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Communication

Adhesives to empower a manipulator inspired by the chameleon tongue

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A B S T R A C T

Existing grasping technologies have persistent challenges with unstructured objects and environments, highlighting an increasing demand for methods that conform to various application scenarios. Inspired by the chameleon tongue, a soft-contact grasping manipulator empowered by a class of adhesive gels has been demonstrated. The adhesives enable the manipulator to rapidly and strongly adhere to diverse substrates with varied surfaces, shapes and sizes, also to release objects under mild conditions. The robustness of such adhesive gels was highlighted with the remarkable recyclability, broad temperature tolerance and long-term stability. Furthermore, a general approach was developed to reconcile the contradiction of simultaneously enhancing their interfacial adhesion and cohesion strength that exists in conventional glues. We anticipate that this work will offer a strategy of developing adhesive materials and pave the way towards new applications of soft materials in the emerging fields of soft robotic devices and smart manufacturing.

Manipulators have been applied in prevalent fields and replaced considerable manpower to reduce labor costs or human exposure to unpleasant environments. Traditional grasping techniques including grippers and suction cups are based on mechanical occlusal or pressure difference. These methods can hold objects tightly but may easily cause irreversible damages by rigid components at delicate contacts [1]. These manipulators are also only applicable to structured objects and environments. As substitutes for them, a few contactless grasping technologies have been developed based on electromagnetic [2], optical [3] or acoustic fields [4]. Electromagnet manipulators can grasp heavy objects by magnetic interactions, whereas the objects need to be magnetized. Optical and acoustic manipulators need sophisticated instruments and restricted environments in contrast to offering tiny grab forces. Therefore, innovative grasping methods are still highly demanding.

Nature predominantly uses soft materials [5,6] to create versatile grasping systems that conform to the environments. As an example, a chameleon preys on an insect by projecting its adhesive tongue, sticking the insect on the tip and pulling it back into the mouth [7] (Fig. 1A). In the mouth, the adhesion becomes weaker, allowing the chameleon to chow down the prey. The specialized tongue which elongates at high speeds and accelerations with a flexible mobile part, and paramountly, bears adhesives on its tip, endows the grasping techniques efficiency and tenderness (Fig. 1B). The adhesive glue allows this grasping method adaptive to widest possible range of object properties, shapes and sizes.

Inspired by the predation of the chameleon, a class of soft adhesive gels (AGs) to capture and release cargoes in a desired manner for a manipulator were designed. To meet the requirements of the manipulator operation, these adhesive materials were expected to achieve a rapid and strong adhesion to different surfaces and be capable of discharging cargoes in a controlled manner under mild conditions. It will be beneficial to have remarkable recyclability, broad temperature tolerance and long-term stability for various application scenarios (Fig. 1C). Although a variety of adhesives have been developed based on different mechanisms including mechanical interlocking [8], charge combinations [9,10], surface modification [11–13], mussel-inspired polymer [14–18], supramolecular recognition [19,20], dynamic covalent [21], adsorption by nanoparticles [22], a contradiction is often encountered, *i.e.*, the increase of cohesion strength is often accompanied by the decrease of adhesion forces, and *vice versa*. A method that can improve both adhesive force and cohesion strength is still on demand.

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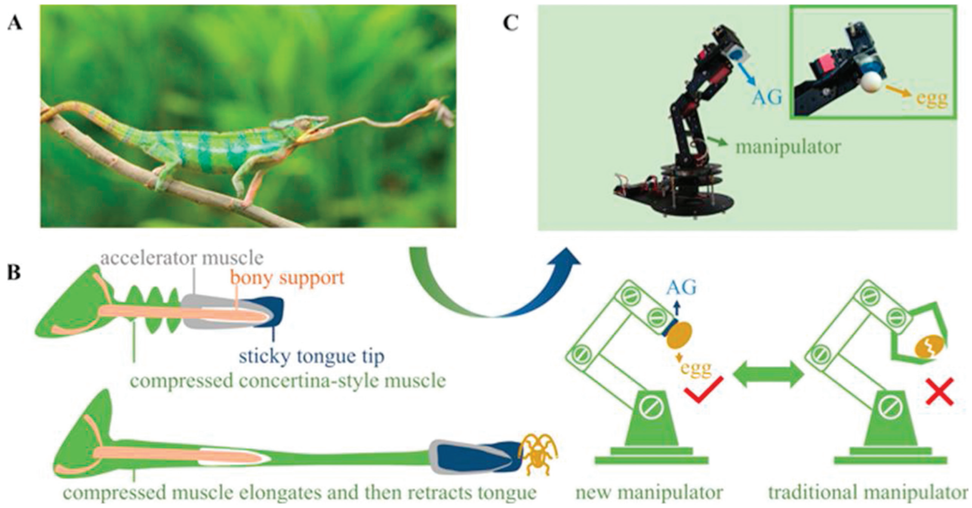

Fig. 1. Chameleon tongue inspired design of a soft-contact grasping manipulator empowered by adhesives. (A) Chameleon preys on an insect by its adhesive tongue. (B) Schematic view of the chameleon tongue with a mucilage-functionalized tip (dark blue), and a manipulator empowered by an adhesive gel (AG, dark blue) that can grasp an egg. A traditional manipulator is supposed to damage the fragile egg. (C) A photo of an AG-empowered manipulator capable of capturing a chicken egg (inset). The AG was stained in dark blue for highlight.

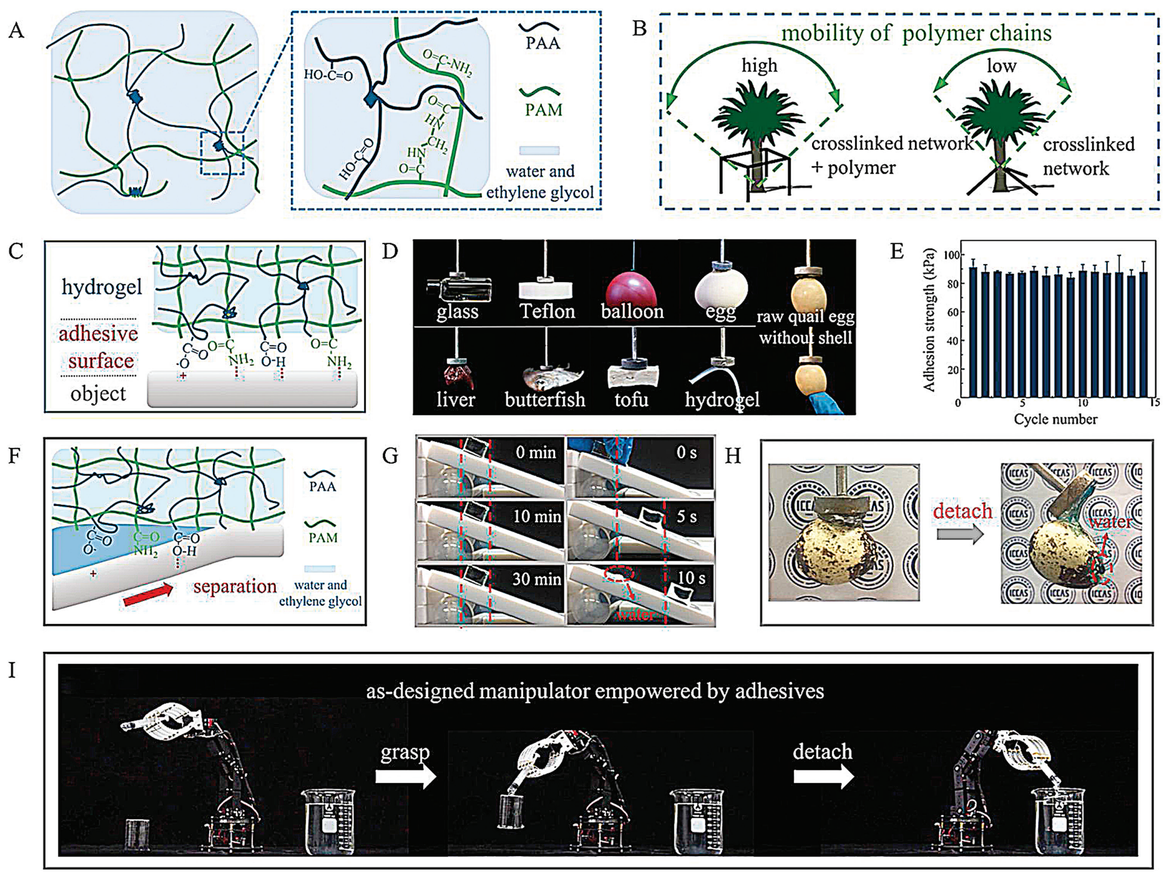

Fig. 2. The design and performance of AGs for a grasping manipulator. (A) AGs were designed by restricting adhesive PAA chains (blue lines) in the supporting PAM network (green lines). (B) Schematic illustration of polymer chain mobility in AG (left) and P(AM-co-AA) (right) system. (C) Schematic illustration of electrostatic interactions and hydrogen bonding between AG functional groups (*e.g.*, amino, carboxyl and carboxylic acid groups) and the objective surface. (D) Photos showing the AG-empowered manipulator can grasp diverse objects with different surface properties, shapes and sizes. Two photos on the right side: a shell-less quail egg displayed obvious deformation but without damage by gentle touching. (E) Recovery test of AG showing no substantial decrease in adhesion strength after 15 cycles. Error bars represent standard deviation; sample size n = 6. (F) The infiltration of water competed with the AG-substrate bonding, which facilitated the detachment of AGs. (G) The AGs can adhere to the Teflon surface for more than 30 min (left), but immediately slipping down a wet surface (right). (H) Water-assisted detachment of quail egg from AG without any detectable damages. Water was stained in blue for highlight. (I) Photos of a designed soft-contact grasping manipulator empowered by adhesives can grasp, move and detach a beaker.

To design mucus-like AGs with certain soft support, multivalent interactions between adhesives and surfaces are required. Herein, a composite system consisting of polyacrylic acid (PAA) and polyacrylamide (PAM) was developed into an AG, where both PAA and PAM serve as the adhesive components and the PAM network was also used as supporting matrix (Fig. 2A). To prepare this soft gel, acrylamide (AM, monomer) and *N*,*N*'-methylenebisacrylamide (MBAA, cross-linker) were mixed with PAA matrix in water/ethylene glycol solution, followed by *in-situ* polymerization initiated by ammonium persulfate (APS). It is worth mentioning that in this synthetic method, PAA rather than its monomer AA was physically mixed with AM (monomer) as the starting material. With this design, high mobility of PAA chains in the PAM matrix was maintained, giving rise to effective interactions between PAA and substrate, and thus a better adhesion performance (Fig. 2B left). In a control experiment, AGs were prepared *via* co-polymerization and cross-linking of AA and AM, and the as-prepared P(AM-co-PAA) gels with strongly intertwined and displayed a weaker adhesion strength (Fig. 2B right, Fig. S1 in Supporting information). This suggests the important role of polymer mobility in determining the adhesive performance of AGs.

The polymeric network of PAM and PAA chains displays a high density of functional groups, such as polar amide, carboxyl and carboxylic acid groups, which contribute to the high interfacial adhesion *via* the formation of electrostatic interactions and hydrogen bonds. The strong PAM hydrogel network was expected to provide the cohesion strength (Fig. 2C). The interfacial forces are expected to be dependent of ionic strength and ionization degree of carboxylic groups (Fig. S2 in Supporting information). Indeed, the addition of sodium chloride was found to reduce the interfacial adhesion forces due to the screening of electrostatic attractions. Alternatively, lowering solution pH or the presence of calcium ion can also inhibit adhesion by reducing the ionization degree of carboxylic groups or form calcium-carboxylate coordination complexes.

Due to the presence of strong adhesion force and cohesion strength, the PAA-PAM AGs are capable of capturing objectives with different substrates, such as glass, Teflon, balloon, liver, butterfish, tofu, hydrogel, egg, shell-less raw quail egg, and rose petal (Fig. 2D, Fig. S3 and Movies S1 to S3 in Supporting information). Quantitatively, the adhesion strength of the AG can reach to 71.4 ± 3.1, 82.0 ± 5.3, and 82.9 ± 9.2 kPa on the surface of aluminum, steel and glass, respectively (Fig. S2). These values are remarkably higher than that of commercially available adhesive hydrogels (typically ~ 10 kPa) [13]. Due to the physical (noncovalent) nature of surface binding, the adhesion strength of AGs maintained at the level of ~ 87 kPa without any substantial decrease after 15 cycles of adhesion-peeling test (Fig. 2E).

Ease of cargo detachment in a controlled manner is another key requirement for an AG-empowered manipulator, which remains a challenge to most adhesives. As by design, the detachment of cargos from our AGs was achieved by reducing the strength of surface affinity. This is achieved by inhibiting the electrostatic interactions or hydrogen bonding at the gel-substrate interface. To this end, water infiltration into the adhesive interface was applied to compete with the interactions between the adhesive polymer and the substrates [23] (Fig. 2F). As shown in Fig. 2G and Movie S4 (Supporting information), AGs could slide down a 30° Teflon slope in 10 s when the surface was wetted with water. In contrast, the AGs on the dry Teflon surface did not move. This property is especially useful for the detachment of fragile objects like a quail egg, benefitting from the soft contact between AGs and cargoes. As shown in Fig. 2H, the egg detached from the AG with water treatment remained intact, while the one detached from the cyanoacrylate glue was broken (Fig. S4 in Supporting information). Importantly, the adhesion property of AGs can be restored after the surface water was removed and such regeneration process can be repeated for at least 7 times without substantial decrease of adhesion strength (approx. 90 kPa during 7 circles) (Fig. S5 and Movie S5 in Supporting information).

Taken together, a soft-contact grasping manipulator empowered by adhesives mimicking chameleon tongue can be designed and it can be used to grasp, move and release a beaker (Fig. 2I).

The soft AGs display a tolerance towards a broad environmental temperature change, ensuring various application scenarios of manipulators. Ethylene glycol is a widely used anti-freezing agent due to its capability to disrupt the hydrogen bonds between water molecules [24]. The incorporation of ethylene glycol to the AGs stabilized the adhesive property in a wide temperature window. According to the literature [25], the freezing point of the water/ethylene glycol mixture can be decreased to −40 °C or even lower temperatures with incorporation of polymers, which ensures AGs to be valid in the subzero environment. As shown in Fig. 3A, an AG-empowered manipulator was able to grasp an egg at −20 °C. In contrast, the AG with the same polymer composition in ethylene glycol-free aqueous system was frozen and incapable of grasping the objects (Fig. S6 in Supporting information). Quantitatively, the shear adhesion of AG was measured to be 2.5 ± 0.5, 2.7 ± 0.3, 2.9 ± 0.1, 6.5 ± 0.2 and 14.9 ± 0.6 kPa at 40, 20, 0, −20 and −40 °C, respectively (Fig. 3B), where a stronger adhesion was achieved below zero. Dynamic rheology data suggest both the storage modulus (G') and loss modulus (G") increased significantly with the decrease of temperature in a sub-zero environment (Fig. 3C). No abrupt change was observed in this process [26], indicating the AGs did

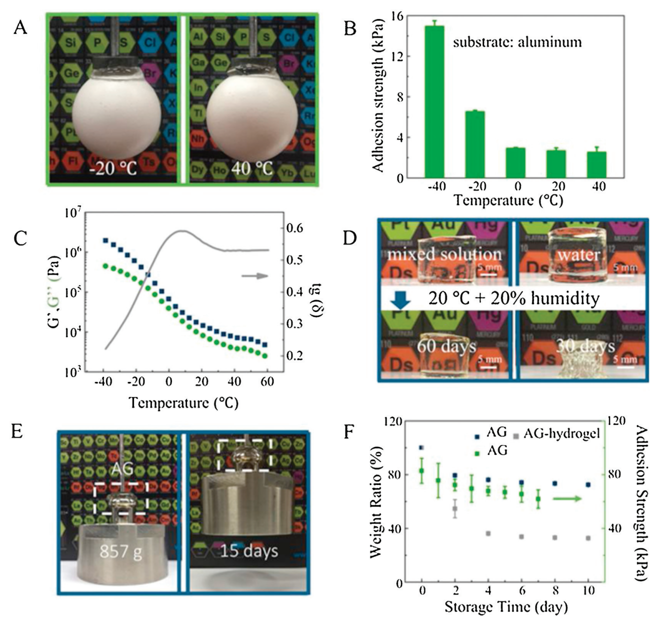

Fig. 3. Temperature tolerance and long-term stability of the AGs. (A) Photos of AG-empowered manipulator grasping eggs at -20 °C and 40 °C. (B) The shear adhesion strength of AG on aluminum plate under -40~40 °C illustrating the thermal tolerant of AG to maintain adhesion in a wide temperature window. Error bars show standard deviation; sample size $n = 6$. (C) Temperature-dependent dynamic rheology of the AG on a temperature sweep in the range of -40~60 °C at a constant shear strain (γ) of 0.1% and frequency (ω) of 1 rad/s. (D) Photos of AG (on the 1st day and 60th day) and the AG-hydrogel (on the 1st day and 30th day) exposed to air (25 °C, 20% humidity). (E) The AG can lift an 857 g object after exposure to air for 15 days (25 °C, 20% humidity). (F) Weight ratio and adhesion strength of AG and AG-hydrogel after different exposure time (25 °C, 20% humidity) indicating the long-term stability of AG. Error bars show standard deviation; sample size $n = 6$.

not freeze between 0 °C and −40 °C. When the temperature decreased from 40 °C to −40 °C, the shear adhesion strength significantly increased, and G' also increased from 4 kPa to 110 kPa, probably because the intermolecular forces (*e.g.*, hydrogen bonding) were strengthened and the movement of the polymer chains were restricted, which reinforced the mechanical interlocking between AGs and the substrate.

Solvent evaporation becomes challenging in the case of long-term stability of the AGs. The incorporation of ethylene glycol to the solvent is known to reduce the saturated vapor pressure of water by forming molecular clusters with water molecules, which is expected to increase the long-term stability of AGs. Indeed, no performance deterioration of AGs was observed after a prolonged storage under mild condition (with coverage, 25 °C, 20% humidity) for more than 120 days. It is also verified that the AGs remained moist after being exposed to the air for 60 days (25 °C, 20% humidity) with a mass loss of ~29%, while the AG-hydrogel (without ethylene glycol in solvent) shrunk significantly with a mass loss of ~67% in 30 days (25 °C, 20% humidity) (Fig. 3D). The AG stored for 15 days still showed an adhesion strength higher than 30 kPa, enabling it to lift an object of 857 g (Fig. 3E). A systematic investigation in Fig. 3F showed that AG remain ~80% of its mass after 4 days exposure to air, with a better long-term stability than AG-hydrogel. The loss of weight slightly decreased the adhesion strength of AG from 82.9 ± 9.2 kPa to 62 ± 6.9 kPa after 7 days' exposure.

Adhesives for a grasping manipulator require both high adhesion and cohesion strength. Strong adhesives with week cohesion strength will fail to capture objects (Fig. S7 in Supporting information). The incorporation of PAA in the AG system plays a crucial role in enhancing both the adhesion and cohesion strength. The adhesion strength, tensile and compression modules increased from 16.6 ± 1.6, 14.6 ± 2.4 and 2.7 ± 0.2 kPa (control experiments without PAA) to 71.4 ± 3.1, 17.9 ± 2.6 and 4.9 ± 0.2 kPa (AGs in the presence of PAA) (Figs. 4A-C). This is presumably due to the formation of the C=O···H-N hydrogen bond between PAA and PAM that conferred the strong polymer network, as demonstrated by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Fig. 4D). The red-shift of amide I band and blue-shift of amide II band [27,28] demonstrated the formation of intermolecular hydrogen bonding between PAA and PAM. It is assumed that the inclusion of different polymers to build gel networks can reconcile the adhesion-cohesion contradiction. With this design principle, more AGs can be obtained. For example, a synergistic increase of adhesion and cohesion strength was achieved in the complex system of poly(*N*,*N*-dimethyl acrylamide) (PDMA) and PAA due to the interaction between PAA and PDMA (Fig. 4E, Figs. S8 and S9 in Supporting information). The properties of AGs can be finely tuned with the PAA content, PAA molecular weight and cross-linking degree of matrix, for different application scenarios (Figs. S10-S13 in Supporting information).

To summarize, a soft-contact grasping manipulator inspired by the chameleon tongue was demonstrated. Key to this manipulator design is a class of AGs that are able to stick to a variety of unstructured objects. The rapid and strong adhesion of AGs to diverse surfaces was attributed to the multivalent non-covalent forces (*e.g.*, electrostatic force and hydrogen-bonding) between AGs and different surfaces. Due to the non-covalent nature of surface forces, the adhered objects can be released in a well-controlled manner by introducing competing intermolecular forces. The regeneration of soft adhesives was achieved, allowing repeated cargo adhesion/detachment operation without losing notable adhesive strength. Furthermore, a broad temperature tolerance, long-term stability, as well as a considerable high cohesion strength was demonstrated. This work offers a design of grasping manipulator by using adhesive soft gels and illustrate the wide potential of applications in next-generation soft robotic devices and smart manufacturing.

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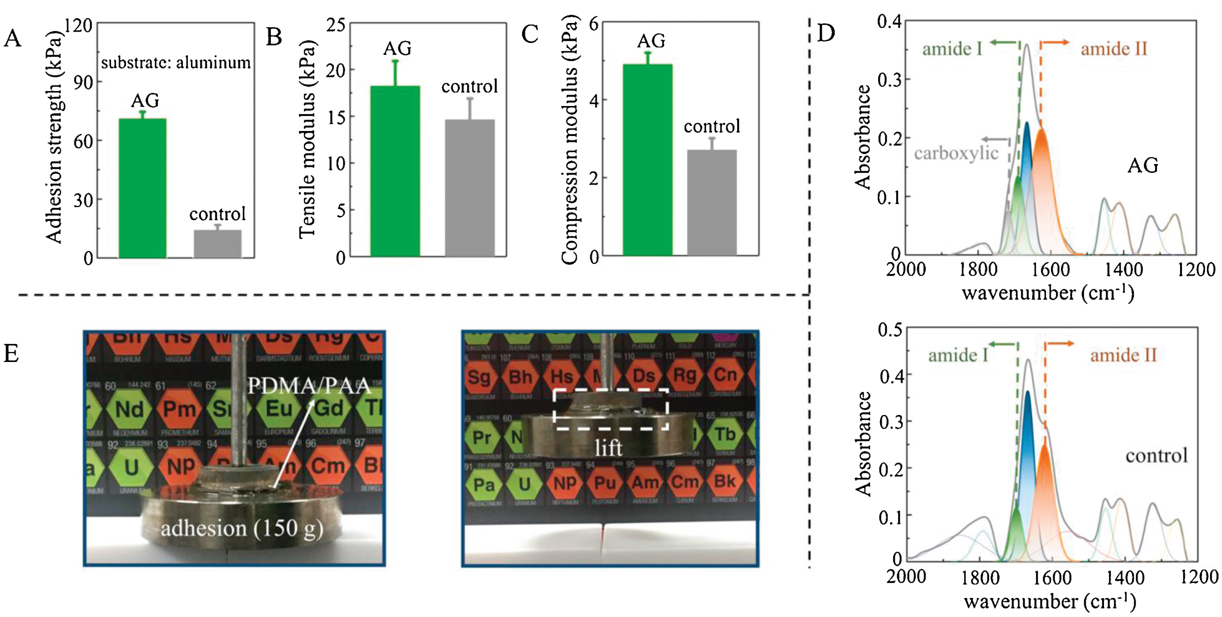

Fig. 4. Enhancement of AG mechanical properties and cohesion strength with addition of PAA. (A) Adhesion strength, (B) tensile and (C) compression modules of AG (with PAA) and control (without PAA). Error bars show standard deviation; sample size $n = 4$ for modulus calculate and sample size $n = 6$ for adhesion strength. (D) ATR-FTIR spectra of AG (with PAA, top) and control (without PAA, bottom). (E) Photos of PDMA/PAA which can sustain a 150 g iron block.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2019.05.018.

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