

Recovery behaviour of shape memory polymer with laser-inscribed hierarchical micro/nanoscale features

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Abstract

This report studies the recovery behaviour of a shape memory polymer (SMP) with femtosecond laser-machined hierarchical micro- and nano-scale surface structures over the course of multiple deformation and recovery cycles. In an effort to identify the respective contributions of the nano and microscale texture, we investigate samples with a typical laser-induced porous network of nanostructures in comparison to microstructures such as pillars and holes of square and triangular shape covered in alike laser-induced nanostructures. Square microstructures recovered fully even after multiple cycles. In contrast, triangular shaped microstructures, which exhibited good recovery after one cycle, lost their structural integrity after multiple deformations. The difference in recovery between the different geometries is explained by the respective elongation of the geometrical features under deformation. The porous nanostructure showed poor recovery over the course of repeated deformations, which we attribute to surface energy minimization during the squeezed deformation stage. Contact angle measurements on all surfaces before and after deformations correlated well with the detailed topographical analysis. The observations of this SMP on these small scales shed some light on the limitations of these materials and of laser micromachining as an industrially versatile processing method.

Keywords: Shape memory polymer, laser micromachining, hierarchical structure, deformation, contact angle

1. Introduction

Shape memory polymers have been investigated for various medical applications (e.g. as stents, sutures or deployable structures), smart textiles, and structural materials with self-healing properties [1]. More recently, shape memory polymers have also gained interest in microtechnology and more specifically in sensing or attachment [2] applications, where the difference in macro or microgeometry results in a difference in wetting [2–5] or optical response [6,7].

Shape memory polymers (SMPs) are considered as smart materials which can be moulded or machined to a permanent shape, be deformed into a temporary state by mechanical stress, and can then “remember”

and recover their permanent shape with the help of thermal or chemical stimulation. Thermal stimuli include direct application of heat, and exposure to optical or electromagnetic fields. The underlying structure-property relations of SMPs are complex, yet the general principle is briefly outlined here: SMPs, being block copolymers, consist of hard and soft segments, each with their own transition temperatures. The hard segments constitute the so-called netpoints of the permanent shape, while the soft segments stabilize the structure given by these netpoints. Upon heating above the SMP's transition temperature T_{trans} the soft segments no longer stabilize the permanent shape. The material becomes rubbery and elastic, and in this state can be deformed. If the temperature is reduced below T_{trans} while the material is kept under constant stress or strain, the soft segments solidify and upon relaxation of the stress or strain the temporary shape remains fixed. The material recovers its permanent shape upon reheating to T_{trans} , which allows for mobility of the polymer chains within the soft segment. Stored energy is released, and the material relaxes into its energetically favourable permanent shape [5].

The recovery quotient [1] provides a measure for the efficacy of shape recovery and is a ratio determined by the following equation:

$$R = \frac{x_{temp} - x_{rec}}{x_{temp} - x_{perm}} \quad \text{Equation 1}$$

where R is the recovery quotient, x is the characteristic dimension of the topographical surface features (which in our study corresponds to the feature height), and the suffixes *temp*, *rec*, *perm* refer to the temporary, recovered, and permanent states. Based on this equation, a recovery quotient of $R = 1$ indicates a structure with perfect recovery properties, whereas a value of $R = 0$ denotes a surface that does not recover its shape at all after compression.

Most research efforts and applications concentrate on deformations of the microgeometry. Table 1 summarizes a non-exhaustive list of relevant works addressing SMPs with pillar, hole or grating structures of small length scales and the respective fabrication methods.

Table 1. Prominent research on micro- and nanostructure SMPs ordered by characteristic feature dimensions from micro to nano.

Author	SMP used	Type of Geometry	Length scale (width and height)	Machining Method	Deformation applied	Recovery of characteristic dimension
Wang et al. (2017)[2]	thiolene/acrylate copolymer	Reentrant mushroom-like pillars	w: ~10 - 55 μm h: ~30-50 μm	Lithography	10 MPa	Full recovery (5 cycles) based on contact angle; no dimensional characterization
Garcia-Huete et al. (2017)[4]	PCO + 2%DCP	Square pillars	w: 50 μm h: 16 μm	Fs laser micro-machining	0.6 MPa	h: 100% (2 cycles)

Zhang et al. (2020)[8]	DGEBA+OA+MXD A (8:2:3 molar ratio)	Pillars	w: 2-5 μm h: 10 μm	Molding	Pressing with glass	h: 100% (11 cycles)
Reddy et al. (2007)[1]	Tecoflex 72D	Pillars	w: 0.5 - 50 μm h: 10 -100 μm	Molding	Tilting with 300 μN	R = 67% (of tilt angle)
Meier et al. (2015)[6]	Tecoplast® TP 470	Optical grating	w: 10 μm h: 0.6 μm	Molding	6 GPa 10 cycles	Grating: h: ~95% (10 cycles)
Turner et al. (2014)[3]	POAOD	Boomerang, elbow and square pillars	w: 2-10 μm h: ~0.67 μm	Molding	0.55 MPa	unquantified full recovery (3 cycles)
Lee et al. (2016)[5]	Tecoflex EG72D	Gratings, pillars and holes	w: 0.2 - 2 μm h: 0.2 - 2 μm	Molding	Stretching, 50-200% of Young Modulus (7 MPa at 80°C) 10 cycles	Gratings: w: 85-100% Nanopillars: w: 90%, h: 50% Nanoholes: w: 98%, h: 4%
Wang et al. (2011)[7]	Acrylate based SMP	optical gratings	period: 834 nm h: 0.2 μm	Lithography	4 MPa 1 cycle	h: 97-100%

While direct comparison is not always possible due to the different chemical nature, fabrication process and deformation applied, some general trends can be summarized. Many works highlight close to full recovery over several deformation cycles either measured from geometrical analysis or indirectly through wetting analysis. Wang et al. (2017) [2] used photolithography to create re-entrant pillars with the goal of testing the omniphobicity of a reversible surface. They tested 5 deformation cycles and showed 100% recovery in the wetting behaviour of the structured surface. However, this contribution did not assess recovery through a quantification of the dimensions of the microstructure before and after deformation.

Garcia-Huete et al. [4] textured the surface of a SMP by femtosecond laser micromachining to induce permanent surface patterns. Their study concentrates on the recovery and wetting characteristics of square pillar structures. However, their study focused only on the recovery of the microstructures and did not provide scanning electron microscope (SEM) images to assess the effect of the deformation cycles on the characteristic laser-induced nano/microstructures that is expected to have formed on all areas subjected to laser irradiation.

Zhang et al. [8] also tested the reversible wetting characteristics of their round pillared structures created by replica-molding. They varied the surface pattern and pillar angles by different compression methods

and highlighted full recovery over multiple deformation cycles through geometrical analysis using confocal imagery and contact angle measurements.

Similarly, for micrometric surface features with low aspect ratios, the works of Turner et al. [3] and Meier et al. [6] highlight good recovery, with a recovery of the characteristic dimension at 95% which is approaching a perfect recovery. However, Reddy et al. [1], who investigated micropillar surfaces on a Tecoflex surface, found a recovery of only 67% after the first cycle assessed through the pillar tilt angle upon tilted deformation, citing possible overstressing as the cause of incomplete recovery. Lee et al. [5], who also worked with Tecoflex, highlighted differences between the recovery characteristics of different micro- and nanometric geometrical features. Their results present excellent recovery for stretched grating structures, which also correspond to the excellent recovery of Wang et al.'s gratings [7]. On the contrary, nanometric pillar and hole features presented rather poor recovery in the dimension perpendicular to the direction of deformation. Overall, these findings indicate that strain recovery, which explains the satisfactory recovery of microstructures, competes with surface energy minimization for nanostructures, which gains in importance with increasing surface to volume ratio.

The variety of methods suitable for structuring SMPs on the nanoscale is limited. As seen from Table 1, micro-molding is a popular method to apply the permanent shape to the different SMPs. However, micro-molding alone is not easily adaptable to the synthesis of complex, possibly reentrant nanostructures. And while lithographic fabrication is suitable for fundamental investigations on flat substrates, it is less practical for widespread and economically competitive applications on complex part geometries. This is where ultrafast laser micromachining provides advantages, as microstructures can be directly written onto surfaces in a single step, without the need for a cleanroom or vacuum equipment. This route to SMP structuring has already been exploited by Garcia et al. [4]. As an added bonus, polymers subjected to pulsed ultrafast laser radiation slightly above the threshold fluence typically exhibit a porous network of nanostructures overlaying the microscale geometry, resulting in a hierarchical structure [9]. The formation of these characteristic small-scale features can be attributed to explosive boiling of a superheated melt layer and its rapid quenching upon irradiation with ultrafast laser pulses [10]. Yet, Garcia et al.'s contribution was limited to wetting characterization and has not assessed recovery characteristics of the laser-induced nanostructure.

Therewith, the objective of the present study is to assess the suitability of ultrafast laser machining for the fabrication of permanent shapes consisting of microfeatures with superimposed laser-induced nanostructures on shape memory polymers. Our study focuses on the SMP behaviour upon thermomechanical cycling, where the temporary form is achieved via compression and recovery is induced by temperature change [11]. We have laser-textured SMP surfaces with protruding pillars and recessed holes of both square and triangular geometry in addition to a nanostructure-only sample. The load-bearing solid surface fraction of each microgeometry was designed to facilitate equivalent analysis

of their recovery abilities assessed from geometric analysis through confocal and scanning electron microscopy. Thus, the load-bearing solid surface fraction of square pillars, square holes and triangular pillars ranged from ~0.2-0.3, while triangular holes showed the exact negative pattern of triangular pillars with a load-bearing solid surface fraction of ~0.7.

2. Materials and methods

The SMP investigated in this report is Desmospan 2795A[®], a copolymer produced by Covestro, Germany with a switching temperature (T_{trans}) of 40°C [12] and a melt temperature around 200°C [13]. The soft segment consists of poly(1,4-butylene adipate) (PBA) ($M_w = 3500$ g/mol)¹¹ and the hard segment is composed of 4,4'-methylenediphenyldiisocyanate (MDI) and 1,4-butanediol (BD) as a chain extender [12]. The material was received as sheets of 2 mm thickness, from which samples were cut with a sharp metal blade for subsequent laser machining. The arithmetic mean roughness of the raw material was measured via confocal microscopy (Olympus LEXT OLS4000), yielding a value of $R_a = 28$ nm.

2.1 Laser micromachining

An amplified Ti-Sapphire laser system (Coherent Libra) was used for micromachining the polymer samples. The laser provides a horizontally polarised Gaussian beam of 800 nm wavelength, in pulses of 100 fs duration with a repetition rate of 1 kHz. The power of the laser beam is adjusted by a computer controlled variable attenuator which consists of a half-wave plate and a polarizing beam splitter. The beam was focused on the samples using a 50 mm plano-convex lens, to a theoretical spot size of 20 μ m. To develop the various micro- and nanostructures tested in this report, a custom laser trajectory was developed for each surface. Custom Python codes were written to synchronize translation stages in 3 axes (Newport Corporation) and a mechanical shutter (VS25, Vincent Associates) so that the sample was translated under the beam to inscribe the desired geometry.

Table 2 lists the beam power, scanning velocity, line overlap percentage, and number of overscans used to micromachine each sample. Experiments were carried out in atmospheric conditions. The machined samples were cleaned after machining by ultrasonication in methanol for 5 minutes to remove any remaining debris.

Table 2 Parameters used for micromachining of each sample surface.

Structure	Velocity (mm/s)	Power (mW)	Overlap %	Overscan #
Nanostructure	2	15	80	1
Square Pillars	0.5	30	87	3
Square Holes	0.5	15	87	1

Triangular Pillars	0.5	30	87	4
Triangular Holes	0.5	20	87	1

Figure 1 and Table 3 summarize the average dimensions of the different microstructures after laser machining. As per Figure 1 **Error! Reference source not found.**, the load-bearing surface fraction (f_{LB}) is the ratio between the load-bearing area of the microscale feature tops (A_{LB}) and the overall area of the polymer sample (A_{total}), such that $f_{LB} = A_{LB}/A_{total}$. The aspect ratio (AR) summarizes the ratio of the feature height (H) to the average width of the raised feature dimensions (indicated by grey shading in Table 3).

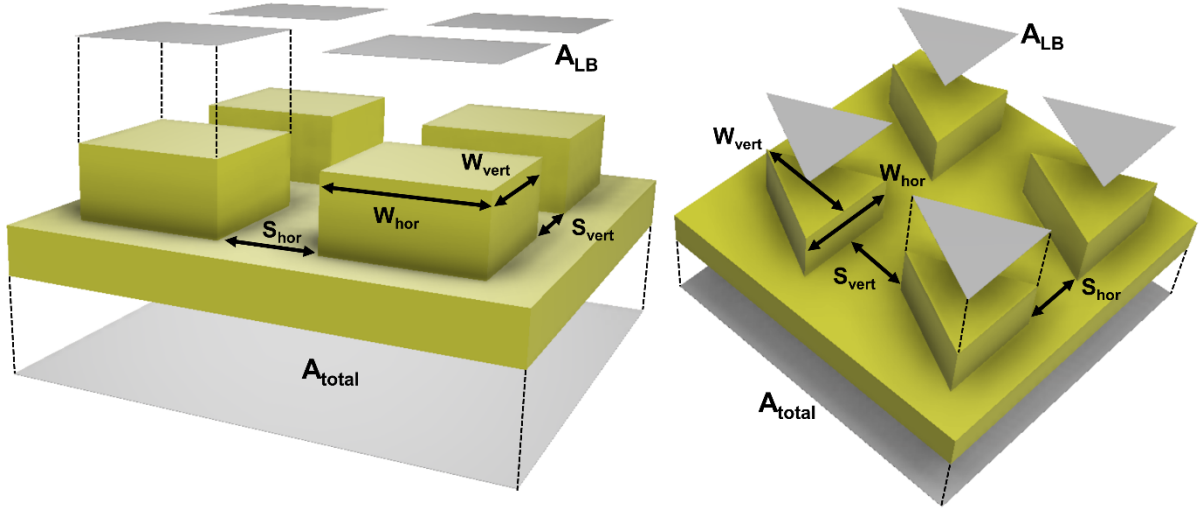


Figure 1. Characteristic dimensions for microtextured pillar samples (the alike nomenclature holds for hole samples where the characteristic features are machined into the surface).

Table 3. Average feature dimensions of pristine samples after laser machining

Geometry	W_{hor} (μm)	W_{vert} (μm)	S_{hor} (μm)	S_{vert} (μm)	H (μm)	AR (-)	f_{LB} (-)	P_{LB} (MPa)
Square pillar	105.2 +/- 0.8		83.5 +/- 9.6		113.7 +/- 1.2	1.08	0.31	3.00
Square hole	184.3 +/- 9.6		18.5 +/- 3.7		51.4 +/- 2.0	2.78	0.17	5.47
Triangular pillar	143.6 +/- 0.9	150.9 +/- 1.7	52.1 +/- 2.8	44.8 +/- 3.3	151.9 +/- 6.6	1.03	0.28	3.32
Triangular hole	172.4 +/- 2.8	178.0 +/- 3.2	23.6 +/- 1.9	30.9 +/- 2.4	62.9 +/- 1.8	2.31	0.63	1.47

2.2 Deformation cycles

For a single deformation cycle, first the samples were placed, structured side down, on the polished base plate in a 60°C oven (VWR Symphony) for ten minutes with no applied weight to allow the surface temperature, monitored with a thermocouple, to reach the soft transition temperature.

Then, weights were loaded onto the samples, as shown in Figure 2, which provides a schematic diagram of exactly how the sample surfaces were compressed using iron weights. The resulting pressure applied to the samples can be calculated either with respect to the overall area of the samples ($P_{total} = F_{applied}/A_{total}$) or with respect to the load-bearing area of the respective sample ($P_{LB} = F_{applied}/A_{LB}$). In our experiments, P_{total} was held constant at 0.93 MPa, but the load-bearing pressure P_{LB} varied according to the value of f_{LB} for each sample (Table 3). With this applied load, the samples were left to deform in the oven for 30 minutes. Additionally, the load remained on the samples as they were moved from the oven to a freezer which operated at -10°C to promote rapid cooling for fifteen minutes. The load was left on the samples in the freezer to prevent recovery, while the surfaces cooled to below the soft transition temperature. The permanent shape of the samples was recovered by placing the deformed samples in the oven at 60°C for 50 minutes. In between deformations or recoveries, the samples were stored in a refrigerator at 4°C to prevent unintended recovery of samples before analysis due to fluctuations in the ambient temperature.

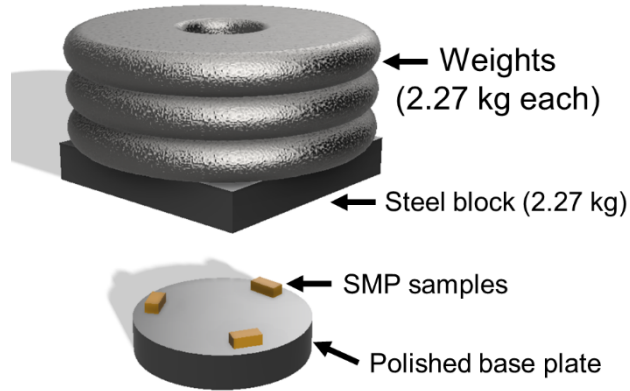


Figure 2. Schematic diagram of how the SMP samples were compressed using weights.

To explore the nature of the material's resilience over time, multiple deformation/recovery cycles were performed on each sample. We chose to apply 5 cycles to each sample, based on the results from works by Garcia et al. [4] and Turner et al. [3], where no significant change in material behaviour on the microscale was observed beyond 3 cycles. However, we note here that due to an oversight in the experimental procedure, the square holes sample underwent one additional deformation/recovery cycle. But we are confident that this one extra cycle did not significantly affect our observations of this sample after the 5 previous cycles. Therefore, for the sake of conciseness, and to avoid needlessly complicated figure and table headings, images and measurements of this sample are included alongside the other samples in the "5 cycle" columns of Figure 3, Figure 4, and Table 4.

2.3 Topography measurements, imaging analysis, and wetting behaviour

Width and depth measurements on the laser machined, deformed, and recovered microstructures were performed by confocal microscopy (Olympus LEXT OLS4000). Feature dimensions were retrieved from height maps of the confocal images and illustrated in Figure 4 (the detailed summary of dimensions is found in Supporting Information). Because of the normal distribution in feature shape, the height (H) or depth of a feature is reported as 95% of the height between highest peak and valley ($H_{\max}$). Distances of raised features (W) are accordingly measured between the 95% height on each feature edge. The spacing between raised features (S) was taken as the distance between features at the accepted height, as illustrated in Figure SI.1 in Supporting Information.

The dimensionless recovery quotient based on microstructure feature height was further calculated for geometry comparison. The nanostructure's recovery quotient was calculated using the root mean square roughness determined from the confocal analysis.

Confocal analysis was complemented with images of the detailed surface topography from scanning electron microscopy (SEM) (FEI Inspect F50). As the samples are polymer, a 5 nm thick gold coating was added via low-vacuum sputtering in order to avoid charge accumulation on the surface.

Dynamic contact angle measurements were performed using a goniometer (Data Physics OCA 15E). First, a 2 μL droplet of deionized water was placed on the surface. Then the drop's volume was increased to 7 μL at a rate of 0.1 $\mu\text{L/s}$. Finally, the entire 7 μL volume was removed from the droplet at 0.1 $\mu\text{L/s}$. The reported contact angles are averages from 4 measurements.

3. Results

3.1 Structural recovery

Figure 3 presents scanning electron micrographs of the samples' microgeometry in its pristine state, after 1 deformation (Def1), after one recovery (Rec1), and after 5 recoveries (Rec5). These SEM images visualize the differences between the different geometries and the scale of their dimensions with respect to each other. Furthermore, Figure 3 provide a qualitative perspective of the deterioration of the nanotexture's texture with multiple deformations.

These images are complemented by Figure 4, which provides confocal images, in which the height distribution of the samples throughout the deformation and recovery cycles are visualized by heat mapping, such that the colour at any location in an image indicates the local height as a percentage of the maximum, with respect to the colour bar beneath the images.

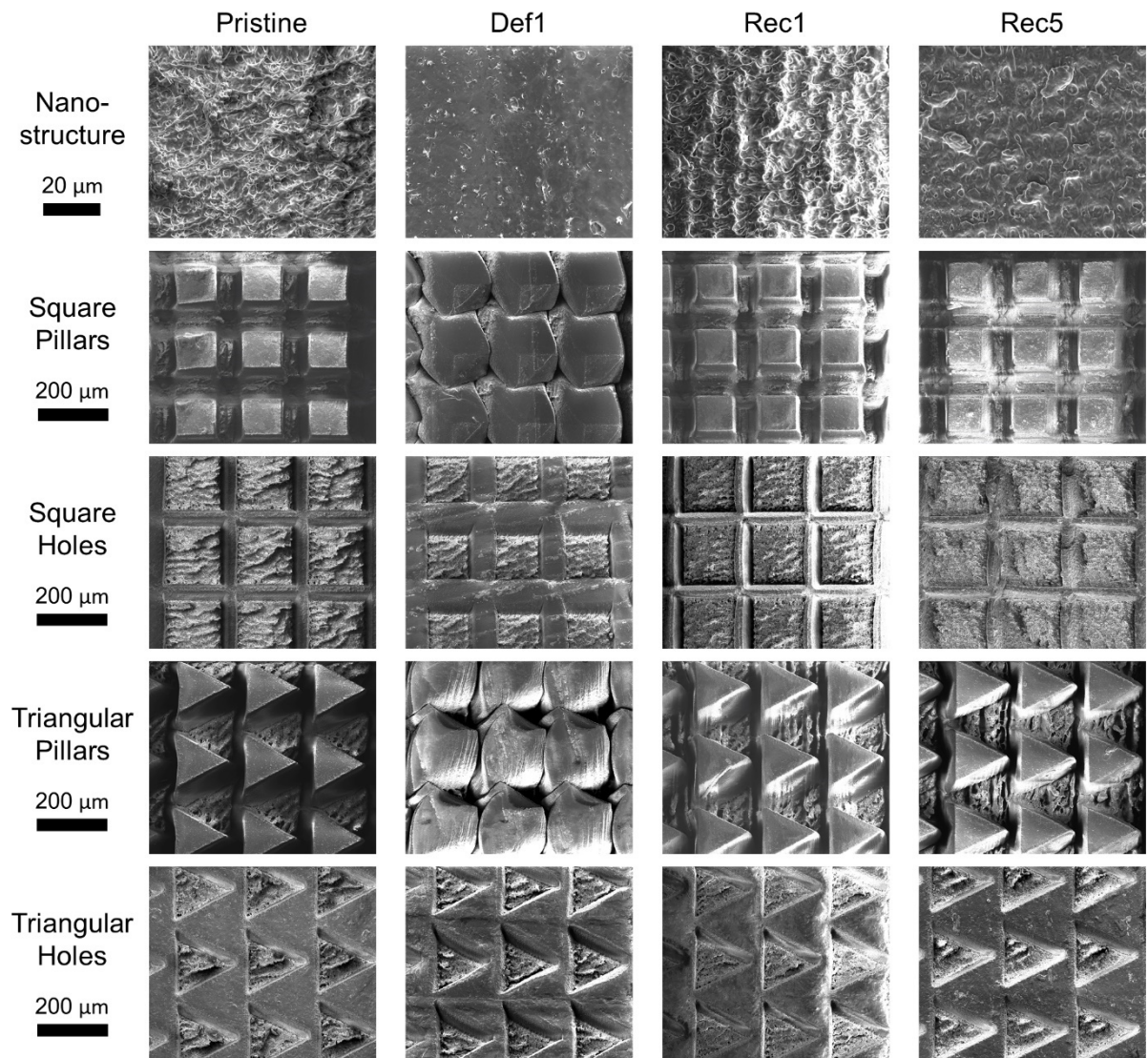


Figure 3. SEM images of samples throughout deformation process.

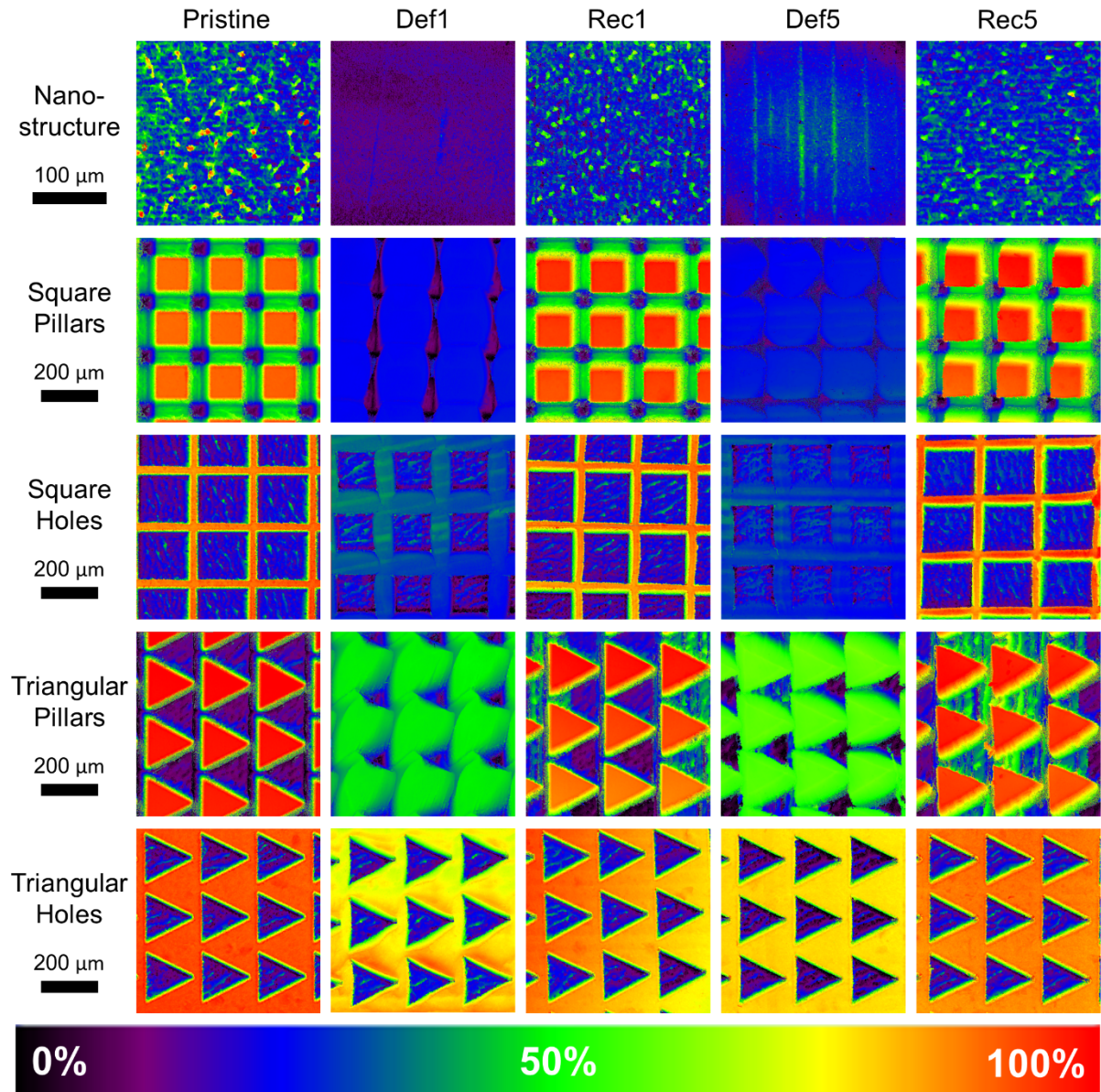


Figure 4. Confocal heat maps for samples throughout deformation cycles. The coloured bar underneath maps each colour to its respective height as a percentage of the height of the pristine structure. The height range for each surface is: Nanostructure (11 μm), Square pillars (220 μm), Square Holes (68 μm), Triangular Pillars (210 μm), and Triangular Holes (77 μm).

Comparing the first two columns of heat maps in Figure 4, the transition from warm colours (red and orange) towards cool colours (blue and green) clearly demonstrates that after one deformation, each structure is significantly flattened by the applied load. Further, the structures recover well to the permanent state even with repeated cycles of deformation and recovery. For example, due to the especially low weight-bearing area of the square holes structure, at the Def1 and Def5 stage this sample is completely flattened, and the entire image appears blue when heat mapping is applied. However, at the Rec1 and Rec5 stages, the presence of red colours indicates that the height of the microstructure has recovered fully to its original size. However, some degradation of the structures can be observed. This is analyzed more closely by considering the 2D height profiles displayed in Figure 5.

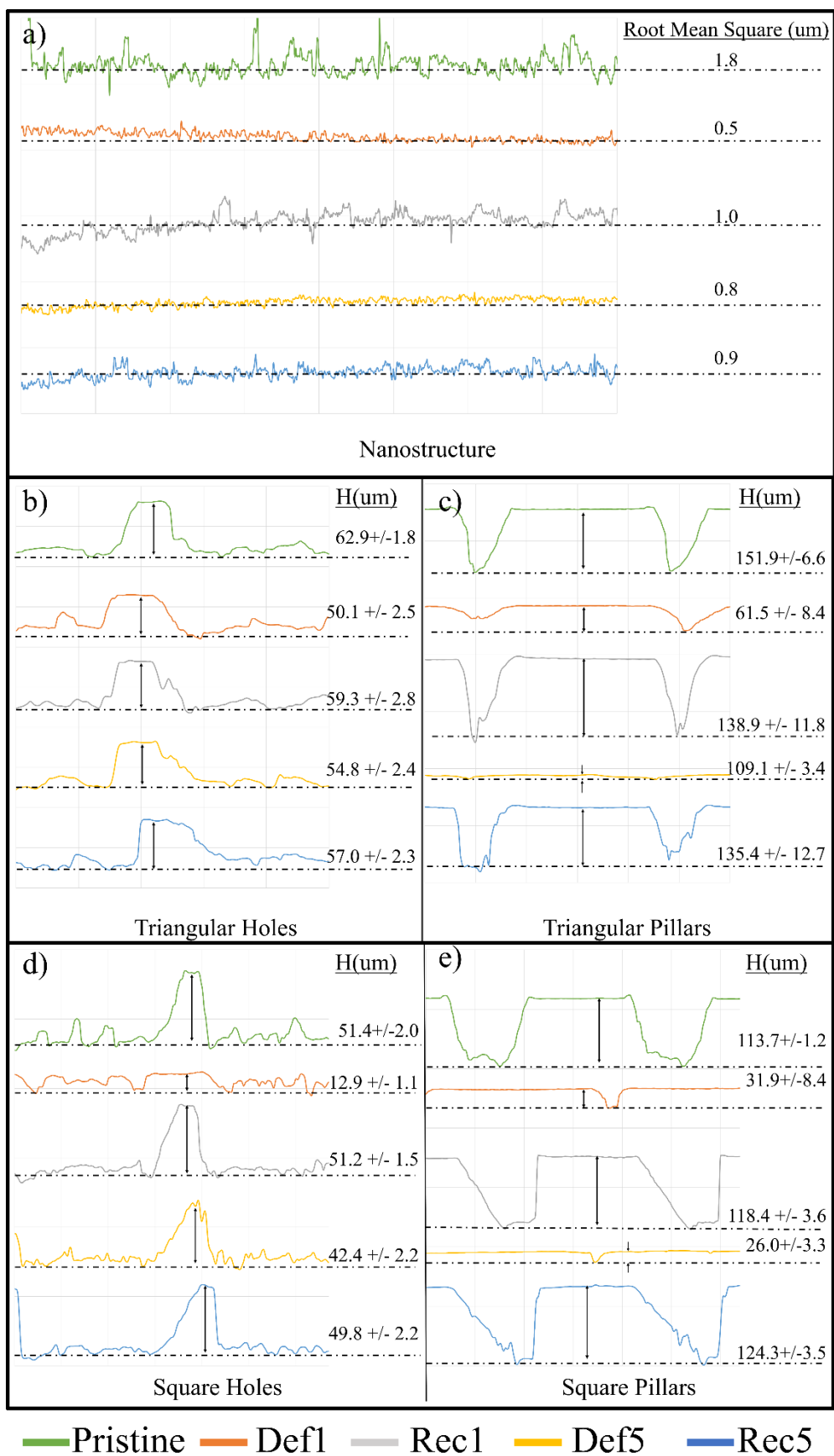


Figure 5. Evolution of height profiles for all samples. The mean measured height is listed in μm next to the relevant profiles. The heights are displayed in descending order from pristine (laser-machined samples), first time deformed (Def1), first time recovered (Rec1) samples, last time deformed (Def5), and last times recovered (Rec5) samples.

As a first observation we note that microstructure edges become less distinct on raised features, this is particularly noticeable for the pillar geometries in Figure 4 as the heat map shows fuzzy edges on the shapes' borders after multiple deformations compared to the crisp borders of the pristine samples. The square and triangular holes also show deterioration near raised feature edges as depicted in the images of Figure 3 and Figure 4 and in the appearance of more rounded height profiles in Figure 5c and e. Yet, while the microstructure can be recovered almost completely to the permanent form (Pristine, Rec1, and Rec5), we observe a significant level of permanent deformation of the nanostructures (refer to first line of Figure 3 and 4 and Figure 5a).

To further quantify the recovery properties of the nano- and microstructures, the dimensionless recovery quotients of the features' heights after one and after multiple deformation/recovery cycles were calculated, as summarized in Table 4. Several of the square geometries' recovery quotients were calculated to be greater than 1, which is merely a result of the surface variability as reflected in standard deviations of the relevant measurements (Figure 5). Measurements of microscale dimensions may have been affected by changes in the nanofeatures (as further discussed in the following) between raised features. A normalized baseline within these rough areas was difficult to determine, and so the lowest valley was used as a baseline for height measurements and subsequent width determinations.

Table 4. Summary of recovery quotients R based on structure height

Geometry	Recovery Quotient R	
	1 cycle	5 cycles
Nanostructure	0.38	0.11
Square Pillars	1.06	1.12
Square Holes	0.99	1.02
Triangular Pillars	0.86	0.61
Triangular Holes	0.72	0.27

Comparing the nanostructure surface to the others, it is evident that nanoscale recovery is considerably lower than recovery on the microscale. Figure 6 highlights details of the SEM images of the nanostructure sample and demonstrates that over the course of several deformation/recovery cycles, the complexity of the nanofiber layers decreased, and the overall structure became flatter (Figure 6a-c). A similar trend is observed for the square pillar and hole structures, where nanostructures between

the square pillars (Figure 6d-f) or inside the square hole (Figure 6g-i) also became less textured and less distinct with multiple deformations.

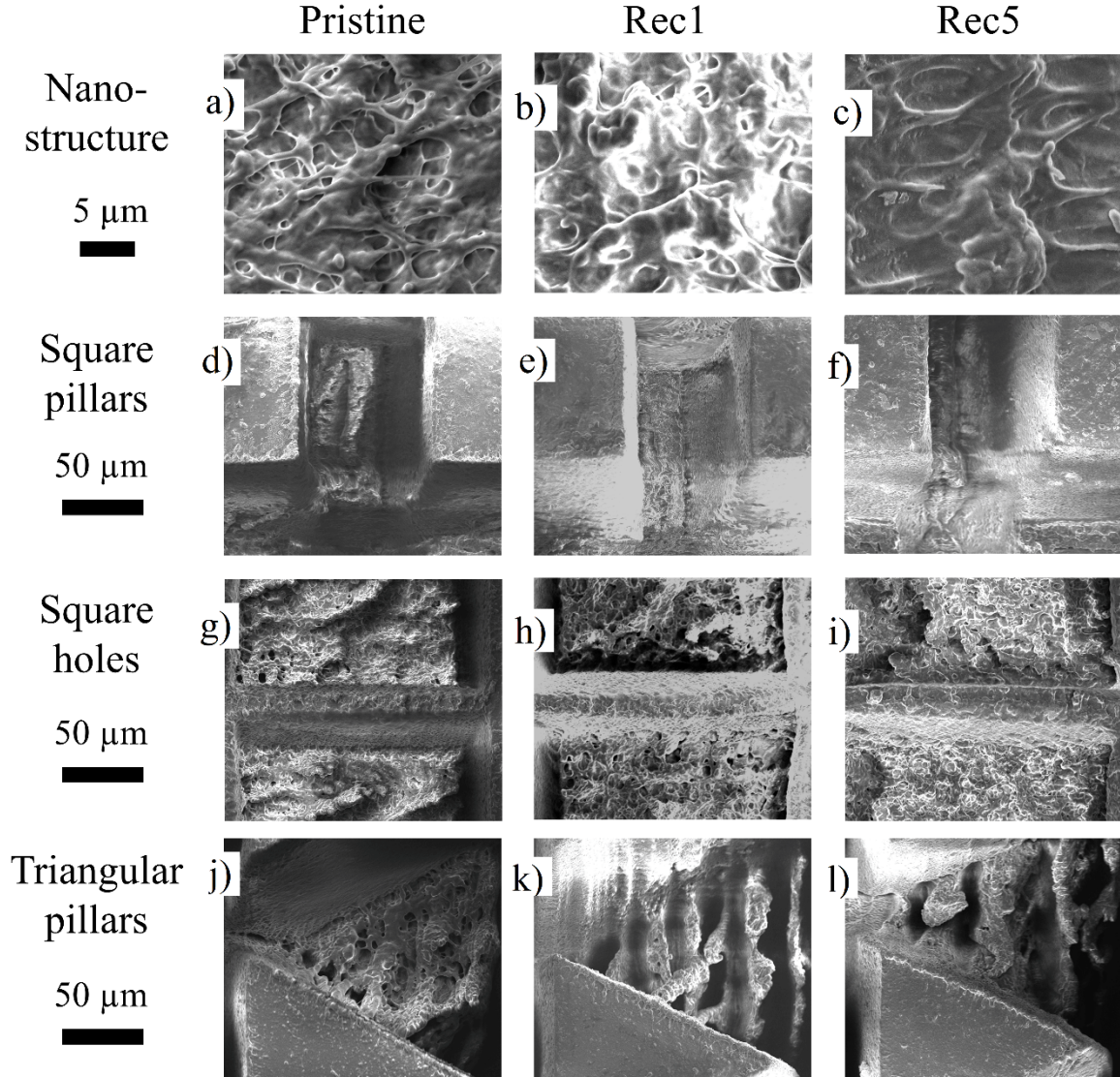


Figure 6. Changes in nanostructure from pristine sample to after 5 recoveries

This flattening and smoothing of the nanostructures with repeated deformation cycles correspond to the observations made by Lee et al. for their nanopillar and nanohole structures [5]. Along their reasoning, we suggest an explanation for the very low recovery of our nanostructures with regards to surface energy. Inherently, nanostructures have high surface energy owing to their very high surface-to-volume ratio. When these structures are heated to above T_{trans} and compressed, the soft segments of the shape memory polymer have a chance to reorient and realign into energetically more favourable locations and to thereby relax inherent stresses induced in the laser micromachining process. As such, surface tension minimization causes a gradual redistribution of soft and hard segments within a feature of high surface-

to-volume ratio (such as e.g. our laser-induced porous network structure) which consequently leads to a change in the overall yield strength of this nanostructure. Thus, in comparison with the bulk material, nanostructures progressively lose their capacity to elastically deform with each heating and deformation cycle as observed with the flattening of the height profiles (Figure 5) and evidenced by the extremely low values of $R = 0.38$ (1 cycle) and $R = 0.11$ (5 cycles).

Careful investigation of the nanostructure in between the triangular pillars (Figure 6 j-l) might suggest an opposite trend, as the nanotextured areas between the pillars become less distinct and more clustered with multiple deformations. This increases the range of the roughness height in between pillars. The variability of the depths between pillars is also made evident in the confocal data as shown in Figure 4. Yet, considering how the triangular features deformed (Figure 3 or 4) already in the first deformation, where the pillars got folded over sideways (likely caused by an uneven weight application), flow and material exchange is likely occurring not only between the nanostructure and the underlying bulk but also from the sidewalls of the originally raised but then squished microfeatures to the nanotextured pores during deformation.

Overall, the poor recovery of the nanostructures is observed for all samples (nanometric features either flatten out and seem to merge with the bulk material or bundle up in microclusters) and is explained by the relaxation of inherent stresses and surface energy minimization upon repeated heating and deforming cycles.

3.2 Effects of geometry

Returning to Table 4, we can further state that in contrast to nanoscale recovery, most microstructures recover very well. Both square geometries recover completely ($R \approx 1$) even after multiple cycles. This is noteworthy especially, since square holes exhibited a 45% lower load-bearing surface fraction than square pillars and were therefore deformed with the corresponding higher load-bearing pressure (Table 3). In contrast, we note that triangular pillars exhibit incomplete recovery already after the first cycle. This discrepancy is surprising since the triangular pillars were compressed by a load-bearing pressure within the range of square holes and square pillars, which could have suggested that the recovery quotient of triangular pillars would be similar to that of the square structures. However, where R for the square structures was close to unity, for triangular pillars we observe lower values of $R = 0.86$ (1 cycles) and $R = 0.61$ (5 cycles). This discrepancy suggests that the actual feature geometry might be responsible. Specifically, we suggest that highly angular structures (like triangles) are especially prone to experiencing plastic deformation, as opposed to recoverable elastic deformation, when compressed. Figure 9 presents a geometrical argument to support this hypothesis: shown in gray are cross-sections of square and triangle pillar geometries with equal areas. Considering a scenario where the pillar structures are compressed to half of their original height, the pillars must spread out laterally to conserve volume. Accordingly, cross-sections are expected to double in area, as illustrated by the blue sections

surrounding each shape. Then, as shown in Figure 7, the lateral displacement of a given feature's extremities under compression varies among different feature geometries. Taking the square as a reference, with a displacement of 1.00 unit length at its corners, the corners of the triangular geometry must spread 24% further to accommodate the shape change under compression. This comparison suggests that the low recovery quotient of very angular pillar geometries like triangles can be explained by the comparatively higher strain, which the material is subjected to. High strain on the crystalline netpoints in the SMP can lead to fragmentation of the crystalline regions. This fragmentation leads to an alteration in the crosslinking which affects the polymer's ability to recover to its original shape and thus leads to a degradation in the integrity of the permanent structure [14]. Following this logic, square structures sustain less structural damage during the deformation/recovery cycles because the perimeter of the structural features does not need to elongate as far, which therefore better preserves the crystalline cross-linking in the hard segments of the polymer. This argument also explains why, as can be seen in Figure 3, the corners of the triangular pillars structure become less sharp and more rounded throughout the deformation/recovery cycles applied.

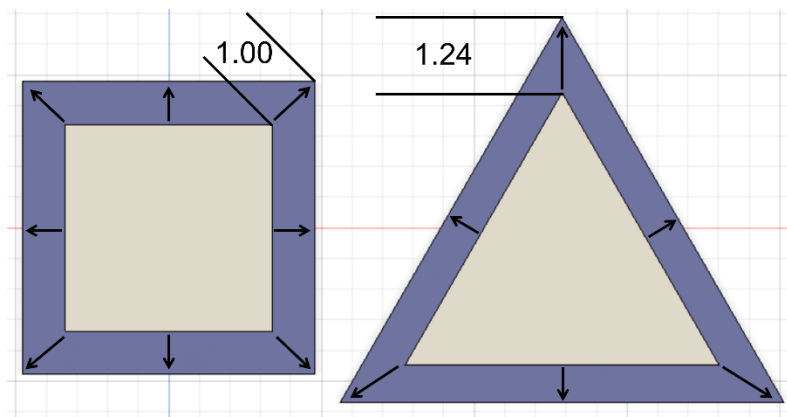


Figure 7. Geometric illustration of the change in horizontal size of square and triangular microscale features when deformed.

Lastly, we consider triangular holes, which show a much lower recovery quotient after 5 cycles ($R = 0.27$) than any of the other geometries. Interestingly, this discrepancy occurs due to the fact that of all the samples tested, the triangular holes structure had the highest load-bearing solid surface fraction ($f_{LB} = 0.63$), and thus the lowest load-bearing pressure (Table 3). Accordingly, even after 5 deformations, the triangular holes microstructure was compressed by only $8.1 \mu\text{m}$ (or 13%) from its pristine height of $62.9 \mu\text{m}$. This slight compression is significantly less than that of the other microstructures, for example the square pillars which were flattened down by $87.6 \mu\text{m}$ (or 77%) to one fifth of their pristine height. Hence, the low value of R for triangular holes is largely an artefact of its mathematical equation

(Equation 1). With the denominator being equal to only 8.1 μm , a change in only 1 μm in the structure's recovered height accounts for a shift in R of 0.12, which is very significant. Therefore, while at a glance the recovery quotient of $R = 0.27$ appears to indicate poor recovery of the triangular holes structure, the reality is that this microstructure maintained most of its pristine height throughout the deformation cycles, which is not reflected in the low value of R for this sample.

To support this explanation, we performed an extra deformation cycle on the triangular holes microstructure using an increased load-bearing pressure of $P_{LB} = 3.00$ MPa, which corresponds to the load-bearing pressure applied to the square pillar sample. As shown in Figure 8, this resulted in a much greater change in the feature height when deformed, and also much greater recovery, with a recovery quotient of $R = 0.96$, which now falls into the range of R for other microstructures as listed in Table 4. This experiment indicates that when the SMP is deformed by only a few μm from its permanent structure, the recovery quotient does not provide a meaningful quantification of the material's recovery properties.

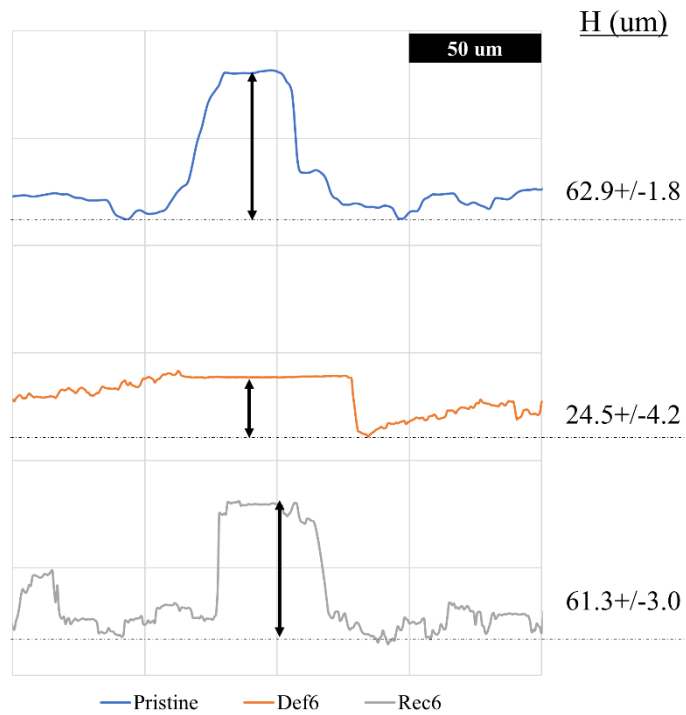


Figure 8. Evolution of height profile for the Triangular Holes sample when deformed at $P_{LB} = 3.00$ MPa.

3.3 Wetting behaviour

Wetting analysis has been used in several previous reports on textured SMPs to assess the recovery characteristics of microstructures [2,4,8]. Our Despoman 2795A[®] sample as received from the supplier showed an advancing contact angle of 89°. Yet, this value is not directly comparable to the contact angles of the micromachined samples, because femtosecond laser machining results in photochemical

reactions, which influences the surface chemistry. Accordingly, we assess the differences in wettability of different microstructures with respect to the laser-induced porous nanostructure. Figure 9 presents our samples' wettability through measurements of the advancing contact angle of each sample surface throughout 5 deformation cycles.

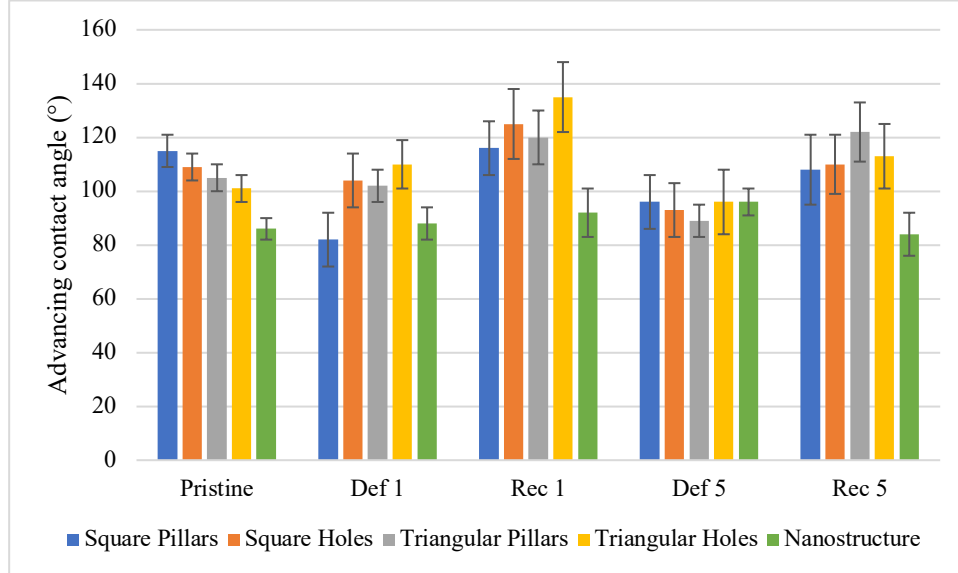


Figure 9. Advancing contact angles of microstructures throughout deformation and recovery cycles

All samples exhibited a high degree of contact line pinning and strong wetting which resulted in receding contact angles ranging from 0 to $\sim 59^\circ$ (Supporting Information: Figure SI2). Therewith, the contact angle measurements indicate that for all surfaces the high adhesion Wenzel wetting state is the dominant wetting state, which means that the liquid fills all depressed features on the samples [15]. One characteristic of Wenzel wetting is that the inherent surface wettability gets amplified by roughness and texture. This coincides with our observations for all microstructures, which show higher contact angles than the nanostructure sample. The comparison between different microstructure types does not allow for a clear conclusion, especially because statistically no significant differences are observed between most of the microstructures for any given deformation/recovery state. However, certain trends within each microstructure type across the different deformation states can be observed. As such, it is not surprising that deformed square pillar microstructures with flattened features and thus lower roughness show lower contact angles and thus wet more easily. Alike trends are observed for square holes and triangular pillars, yet without statistically significant differences between the pristine and first deformed surface. Differences for the contact angles measured on the triangular holes sample are even less significant, yet the general trend can be perceived. Finally, we note that the measured contact angles for recovered triangular features increase from the pristine structure upon deformation, which we attribute to bundling of the nanostructure and thus rougher appearance in between the microfeatures, as outlined

previously. Overall, our wetting analysis highlights that generally the contact angle results correlate as expected with the observations from the topographical analysis. Yet, the latter is more conclusive and thus better suited to fully understand a surface's recovery behavior.

4. Conclusions

The goal of this study was to identify the recovery potential of laser textured shape memory polymer surfaces and thereby also assess laser-micromachining as a possibly industrially relevant fabrication method for SMP related sensing applications. Our findings provide insights into the mass transfer occurring between nano- and microstructures as well as microfeatures and the bulk polymer. With repeated deformation and recovery cycles, the overall roughness and complexity of the nanoscale features decreased significantly, which is explained by surface energy minimization. In contrast, the microstructures showed minimal degradation; the edges of the structures became slightly frayed, but overall the microstructures maintained their structural integrity and shape, even after 5 deformation/recovery cycles. Among the 5 different samples tested, the square holes and square pillars microstructures had the highest performance, recovering completely to their pristine height even after 5 deformation cycles. Lower performance was observed for the triangular pillar and hole microstructures. We attribute this difference to the angular corners of triangular structures, which are more prone to experiencing irreversible plastic deformation while under stress than the square structures. Hence, small scale SMP applications should carefully consider the actual geometry in the microscale to ensure consistent recovery even with repeated use. Finally, our work highlights that manipulation of microstructure dimensions in future works, can lead to laser-textured SMPs with switchable wettability between temporary and deformed states, which is of interest to large volume manufacturing of microfluidics' sensing applications.

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