

Communication

Shape Memory Effect in Micro-Sized Shape Memory Polymer Composite Chains

Xin Lan ^{1,*} , Weimin Huang ² and Jinsong Leng ^{1,*}¹ Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150001, China² School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore

* Correspondence: lanxin@hit.edu.cn (X.L.); lengjs@hit.edu.cn (J.L.); Fax: +86-451-86402328 (X.L. & J.L.)

Received: 6 June 2019; Accepted: 8 July 2019; Published: 22 July 2019

**Featured Application:** The potential applications of SMP/Ni vertical chain arrays may contain micro electro mechanical systems (MEMS) and biomedical devices.

Abstract: Since the shape memory effect (SME) has been confirmed in micron and submicron sized polyurethane (PU) shape memory polymer (SMP), it might be used in novel micro/nano devices even for surgery/operation inside a single cell. In this study, micron sized protrusive PU SMP composite chains are fabricated via mixing ferromagnetic nickel micro powders with PU SMP/dimethylformamide solution and then cured under a low magnetic field. Depending on the amount of nickel content, vertical protrusive chains with a diameter from 10 to 250 μm and height from 200 to 1500 μm are obtained. The SME in these chains is investigated to confirm the SME in SMP composites at microscale. An array of such protrusive chains may be utilized to obtain re-configurable surface patterns in a simple manner for applications, such as remarkable change in wetting and friction ability. Finally, its potential applications for micro electro mechanical systems (MEMS) and biomedical device are proposed.

Keywords: shape-memory polymer; nickel powder; protrusive chain; shape-memory effect; surface morphology

1. Introduction

As a smart material, shape-memory polymers (SMPs) attract much interest owing to the capability to fully recover a remarkable pre-strain (on an order of hundred percent) upon applying a variety of external stimulus [1,2], including Joule heating [3,4], magnetism-induced heating [5,6], moisture [7], light [8,9], and pH change [10]. The shape memory effect (SME) could be realized on the basis of the following mechanism and the associated shaping procedure in a SMP [11]. In a glass transition based thermo-responsive SMP with the hard/soft-segment system, the function of hard segments is to act as physical crosslinks, and the SME is driven by the entropic forces which tend to shape the stretched polymer chains in the soft elements back to their original coiled configuration [12,13]. During a typical shape memory procedure, the original shape of SMP is synthesized and solidified at below glass transition temperature (T_g), then it is deformed to a temporary and large-deformation shape above T_g . Then, it is cooled well below T_g and the frozen soft segment lock the large-deformation configuration. When it is heated above T_g again, the soft segment release the hard segment, and the SMP recover toward the original shape.

The SME has occurred in macroscale and microscale in recent years, and also demonstrated at nanoscale in SMPs [14,15]. Hence, the prospect of SME applying in microscale or even nanoscale patterning receives great attention, including adaptive programmable materials [15], switchable

molecule-based materials [16], photoactive electroactive applications [7,8], soft electronics [17,18], biomedical applications (e.g., cell mechanobiology [19], biomimetic 4D printing [3], switchable dual pH-Responsiveness [10], robust microcarriers [20], soft microgrippers [21], and micropatterned containers [22]). At present, a number of SMPs are available in the market and many more are under developing [1]. Among these SMPs, some polyurethane SMPs are both thermo-responsive and moisture-responsive [9], which shows a prospective way to realize the operation and surgery in live cell at microscale and nanoscale. Some microscale polymeric machines have been developed [23,24] for operation or surgery at cell scale, and can be actuated outside the cells. But, it is still difficult to deliver those machines into cells and the following stimulus for the artificially controlled operation. Those polymeric machines may be fabricated with SMPs to deliver and operation inside the living cells on the basis of shape memory effect.

Considering the formation of chain structures of ferromagnetic particles of magnetorheological fluids and elastomers [25,26], the suspended ferromagnetic particles form chains, columns, or aggregates along the direction of magnetic field. To explain the above phenomenon, several research methods have been used, including macroscopic mechanical element combination method, macroscopic continuum mechanics, microscopic dipole mechanical method, and finite element method based on multi-field coupling [26–29]. Based on these methods, many models or theories have been proposed, and two typical theories among them are phase-nuclear theory and field-induced dipole moment theory [30]. Among those models, the main parameters include strength and distribution of magnetic field, properties of particles (volume fraction, size, and microstructures), viscosity of solvent, interface between particle and solvent, and time of action. However, the formation mechanism of particle chains under magnetic field is still unclear [25–30], and the testing results are not completely consistent with the theoretical predictions [31,32].

In this study, we prepared nickel (Ni) particles polyurethane-SMP chains in micron and submicron scale, and the shape memory effect and associated properties are demonstrated for those vertical protrusive chains upon thermal stimulus.

2. Sample Preparation and Formation of Shape Memory Polymer/Nickel (SMP/Ni) Vertical Chains

In this study, the polyurethane (PU) SMP solution (MS 5510) was bought from Diaplex Co. Ltd. (Tokyo, Japan), with 70 wt% dimethylformamide (DMF) solution and 30 wt% SMP solution. The nickel powders with average diameters 3–7 μm (99.8% purity, Good fellow, Delson, Canada), are electrically and ferromagnetic conductive. The array of microscale protrusive SMP-nickel composite chains in vertical direction was prepared in the following procedure. The nickel particles were blended into the SMP/DMF solution with the different volume fraction, namely 1%, 2%, 3%, and 5%. The well stirred nickel-particle/SMP/DMF mixture with a certain content of nickel particles was immediately injected into a petri dish (8 mm height, and 30 mm diameter) with a height of 4 mm. At this time, without applying the magnetic field, the nickel particles distributed uniformly and randomly in the well stirred Ni/SMP/DMF mixture. To avoid the deposition of nickel particles to the bottom of petri dish, the petri dish with SMP/DMF/Ni mixture was immediately placed in the middle of a pair of magnets as shown in Figure 1b, and the vertical chains immediately formed. The magnetic intensity was controlled at about 0.4T tested by a Gauss meter. The setup of magnets and petri dish was placed into an oven and kept at 80 °C for 48 h for solidification. The scanning electron microscope, SEM (JEOL 5600LV, MA, USA) and optical microscope was used to observe the morphology of SMP/Ni vertical chains. The differential scanning calorimetry, DSC (Modulated DSC, DSC-2920, TA Instruments, New Castle, DE, USA) was used to characterize the glass transition behavior of SMP/Ni composite.

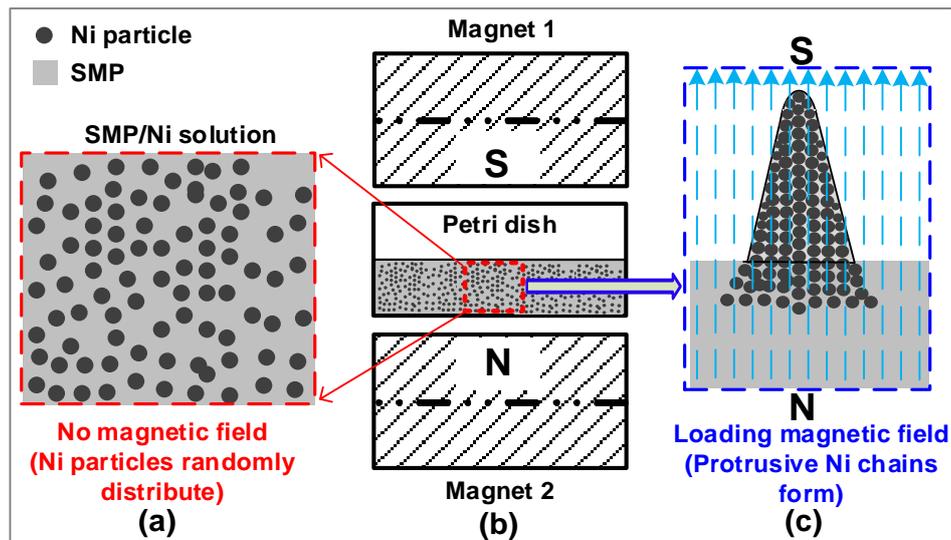


Figure 1. Illustration of preparation setup for vertical protrusive Shape Memory Polymer/Nickel (SMP/Ni) chains. (a) Random distribution of SMP/Ni solution without applying magnetic field; (b) Setup for preparing SMP/Ni vertical chain arrays; (c) Formation of SMP/Ni vertical chain arrays with applying magnetic field.

As revealed in Figure 1a, without loading a magnetic field, the ferromagnetic nickel particles were randomly distributed in the SMP/DMF solution. After loading a magnetic field, the ferromagnetic nickel particles aligned one by one in a line along the direction of magnetic field. In this way, the array of vertical protrusive nickel chains formed in the SMP/DMF solution as shown in Figure 1c. After evaporation of DMF from the SMP/DMF/Ni mixture, the aligned nickel particles were kept as shown in Figure 2; hence, the array of vertical protrusive SMP/Ni chains in solid state was obtained.

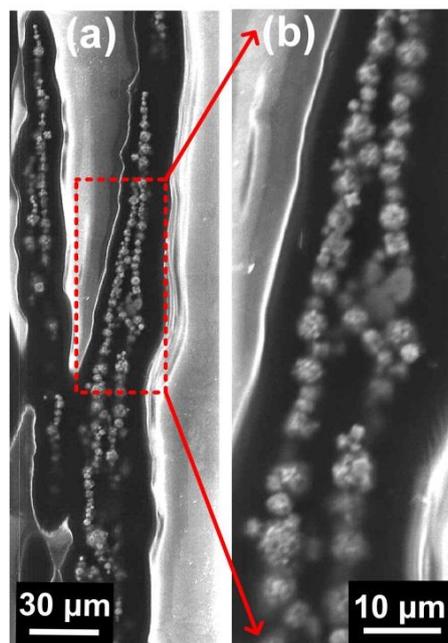


Figure 2. Nickel particles chains in Shape Memory Polymer (SMP) matrix. (a) Morphology of nickel particles chains; (b) Zoomed-in view of (a).

The typical vertical protrusive SMP/Ni chains and the morphology of separated nickel chains are exhibited as Figure 3. This protrusive SMP/Ni chain shows the dimension with approximate 1 mm

height and 40–100 μm diameter. As shown in the zoom-in image of Figure 3b, the tip of this SMP/Ni chain is a mixture of SMP and separated nickel chains aligned along the direction of magnetic field. In more detail, Figure 3c reveals the typical morphology of separated nickel chains distributed within the SMP matrix at micro/nano scale. Under the loading of magnetic field, the separated nickel particles moved and aligned one by one into regular array, and all the orientated lines are almost parallel in this field of view.

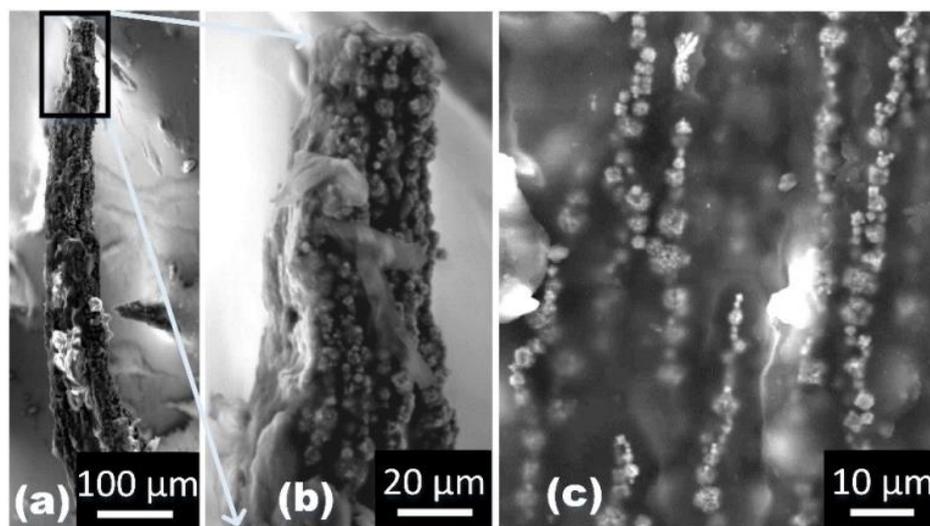


Figure 3. Typical chain structures of nickel particles in Shape Memory Polymer (SMP) matrix (3 vol% Ni). (a) Morphology of SMP/Ni vertical chain pillar; (b) Zoomed-in view of (a); (c) Typical morphology of nickel particles chains.

3. Morphology of Shape Memory Polymer/Nickel (SMP/Ni) Chain Arrays in Horizontal Plane

The distribution of nickel particles in SMP/DMF solution is essential for the formation of chain-like structures. After well stirring of the nickel-particle/SMP/DMF mixture, the nickel particles distribute uniformly and randomly at the initial time. As time flows, the nickel particles slowly deposit on the bottom of the petri dish. Hence, the uniform and random distribution of nickel particles in SMP/DMF solution is difficult to be observed by an optical microscope or SEM. Alternatively, to observe and study the formation characteristics of nickel chains, the magnetic field was applied in the direction parallel to the bottom of petri dish. The nickel chains formed, and finally solidified in horizontal plane with the volatilization of DMF solvent. Figure 4 indicates the distribution morphology of nickel particles under the magnetic field in horizontal plane. The straight nickel-chain structures along with the direction of magnetic field are obvious especial for the low volume fraction of nickel fillers, namely 0.25%, 0.5%, 1%, 2%, 3%, and 5%. The width of nickel chains gradually increases with the increasing of nickel contents. For the 0.25% sample, most of the cross sections of nickel chains only contain one nickel particle (3–7 μm width), and the length of nickel chains is general over 1000 μm , with an aspect ratio around 200. For the samples with higher nickel contents, they contain more nickel particles in one cross section, and the length limits of nickel chains approach 1500–3000 μm . In summary, for the varied contents of nickel fillers (0.25%, 0.5%, 1%, 2%, 3%, and 5%), the general widths of nickel chains are 3–7 μm , 10–50 μm , 20–80 μm , 20–100 μm , 100–300 μm , and 200–400 μm , respectively, and the general lengths are 1000–3000 μm .

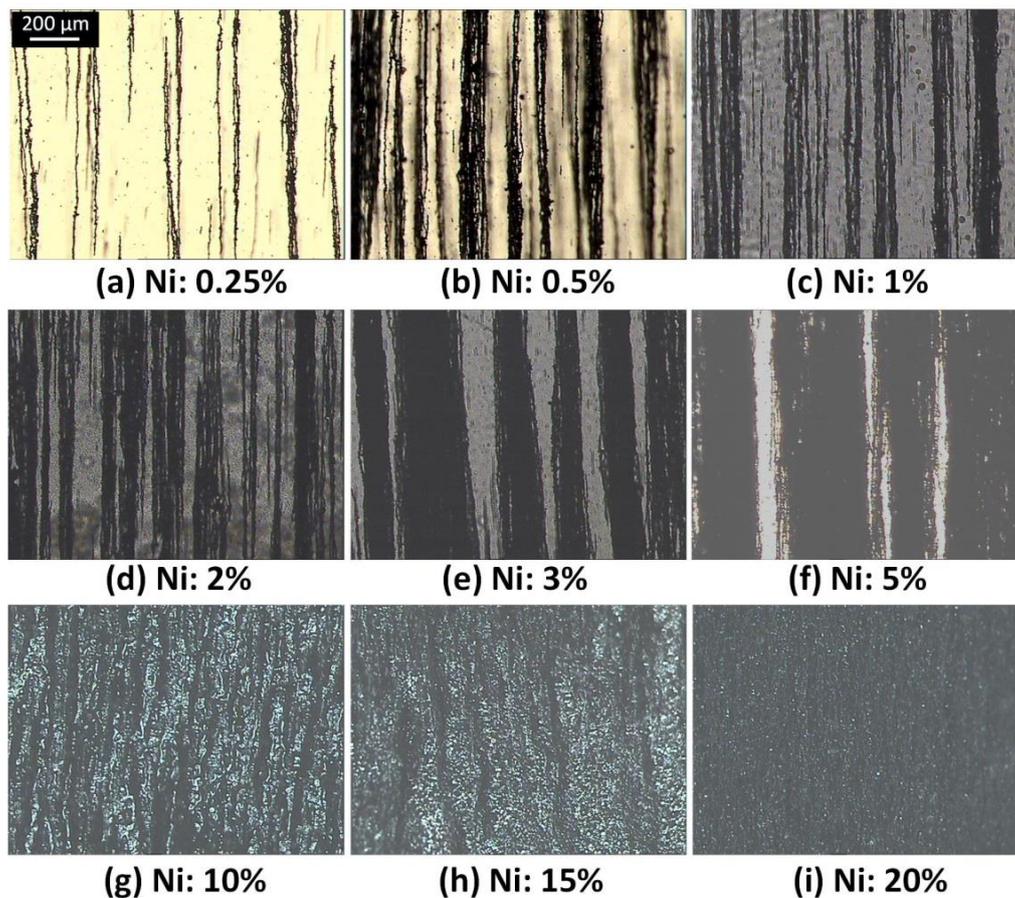


Figure 4. Distribution morphology of nickel particles in Shape Memory Polymer (SMP) matrix under the magnetic field in horizontal plane.

4. Differential Scanning Calorimetry (DSC) Test of Shape Memory Polymer/Nickel (SMP/Ni) Composite

In order to evaluate the fundamental material performance for pure polyurethane-based SMP and SMP/Ni composite, the DSC test was performed and the glass transition behavior was characterized (Figure 5). For SMP/Ni composite, the thin sample (around 100 μm) without applying magnetic field was prepared to maximally maintain the uniform distribution of nickel fillers in SMP matrix. The weight of sample for DSC test was 10–15 mg. The heating or cooling rate is 5 $^{\circ}\text{C}/\text{min}$ at the temperature range from -50 $^{\circ}\text{C}$ – 150 $^{\circ}\text{C}$. Figure 5 indicates the DSC curves in the cooling process, and the median point (half-height) was used to define the T_g . The glass transition temperatures of pure polyurethane-based SMP and SMP/Ni composite are 46 $^{\circ}\text{C}$ and 43 $^{\circ}\text{C}$, which indicate that the T_g of pure SMP reduces a little bit when bending nickel powders into SMP. Furthermore, because the T_g is 6–9 $^{\circ}\text{C}$ higher than the temperature of human body, the SMP/Ni composites are suitable for thermal responsive actuation using for human (e.g., live cell operations).

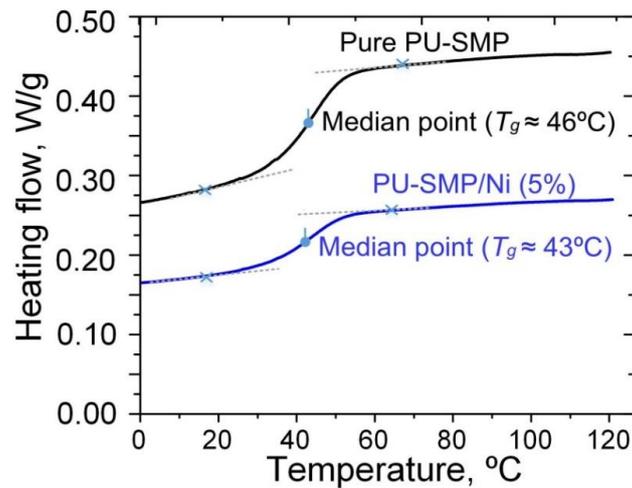


Figure 5. Differential Scanning Calorimetry (DSC) results of pure polyurethane-based Shape Memory Polymer (SMP) and SMP/Ni (Nickel) composite.

5. Morphology of Shape Memory Polymer/Nickel (SMP/Ni) Vertical Chain Arrays

The arrays of protrusive SMP nickel chains formed perpendicular to the SMP substrate. As shown in Figure 6, the morphology comparison of protrusive chains at four different volume fractions of nickel powders is presented. Statistical results of dimensions of protrusive chains, including diameter, height and separation were also obtained. Here, the diameter of a chain is defined as the measured diameter at the middle height of a chain. The interval distance is defined as the distance between the centrals of two adjacent chains. As shown in Table 1, it is clear that both the diameter (from 10 μm to 250 μm) and height (from 200 μm to 1500 μm) increase with the increasing of nickel contents, while the interval distance (from 100 μm to 700 μm) is relatively stable at five different nickel contents.

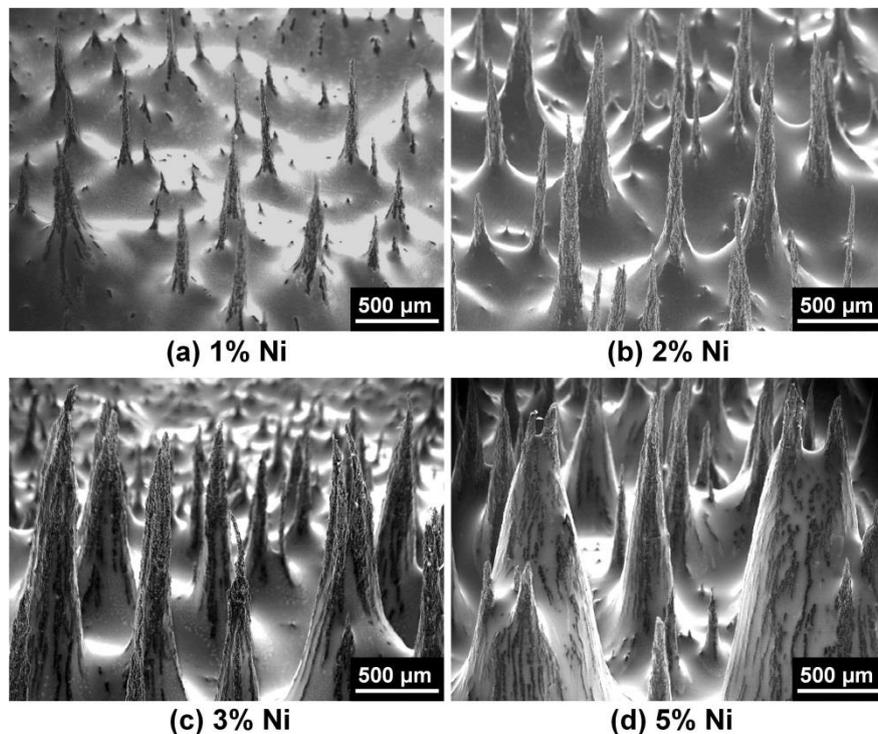
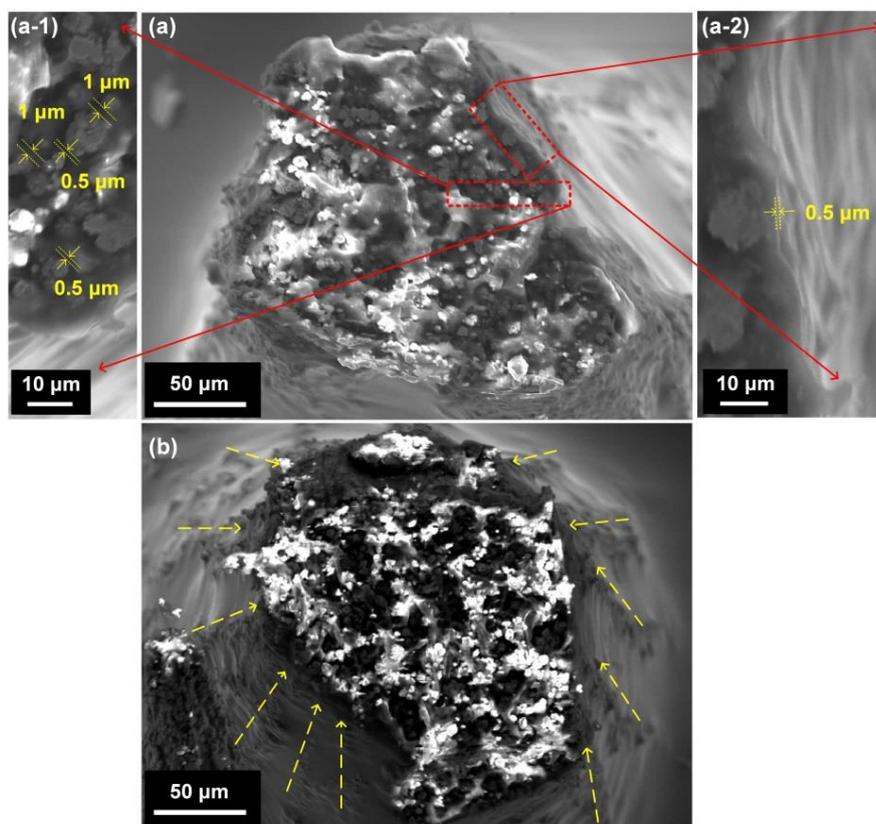


Figure 6. Typical array of vertical protrusive Shape Memory Polymer/Nickel (SMP/Ni) chains with varied volume fraction of nickel particles: 1%, 2%, 3%, and 5%.

Table 1. Dimensions (diameter, height, and interval distance) of vertical Shape Memory Polymer/Nickel (SMP/Ni) chains.

Filler Contents	Diameter (μm)	Height (μm)	Interval Distance (μm)
1%	25–45	270–310	100–400
2%	100–135	750–1000	300–550
3%	180–220	1100–1300	400–700
5%	200–240	1200–1400	450–600

Figure 7 reveals the patterns of the cross section cut from a vertical protrusive SMP/Ni chain with average 2% (Figure 7a) and 5% (Figure 7b) nickel particles in SMP matrix. The particles distributed randomly, which implies that the aligned nickel particles are also in random distributions in the horizontal cross-section plane (the direction of magnetic field is in the vertical direction). Furthermore, referred to the observed distributions of nickel particles, the volume fraction in this cross section is much higher than 2% (Figure 7a) and 5% (Figure 7b). Due to the attraction effect of magnetic field to the nickel particles, the nickel particles concentrate towards each vertical protrusive SMP/Ni chain, where the nickel content is much higher than those located far from the SMP/Ni chains. As shown in Figure 7a-2, the thin films of pure SMP are obvious at the exterior surface of the cross section, which ensure the strong banding of nickel particles on the surface. Furthermore, as shown in Figure 7b, a series of nickel chains are also embedded under the surface of a big vertical SMP/Ni chain, and the thin films of pure SMP also cover nickel particles. Moreover, on the tips of SMP/Ni vertical chains, the particles may be exposed to the air. However, due to high porosity of nickel particles, the nickel particles are still strong bonded with the SMP matrix.

**Figure 7.** Cross section of the vertical protrusive Shape Memory Polymer/Nickel (SMP/Ni) chain ((a) 2 vol% Ni; (b) 5 vol% nickel).

6. Shape Recovery Properties of Shape Memory Polymer/Nickel (SMP/Ni) Vertical Chain Arrays

As illustrated in Figure 8, we heat initially vertical chains (Figure 8a) to 120 °C (well above T_g , $T_g = 43$ °C–46 °C) for 20 min. After that, a piece of aluminum plate is placed atop the sample. Hence, the chain is flattened (Figure 8b). Subsequently, the SMP/Ni vertical chains are gradually cooled in the bending and flattened configuration while keeping the aluminum plate there. After the removal of the aluminum plate, the nickel protrusive chains are still in the bend-shape as shown in Figure 8c. Upon heating to 120 °C, if the chains can recover its initial shape (Figure 8d), the shape memory effect of SMP is demonstrated at microscale and nanoscale.

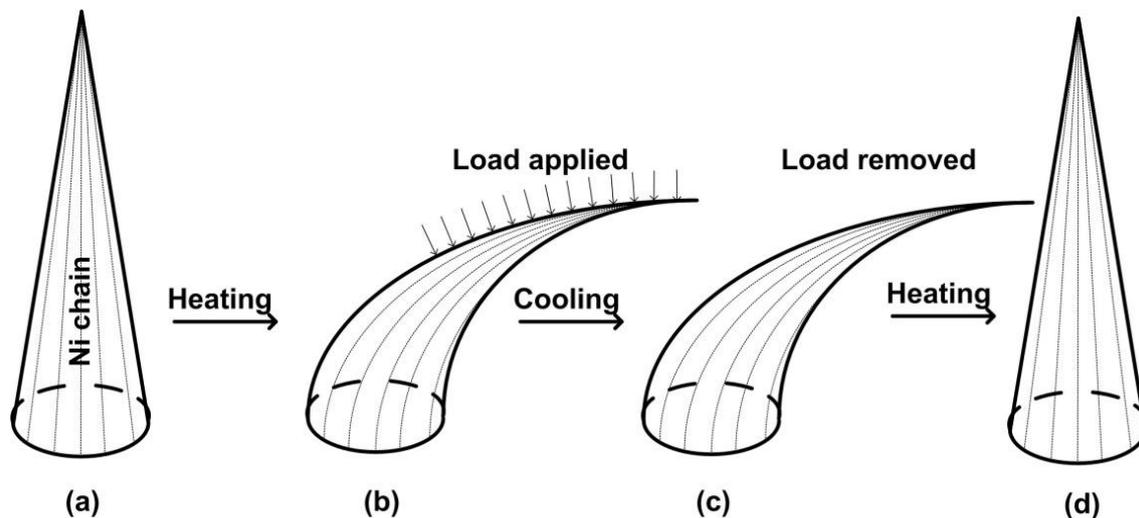


Figure 8. Illustration of a thermomechanical cycle to evaluate the shape memory effect of a vertical protrusive chain. (a) Initial shape; (b) pre-deformed shape; (c) flattened shape; (d) recovered shape.

The shape memory effect of vertical chains atop different samples with different nickel contents was tested following the procedure described above. Figure 9a shows one typical flattened chain of two samples with 2 vol% nickel. It is obvious that thin chains are easier to be flattened as compared with the thick chains. Hence, the chains obtained in samples with lower nickel content are preferred to demonstrate the SME. Furthermore, the local buckling phenomenon of SMP matrix can be found in the inner surface of the bending chain, which implies that the local compression strain is high. Figure 9b is the zoom-in view of chains of 2 vol% nickel content. Given that the size of nickel powders is around 3 to 7 μm , it reveals that the dimension of SMP (in particular, the thickness) is around 1 μm or less (i.e., at submicron scale), which is also indicated in Figure 7a. Hence, if the chains, although they are composite in nature, are demonstrated as with the SEM, we can conclude that the SMP/Ni chains structure does have the shape memory effect at around 1 micron and even submicron scale.

Figure 10 reveals the patterns of several SMP/Ni vertical raised chains in shape memory recycle. In the original shape Figure 10a, the SMP/Ni protrusive chains are strictly straight along with the direction of magnetic field. After heated above the T_g , the SMP matrix in the SMP/Ni chain became soft, and then the SMP/Ni protrusive chains were forced to be bent to approximate 180° to the flatten shape with a flat board. When cooled below T_g , after releasing the external constraint, this flattened pre-deformed configuration were obtained as shown in Figure 10b. The bending areas of vertical chains are mainly located at the root. When re-heating the SMP/Ni vertical chains, they gradually recovered toward the original vertical configuration. The macroscopic shape memory effect of pure SMP is the same as that at microscale, with shape recovery ratio 95–100% above T_g . However, with bending in solid and hard nickel particles, the shape recovery ratio of SMP/Ni vertical chains will reduce. The biggest unrecoverable angle in the recovered shape of SMP/Ni vertical chains is approximate 30° compared with the original straight shape, namely shape recovery ratio around 83%.

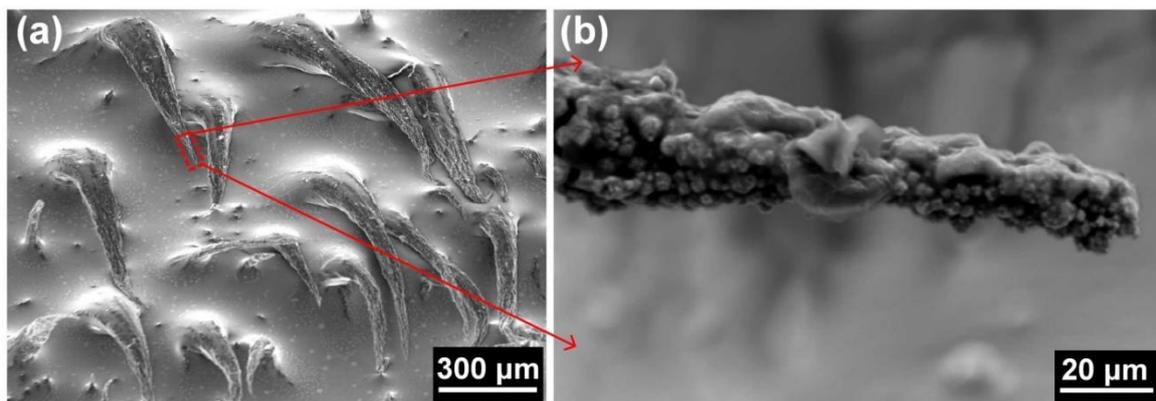


Figure 9. Typical configurations of flattened Shape Memory Polymer/Nickel (SMP/Ni) chain array with 2% nickel particles. (a) Morphology of flattened pillars; (b) Zoomed-in view of (a).

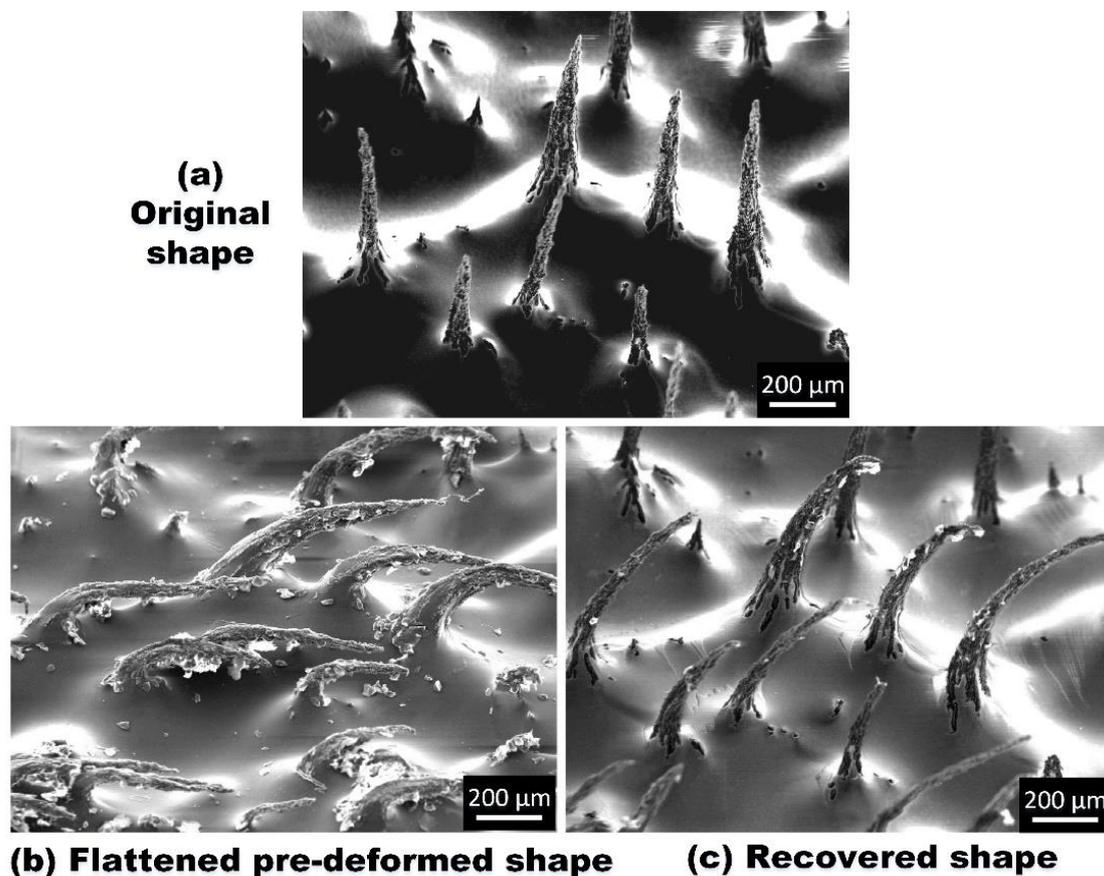


Figure 10. Typical shape recovery cycle of the vertical protrusive Shape Memory Polymer/Nickel (SMP/Ni) chains (2 vol% Ni). (a) Original shape; (b) Flattened pre-deformed shape; (c) Recovered shape.

7. Formation Mechanism and Dimensions Control Method of Shape Memory Polymer/Nickel (SMP/Ni) Vertical Chain Arrays

Considering the formation mechanism for nickel chains aligned along the magnetic field direction, the general explanation could be referenced to magnetomechanical coupling theory of the magnetorheological fluids [26]. Without loading a magnetic field, there are no permanent dipole moments in nickel particles; hence, all the nickel particles are in Brown motion and distributed randomly in the SMP/DMF solution prior to curing. Upon loading a permanent static magnetic field H , the permanent dipole moments in all ferromagnetic particles were induced and interacted. In

local nonuniform magnetic field, they rotate, repel or attract between two adjacent nickel particles depending on the direction of induced dipole moments and their relative position [33–36]. Referenced to the aforementioned studies of magnetorheological fluids, the formation of nickel chain structures in SMP matrix should consider the following forces applied on nickel particles:

- Magnetic force. SMPs are macromolecule and not ferromagnetic materials, and their magnetic susceptibility is negligible. The magnetic forces $\mathbf{F}_j^{\text{mag}}$ acting on a single particle j are induced by external magnetic field as well as induction field among nickel particles themselves [35]: $\mathbf{F}_j^{\text{mag}} = \mathbf{m} \cdot \nabla(\mathbf{B}_0 + \sum_{i \neq j} \mathbf{B}_i)$, where \mathbf{m} indicates dipole moment, \mathbf{B}_0 reveals magnetic induction intensity of external magnetic field, \mathbf{B}_i indicates magnetic induction intensity of particle j induced by particle i .
- Repelling force. Repelling forces exist when a nickel particle j approaches other particles ($\mathbf{F}_j^{\text{sphere}}$). Moreover, repulsive forces of a nickel particle j from walls of container ($\mathbf{F}_j^{\text{wall}}$) are included.
- Gravitation force. $\mathbf{F}_j^{\text{gav}}$. The gravitation of a nickel particle j .
- Hydrodynamic force. The hydrodynamic force $\mathbf{F}_j^{\text{hydro}}$ of a moving nickel particle j for small Reynolds can be described by Oseen's equation $\mathbf{F}_j^{\text{hydro}} = -D \frac{d\mathbf{r}_j}{dt}$, where $D = 6\pi a\eta$ reveals Stokes drag coefficient of a nickel sphere. η is the viscosity coefficient of the SMP/DMF solution. Note that, the viscosity coefficient increases during solidification process.

Hence, on the basis of references [33,34], the motion governing equations of a nickel particle j in the SMP/DMF solution can be expressed as

$$m \frac{d^2 \mathbf{r}_i}{dt^2} + D \frac{d\mathbf{r}_i}{dt} = \mathbf{F}_i^{\text{mag}} + \mathbf{F}_i^{\text{sphere}} + \mathbf{F}_i^{\text{wall}} + \mathbf{F}_i^{\text{gav}}. \quad (1)$$

The properties of vertical protrusive chains (diameter, height, and interval between two adjacent chains) can be explained as follows according to Equation (1). For finitely long chains, the interaction between two adjacent chains may be attraction or repelling forces depending on their interval, and height of the two chains. Those interaction forces cause the local gather of adjacent nickel chains in local nonuniform magnetic field; hence, big and high nickel chains atop SMP substrate form. Naturally, with more nickel particle fillers, the diameter and height of nickel chains will be larger, and the interval will be smaller. After solidification of SMP/DMF/Ni mixture, the SMP/Ni chains form with different diameter, height, and interval. On the other hand, the forces among nickel chains are in short range, and the stable protrusive array forms. The field between neighboring protrusive chains is relatively stable and almost independent on the exact nickel content.

Because of the complexity and imperfection of the above theoretical models referenced to magnetomechanical coupling theory of the magnetorheological fluids [26,33–36], it is still difficult to quantitatively design the distributions or accurately control the dimensions (diameter, height, and interval distance). Alternatively, in order to form well distributions of SMP/Ni chain arrays as much as possible, the experimental methods are still employed. Base on the preliminary analysis of theoretical models (Equation (1)), the following key parameters in the preparation procedure of SMP/Ni vertical chain arrays were considered, including strength of magnetic field, volume fraction of nickel contents in SMP matrix, size of nickel particles, viscosity of SMP/DMF solution.

7.1. Strength of Magnetic Field

In this study, the strength of magnetic field was controlled within 0.35–0.4 T. When it was weaker than 0.35–0.4 T, the height of SMP/Ni chains was small, although the chain arrays are dense. If it was stronger than 0.35–0.4 T, the nickel particles aggregated into relative thick chains; hence, the uniform chain arrays were difficult to form.

7.2. Volume Fraction of Nickel Particles in Shape Memory Polymer (SMP) Matrix

The volume fraction of nickel particles was also controlled in a proper range, namely 1–5%. When it was lower than 1% (e.g., 0.5%), the diameter of vertical chains reduced to 3–20 μm with the interval distance 200–1000 μm (Figure 4a,b). Alternatively, when it was higher than 1% (e.g., 10%, 15% and 20%) the nickel particles aggregated into relative thick chains without forming regular chain arrays (Figure 4g–i). Therefore, for the fabrication of SMP/Ni vertical chains, the volume fractions 1%, 2%, 3%, and 5% were employed in this study.

7.3. Size of Nickel Particles

Considering the size of nickel particles, its diameters 3–7 μm are at microscale level, and the proper volume fractions for SMP/Ni mixture to form relative well vertical arrays are around 2–3%, as shown in Figures 3, 4, 6 and 7. Moreover, it is predicted that, when the size of nickel particles is smaller, the appropriate volume fractions as well as dimensions will also reduce.

7.4. Viscosity of Shape Memory Polymer/Dimethylformamide (SMP/DMF) Solution

Viscosity of SMP/DMF solution is essential for the formation of SMP/Ni chains. With a low viscosity of solvent, the nickel particles will quickly deposit at the bottom, and they will aggregate but not chains form when loading magnetic field. If the viscosity of solvent is too high, the movement of particles will be constrained in a small area, and therefore the nickel particles are difficult to align into chain structures along magnetic field.

8. Discussion, Future Work, and Potential Applications

The current investigation of SMP/Ni vertical protrusive chains in this paper is just a preliminary stage to study this type of ferromagnetic particle-filled composite under magnetic field. There are three purposes to prepare those pillar arrays with applying magnetic field. First, mechanism and experimental research are prospective to be studied to prepare designable microscale structures (e.g., aligned chains) for ferromagnetic particle-filled composite through the operation of magnetic field. The main research contents contain physical mechanism and associated theoretical model of chain formation of nickel particles under magnetic field, and the crucial parameters in the preparation and experimental study with the aim to control the distribution and dimensions of SMP/Ni chain arrays. Second, it is proposed to investigate special performance of SMP/Ni composite with nickel particle chain morphology, such as reinforcement of mechanical and electrical-conductivity along the direction of nickel chains. Third, the SMP/Ni pillar arrays are prospective to be fabricated into micro, sub-micro, and even nano size, and to realize the artificial and controllable operation at the corresponding scale levels. Hence, the nanoimprinting [37,38] and mold preparation method without applying magnetic field were not used in this study, although they are alternative methods to prepare more uniform pillar arrays for SMP/Ni composite. Based on the above three purposes, the further and more detailed study will be carried out in near future.

Additionally, the size of nickel particles is at microscale level (3–7 μm), and the diameters of SMP/Ni vertical chains are approximate at the magnitude of tens of micron for 1% or even lower filler contents, and hundreds of micron for 2%, 3%, and 5% filler contents. However, those dimensions are not suitable for the operations in sub-micro size. Alternatively, nanoscale nickel particles are a choice to be filled into SMP to prepare SMP/Ni vertical chains in sub-micro or even nano size. As a preliminary investigation, the nanoscale nickel particles with diameters of 100–500 nm have been used to prepare the nickel chains in horizontal plane with loading magnetic field. As shown in Figure 11, the nickel chains are in sub-micro, which provide a possibility to prepare SMP/Ni vertical chain arrays and for the corresponding operations in sub-micro size in future work.

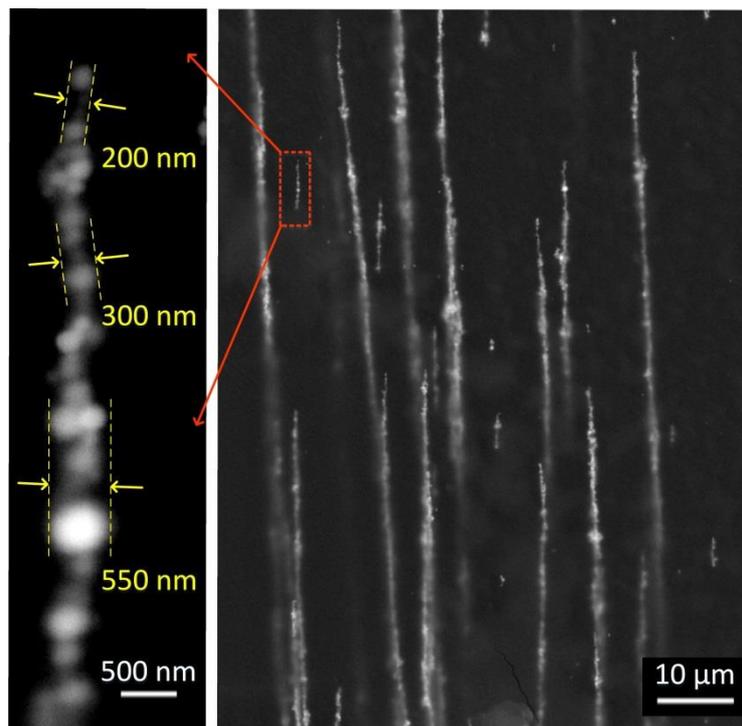


Figure 11. Typical array of Shape Memory Polymer/Nickel (SMP/Ni) chains with 1% volume fraction of sub-micro nickel particles.

Thermal-sensitive shape memory polymers have gained much attention because of their physical or chemical responses to quick changes by thermal-stimuli around the critical transition temperature. The vertical protrusive SMP chains show great prospects for the microscale and sub-micro actuation for biomedical materials and device, microscale patterns, and micro electro mechanical systems (MEMS), such as drug delivery, bioseparation, biomimetic 4D printing, switchable dual pH-Responsiveness, robust microcarriers, and soft microgrippers. For the microbrush or microgripper, the potential application may be described as follows: the chains of the microbrush or microgripper, which is flexible above transition temperature, can be used for finishing, cleaning, burnishing or gripping MEMS devices. The nature of the microbrush or microgripper is flexible to access the surface where the conventional tools are hardly applicable. After using, the protrusive chains can recover to the original shape by heating above the T_g . In this way, the shape memory microbrush or microgripper is recycling-used. For instance, Figure 12 illustrates the typical delivery and operation procedure of protrusive chains of microscale SMP brush machine. The array of protrusive SMP chains (Figure 12a) was compressed and bent to a flatten shape (Figure 12b) above T_g , and easily delivered into a live cancer cell in this compressed shape in a small volume. The bent SMP chains can recover to the original protrusive shape triggered by outside alternative magnetic field or moisture. In special, the T_g will reduce when the polyurethane SMP immersed into water or in moisture atmosphere. In this way, the pre-deformed polyurethane SMPs can be “actuated” by water or moisture, which is suitable to be used in human body.

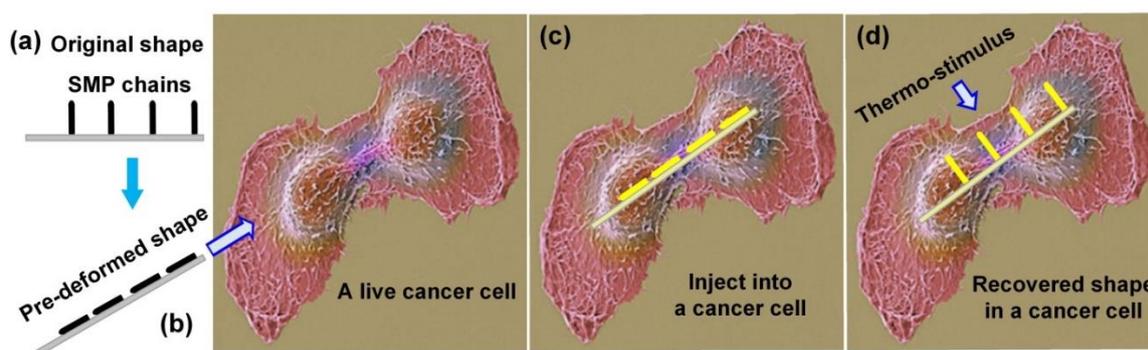


Figure 12. Schematic illustration of the delivery and operation procedure of microscale Shape Memory Polymer (SMP) brush machine in a live cancer cell. (The live cancer cell is referred to in Reference [39]). (a) Original shape of SMP chain pillars; (b) Pre-deformed SMP chain pillars; (c) Pre-deformed SMP chain pillars injected into a cancer cell; (d) Recovered SMP chain pillars in a cancer cell.

9. Conclusions

Arrays of SMP/Ni microscale chains were prepared along the direction of magnetic field. Depending on the volume fraction of nickel particles, protrusive chains were obtained with a diameter from 10 to 250 μm and height from 200 to 1000 μm . The shape memory effect in such vertical protrusive chains was demonstrated in microscale. As the SMP is thermo/moisture-responsive, it can be used for novel microscale devices. These micro protrusive chains may be utilized to significantly alter the surface morphology, and hence induce a dramatic potential for microscale actuation for biomedical materials and device, MEMS, such as microbrush or microgripper.

Author Contributions: X.L., W.H. and J.L. conceived and designed the experiments; X.L. performed the experiments; X.L. and W.H. analyzed the data; X.L. wrote the paper.

Funding: This work is supported by the National Natural Science Foundation of China (grant numbers: 11872020, 11632005, U1637207, and 11772109).

Conflicts of Interest: The authors declare no conflict of interest.

References

- Leng, J.S.; Lan, X.; Liu, Y.J.; Du, S.Y. Shape memory polymers and their composites: Stimulus methods and applications. *Prog. Mater. Sci.* **2011**, *56*, 1077–1135. [[CrossRef](#)]
- Xie, T. Tunable polymer multi-shape memory effect. *Nature* **2010**, *464*, 267–270. [[CrossRef](#)] [[PubMed](#)]
- Sydney, G.A.; Matsumoto, E.A.; Nuzzo, R.G.; Mahadevan, L., J.A. Biomimetic 4D printing. *Nat. Mater.* **2016**, *15*, 413–418. [[CrossRef](#)] [[PubMed](#)]
- Lan, X.; Liu, L.W.; Liu, Y.J.; Leng, J.S. Thermomechanical and electroactive behavior of a thermosetting styrene-based carbon black shape-memory composite. *J. Appl. Polym. Sci.* **2018**, *135*, 45978. [[CrossRef](#)]
- Yu, K.; Westbrook, K.K.; Kao, P.H.; Leng, J.; Qi, H.J. Design considerations for shape memory polymer composites with magnetic particles. *J. Compos. Mater.* **2013**, *47*, 51–63. [[CrossRef](#)]
- Marco, D.; Eckhouse, S. Bioerodible self-deployable intragastric implants. U.S. Patent 8,864,784 B2, 21 October 2014. Application granted.
- Ayesha, K. Review on Technological Significance of Photoactive, Electroactive, pH-sensitive, Wateractive, and Thermo-responsive Polyurethane Materials. *Polym. Plast. Technol.* **2017**, *56*, 606–616.
- Jin, B.J.; Song, H.J.; Jiang, R.Q. Programming a crystalline shape memory polymer network with thermo- and photo-reversible bonds toward a single-component soft robot. *Sci. Adv.* **2018**, *4*, 05195. [[CrossRef](#)]
- Bertrand, O.; Gohy, J.F. Photo-responsive polymers: Synthesis and applications. *Polym. Chem.* **2017**, *8*, 52–73. [[CrossRef](#)]
- Hu, Y.; Lu, C.H.; Guo, W.; Aleman-Garcia, M.A.; Ren, J.; Willner, I. A shape memory acrylamide/DNA hydrogel exhibiting switchable dual pH-responsiveness. *Adv. Funct. Mater.* **2015**, *25*, 6867–6874. [[CrossRef](#)]

11. Wang, X.; Sparkman, J.; Gou, J.H. Electrical actuation and shape memory behavior of polyurethane composites incorporated with printed carbon nanotube layers. *Compos. Sci. Technol.* **2017**, *141*, 8–15. [[CrossRef](#)]
12. Behl, M.; Lendlein, A. Shape-memory polymers. *Mater. Today* **2007**, *10*, 20. [[CrossRef](#)]
13. Lendlein, A.; Kelch, S. Shape-memory polymers. *Angew. Chem. Int.* **2002**, *41*, 2034. [[CrossRef](#)]
14. Wang, C.C.; Zhao, Y.; Purnawali, H. Chemically induced morphing in polyurethane shape memory polymer micro fibers/springs. *React. Funct. Polym.* **2012**, *72*, 7575–7764. [[CrossRef](#)]
15. Fan, X.S.; Chung, J.Y.; Lim, Y.X.; Li, Z.B.; Loh, X.J. Review of adaptive programmable materials and their bioapplications. *ACS Appl. Mater. Interfaces* **2016**, *8*, 33351–33370. [[CrossRef](#)]
16. Manrique-Juárez, D.M.; Rata, S.; Salmona, L.; Molnára, G.; Quinterob, C.M.; Nicub, L.; Shepherd, H.J.; Bousseksou, A. Switchable molecule-based materials for micro- and nanoscale actuating applications: Achievements and prospects. *Coord. Chem. Rev.* **2016**, *308*, 395–408. [[CrossRef](#)]
17. Wang, Q.M.; Zhao, X.H. Beyond wrinkles: Multimodal surface instabilities for multifunctional patterning. *MRS Bull.* **2016**, *41*, 115–122. [[CrossRef](#)]
18. Lagrange, R.; LópezJiménez, F.; Terwagne, D.; Brojan, M.; Reis, P.M. From wrinkling to global buckling of a ring on a curved substrate. *J. Mech. Phys. Solids* **2016**, *89*, 77–95. [[CrossRef](#)]
19. Ebara, M. Shape-memory surfaces for cell mechanobiology. *Sci. Technol. Adv. Mater.* **2015**, *16*, 014804. [[CrossRef](#)]
20. Shim, T.S.; Kim, S.H.; Heo, C.J.; Jeon, H.C.; Yang, S.M. Controlled origami folding of hydrogel bilayers with sustained reversibility for robust microcarriers. *Angew. Chem. Int. Ed.* **2012**, *51*, 1420–1423. [[CrossRef](#)]
21. Breger, J.C.; Yoon, C.; Xiao, R.; Kwag, H.R.; Wang, M.O.; Fisher, J.P.; Gracias, D.H. Self-folding thermo-magnetically responsive soft microgrippers. *ACS Appl. Mater. Interfaces* **2015**, *7*, 3398–3405. [[CrossRef](#)]
22. Azam, A.; Laflin, K.E.; Jamal, M.; Fernandes, R.; Gracias, D.H. Self-folding micropatterned polymeric containers. *Biomed. Microdevices* **2011**, *13*, 51–58. [[CrossRef](#)] [[PubMed](#)]
23. Maruo, S.; Ikuta, K.; Korogi, H. Optically-driven nanomanipulators fabricated by two-photon microstereolithography. *Mat. Res. Soc. Symp. Proc.* **2003**, *739*, 269.
24. Ionov, L. Biomimetic 3D self-assembling biomicroconstructs by spontaneous deformation of thin polymer films. *J. Mater. Chem.* **2012**, *22*, 19366–19375. [[CrossRef](#)]
25. Sasena, P.; Hossain, M.; Steinmann, P. Nonlinear magneto viscoelasticity of transversally isotropic magneto active polymers. *Proc. Math. Phys. Eng. Sci.* **2014**, *470*, 20140082. [[CrossRef](#)] [[PubMed](#)]
26. Yuan, F.Y.; Wan, Q.; Zhang, C.Y.; Li, X. Advances in Magnetomechanical coupling constitutive relations of magnetorheological elastomers. *Mater. Rev. A* **2017**, *31*, 10.
27. Zhou, G.Y.; Jiang, Z.Y. Deformation in magnetorheological elastomer and elastomer-ferromagnetic composite driven by a magnetic field. *Smart Mater. Struct.* **2004**, *13*, 309. [[CrossRef](#)]
28. Ivaneyko, D.; Toshchevikov, V.; Borin, D.; Saphiannikova, M.; Heinrich, G. Mechanical properties of magneto-sensitive elastomers in a homogeneous magnetic field: Theory and experiment. *Macromol. Symp.* **2014**, *338*, 96. [[CrossRef](#)]
29. Sasena, P.; Hossain, M.; Steinmann, P. A theory of finite deformation magneto viscoelasticity. *Int. J. Solid Struct.* **2013**, *50*, 3886. [[CrossRef](#)]
30. Galipeau, E.; Rudykh, S.; Castaneda, P.P. Magnetoactive elastomers with periodic and random microstructures. *Int. J. Solid Struct.* **2014**, *51*, 3012. [[CrossRef](#)]
31. Itskov, M.; Khiem, V.N. A polyconvex anisotropic free energy function for electro and magneto rheological elastomers. *Math. Mech. Solid.* **2014**, *21*, 1126. [[CrossRef](#)]
32. Chen, S.W.; Li, R.; Zhang, Z.; Wang, X.J. Micromechanical analysis on tensile modulus of structured magneto rheological elastomer. *Smart Mater. Struct.* **2016**, *25*, 035001. [[CrossRef](#)]
33. Ly, H.V.; Reitich, F.; Jolly, M.R.; Banks, H.T.; Ito, K. Simulations of particle dynamics in magnetorheological fluids. *J. Comput. Phys.* **1999**, *155*, 160. [[CrossRef](#)]
34. Mohebi, M.; Jamasbi, N. Simulation of the formation of nonequilibrium structures in magnetorheological fluids subject to an external magnetic field. *Phys. Rev. E* **1996**, *54*, 5407. [[CrossRef](#)]
35. Gross, M.; Kiskamp, S. New long-range interaction between dipolar chains. *Phys. Rev. Lett.* **1997**, *79*, 2566. [[CrossRef](#)]
36. Zhou, L.; Wen, W.; Sheng, P. Ground states of magnetorheological fluids. *Phys. Rev. Lett.* **1998**, *81*, 1509. [[CrossRef](#)]

37. Dumond, J.J.; Low, H.Y. Recent developments and design challenges in continuous roller micro- and nanoimprinting. *J. Vac. Sci. Technol. B* **2012**, *30*, 010801. [[CrossRef](#)]
38. Sharstniou, A.; Niazorau, S.; Ferreira, P.M. Electrochemical nanoimprinting of silicon. *PNAS* **2019**, *116*, 10264. [[CrossRef](#)]
39. University of California, San Diego Health Sciences. Live and Let-7: microRNA Plays Surprising Role in Cell Survival. *ScienceDaily*. 7 October 2014. Available online: <https://phys.org/news/2014-10-let-microrna-role-cell-survival.html> (accessed on 17 July 2019).



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).