

A Soft Shape Memory Reversible Dry Adhesive

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 Electronic Supplementary Information

Abstract Transfer printing is a critical procedure for manufacturing stretchable electronics. During such a procedure, stamps are utilized to transfer micro devices from silicon wafers to stretchable polymeric substrates. In addition to conventional silicone rubber stamps, epoxy resin based shape memory stamps have been developed and the transfer yield is thus significantly promoted. However, elastic modulus of the epoxy stamps is too high at both glassy and rubbery states, which may break the brittle micro devices during the adhesion process under mechanical pressure. In this work, we synthesized a copolymer of butyl acrylate (BA) and polycaprolactone diacrylate (PCLDA) as a soft reversible dry adhesive enabling a shape memory capability based on crystalline transition of polycaprolactone (PCL) segments. For the sample containing 40 wt% BA and 60 wt% PCLDA, Young's modulus was 8.3 and 0.9 MPa respectively below and above the thermal transition temperature, which was much lower than that of the epoxy adhesive. On the other hand, the soft material still provided nearly ideal shape memory fixity and recovery ratios. Subsequently, shape memory surface with cone-shaped microstructure was prepared, which enabled a heating induced strong-to-weak adhesion transition when the microstructure recovered from a pressed temporary morphology to the permanent cone-shaped morphology. Such a soft reversible dry adhesive may contribute to large-scale and automated transfer printing processing.

Keywords Stretchable electronics; Shape memory polymers; Reversible adhesives

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INTRODUCTION

Flexible electronics, such as flexible circuits, flexible display, and skin-like sensors, are developing rapidly for their human friendly nature^[1, 2]. As a special and important class, stretchable electronics provide increasing opportunities since they can tolerate much larger deformation than other flexible electronics^[3–5]. In the manufacturing of the stretchable electronics, however, traditional fabricating methods are no longer suitable for the assembly of rigid inorganic devices and deformable polymeric substrates. Elastomeric stamps are used to transfer well-organized micro-scaled components from silicon wafers where they had been produced to soft polymer substrates which endow the functional devices with flexibility. Such a process is called transfer printing. Different from commonly used adhesives which require stable yet strong adhesion to bind interfaces together, the transfer printing stamps should provide tunable and reversible adhesion upon various stimuli or operating conditions taking advantage of surface morphology and physical (or chemical) interactions^[6–10].

A great many attempts have been made to meet the practical and specific requirements of the adhesives using as the transfer printing stamps. Viscoelastic silicone rubber

stamps were designed^[8]. Upon fast or slow peeling rates, strong or weak adhesion strength can be respectively conducted, achieving pick-up or release of the devices in a kinetically controlled manner. However, such a process is not very reliable since the peeling action is extremely hard to be controlled and the time window for the release is too small. As a result, the transfer suffers from a high failure rate, which cannot be applied in large-scale industrial processing. To solve this problem, shape memory stamps enabling thermally induced reversible strong-to-weak adhesion have been developed^[11–17]. The stamps provided micro-structure on the surface which can be flattened upon heating when they were pressed on to the micro-devices. The flattened surface can be fixed when cooling down the stamps while maintaining the pressure, providing a strong adhesion due to the large interfacial contacting area. At this stage, the micro-devices can be picked up. Upon heating again, the flattened surface would recover to its original micro-structure, which largely decreased the contacting area and the adhesion force. The micro-devices can thus be released and transferred onto the stretchable substrates. Recently, spatially selective transfer has also been developed *via* light induced local heating^[12]. The heating induced release provided a very large time window for the operation and the shape memory stamps thus enabled highly controllable transfer processing, which ensured a nearly perfect transfer yield. However, the currently applied shape memory stamps are

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based on epoxy resins which exhibit high modulus at both glassy and rubbery states^[12, 18, 19]. While the high modulus makes the detachment more efficient when the microstructure recovers to its original shape, the excessive stiffness is more likely to hurt the delicate micro-devices, which restrains its application in high-speed automated manufacturing.

In addition to the surface micro-structure, ideal shape memory stamps should provide suitable modulus and high shape fixity/recovery ratios at the same time. The stamps are not necessary to be ultra-soft, whereas the modulus had better be lower than 10 MPa and not damage the brittle devices no matter whether there is a stimulus or not. However, the low modulus and the high shape fixity are usually conflicting. Although a variety of soft shape memory polymers have been developed recently^[20, 21], their shape fixity was commonly not so perfect which may result in poor adhesion at the temporary strong adhesion due to the poor contacting, since the surface patterns cannot be totally flattened with an imperfect shape fixity. In addition, they generally required sophisticated synthesis to push the modulus till ultra-low since they usually involved liquid crystal transition or molecular switches as the mechanism for the shape memory transition. Facile and soft shape memory stamps with a good shape fixity ratio are still to be found.

In this work, we develop a butyl acrylate (BA)/polycaprolactone diacrylate (PCLDA) copolymer as the soft shape memory stamp. Both the crosslinking density and the crystallinity can be facilely tuned by the BA content, which can provide suitable modulus both at room temperature and beyond the melting temperature of the polycaprolactone (PCL) segments. When the BA content is higher than 60 wt%, the room temperature modulus can be lower than 10 MPa while the shape fixity ratio is nearly perfect (> 96%). Although similar copolymers have been developed^[22, 23], it should be noted that there is no emergent application for the reported materials. Moreover, microstructure on the surface enables large contrast between strong and weak adhesion states. No external mechanical force is even necessary in the releasing process, making it a competitive candidate for transfer printing. The transfer process is schematically shown in Fig. 1(a). The chemical structures of PCLDA and BA are shown in Fig. 1(b).

EXPERIMENTAL

Materials

Polycaprolactone diol ($M_n = 1.0 \times 10^4$, Sigma Aldrich), acryloyl chloride (TCI), triethylamine (TEA, TCI), methylbenzene (TCI), butyl acrylate (BA, TCI), and 1-benzoylcyclohexanol (UV-184, photoinitiator, TCI) were used as received.

Material Synthesis

Polycaprolactone diacrylate (PCLDA) was synthesized according to the method reported in the literature^[24]. Briefly, 10 g of PCL diol was dissolved in 100 mL of methylbenzene in a 300 mL of round-bottomed flask. And then, 1 mL of triethylamine and 1.2 mL of acryloyl chloride were added to the flask, and the reaction mixture was stirred for 6 h at 80 °C. The reaction mixture was filtered to remove

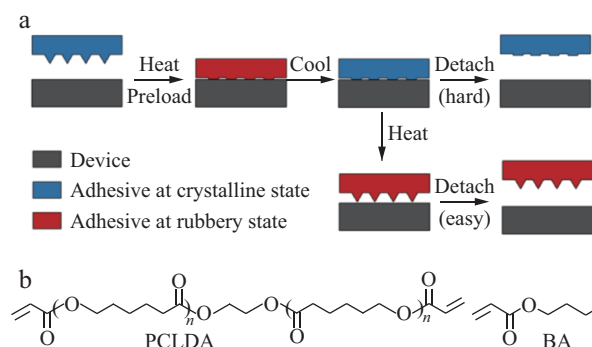


Fig. 1 (a) Illustration of the transfer process enabled by adhesive with shape memory microstructure; (b) Chemical structures of PCLDA and BA

triethylamine hydrochloride, and then the macromer was obtained by dropping the filtrate into an excess of *n*-hexane. Finally, the precipitated PCLDA was dried at 40 °C under reduced pressure for 24 h.

The copolymers of BA and PCLDA were prepared by UV polymerization. A certain amount of PCLDA was dissolved in BA with varied mass fractions (the BA mass content is 40%, 50%, 60%, 70%, respectively) at 80 °C. The photoinitiator (0.5 wt%) was added into the solution and stirred till solved. The precursor was poured into the mould composed of two glass slides with a silicon rubber spacer. Then the mixture was irradiated under UV light for 5 min. The cured material was then vacuum dried (100 °C) overnight. For the micro-structured material, the procedure was the same as above except that a hollow patterned silicon chip was stacked on the inner side of one glass slide during curing.

Chemical structure of the obtained material (BA60) was characterized by FTIR and ¹H-NMR. Specifically, due to the insolubility of the crosslinked film, the sample was cut into powder and swollen in the CDCl₃ for the ¹H-NMR test.

Thermal and Mechanical Properties Characterization

Melting and crystallization of the samples were tested *via* differential scanning calorimetry (DSC Q200, TA instruments).

Shape memory behavior of the non-structured samples was tested using dynamic mechanical analyses (DMA Q800, TA instruments). Shape fixity (R_f) and shape recovery (R_r) can be calculated using the following equations where ϵ refers to the fixed strain after cooling and load removal, ϵ_{load} refers to the maximum strain under load and ϵ_{rec} refers to the recovered strain.

$$R_f = 100\% \times \frac{\epsilon}{\epsilon_{load}}$$

$$R_r = 100\% \times \frac{\epsilon - \epsilon_{rec}}{\epsilon}$$

The Young's modulus of the samples was tested using a universal tensile test machine (Zwick/Roell Z005).

The adhesion strength was tested using the universal tensile test machine with self-made clamps. Each clamp of the pair consists of the disk part to contact the material and the binder part to connect the tensile machine. The two parts were joint together with a mobilizable ball bearing to guarantee a vertical testing force and avoid any shearing

strength. The disk was capable of being disassembled to allow load manipulation. The material in a flat film was cut into a 1 cm × 1 cm square with one side stick on the clamp disk surface using strong glue. A constant preload (2 N) was given when the material surface to be tested attaches the other clamp disk surface. The adhesion strength of the materials in different recipes and at different states were tested. Three protocols were conducted: (a) the preload was given at room temperature (*i.e.* the crystalline state) and the pulling test was also conducted at room temperature; (b) the preload was given at 70 °C (*i.e.* the rubbery state) and the pulling test was conducted at room temperature; (c) both the preload and the pulling test were conducted at 70 °C. The climax stress upon adhesion failure was defined as the detach stress to identify the adhesion strength.

The surface microstructure was observed *via* a confocal laser scanning microscope (Zeiss LSM 700).

RESULTS AND DISCUSSION

Material Synthesis

The material was obtained by simple radical initiated

copolymerization of PCLDA and BA. The diacrylate functionalized PCL ($M_n 1.0 \times 10^4$) serves as both the crosslinker and the crystallization segment, while their ratio is varied to tune the crosslinking density. Some basic characterization results are shown in Table 1 and Fig. 2. All the samples provide high gel contents (> 95%). As the BA content increases from 40 wt% to 70 wt%, the T_m of the materials maintains at around 45 °C, while the melting enthalpy decreases steadily. The PCL segment is dominantly responsible for the crystallization, thus a larger content of PCL results in a higher crystallinity of the material. The modulus drops acutely at both 70 °C (above T_m) and room temperature (below T_m) with the increase of the BA content. The decrease of crosslinking density effectively reduces the modulus of the sample at its rubbery state, while at the crystalline state, the decrease of crystallinity contributes to the modulus drop. Particularly, the modulus of the sample BA60 is about 0.9 MPa at 70 °C and 8.3 MPa at room temperature. In comparison, the previous reported epoxy-based shape memory stamps provided modulus of about 10 MPa above the glass transition and over 2 GPa at room temperature, much stiffer than the presented crystalline shape

Table 1 Characterizations of the samples

Sample name	BA content (wt%)	T_m (°C)	ΔH (J/g)	Gel content (%)
BA40	40	44.3	25.7	97.5
BA50	50	46.9	22.4	96.8
BA60	60	44.2	18.9	95.2
BA70	70	45.3	14.1	95.1

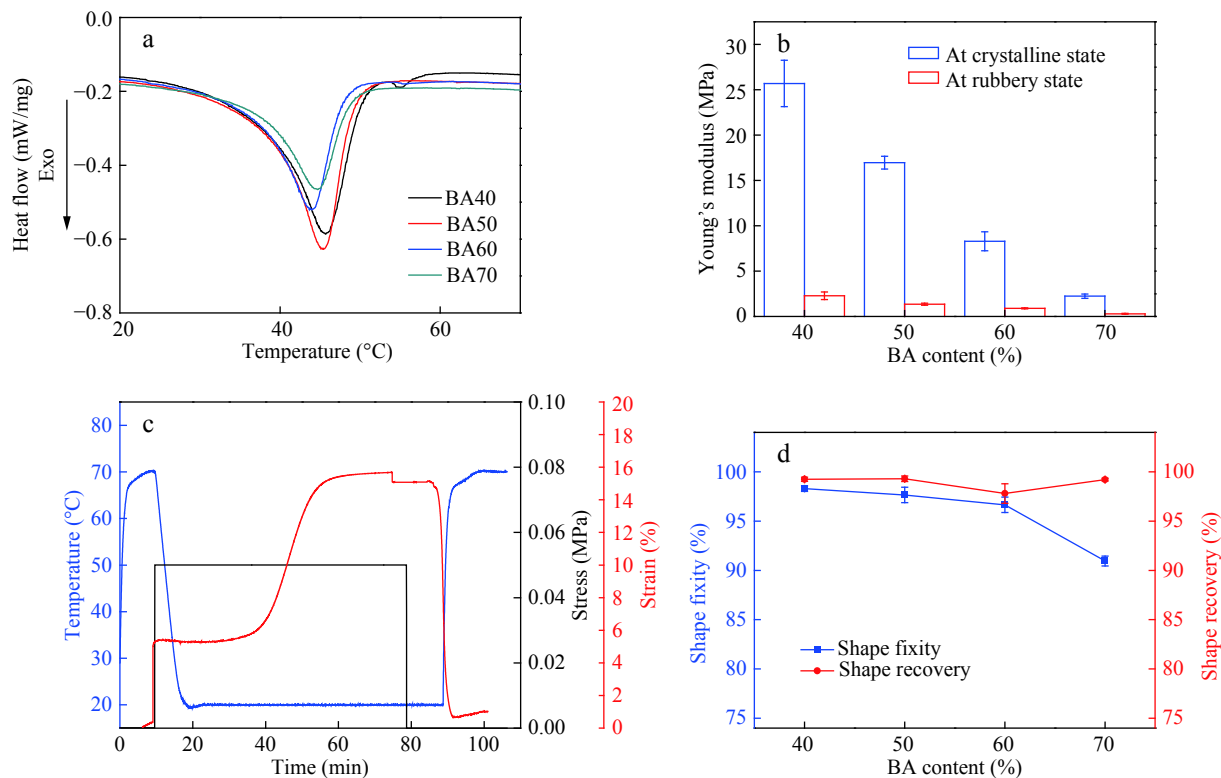


Fig. 2 Thermal and thermomechanical characterization: (a) DSC curves of the samples with different BA contents; (b) Young's modulus of the samples with different BA contents at crystalline and rubbery state; (c) a thermomechanical shape memory cycle; (d) shape fixity and shape recovery of the samples with different BA contents

memory stamp and more likely to damage the devices (see Fig. S1 in electronic supplementary information, ESI). FTIR and ^1H -NMR spectra of the typical sample BA60 are presented in Figs. S2 and S3 (in ESI), which supports the copolymerization of BA and PCLDA.

A typical thermomechanical shape memory curve is presented in Fig. 2(c). With the reduction of the crystallizable PCL content in the network, the shape fixity ratio should be accordingly reduced since network cannot provide sufficient switching segments to fix a temporary shape. However, as shown in Fig. 2(d), all the samples except BA70 provide almost ideal shape memory capability with both R_f and R_r higher than 96%. The R_f of BA70 that contains too small PCL amount decreases remarkably to 90%. In this case, BA60 is chosen as the base material for preparing the micro-structured stamp as well as further characterizations, although the modulus of BA70 is even smaller than that of BA60.

Adhesion Strength Characterization

We characterized the adhesion strength of the samples *via* testing the pulling strength of detaching the adhered surfaces as illustrated in Fig. 3(a). Fig. 3(b) shows a representative detaching curve. A 46 kPa adhesion strength is examined at a displacement of 0.04 mm. Such magnitude of strength is comparatively suitable for picking up the light devices.

The adhesion strength was measured *via* three different testing protocols for the same samples. As shown in Fig. 3(c), the samples can hardly adhere the surfaces together

when the preload is given at the crystalline state. This is owing to the fact that the mobility of molecular chains was restrained by the crystalline phase which led to a poor interfacial contact. On the contrary, when a preload was imposed at the rubbery state, much larger adhesion strength can be detected after complete crystallization. In comparison, when such a prepared bonding was tested over the melting temperature, a much lower (but still some) strength was detected. It is believed that the sharply reduced modulus at rubbery state of the samples is responsible for the decrease of adhesion strength. Typically, the adhesion strengths were approximately 10 and 2 N/cm^2 for the sample BA60 respectively at the crystalline and rubbery states. Although the variation is remarkable, the adhesion strength at the rubbery state (2 N/cm^2) is still too large for self-detachment for the light micro devices. In this case, micro-structured samples were to be developed.

Microstructure Assisted Adhesive

To effectively reduce the adhesion strength at the weak adhesion state, a much smaller contacting area at the rubbery state shall be desirable. Microstructure was fabricated on the adhesive's surface to boost the detaching efficiency. A silica chip with arrayed cone hollows was utilized as a mould to obtain the reversible adhesive with convex cones. When the structured adhesive was compressed on a flat object at a relatively elevated temperature (*i.e.* above its T_m), the cones on the surface were flattened, leading to a large contacting area. After the temperature dropped down to room

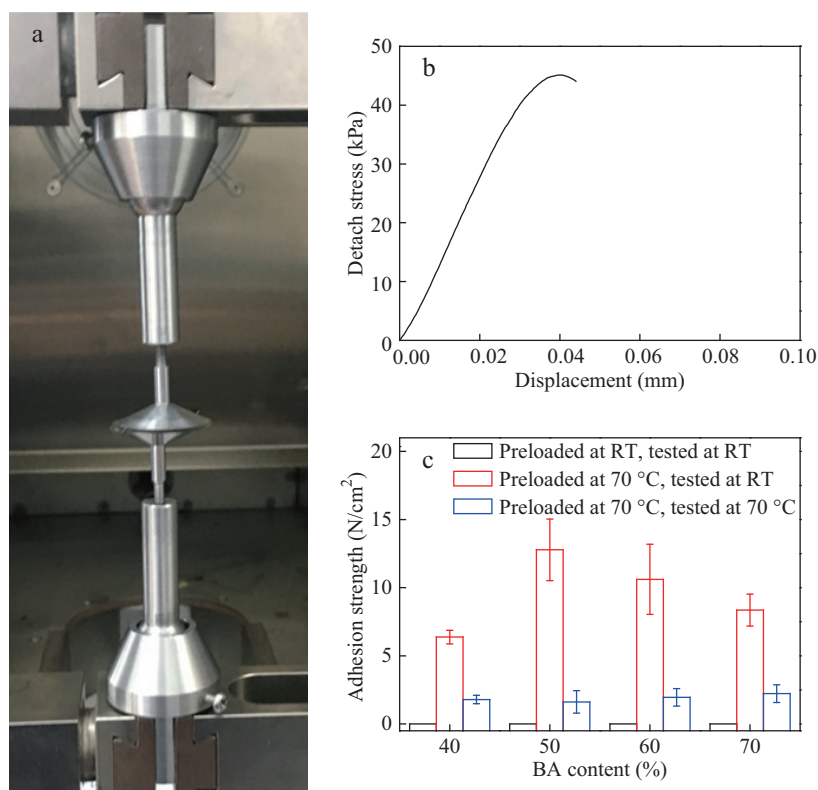


Fig. 3 Characterization of the adhesion performance: (a) illustration of the self-made clamps; (b) a representative curve of detaching process; (c) adhesion strength of nonstructured samples with different BA contents utilizing different protocols

temperature (*i.e.* below its T_m), the crystallization allowed the flattened surface of the adhesive to be temporarily fixed, making a relatively strong adhesion force between the surfaces. When heating above the T_m again, the entropy driven shape shifting enabled the cones to recover, leading to a peeling effort. As such, the contacting area was largely reduced and the adhesion force was greatly weakened.

Fig. 4 shows the morphology transformation of BA60 sample with patterned cones. At an original state, each cone is about 10 μm in diameter and 9 μm high. The confocal image confirms that the cones are almost flattened after programming (Fig. 4b). When heated to 70 $^{\circ}\text{C}$ again, the cones appear again though a minor shape deviation is found. The diameter of the underside is about 10.5 μm and the height is about 8 μm . It is understandable as the shape recovery is not perfectly 100%. The strain of flattening is undoubtedly very large, which may result in some permanent damaging of the materials. Nevertheless, we consider that such recovery is still acceptable.

The adhesion strength of the structured materials is tested in the same fashion with the nonstructured materials. As shown in Fig. 5(a), the absolute adhesion strength at strong state of the structured materials is somehow reduced in comparison to the nonstructured materials. This is mainly because the microstructures on the surface interfere in fitting of the surfaces. However, it is still acceptable because such

strength is large enough to pick up light devices. On the other hand, the adhesion strength at the weak state after shape recovery is too low to be detected. It is highly desired that the adhesion strength should be as low as possible at the weak adhesion state to achieve self-detaching, which can largely accelerate the entire transfer process. A video demonstrating the self-detaching process of a light glass sheet as a simplified transfer printing model instead of micro devices is available in ESI. The glass sheet weighed as 1 g is picked using the microstructured adhesive and the bonding can last for days (1 h illustrated in the video). Upon heating, the glass sheet drops immediately without any assistance of external force (as shown in Fig. 5c). The repetitive adhesion test in Fig. 5(b) shows that the structured material is quite durable in function, exhibiting nearly constant adhesion upon 10 times' repeating. Notably, such a self-detaching cannot be achieved *via* neither the nonstructured materials nor the previous epoxy reversible adhesives for their non-neglectful adhesion force during detaching. Furthermore, an array of chip resistors is adhered on the structured stamp and then transfer printed onto a silicon rubber substrate (shown in Fig. 5d). The micro-images confirm a successful transfer.

CONCLUSIONS

In this work, we prepared BA/PCLDA copolymers as

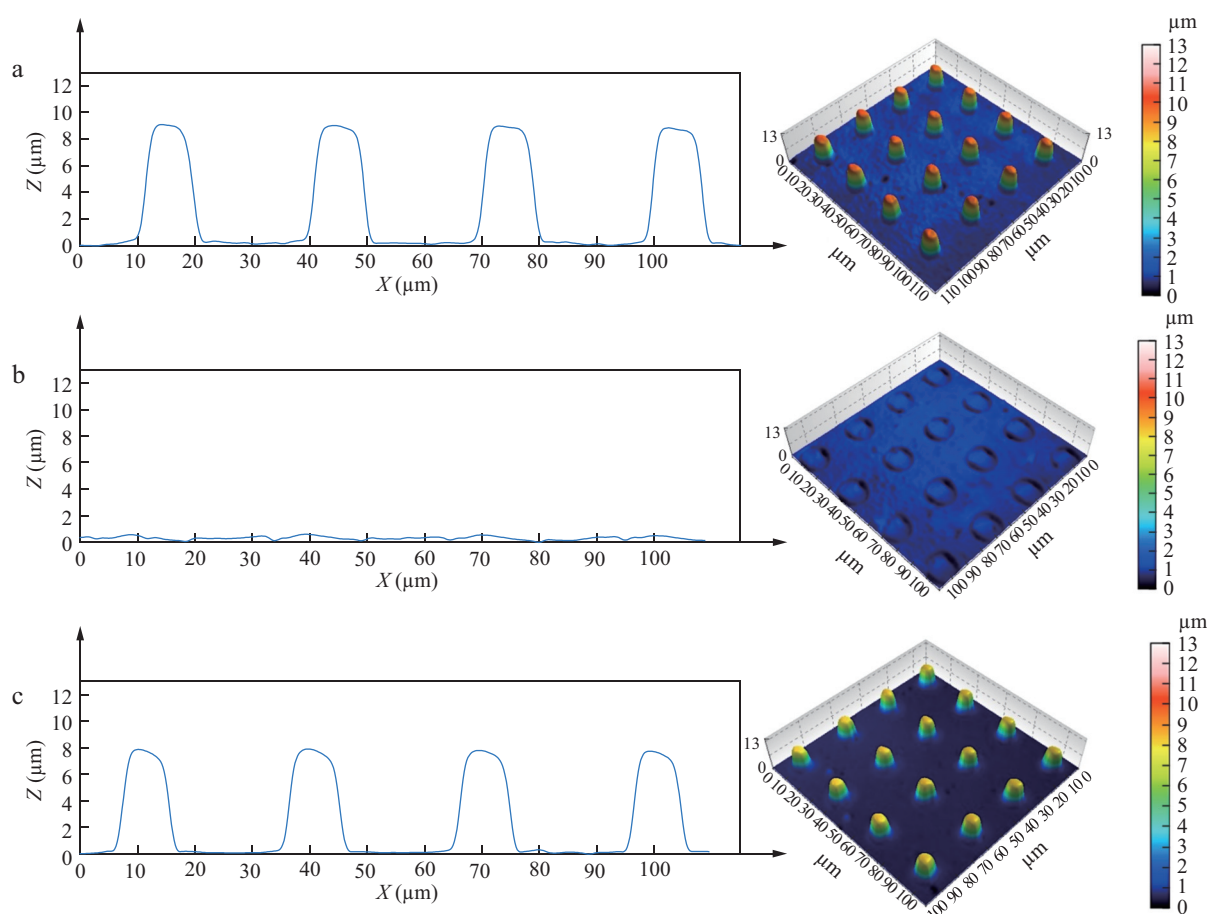


Fig. 4 Configuration curves and confocal images of the structured sample at (a) its original state, (b) temporarily flattened state, and (c) recovered state

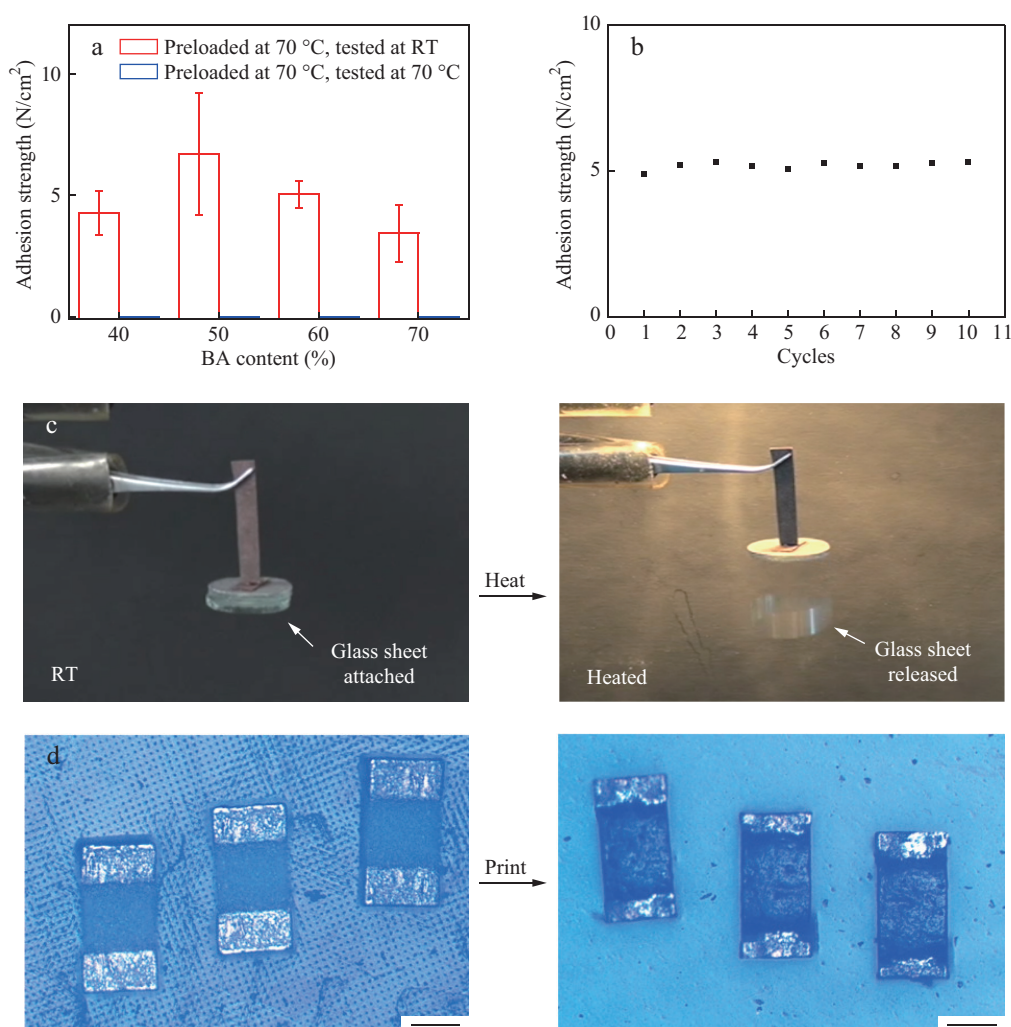


Fig. 5 Adhesion performance of the shape memory stamps with surface structure: (a) adhesion strength of the samples with different BA contents; (b) adhesion strength in repetitive tests for the sample BA60; (c) releasing process of transferring a light glass sheet using the structured BA60 upon shape recovery; (d) micro-images of an array of chip resistors (Spec: 0201, 0.60 mm × 0.30 mm × 0.23 mm) adhered on the microstructured SMP stamp (left) and transfer printed on to a silicon rubber substrate (right) (The scale bars are 200 μm .)

reversible dry adhesives which may perfectly meet the requirements for transfer printing. The copolymers enabled nearly ideal shape memory performance. When the copolymer was synthesized using 40 wt% PCLDA and 60 wt% BA, the resulted adhesive could be soft enough to avoid damaging the delicate microelectronic devices during the transfer. With the assistance of the thermally induced shape recovery of micro cone structure on the surface, the adhesive enabled a self-detaching capability upon heating. The adhesion-detaching process can be repetitively manipulated with negligible performance loss. The soft, responsive, and reversible dry adhesive may contribute to a more efficient transfer printing process.

E Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2119-6>. Video S1 shows a shape memory assisted self-detaching process.

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