

Formation of Protrusive Micro/nano Patterns atop Shape Memory Polymers

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Abstract: The surface morphology of materials is of fundamental importance to many applications (e.g., surface wetting, friction, surface roughness, reflection, drag, adhesion, etc). Various approaches for micro/nano patterning atop polymer surfaces have been proposed in recent years. However, a cost effective technique is still highly in demand. In this paper, we demonstrate a few novel but rather simple and generic approaches for surface micro/nano patterning using shape memory polymers (SMPs). Reversible micro vertical chains, crown shaped protrusion arrays and strip/labyrinth wrinkles atop SMPs are presented.

1. Introduction

The surface morphology of materials is of fundamental importance to many applications (e.g., surface wetting, friction, surface roughness, reflection, drag, adhesion, etc). The investigation and findings in plants and animals reveal the fantastic surface features in natural creatures.[1] However, to realize those surface patterns atop a man made material in a cost effective manner is not an easy task. Although various novel techniques (e.g., [2]) have been proposed to realize micro/nano patterns atop polymer surfaces, low cost, simple and generic approach is still highly in demand.

Shape memory polymer (SMP) can fully recover its original shape after a severe pre-deformation. Although the recover stress is small, the recoverable strain in SMPs is on an order to 100%. A number of applications have been proposed and demonstrated in recent years (e.g., [3]). The most significant advantage of SMPs as compared with other smart materials (e.g., shape memory alloys) is the low cost and easy in processing.

In this paper, we demonstrate a few novel techniques for micro/nano patterning atop SMPs. Reversible micro vertical chains, crown shaped protrusion arrays and strip/labyrinth wrinkles atop SMPs are presented.

2. Surface Patterning

Vertical protrusive micro chains

We have demonstrated in [4] that the electrical conductivity of a polyurethane SMP can be significantly improved if chained (instead of randomly dispersed) Ni particles are formed inside the polymer matrix. The Ni particles (a few microns in diameter) align into chains inside the SMP solution upon applying a weak magnetic field. After drying, these chains, which are continuous long ones if the amount of Ni particle is not small, are well kept serving as conductive channels for achieving good electrical conductivity. The Ni particle chains are short discontinuous ones if Ni particles are lightly loaded in the Ni/SMP composite.

Inspired by this work, we fabricated vertical chains atop a SMP instead of inside SMP. The thermo-responsive polyurethane SMP solution from Diaplex Co. Ltd. (MS-5510) was used in this

study. It consists of 30 wt% of SMP (glass transition temperature, T_g : about 40°C) and 70 wt% of dimethylformamide (DMF). Its molecule chain consists of alternating sequences of soft segment with low molecular weight, and hard segment built from diisocyanates and extenders to form the points for physical linking. Ni powders, which are magnetic and electronically conductive, with an average size from 3 to 7 μm and a purity of 99.8%, were bought from Goodfellow, UK.

The experimental setup and procedure is more or less the same as that reported in [4], except that one magnet was placed above the polymer solution and another was placed underneath it. Hence, the Ni chains were along the vertical direction instead of in the horizontal direction as in [4,5]. Different volume fractions of Ni particles (from 0.5 to 5%) were mixed into the SMP solution.

Micro/nano crown shaped array

In [6-7], we have demonstrated two novel techniques to produce protrusive arrays atop SMP. One is to use a laser to locally heat a pre-compressed SMP to form bumps. Another is to form various sized and shaped protrusions through an indentation-polishing-heating process. In order to improve the efficiency in make indents atop SMP, in [7], we have used hard spherical balls (300 μm in diameter), which were well packed atop SMP (polystyrene SMP sheet, about 4 mm thick, T_g about 65°C, bought from CRG, USA), and then compressed them into SMP to form an array of indents in one step. To make protrusion crowns with an even higher density, we used 30.1 μm diameter soda lime glass micro spheres (with standard deviation of 2.3 μm and uncertainty of 2.1 μm , from Duke Scientific Corporation, USA) in current study. In addition, we have pre-stretched some SMP samples by 50% before indentation.

Wrinkles atop SMP

Wrinkling in a thin elastic layer atop a polymer is not a new phenomenon, but still attracting, since the formed wrinkling patterns can be highly in order and at micrometer and even nanometer scale.[8] The wrinkling is resulted by the elastic buckling of the elastic layer due to the thermal mismatch between the elastic layer and soft substrate. Such phenomenon has been utilized to characterize the mechanical properties of an ultra-thin elastic layer.

The same polystyrene SMP sheets as used in forming micro/nano crown shaped array were used here to produce different wrinkling patterns. All samples were polished to ensure a very smooth surface. Some of the samples were pre-stretched (from 0.5% to 40% pre-strain). After sputter coating with a thin layer of metal (Ni or gold), the samples were heated to 100°C for shape recovery. In other samples, which were not pre-strained, were sputter coated with Ni or gold and then heated to 150°C for 20 minutes. After cooling back to room temperature (about 22°C), different wrinkle patterns were produced atop SMP.

3. Results and Discussions

A Scanning Electron Microscope (SEM, JEOL 5600LV) was used to observe the protrusions. In addition, a WYKO interferometer and a Confocal image profiler were used to obtain 3-D morphology and cross-sectional view.

Figure 1 reveals the SEM image of micro chains atop SMP (at 1% volume fraction of Ni particles). Figure 2 shows a zoom-in view of one chain, which is originally vertical and about 30 μm in diameter. The chain can be easily deformed at above its T_g . After cooling back to room temperature, the deformed shape can be well maintained. Upon heating to above T_g again, the deformed chain becomes vertical again due to the shape memory effect. The chains are aligned Ni particles covered by SMP. The reversible feature of such vertical chains enables a dramatic change in surface morphology, and hence a significant altering in wetting, friction, roughness and reflection etc.

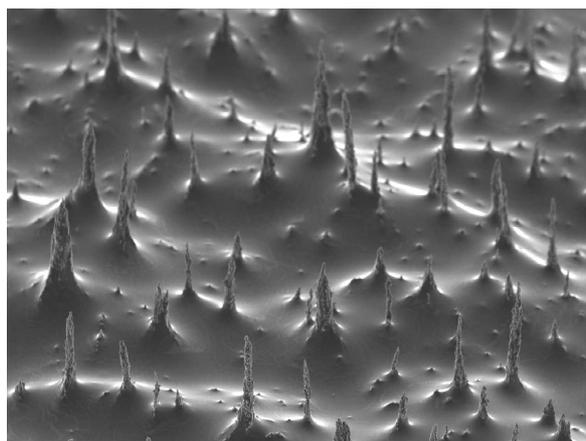


Figure 1 Micro chains atop SMP (at 1% volume fraction of Ni particles).

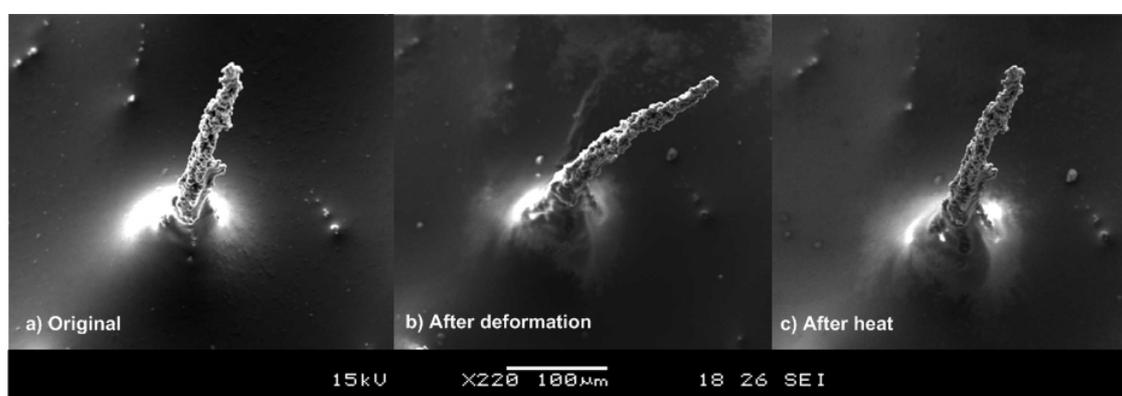


Figure 2 One reversible protrusive micro chain.

Figure 3(a) (SEM image) reveals that the surface of SMP is fully occupied by micro dots everywhere. These dots are pretty well distributed forming a rather regular pattern. Figure 3(b) is a 3-D zoom-in view showing a few crown shaped protrusions. The height of these protrusions is less than 1 μm . Top-view (Figure 3c) reveals that these bumps are circular shape and about the same size. Cross-sectional view of two bumps (Figure 3d) shows that the height of them is actually less than 500 μm . In 50% pre-stretched samples, the resulted dots are not circular but elliptical (Figure 4). This study successfully demonstrates a convenient approach to realized micron and submicron sized both isotropic and anisotropic bump array.

Figure 5 reveals strip-shaped wrinkles atop pre-stained SMP sheets (from 5% to 40% pre-strain). They were all coated with 50 nm thick of Ni by sputtering before heating to above the T_g for shape recovery. In fact, we can see many crack-like lines, which become denser with the increase in the amount of pre-strain. An enlarged image by Wyko scanning (Figure 6) of a crack-like line shows slight shear of the wrinkles. It is observed that the wavelength of the wrinkles is more or less independent of the pre-strain. These cracks are resulted by the remarkable expansion of SMP in the transverse direction (perpendicular to the pre-stretching direction) during shape recovery.

In another set of experiments, the pre-strain was 5% and the coated material was gold (about 50 nm). As we can see in Figure 6(a) (3-D confocal image), there is no crack but regular parallel wrinkles. The surface roughness of this surface is about 181 μm and the wavelength is about 13 μm . Figure 6(b) is 3-D confocal image of labyrinth like wrinkles. The surface roughness is only about 94 nm and the wavelength is estimated as 4.3 μm , both are much smaller than the ones in strip-shaped wrinkle samples. Further study, which will be reported elsewhere, shows the remarkable influence of wrinkles and their patterns on the contact angle between water and SMP surface (coated with gold).

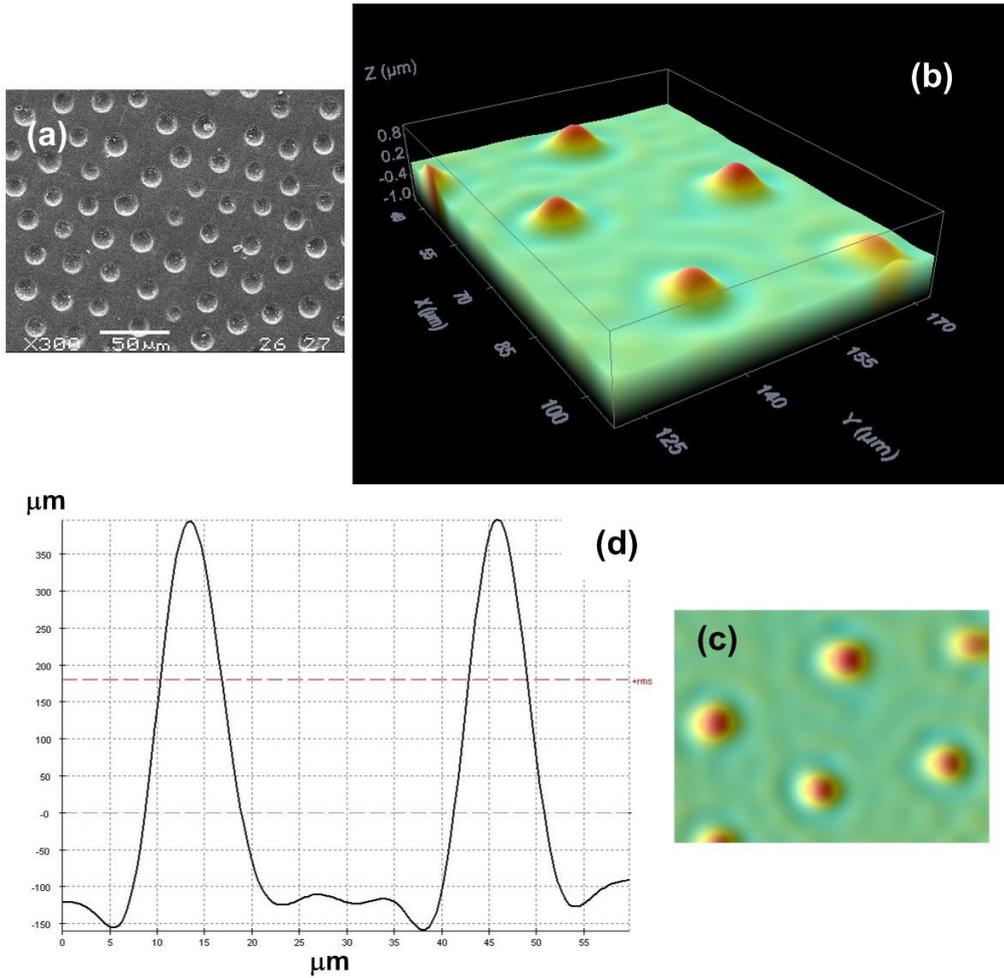
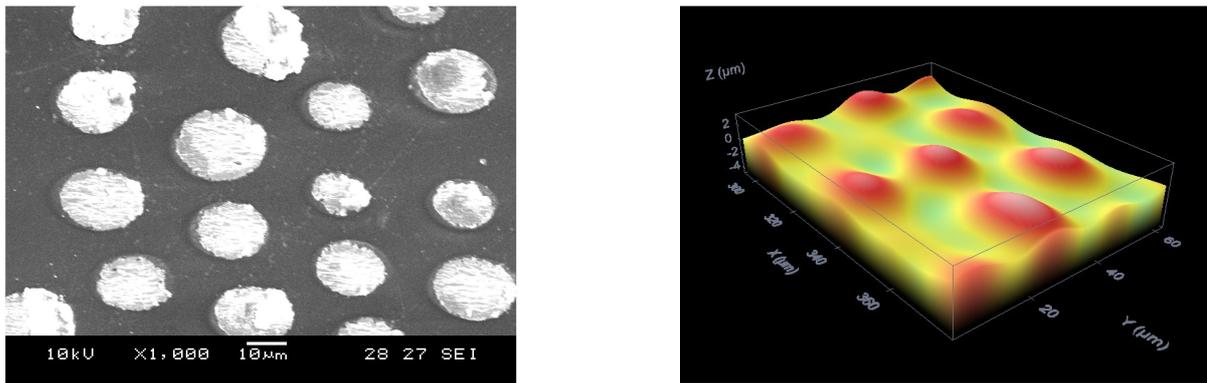


Figure 3 Details of a protrusion array. (a) SEM image showing the surface fully covered by micro dots; (b) 3-D profile (a zoom-in view); (c) top view; (d) cross-sectional view.



(a) SEM image

(b) 3-D Confocal scanning

Figure 4 Elliptical shaped protrusion array.

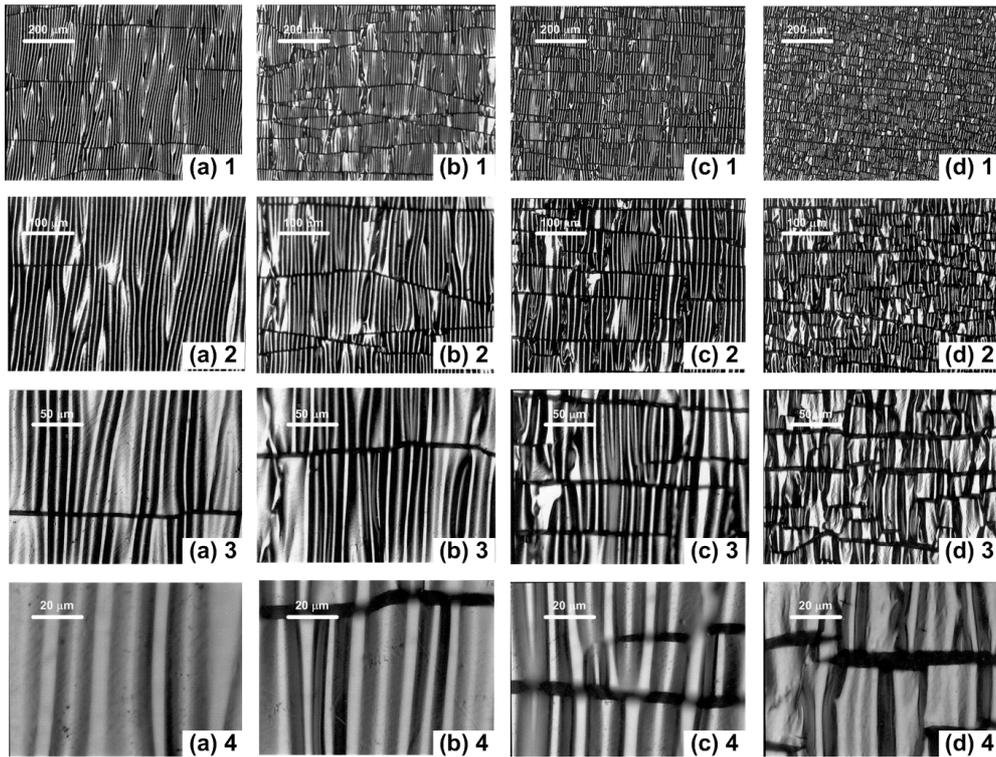


Figure 5 Strip shaped wrinkles formed atop a pre-stretched SMP (coated with a thin layer of 50 nm Ni). (a) 5% pre-strained; (b) 10% pre-strained; (c) 20% pre-strained; and (d) 40% pre-strained.

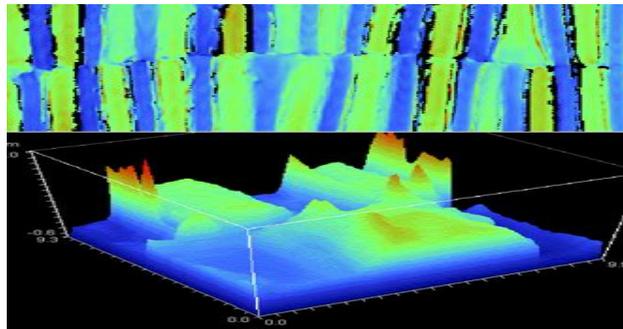
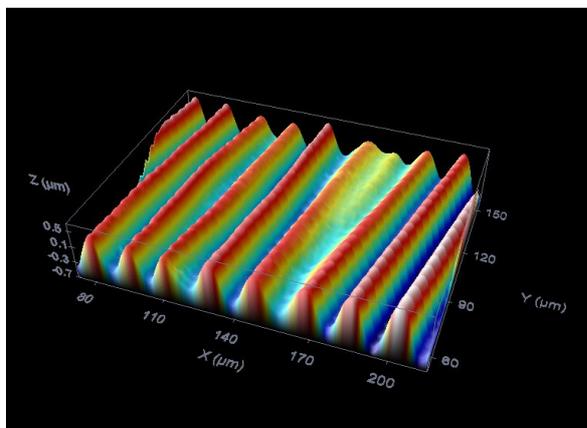
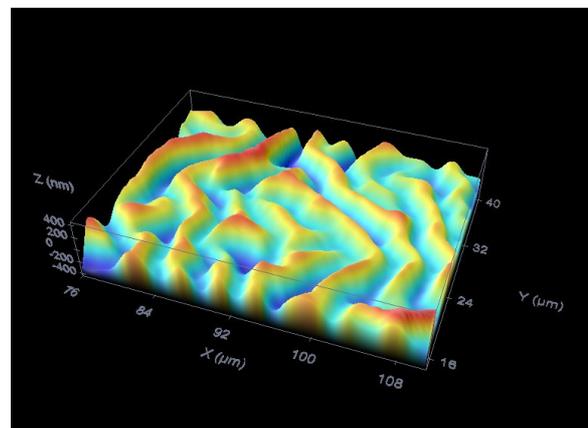


Figure 6 Enlarged image (top view and 3-D view, by Wyko scanning) of a fine hairline crack that causes slight shear of the wrinkles.



(a)



(b)

Figure 7 Wrinkles atop SMP (50 nm thick gold coated). (a) Strips; (b) labyrinths.

4. Conclusions

We demonstrate a few novel techniques for micro/nano patterning atop SMPs. Reversible micro vertical chains, crown shaped micro/nano protrusion arrays and strip/labyrinth wrinkles atop SMPs are realized and characterized. This study confirms the feasibility and convenience in micro/nano patterning utilizing SMPs, in particular, for protrusions.

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