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Electronic Supplementary Information

Soft Stimuli-Responsive Grippers and Machines with High Load-to-Weight Ratios

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Supplementary Materials

Supplementary Figures S1-S5

Table S1

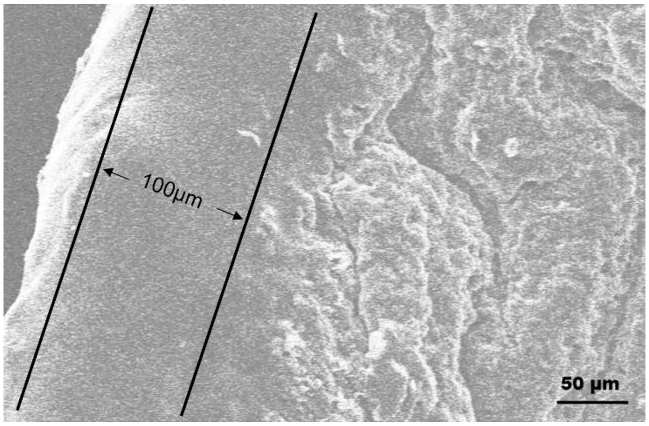

Fig. S1. SEM image of the edge of a temperature-responsive gripper. The layer of adhesive around the gripper appeared smoother than the temperature-responsive hydrogel and had a thickness of ~ 100 µm.

1. Optimizing the composition of the temperature-responsive gripper

We optimized the gripping strength of the temperature-responsive gripper by changing the amount of monomer, *N*-isopropylacrylamide, used for preparing the hydrogel. Specifically, we prepared the hydrogel using exactly the same procedure as described for the fabrication of the temperature-responsive gripper, except that we varied the amount of *N*-isopropylacrylamide used from 0.2 g to 0.4 g. Results show that the load-to-weight ratio is highest when 0.3 g of *N*-isopropylacrylamide was used compared to 0.2 g and 0.4 g (Fig. S2). Hence, we used 0.3 g of *N*-isopropylacrylamide for the fabrication of all the temperature-responsive grippers discussed in this study.

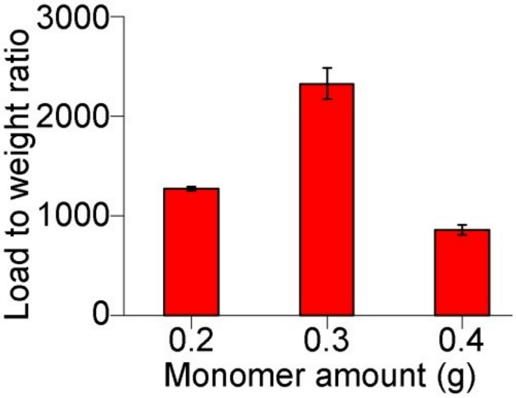

Fig. S2. Optimizing the load-to-weight ratio of the temperature-responsive gripper.

2. Dependence of the gripping force and the mechanical properties of the stimuli-responsive hydrogel.

We investigated the relationship between the gripping force and the mechanical properties of the grippers. First, we fabricated pieces of temperature-responsive hydrogels as described in the Experimental Section but with varying amounts of cross-linker (i.e., *N*,*N*'-

methylenebisacrylamide) added for polymerization. Specifically, we fabricated the same type of temperature-responsive hydrogel typically used for the grippers described in the main text (i.e., by using 5 mg of the cross-linker; the “1×cross-linker”) and three other types of hydrogels with different amounts of cross-linker: ¼×cross-linker, 4×cross-linker, and 6×cross-linker of the typical amount of cross-linker used. After preparing the different types of temperature-responsive hydrogels, we used them to fabricate the grippers and measured their load-to-weight ratios (by gripping onto a rod with a diameter of 0.4 mm). We observed an increasing load-to-weight ratio with increasing amount of cross-linker for the hydrogels that were composed of ¼×cross-linker, 1×cross-linker, and 4×cross-linker (Fig. S3a). For the gripper that consisted of a hydrogel with 6×cross-linker, however, we observed that the hole in the center did not close completely; hence, the gripping force was negligible. Subsequently, we measured the tensile modulus (Instron 5542 Single Testing Column System) and the compressive modulus (Instron 3342 Single Testing Column System) of the pieces of temperature-responsive hydrogels polymerized with different amounts of cross-linkers (Fig. S3b, c). Results showed that the tensile modulus and the compressive modulus increased with the amount of cross-linker used to polymerize the hydrogels as expected. In general, the gripping force of the grippers increases when the stimuli-responsive hydrogels are fabricated to be mechanically stronger, until the point when the gripper can no longer close its hole in the center.

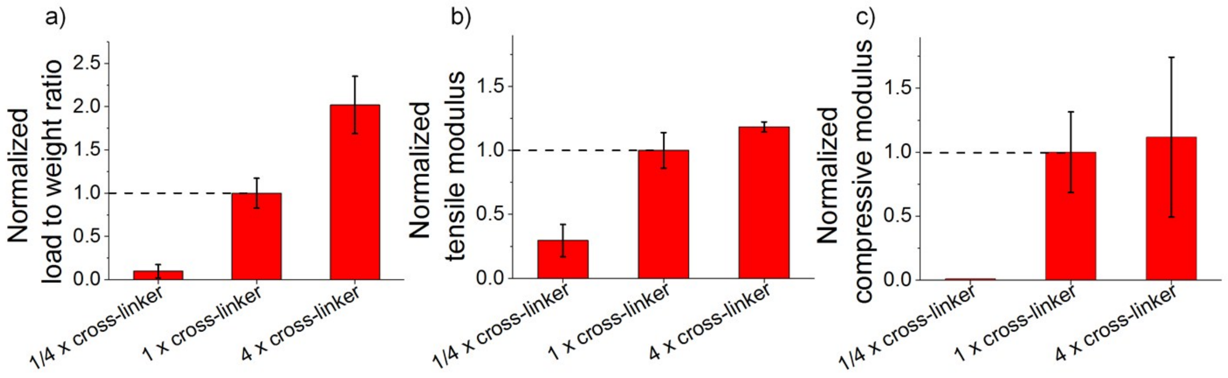

Fig. S3. Dependence of gripping force (i.e., the load-to-weight ratio) with the amount of cross-linker used for polymerizing the temperature-responsive hydrogels.

3. Change in Size of the Hole of the Gripper with Time

We investigated the change in the size of the hole in the center of the gripper with respect to time. We first fabricated a temperature-responsive gripper and a pH-responsive gripper as described in the Experimental section. After fabrication, we immersed the temperature-responsive gripper in a water bath at room temperature and allowed the hole to close. The changes in the size of the hole were monitored with time as shown in Figure S4a. Subsequently, we immersed the temperature-responsive gripper in a water bath at 40 °C and allowed the hole to open (Figure S4b). We repeated the experiment for a pH-responsive gripper. The gripper was first immersed in a pH 12 solution so that the hole in the center closed (Figure S4c). We then immersed the gripper in a pH 2 solution to reopen the hole (Figure S4d). The changes in the size of the hole with time were observed by an optical microscope.

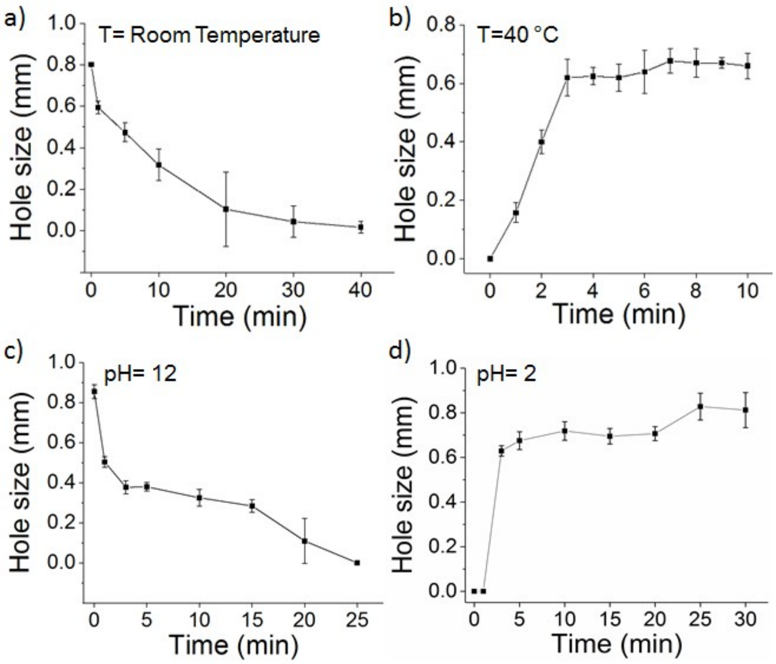

Fig. S4. Changes in the size of the hole in the center of the gripper with time.

The grippers that we fabricated usually take around 20 – 30 min to close their holes in the center and less than 10 min to reopen their holes. If the specific application requires the speed of response to be reduced, it will be necessary to increase the rate of change in size of the stimuli-responsive hydrogel under the influence of a stimulus. In general, the rate of change in size of stimuli-responsive hydrogels can be increased by a few ways. A common way is to decrease the size of the stimuli-responsive hydrogel. Previous studies have reported that the characteristic time, τ_c, at which the size of a stimuli-responsive hydrogel changes scales with $\tau_c \sim L_c^2/D$, where L_c is the characteristic length of the stimuli-responsive hydrogel and D is the diffusion coefficient of the hydrogel.[1,2] Because the time scales with the square of the dimension of the hydrogel, a reduction in the size of the hydrogel greatly decreases the time needed for the hydrogel to respond. It is most effective to reduce the shortest dimension of the hydrogel to decrease the time of response. Specifically, for the gripper that we fabricated, it will be most effective to reduce the thickness of the gripper. The second way by which the rate of expansion of the hydrogel can be increased is by fabricating the hydrogel with more pores. Previous studies have found that hydrogels with pores can change their sizes faster than those without pores.[3,4]

4. Gripping onto rods of different materials

In the previous section, we described the experimental setup and procedure for measuring the maximum amount of load that the gripper can hold onto. In the setup, the gripper gripped onto a metallic rod that was attached to a bin. The metallic rod is a syringe needle made of stainless steel, which is reported to have a coefficient of friction of around 0.5 – 0.8.[5] Besides these metallic rods, we also investigated materials that are known to have relatively low coefficients of friction. Specifically, we used a perfluoroalkoxy alkane (PFA) tubing (outer diameter: 0.60 mm) with a coefficient of friction of 0.1 – 0.3, and a graphite rod (outer diameter: 0.58 mm) with a coefficient of friction of 0.1.[6,7] We found that the load-to-weight ratios of the temperature-responsive gripper were around 11,500 ± 2,300 for gripping onto the PFA tubing, and 10,700 ± 1,300 for gripping onto the graphite rod. Hence, the load-to-weight ratios were still large (i.e., > 10,000) even when the gripper was gripping onto materials of low coefficients of friction.

5. Fabricating another pH-responsive gripper with high load-to-weight ratio

In order to demonstrate that the generality of the grippers (i.e., different types of stimuli-responsive hydrogels can be fabricated to have high gripping strength), we fabricated another type of pH-responsive hydrogel, and determined its load-to-weight ratio. This pH-responsive hydrogel was prepared by first mixing 2-hydroxyethyl methacrylate (HEMA; 0.381 g), methacrylic acid (MAA; 0.243 g), *N*,*N'*-methylenebisacrylamide (Bis; 0.009 g), deionized water (0.44 mL), methanol (0.44 mL), 5 wt% ammonium persulfate solution (APS; 0.06 mL) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TEMED; 0.04 mL) in a vial. Nitrogen was introduced into the solution for 20 min. We then poured the pre-hydrogel solution into an ABS mold with a cavity of dimensions 30 mm × 30 mm × 5 mm. The relatively large dimensions of this mold were used for making nine grippers at the same time. In the mold, we placed nine syringe needles (each of them had a diameter of 0.9 mm) arranged in a 3 by 3 configuration for creating the hole in the middle of each gripper. The hydrogel was then allowed to polymerize for ~24 h; the ABS mold that contained the pre-hydrogel solution was covered completely in order to prevent the solvent from evaporating. After polymerization, we removed the hydrogel from the mold and the needles, and soaked it in a pH 2 solution for 5 h (so that they were easier to cut). We then cut the hydrogel into dimensions of 1.3 mm × 1.3 mm × 0.6 mm, with the hole of diameter 0.9 mm in the center. This piece of hydrogel was dried in an oven at 80 °C for 30 min. After drying, the hydrogel shrunk to a size of 1.2 mm × 1.2 mm × 0.5 mm, and the hole shrunk to a diameter of 0.8 mm. At this state, the four sides of the hydrogel was coated with adhesive, and was left to dry for 20 min.

This pH-responsive hydrogel has a different chemical composition than the pH-responsive hydrogel described in the main text (e.g., Fig. 3c in the main text). The method of fabrication of this pH-responsive hydrogel is also different. This method is modified slightly from a procedure reported previously.[8] Using this pH-responsive hydrogel, we determined the load-to-weight ratio to be ~10,000 when a syringe needle of 0.6 mm in diameter was used. This ratio is similar to the pH-responsive hydrogel described in the main text. Therefore, it seems that the high load-to-weight ratios are achievable for different types of stimuli-responsive hydrogels.

6. Determining the adhesive force of the surface of the stimuli-responsive hydrogels

We determined the adhesive force of the stimuli-responsive hydrogel by measuring the maximum load that the surface can stick to. The adhesive force was measured for a temperature-responsive hydrogel and a pH-responsive hydrogel for both the contracted and expanded states.

In the first experiment, we contracted a temperature-responsive hydrogel by immersing it in a water bath (with deionized water) at 40 °C. We then removed the hydrogel from the water bath, and cut it into a size of 1 cm × 1 cm and a thickness of ~0.5 mm. The cutting was done quickly (~ a few seconds) on a heated surface (~40 °C) in order to maintain the contracted state of the hydrogel. After cutting, the hydrogel was immersed in the water bath again to maintain its moisture. Subsequently, we removed it from the water bath, wiped away the excess water on its surface, and placed it onto a rigid substrate (glass slide; 75 mm × 26 mm × 1 mm). This rigid substrate was then clamped and fixed in place (see Fig. 2e in the main text for the scheme of the experimental setup). On the opposite side of the hydrogel, we placed a piece of glass slide (75 mm × 26 mm × 1 mm) that acted as the load. A bin (made of aluminum foil) was glued to the bottom of the glass slide. We then placed smaller pieces of loads (glass slides; 15 mm × 26 mm × 1 mm; 0.91 g) one by one into the bin until the adhesive force of the surface of the hydrogel was insufficient to hold onto the load, and the load fell under its own weight. Drops of water at 40 °C were added to the hydrogel every one minute to maintain the contracted state of the hydrogel. The total weight of the load (i.e., the sum of the weight of the glass slide, the bin, and the smaller pieces of glass slides) was measured using a mass balance. This temperature-responsive hydrogel in its contracted state (at 40 °C) was able to hold onto a load of ~200 g.

In a second experiment, we expanded a temperature-responsive hydrogel by immersing it in a water bath at room temperature of around 20 degrees, and cut it to a size of 1 cm × 1 cm and a thickness of ~ 1 mm. We then repeated the experiment as described in the previous paragraph. The temperature-responsive was kept in its expanded state by placing drops of water at 20 °C on it every minute while we gradually increased the load. This temperature-responsive hydrogel in its expanded state (at 20 °C) was able to hold onto a smaller load of 13 g.

We repeated the experiments for a pH-responsive hydrogel. Specifically, we first contracted a pH-responsive hydrogel in a solution of pH 2, and cut it to a size of 1 cm × 1 cm. The amount of load that it could hold onto was 19 g. In another experiment, we expanded a pH-responsive hydrogel in a solution of pH 10, and cut it to a size of 1 cm × 1 cm. The amount of load that it could hold onto was negligible.

Hence, we found from this set of experiments that the surface of the hydrogel can generally provide an adhesive force for holding onto objects. In addition, the force is greater when the hydrogel was in the contracted state than when it was in the expanded state. The reason is probably because when the hydrogel expanded, it contained more water. With an increase in the amount of water at the surface of the hydrogel, the adhesive force may decrease.

7. Determining the bulk force derived from the expanding stimuli-responsive hydrogels

When the stimuli-responsive hydrogel expanded, the bulk material of the hydrogel that filled into the hole may contribute to a compressive force for gripping onto an object. In order to demonstrate that the bulk force (i.e., as opposed to the surface adhesive force) can contribute to gripping the objects, we performed the set of experiments as follows.

First, we prepared four slabs of temperature-responsive hydrogels that had the same area on their flat side (i.e., 1 cm × 1 cm) when fully expanded, but with different thickness. These hydrogels were prepared by pouring the pre-hydrogel solution into cavities of four molds of different sizes. The cavities of the molds had the same area of 15 mm × 20 mm, but different thicknesses of 272 µm, 400 µm, 528 µm and 672 µm. Each mold was made from multiple layers of aluminum foil (20 mm × 20 mm × 0.016 mm) stacked on top of a glass slide, and arranged so that there was a cavity in the mold. We poured the pre-hydrogel solution into the mold, then covered it with another piece of glass slide, and clamped the top and bottom glass slides together. It was then placed in a humidity chamber (humidity ~90%) for 24 h. After curing, we removed the hydrogel from the mold, immersed it in deionized water at 20 °C for 2 hours, and allowed it to expand fully. At this state, we measured the thicknesses of the four hydrogels to be 380 µm, 560 µm, 760 µm, and 980 µm. We then cut the hydrogels manually so that they had an area of 1 cm × 1 cm on their flat side at their expanded state.

After preparing the hydrogels of different thickness, we determined the maximum load that the hydrogels could grip onto. The experiment procedure involved first placing two pieces of hydrogels of the same dimensions (including their thickness) into deionized water at 40 °C. After they fully contracted, we placed each of them on a rigid substrate (i.e., a glass slide) separately. Due to the adhesiveness of the hydrogels, they naturally stuck onto the glass slides. In a separate step, we prepared the load, which consisted of two pieces of cover slip adhered together (22 mm × 22 mm, and a total thickness of 330 µm), and a bin (aluminum) that was attached below the cover slips for placing smaller pieces of loads. One surface of the cover slips of the load was placed on top of the surface of one of the hydrogels resting on the rigid substrate. On the two far ends of the glass slide, we placed two blocks of ABS (20 mm × 10 mm × 1.5 mm). On top of the blocks, we placed the second glass slide such that the two hydrogels faced each other; hence, the ABS blocks acted as spacers for maintaining the distance of separation between the surfaces of the two glass slides at 1.5 mm. After expansion, the two hydrogels that faced each other on opposite sides could grip onto a load in the middle (see inset of Fig. 2f of the main text for an illustration of the experimental setup).

In order to expand the hydrogels, we placed the whole assembly in deionized water at 20 °C. After approximately 12 h, we removed the assembly from the water, wiped the excess water away, and clamped the two glass slides in place. In this position, the empty bin hung at a position that was vertically below the cover slips. At low temperature, the hydrogels expanded toward each other, and gripped onto the load (with the exception of the thinnest hydrogel). Subsequently, we placed additional loads (i.e., smaller pieces of glass slides, each with dimensions of 15 mm × 26 mm × 1 mm, and a weight of ~0.91 g) one by one into the bin until the hydrogels were insufficient to hold onto the load. The total load (i.e., the smaller pieces of glass slide, the bin and the cover slips) was measured using a mass balance. For the case when we used the thinnest hydrogels (i.e., the hydrogel with a thickness of 380 μm after it fully expanded in water), they were not thick enough to grip onto the load from both sides even after they fully expanded; only the surface of one of the hydrogels was in contact with the load. Hence, the measurement of the load was for determining the adhesive force of the surface of one hydrogel.

Another point to note is that the surface areas of the hydrogels were similar after they fully expanded in the assembly. Specifically, the surface areas were ~9.5 mm × 9.5 mm for the two cases when the thicknesses of the hydrogel were 380 μm and 560 μm after they expanded in the assembly for 12 h. The surface areas were ~9 mm × 9 mm for the two cases when the thicknesses of the hydrogels were 760 μm and 980 μm after they expanded in the assembly for 12 h. Because the surface areas of the stimuli-responsive hydrogels of different thickness were similar after expansion, the adhesive forces of the surface of the hydrogels might be similar; hence, we compared only the compressive force of the hydrogels.

In order to remove the contribution of the adhesive force entirely, we performed another set of experiments in which we measured the force in the same direction as the direction of expansion, instead of measuring the force perpendicular to the direction of expansion (i.e., the experiment illustrated in Figure 2f of the main text). In this experiment, we used temperature-responsive hydrogels of three different thicknesses at the expanded state: 0.8, 1.2, and 1.4 mm. We then used a mechanical testing system (Instron 3342 Single Testing Column System) for measuring the force of expansion of the hydrogels. Specifically, we fixed the distance of separation between the bottom and top substrates of the mechanical testing system at 0.8 mm and placed a piece of contracted hydrogel in between the two substrates. We then allowed the hydrogel to expand at room temperature while keeping the hydrogels hydrated. The expansion allowed the hydrogels to compress against substrates of the mechanical testing system; this force of compression was measured. The experiment was then repeated for the hydrogels with different thicknesses. Results showed that the thicker the hydrogel, the amount of compressive force exerted was larger.

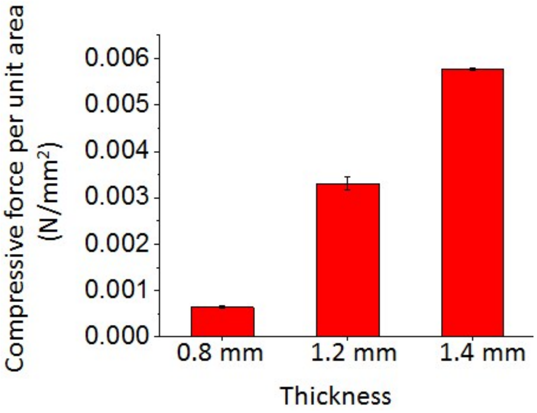

Fig. S5. Compressive force per unit area of hydrogels with different thicknesses.

Besides the temperature-responsive hydrogels, we also determined the bulk compressive force of the pH-responsive hydrogels. These pH-responsive hydrogels with the required dimensions were fabricated by preparing a mold made of PDMS. First, we stacked multiple layers of aluminum foil (each layer of aluminum foil has dimensions 7 mm × 7 mm × 0.016 mm), and adhered them onto the bottom of a petri dish using double-sided tapes. We then poured the PDMS pre-polymer solution in the petri dish, and cured it. After extracting the aluminum foils out of the PDMS, the PDMS had cavities for fabricating the pH-responsive hydrogels of the desired dimensions. By using different number of layers of aluminum foils, we made four PDMS molds with the same area on their flat side (7 mm × 7 mm), but different thicknesses of 304 µm, 448 µm, 576 µm and 720 µm.

Subsequently, we poured the pre-hydrogel solution into the mold, and cured it with ultraviolet light (Omnicure S2000) for 20 min with a wavelength of 365 nm and an intensity of 10 mW/cm^2. After curing, we extracted the hydrogel from the PDMS mold, and soak it in a pH = 2 (HCl) solution for 2 hours. The hydrogel was then fully expanded by immersing it in a pH = 10

(NaOH) solution for 2 hours. At this state, we measured the thicknesses of the four hydrogels to be 390 µm, 610 µm, 840 µm, and 1010 µm. We then cut the hydrogels manually so that they had an area of 1 cm × 1 cm on their flat side at their expanded state.

After preparing the pH-responsive hydrogels, the procedure for determining the bulk compressive force of the hydrogels with different thicknesses was similar to that of the temperature-responsive hydrogel. The one difference was that the hydrogels were initially contracted in a pH = 2 solution, and later, expanded in a pH = 10 solution. After the hydrogels expanded in the assembly for 12 h, the surface areas were ~8.5 mm × 8.5 mm for the two cases when the thicknesses of the hydrogels were 390 µm and 610 µm. The surface areas were ~8 mm × 8 mm for the two cases when the thicknesses of the hydrogels were 840 µm and 1010 µm. Hence, the surface areas of the stimuli-responsive hydrogels of different thickness were again similar after expansion. Similar surface areas may lead to similar adhesive forces; thus, we compared only the compressive force of the hydrogels.

8. Performance Comparison of Artificial Grippers

Table S1. Grippers reported in previous works

Category	Technology	Tethered or not	Source of power	Load-to-weight ratio[a]	Ref.
Actuation	Grippers with finger-like structures driven by motors.	Yes	Electricity	4.5 16.3	[9] [10]
	Soft pneumatic actuators (with internal fluidic channels)	Yes	Air pressure	2 68	[11] [12]
	Electroactive polymers (polymers that deform reversibly in response to an electric field)	No	Electric field	8.7 2 3.5	[13] [14] [15]
Controlled Stiffness	Granular jamming: flexible membrane filled with granular materials.	Yes	Air pressure (for jamming the granular materials and controlling the grip)	7.6-15.1	[17]
	Low melting point alloys	No	Heat	2.2 5.5	[18] [19]
	Shape memory polymers	No	Electric field or heat (e.g., induced by light)	30; 925	[20] [21]
	Shape memory alloys	No	Heat (for changing the phase of the alloy from martensite to austenite)	15 31.4	[16] [25]
Controlled Adhesion	Electro-adhesion	No	Electric field	54.7	[22]
	Geckoadhesion	No	Pressure (for pressing the gripper against the object)	39 286.7	[23] [24]

[a] Object mass to gripper mass

In addition, some studies reported grippers that were able to move under the influence of a magnetic field by doping the grippers with Fe_2O_3 nanoparticles. On the other hand, the class of soft machines that we discussed involved different stimuli-responsive components that can be assembled in a modular manner. With many different stimuli-responsive components, coupled with the many different types of stimuli that can be used for actuating the different components, it is potentially possible to fabricate a variety of soft machines that can perform a wide range of complex functions.

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