Electronic Supplementary Information

Tunable Shape Memory Polymer Mold for Multiple Microarray Replications

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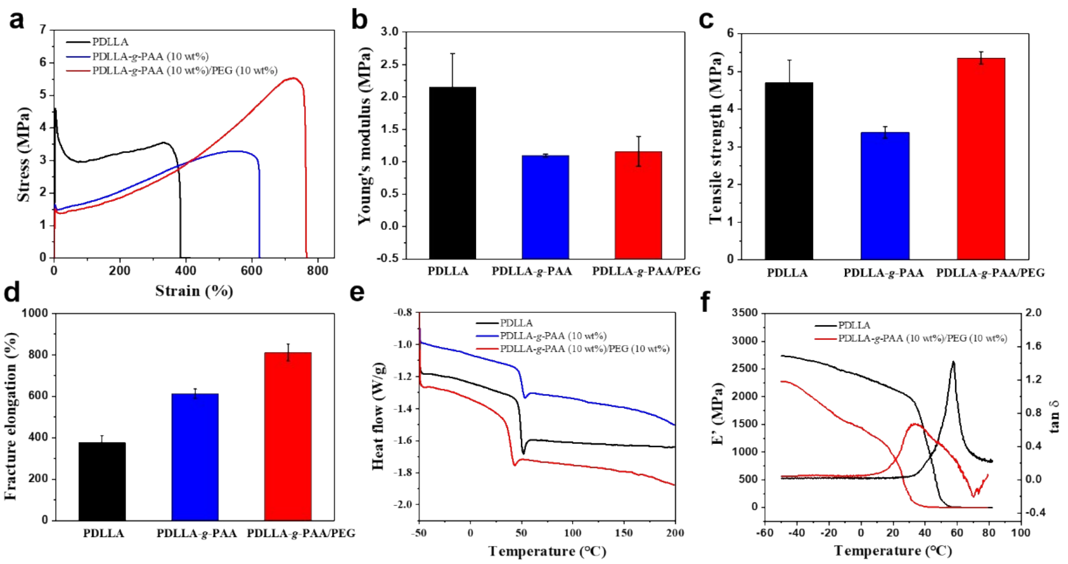

Fig. S1 (a) Stress-strain curves of neat PDLLA, PLDLA-*g*-PAA (10 wt%), and PDLLA-*g*-PAA (10 wt%)/PEG (10 wt%) respectively. It can be seen that the strain at break of these samples is very high, which is above 300%. Specifically, the strain at break of PDLLA-*g*-PAA (10 wt%)/PEG (10 wt%) is the highest, up to ≈ 769%. (b) Young's modulus of PDLLA-*g*-PAA (10 wt%)/PEG (10 wt%) has little loss compared to neat PDLLA due to grafting with PAA and blending with PEG, which approximately decreases from 2.15±0.52 MPa to 1.10±0.23 MPa. (c) Tensile strength increased to 5.36±0.16 MPa for the PDLLA-*g*-PAA (10 wt%)/PEG (10 wt%), which is higher than both neat PDLLA and PDLLA-*g*-PAA (10 wt%). (d) Elongation at break is from less than 400% for neat PDLLA, to 612±22% for PDLLA-*g*-PAA (10 wt%), and nearly 800% for PDLLA-*g*-PAA (10 wt%)/PEG (10 wt%). (e) T_g*s* of PDLLA samples change after chemical blending with PAA (10 wt%) or further physical blending with PEG (10 wt%). Neat PDLLA showed a sharp T_g (50.0 °C), while the T_g decreases gradually with reactive blending with PAA (48.9 °C) or further physical blending with PEG (39.3 °C). (f) Storage modulus E' and loss factor tan δ *vs*. temperature of the pure PDLLA and PDLLA-*g*-PAA (10 wt%)/PEG (10 wt%), measured by dynamic mechanical analysis (DMA).

Table S1. T_gs of PDLLA-*g*-PAA (10 wt%)/PEG varied with different content of PEG.

	Composition		
no	Sample	M_r	T_g (°C)
1	PLA-*g*-PAA (10 wt%)/PEG (30 wt%)	200	14.04
2	PLA-*g*-PAA (10 wt%)/PEG(20 wt%)	200	25.31
3	PLA-*g*-PAA (10 wt%)/PEG(15 wt%)	200	32.58
4	PLA-*g*-PAA (10 wt%)/PEG(10 wt%)	200	39.30
5	PLA-*g*-PAA (10 wt%)/PEG(5 wt%)	200	43.50
6	PLA-*g*-PAA (10 wt%)/PEG(2.5 wt%)	200	50.20

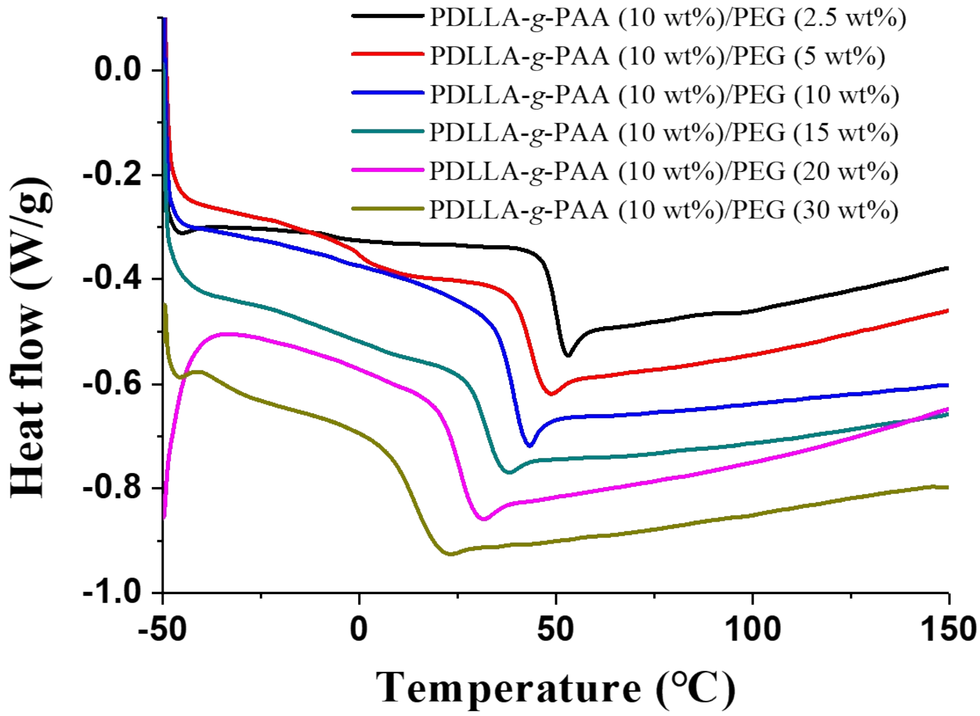

Fig. S2 T_gs of PDLLA-*g*-PAA (10 wt%)/PEG changed with different content of PEG. The T_g of PDLLA-*g*-PAA (10 wt%)/PEG decreases from 50.2 °C to 14.0 °C with increasing the content of PEG from 2.5 wt% to 30 wt%, which results from the enhancing chain mobility of PDLLA blending as the rubbery phase PEG increased.

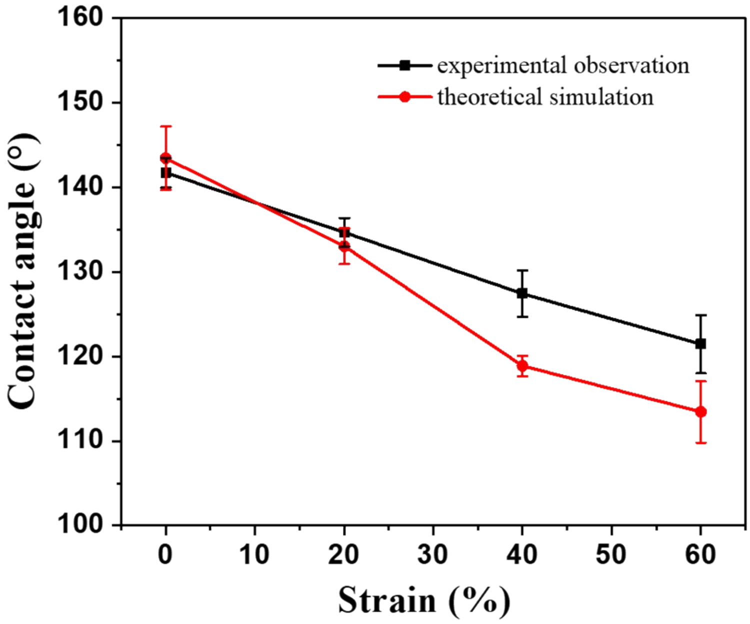

Fig. S3 The comparison of static contact angle (CA) between the theoretical calculation and experimental results of big round micropillars at different strains.

According to Wenzel model, the typical CA on the rough surface given by

$$\cos\theta_{\mathrm{w}} = r\cos\theta$$

where θ is the CA in the equilibrium state on a flat substrate and r is the roughness factor defined as the ratio of the actual area of the rough surface to the geometric projected area.[1] For the Wenzel model, the CA varies proportionally with the roughness factor. Because the roughness factor is always above 1, the wetting properties will be amplified. That means the addition of surface roughness will make hydrophilic surfaces (CA < 65°) more hydrophilic, while the hydrophobic surfaces (CA > 65°) more hydrophobic. In this work, the roughness factor r can be obtained by the following equation

$$r = 1 + \frac{h\cdot\left[2\pi b + 4\times(a-b)\right]}{(2a+\mathrm{s}_1)(2b+\mathrm{s}_2)}$$

where h is the height of patterns, a and b are the maximum and minimum radii of the round pillars in the direction parallel and perpendicular to the stretching, respectively, and s_1 and s_2 are the spacing in the direction parallel and perpendicular to the stretching, respectively. The heights of patterns at different strain were directly measured by scanning electron microscopy (SEM). For the strain of 0%, 20%, 40%, and 60%, the values of r were 1.15, 1.13, 1.12, and 1.11, respectively. The predicted CAs by the Wenzel equation are 143.4° (0%), 133.0° (20%), 118.9° (40%) and 113.4° (60%), respectively, which is in agreement with the literatures.[2, 3]

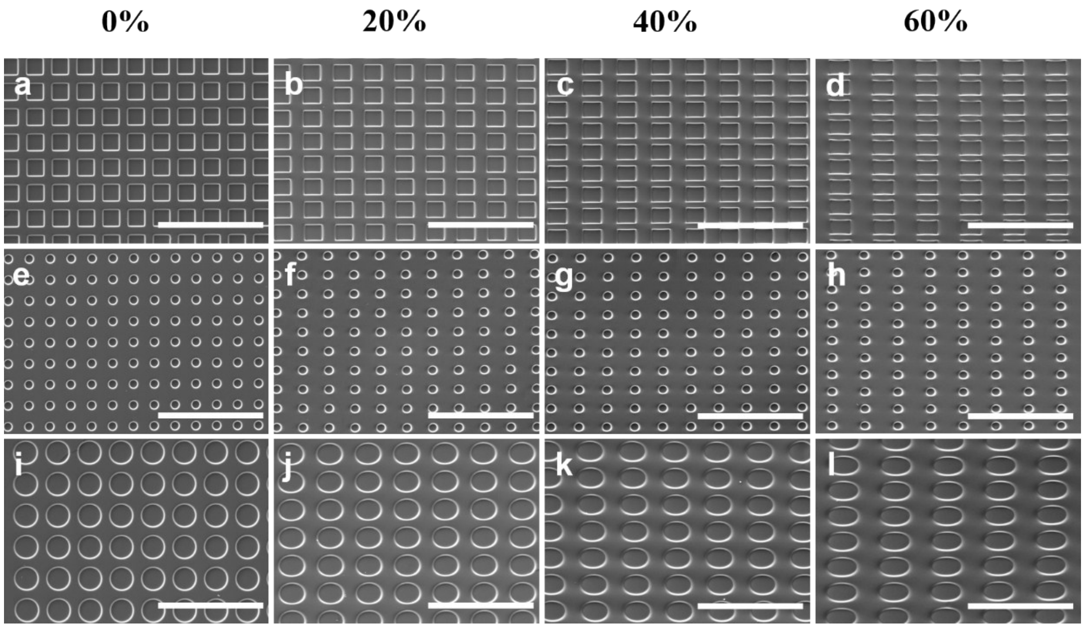

Fig. S4 (a-l) SEM images of large-scale PDMS replicas of square (a), small round (e) and large round (i) micropillars, and their corresponding elongated images at a strain of 20%, 40% and 60%, respectively. The scale bars are 500 μm.

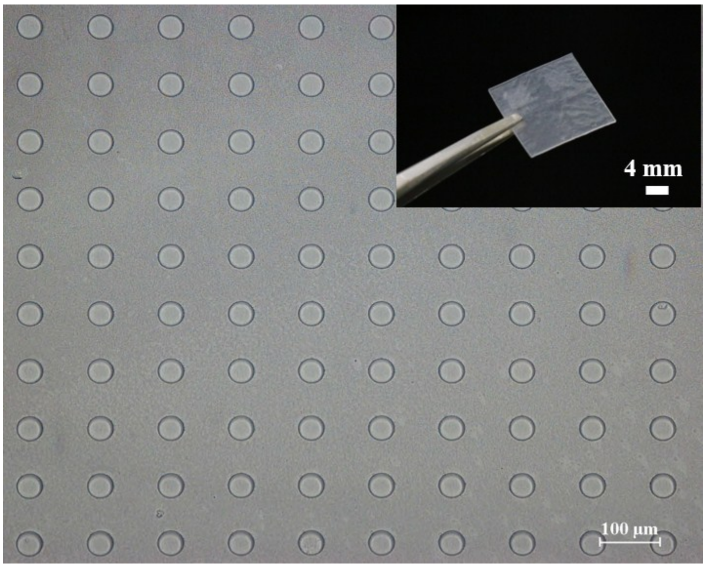

Fig. S5 Microscopic image of patterned EVA and the insertion is the photograph of EVA replica sample.

References

1 T. S. Wong, S. H. Kang, S. K. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, J. Aizenberg, *Nature*, 2011, **477**, 443.

2 B. He, J. Lee, N. A. Patanka, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 2004, **248**, 101.

3 L. Zhao, J. Zhao, Y. Liu, Y. Guo, L. Zhang, Z. Chen, H. Zhang, Z. Zhang, *Small*, 2016, **12**, 3327.