b). Accordingly, FEM also suggests that the residual stress in the reconfigured CAN particles increases with the increase of $\varepsilon_E$, due to the re-deformation of the already relaxed chains during particle recovery.

The use of UV-NIL to reconfigure shapes of CAN particles is attractive because it allows further lithographic control over the particle surface features. To demonstrate that, we used a patterned Si mold (1:1 line-space grating pattern, with an 840 nm periodicity and a groove depth of 200 nm) as supporting substrate for the particle shape reconfiguration process using the UV-NIL. Figure 42 shows the AFM images of the CAN particle after 15 min UV irradiation under a 3 MPa pressure with (Fig. 42a) and without (Fig. 42b) the use of 0.73 μm spacers. The absence of spacers allows the particle to creep outward during imprinting. When the spacers were used, the aspect ratio of the particles obtained was 3.4, the same as particles compressed with
a flat superstrate. The average pattern height replicated on the particle surface was 100 nm, i.e. ~ 50% of that of the mold depth. When no spacers were applied, the corresponding particle aspect ratio and surface pattern height were 5.8 and 45 nm, respectively.
Figure 42: a) Top down AFM scans of particles imprinted using a silicon mold with a line-space grating pattern, without the use of spacers to control vertical deformation and b) with 0.73 µm spacers to prevent lateral creep. Insets in both a) and b) show cross-sectional AFM scans of the surface topography.

In addition to using patterned silicon molds to create non-uniform topologies, photomasks can also be implemented into the NIL procedure to achieve interesting
particle geometries. Previous studies have shown that photomasks can be used to spatially control stress relaxation and have been utilized to generate surface patterns in films.(81) In Figure 43a, an AFM scan is presented of a particle which was imprinted without spacers using a photomask that allows UV exposure of roughly half the compressed particle. The result is a unique, pear-shaped particle. Since the AFM is unable to undercut particle curves, the FEM model was modified to generate an image of the full shape of particle in which only half the particle volume exhibits stress relaxation during NIL, Figure 43b. The current model does not accommodate lateral creep during NIL, so a fixed vertical strain of $\varepsilon_E = 0.69$ was employed. Accordingly, Figure 43a and b, while similar, do not offer a direct comparison of shape. The methodology presented here could potentially be used to generate far more complex particle shapes if various photomask designs are utilized.
Figure 43: a) An AFM obtained side profile of a particle subjected to NIL in conjunction with a photomask preventing UV exposure in half the particle. No spacers were used in this compression. b) FEM model of the full particle shape when a photomask prevents exposure of half the particle volume. The FEM assumes a fixed strain of $\varepsilon_E = 0.69$. 
In conclusion, this work demonstrates the light-stimulated permanent shape reconfiguration of polymer microspheres based on novel covalent adaptive network chemistry. Using RAFT-based chemistry as a model system, we showed that CAN microspheres can be reconfigured into a series of oblate ellipsoidal particles with aspect ratio as high as 3.4 using a UV-NIL setup. By adjusting the UV-NIL process conditions including UV irradiation time and pre-strain, the degree of stress relaxation within the CAN particles can be controlled, which results in different degree of shape reconfiguration. The use of UV-NIL allows program more complex topography onto CAN particle surfaces by either using topographic mold or photomasks. This approach provides a platform to custom fabricate unique non-spherical polymer particles with geometric complexity beyond capability of current top-down lithographic techniques. The FEM methods developed here further allow predictive control over the final particle shape.

Moving forward, this work presents several exciting directions to be explored. One clear question is how mechanical strain affects the degree and rate of stress relaxation in these particles. Preliminary work on a related projects indicates this is a difficult phenomenon to study via DMA stress relaxation on films, since films tend to break at much lower strain energies than the particles. Because their incredibly small volume contains far fewer defects than macroscopic films, particles are an excellent system with which to explore this question. Silica particles of uniform size can be commercially obtained with diameters as small as 60 nm, an order of magnitude
smaller than the spacers used in this work. Systematically measuring aspect ratio (and modeling the corresponding stress relaxation) at greater strains presents a project opportunity of immediate interest. Furthermore, only individual particles have been characterized thus far. In addition to internal bond exchange, RAFT particles should exhibit interfacial bond exchange as well. Particle adhesion of CAN based systems remains totally unexplored. Finally, the rubbery particles are commonly embedded in glassy resins to generate tough composites. The implementation of RAFT particles into such systems could generate very interesting results, and I have recently begun a preliminary investigation of the topic.
Chapter 4: Summary and Prospects

4.1 Summary of Research

In this thesis, we first demonstrated the ability of shape memory micro- and nano-scale particles to be directly compressed to fix highly deformed geometries via Nanoimprinting and recover their original shape upon thermal stimulus. This recovery behavior is shown to be highly dependent on the substrate confinement. By coating programmed particles with thin metal films, particles were then used as the foundation for creating dielectric, topographical Janus particles with highly hierarchical surface features. The wrinkles were controllably tuned by altering the degree of particle compression, thickness and stiffness of the capping layer, and annealing conditions. We then investigated how elastic energy and work of adhesion compete in the recovery process of deformed particles at different particle length scales. The influence of size, strain levels, and substrate adhesion on the shape memory cycle of 4.25 and 0.2 µm diameter cross-linked polystyrene particles was investigated. We found that shape recovery for particles in contact with SiOₓ substrates exhibits a compression dependency that becomes much more severe at smaller length scales. On a low energy SAMs modified substrate, however, no compression dependency is seen in the recovery of particles. As tool for analyzing this system, the elastic and adhesive energies present in the shape memory particle system at different length scales during particle compression were modeled, showing that the while elastic energy is the dom-
inant force in the 4.25 μm particles, adhesive energy grows comparable to elastic energy at sub-micron length scales. To investigate the kinetics of particle recovery as a function of size and substrate we then took in situ scans of compressed particles subjected to annealing at a slow temperature ramp.

In addition to shape memory particles, we also investigated the permanent shape reconfiguration of CAN-based particles by coupling a UV source in the imprinting process. The photoplasticity of particles employing the RAFT mechanism was successfully harnessed to generate particles with controllable, stable, non-spherical geometries. Silica spacers are used to set an initial elastic deformation and the degree to which that deformation is fixed after stress relaxation is examined. Rates at which fixity occurs appear qualitatively similar to macroscopic stress relaxation tests and the degree to which fixity of vertical and lateral deformations is achieved are observed to be dependent upon the initial strain imposed on the particles. When then demonstrate the ability of not only these particles, but RAFT-based films as well, to fix sub-micron surface patterns simply by using a patterned mold in the imprinting process.

4.2 Future Research Directions

For every question answered in this work, new questions arise. In the case of shape memory particles their ability to act as modifiers of rheological properties in fluids or mechanical properties in composites presents be an interesting direction for
applied research. Furthermore, the shape recovery of particles in the presence of favorable solvents is only briefly touched upon in this work and awaits systematic investigation.

Covalent adaptive networks have only garnered significant attention for the past decade and the work presented here contributes to a very young and promising field of research. Fundamentally, the ways in which stress relaxation in these networks changes as a function of UV intensity and mechanical strain are completely unknown. The spatial resolution at which stress relaxation and resulting deformations can be controllably achieved is also an unexplored point of interest.

Most of the work presented in this thesis relies on the use of NIL. Truly, NIL is a useful tool for the compression of large arrays of particles. Its primary limitation, however, is that it does not provide the force feedback or spatial control necessary to directly measure the mechanical properties of individual particles. Recently, some indentation based mechanical measurements on glassy polymer particles (modulus ~1 GPa) have revealed a strong particle-size dependency of the particle stiffness,(158) but the size effect on the properties of elastomeric particles (modulus ~ 1 MPa) is much more sparse. So far, only one study employing a soft colloidal probe atomic force microscopy technique (SCPAFM, (159)) has measured adhesion and stiffness in elastomeric particles.(62) However, this work explored behavior in a single particle size and across only very minor strains (~ 5%). For particles that have complex structure
and/or chemistry, no knowledge of their mechanical responses can be found in literature.

This presents a very promising direction for future. Combining SCPAFM and helium ion microscopy (HIM) measurements to characterize how modulus, work of adhesion, and fracture energy are influenced by the size of elastomeric particles at different strain levels and temperatures is direction I intend to pursue. Furthermore, incorporating CAN-based particles into the SCPAFM methodologies will enable measurements of the material properties of CAN particles during and in the absence of covalent bond exchange across a wide frequency range. Particle-particle and particle-film interfacial adhesion of CAN networks will also be measurable with unprecedented resolutions using SCPAFM techniques.
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