Self-Peeling Reversible Dry Adhesive System

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The unique gecko adhesion phenomenon enabling gecko climbing has attracted tremendous scientific interest.[1–8] Presently, the research focus from the material science community has been to mimic the nanohairy structure of gecko footpads to fabricate the so-called gecko adhesives (or structured dry adhesives).[9–22] Biologists, on the other hand, have been advocating the perhaps more important role of gecko toes.[6] Indeed, while a gecko detaches its footpads via the mechanical toe actions,[4–7] synthetic gecko adhesives have to rely on external peeling forces for detachment[10,17,18] and are not self-reversible like geckos. In this communication, we report a self-peeling reversible dry adhesive (SPRA) system with a unique build-in adhesion reversal mechanism. It consists of a smooth (nonstructured) dry adhesive layer and a shape memory polymer (SMP) layer, with the latter introducing a heat triggered "self-peeling" adhesion reversal mechanism similar to the mechanical roles of gecko toes.[4–7] We note that, while the practical potential for synthetic gecko adhesives is limited by the high cost of microfabrication involved,[9–22] poor durability,[10,11] and low adhesion coefficient (adhesion to preload ratio),[1,10,11] our choice of a nonstructured epoxy based dry adhesive resulted in a robust, low cost, yet strong adhesive.

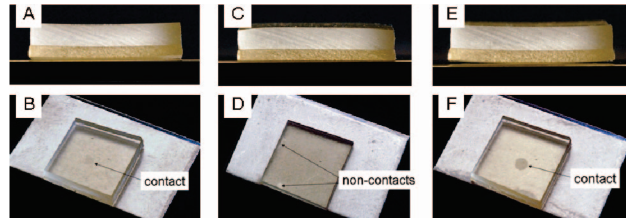

Figure 1. Photographs of the adhesion reversal process. A, B: side and top view of the as prepared SPRA. C, D: side and top view of the bonded sample. E, F: side and top view of the thermal recovered sample. Dark and light colors represent contact and noncontact areas, respectively. Sample dimensions: 1.03 cm × 1.02 cm × 0.21 cm.

The SPRA was fabricated based on a simple two step curing process.[23,24] The glass transition temperatures (T_g's) for the two thermoset epoxy layers in the SPRA are 3.0 and 39.9 °C, respectively (based on differential scanning calorimetry (DSC)). The layer with the lower T_g is an intrinsic sticky layer, which is different from gecko adhesives with fibrous structures. The other layer, with its T_g above room temperature, was expected to possess shape memory properties as it is chemically cross-linked with roughly two orders of magnitude change in storage modulus above and below its glass transition (based on dynamic mechanical analysis (DMA)).[25,26] Figure 1A shows the double layer construction of the SPRA. Figure 1A,B reveals that the SPRA has a slight curvature, resulting from the chemical shrinkage during the curing and the difference in thermal expansion between the layers.

A preload (4 N/cm^2) was first imposed on an SPRA sample placed on a stainless steel surface. Due to the curvature of the SPRA and the rigidity of the SMP layer, the SPRA had poor contact with the substrate (Figure 1A,B), and a pull-off strength of 9.0 N/cm^2 was measured (all adhesive testing was conducted at an unloading rate of 20 N/s). When preheated to 90 °C, the SPRA deformed immediately under the same preload to comply with the surface profile of the substrate. After the subsequent cooling, the preload was removed and the deformed shape of SPRA was maintained due to the SMP layer (Figure 1C). As a result, good contact between the adhesive and substrate surface was achieved

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(23) Materials: The diglycidyl ether bisphenol A epoxy monomer (EPON 826) and the poly(propylene glycol)bis(2-aminopropyl) ether curing agent (Jeffamine D-230) were obtained from Hexion and Huntsman, respectively. Neopentyl glycol diglycidyl ether (NGDE) was purchased from TCI America. All chemicals were used as received.
(24) SPRA fabrication procedure: 3.6 g of EPON 826 was melted at 75 °C and mixed with 2.16 g of NGDE and 2.3 g of Jeffamine D-230. The mixture was immediately poured into an aluminum mold and cured at 100 °C for 1.5 h to produce the first epoxy layer. Next, a mixture of 2.16 g of NGDE and 1.15 g of Jeffamine D-230 was poured into the same aluminum pan on top of the cured first layer, and cured at 100 °C for another 1.5 h and 130 °C for 1 h. After the curing and demolding, the SPRA was cut into small pieces of about 1 cm × 1 cm, heated to 90 °C for 5 minutes, and cooled down to room temperature prior to use.
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(Figure 1C,D), resulting in a pull-off strength of 61.5 N/cm^2, significantly higher than the pull-off strength reported for synthetic gecko adhesives.[9–22]

The bonding procedure was repeated, and the fully bonded sample (Figure 1C,D), instead of being separated by a pull-off force, was heated again to 90 °C under no load. Upon heating, the SPRA returned to its original curved structure (Figure 1E), and the contact area became small (Figure 1F). The sample was then taken out of the oven, and the remaining small adhesive contact was immediately separated by peeling. The recorded peel-off force was less than 0.1 N/cm. Additionally, if the shape recovered sample (Figure 1E,F) was allowed to cool down to 25 °C, the SPRA became rigid and peeling was no longer possible. The separation could still be done in a pull-off mode with a small force corresponding to 6.3 N/cm^2. Clearly, the adhesion was reversed via heating. It is interesting to note that the shape recovery of the SPRA can occur despite the large pull-off strength between the SPRA and the substrate. We believe that the original curvature played a critical role here. During the shape recovery process to return to the original curvature, the interfacial separation started from the edge and gradually propagated to the center. In a way, this was a peeling process, or more precisely a self-peeling process, as no external peeling force was involved.

Overall, the adhesion controllability of the SPRA is twofold: (1) The thermal transition of the SMP from being rigid to flexible turns the ability to peel on and off; in this case, the curvature is not needed, but an external peeling force may be required. (2) The shape recovery ability and the original curved structure create a self-peeling mechanism to control the contact area and, thus, the adhesion. The SPRA curvature originating naturally from the fabrication process allows the second controlling mechanism to occur. We believe that curvatures created through mold design would have the same effect.

Mechanistically, the SMP stores strain energy in the bonded state (deformed temporary state). Upon heating above its T_g, the mobility of the polymer chains is increased to release the strain energy to detach the adhesive layer. Although it is possible that the intrinsic adhesion of the adhesive layer may change with temperature, we believe such change is insignificant within the temperature range of this study. In fact, the adhesion can be reversed similarly at a much lower temperature of 50 °C (still higher than the T_g). The primary function of the temperature increase is thus to overcome the molecular kinetic barrier to release the SMP strain energy, instead of reducing the intrinsic adhesion of the adhesive layer.

We note that, in the absence of heating, the adhesive bonding is very stable. In fact, we observed no adhesion reduction after a bonded sample was kept under ambient conditions for 1 month. This means that the residue stresses in the backing SMP layer in the deformed (bonded) state do not get released over time unless heated. This is due to the excellent shape fixing properties[25,26] of our particular epoxy SMP, which will be published separately in the future.

In principle, this adhesion reversal using an SMP can be applied to other dry adhesives, and the minimum adhesion

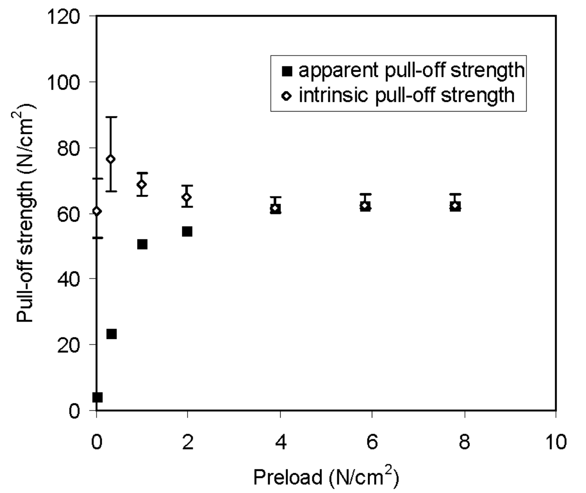

Figure 2. Impact of preload on pull-off strength. The error bars reflect the difficulty in accurately estimating the actual contact areas, particularly when preloads were small.

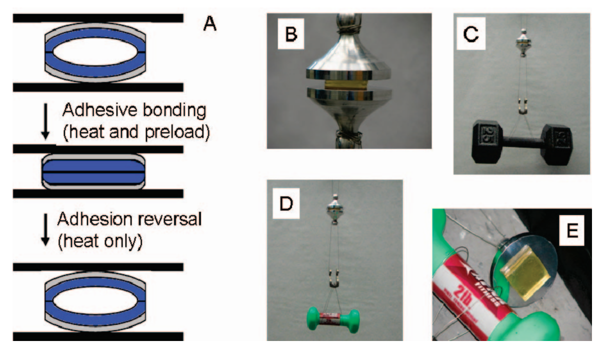

Figure 3. Reversible bonding of rigid substrates using SPRA. A: Schematic cross-section views of the SPRA (blue, SMP; grey, adhesive; black, substrates). B: Adhesive joint. C: Hanging of a heavy load. D: Hanging of the peeling load. E: SPRA after adhesion reversal.

reversal temperature is adjustable based on the thermal transition temperature of the SMP selected. It is worth mentioning that an interesting switchable dry adhesive based on an SMP has been recently reported.[21] In this example,[21] the transition from high adhesion state to low adhesion state was accomplished via an ex situ hot pressing, which is different from our SPRA that reverses the adhesion in situ.

To establish the minimum preload requirement for the SPRA, preloads were varied and the corresponding pull-off forces were measured. As shown in Figure 2, the apparent pull-off strength (force divided by SPRA surface area) increased with the preload until it reached plateau adhesion of 60 N/cm^2 at a preload of 4 N/cm^2, yielding an adhesion coefficient of 15. The intrinsic pull-off strength (force divided by the actual contact areas), however, remains constant within the preload range (Figure 2). This implies that the function of the preload is to deform the SMP and that no significant additional preload is needed for the adhesive layer to reach its adhesion potential.

In summary, our SPRA possesses high adhesion strength, high adhesion coefficient, and excellent durability (no reduction in adhesive strength for eight attaching−detaching cycles). More importantly, its detachment mechanism distinguishes it from any adhesive tape. For instance, if a double side adhesive tape (gecko-like or regular pressure sensitive adhesive) is used to bond two rigid substrates, the adhesive bonding cannot be reversed as the mechanical constraint by the rigid substrates on both sides does not allow peeling to occur. The reversible bonding of rigid substrates is feasible, however, with an SPRA designed as the top structure in Figure 3A. Such an SPRA can be used to bond rigid substrates (middle structure in Figure 3A), and the bonding can be reversed thermally (bottom structure in Figure 3A). The actual images of the bonding and debonding are shown in Figures 3B−E. The bonding between the two aluminum dollies using an SPRA (~4 cm^2) can support a 25 pound dumbbell (Figure 3C). Upon heating, the adhesive bonding can be reversed with a 2 pound dumbbell (Figure 3D,E). The bonding and debonding process can be repeated multiple times.

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