

Bio-inspired Nanosucker Structures for Dry Adhesives

W.-Y. Chang*, Y.-P. Wen* and Y.-C. Chung**

*Research Center of Biomimetics and Medicare Technology, National University of Kaohsiung, Kaohsiung, 811 Taiwan R.O.C.

**Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung, 811 Taiwan R.O.C.

ABSTRACT

We present a facile lithographic nanosucker production process of laminating a nanosphere monolayer with a UV resin and applying various gentle solvent treatments to produce “bottom-up” and “bottom-down” non-close-packed patterns, generating nanosuckers for adhesion. Through mimicking sucker structures on octopus tentacles, we developed a dry adhesive with 6×10^8 nanosuckers per cm^2 via an accessible process. The dry adhesive was produced without complex photolithographic processes and with no sticky wet coatings on it. We produced a biomimetic dry adhesive via UV imprinting, and then applied a slight normal weight on the top of the dry adhesive to generate high average shear force (about 50 N/cm^2) and normal pull-off force (about 54 N/cm^2), which as far as we know is the world record among commercial dry adhesives. In addition, the adhesive can be easily peeled off and repeatedly used without any adhesive residue, and maintain its adhesion force in rigorous environment changes, in temperatures up to 200°C or after washing in a strong acid/base aqueous solution.

Keywords: nanosuckers, dry adhesives, octopus-inspired, non-close-packed patterns, residual-glue-free.

1 INTRODUCTION

Dry adhesives derived from the concept of great van der Waals force in and between the interface of two solids have been developed and correlated with gecko foot nanostructures [1-5]. The hierarchical micro- and nano-structures have then been fabricated on tape surfaces to generate greater contact areas between the dry adhesive and an object when a preload is applied. Such dry adhesives can achieve excellent lateral shear force via orientated adhesion and they can easily be peeled off from the opposite direction, analogous to gecko feet. The gecko-inspired dry adhesives take advantage of nanopillars or nanowires on the tops of microrods, producing greater contact area changes during adhesion, instead of using traditional concepts of wet adhesion, such as pre-treatment of the object surfaces and irreversible chemical bonding force between the adhesive and the object. Therefore, the physical interaction and adhesion established between two solids can be reversibly and repeatedly used without any residual glue or

damage on the object surfaces. Some specific and useful techniques have been used to produce these dry adhesives, such as growing carbon nanotubes in a bottom-up method [6-8], producing polymeric nanohairs from polymer drawing [6,9-11], using elastomer-coated stiff fabrics [12-14], and so on.

However, the normal pull-off force on a gecko-inspired dry adhesive is usually largely decreased compared to the shear force. In some applications, such as silicon wafer transportation, assembly of smart phones, lamination of 3C products, and suspension of drape weights, we need to keep a relatively high shear and normal force endurance, because the adhesive should tolerate pull-off motions in any direction during the lifting process. Inspired by the esteemed professor Kahp Y. Suh's work as well as octopus tentacles, we developed a nanosucker-structured surface, avoiding the complicated processing of nanostructures in gecko-inspired materials. To our knowledge, most dry adhesives are designed using nanohair (gecko-inspired) concepts, but the nanosucker design presented in this article is the only octopus-inspired design, showing astonishingly high shear and normal force endurance [15]. As we know, the suckers on octopus tentacles can produce great suction force. The way it works is that the sucker is pressed against a surface, and the flexible outer margin of skin conforms to it, forming a seal. The octopus-tentacle-inspired design was conceptualized as nanosucker structures behaving like a great deal of suckers on a resin surface, generating a considerable adhesion force. Furthermore, the dry adhesive could also resist shear force as well as normal force, and still be easily peeled off from the surface.

Therefore, this new dry adhesive can be applied but not limited to wafer processing, transportation of optoelectronic materials, 3C product assembly, in-home use, and so on. The adhesion force could be controlled through adjustment of micro/nano patterns, fabrication of master molds, and ingredient design of resins, in order to fit customized designs and required adhesion for special applications.

2 EXPERIMENTAL SECTION

The fabrication of nanosucker structures via solvent immersion method has been described in a previous publication [16]. Briefly, a robot arm with a clamp affixed to it is employed to dip a PET substrate into water in a tank. A nanosphere suspension is then carefully injected onto the water surface via a micro-syringe pump. The nanospheres

float on the water surface and assemble together. 2 wt% sodium dodecane sulfonate is added to the close-packed nanospheres, forming a film. Then the robot arm homogeneously lifts the substrate out of the water, and a 2D photonic crystal monolayer is deposited on the substrate. The substrate is then spin-coated with a UV resin precursor (UVR-1® from BiomiMedTech Co. Ltd. Taiwan). A nanosphere monolayer is adhered to the precursor-coated substrate to be a laminated layer, and then irradiated with UV light (1000W) to cure. The PET is peeled off and the nanospheres are transferred to the UV resin surface. The resin is then dipped into toluene for a certain period. After being gradually rinsed with methanol and water, samples with nanosucker patterns are obtained.

In this experiment, after producing samples with nanosuckers via the above process, the patterned samples were inspected with a scanning electron microscope (SEM, Hitachi S4800). Contact angles on the UV resin were measured via a contact angle analyzer (Han-Kuang High Tech. Co. Taiwan). An atomic force microscope (AFM, NT-MDT Solver PRO-M) attached with a micro-Raman analyzer (NTEGRA Spectra) was employed to explore the chemical structures of the nanosuckers.

3 RESULTS AND DISCUSSION

In preparation of the nanosuckers, we used two resins to fabricate and replicate the nanosucker structures. Only the soft and flexible one was able to display high adhesion force. Addition of multi-functional oligomers led to a highly crosslinked structure, which was conformal and easy to demold from the PS nanosphere mold; however, the hard structure failed to stick to the substrate. Ingredients that were too soft were also tested and found to stick to the PS nanosphere/glass substrate, leading to difficulty in demolding. The soft resin also showed permanent deformation after enduring high forces.

Figure 1 shows the SEM photographs of the nanopores on the resin surface and their cross-sectional view assists in the inference that some good solvents could etch PS nanospheres out of the resin, leaving some nanosuckers on the surface with the same pattern as the nanosphere monolayers. The process could produce non-close-packed nanosucker structures with small open mouths and large empty interiors, resulting in separate and individual nanopores that could serve as nanosuckers to generate partial vacuum adhesion force.

The average shear force endurance was 50.6 ± 13.0 N/cm², which is competitive among gecko-inspired dry adhesives. Interestingly, the average normal force endurance was about 54.3 ± 19.3 N/cm², revealing a relatively high pull-off force among dry adhesives. The partial vacuum effect is predicted in Figure 2, showing a certain preload is applied on the back of the dry adhesive to extrude some air out of the nanosuckers. The van der Waals force (contact area) should be increased, which has been

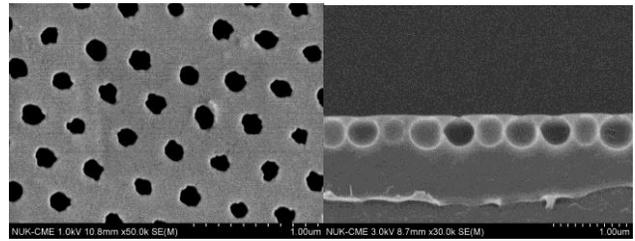


Figure 1. SEM photographs of nanosuckers and their cross-sectional view.

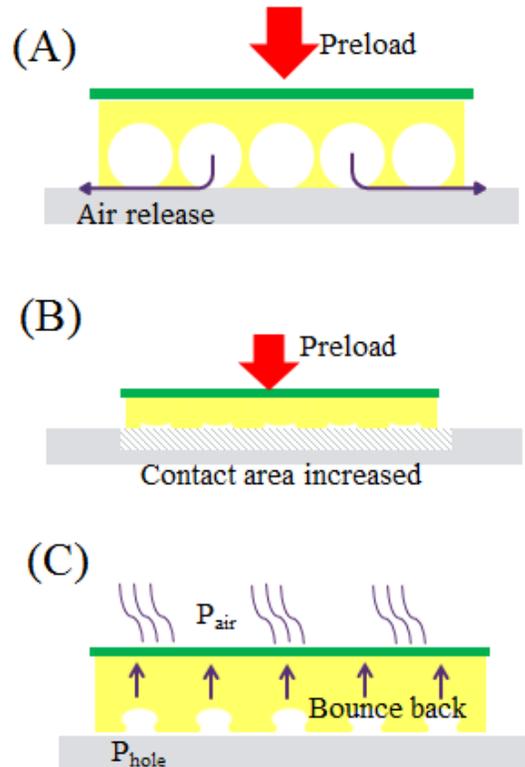


Figure 2. Illustration of mechanism of nanosucker adhesive with preload and partial vacuum adhesion force.

characterized via ATR-FTIR (data not shown). In Figure 2(C), the pressure drops between P_{air} and P_{hole} maintain the adhesion while the flexible resin bounces back a little.

We also compared the nanosuckers with a surface covered in $80 \mu\text{m}$ non-spherical pores in a similar arrangement. Based on the same UV resin, the microporous pattern revealed only 9.29 ± 2.61 N/cm² for shear force endurance and undetectable normal force endurance. Therefore, size and shape seem to significantly affect the adhesion force.

Analysis of the morphology of the nanosuckers showed about 100-125 nm diameter opening mouths on top of 380 nm diameter spherical shapes, with 60 million nanopores in a square cm. Moreover, the thin monolayer of nanopores coupled with flexible UV resin retained the elastomeric surface property enabling close contact with the substrate surfaces due to reversible surface deformation.

Figure 3 shows the suspension test for lifting a 7.52 kg dumbbell. The 1 cm x 1 cm dry adhesive was fixed on a glass slide and physically stuck to the other glass slide that had bound to the dumbbell. The SEM photograph shows the deformation of nanosuckers after being stretched with maximum load.

We performed repeated maximum loading tests on a single adhesive sample. The adhesion force of the nanosucker adhesive decreased each time the test was repeated, shown in Figure 5. While the maximum load endurance of the adhesive was 80 N/cm² for the first test, it was reduced to only 0.73 N/cm² by the 14th iteration, indicating the deformation of nanopores after the load exceeded the adhesive's maximum endurance. In order to analyze the safety of using the dry adhesives, a PMMA slab was lifted and released using an automatically-controlled mechanical test. After lifting the slab 120 times the maximum load of the adhesive was tested and found to be 18 N/cm², which is still high enough to suspend some weights.

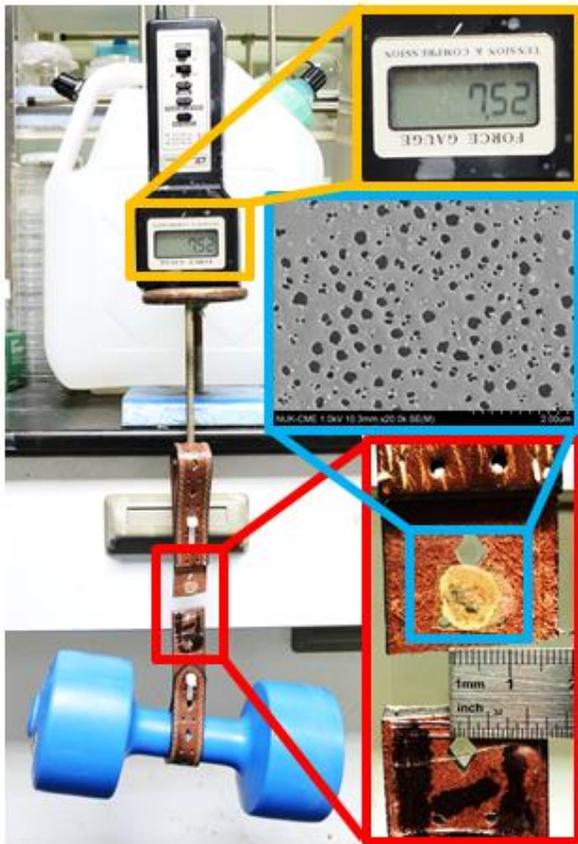


Figure 3. Suspension test for 100 mm² nanosucker adhesive suspending a dumbbell with a total weight of 7.52 kg and close-up of the sample. The SEM photograph shows the deformation of nanosuckers after loading.

The endurance tests were also performed in different pH aqueous solutions (Figure 6). Three-minute immersion time was adopted to imitate the extreme conditions in water. The adhesion between the dry adhesive and the glass slide was found to resist water diffusion, even in acidic or alkaline conditions. Thermal endurance test was also performed from the room temperature to 200 °C to meet the wafer processing requirement. The polymeric dry adhesive turned to slight yellow, but maintained its adhesion on a glass slide, showing the concern of thermal expansion and nanosucker deformation could be solved in choosing a flexible and thermo-durable UV resin as the adhesive substrate.

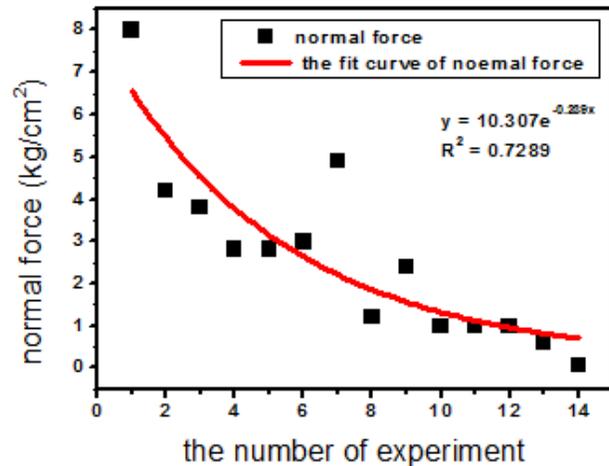


Figure 4. Repeated measurement of the same nanosucker adhesive enduring its maximum normal loading.

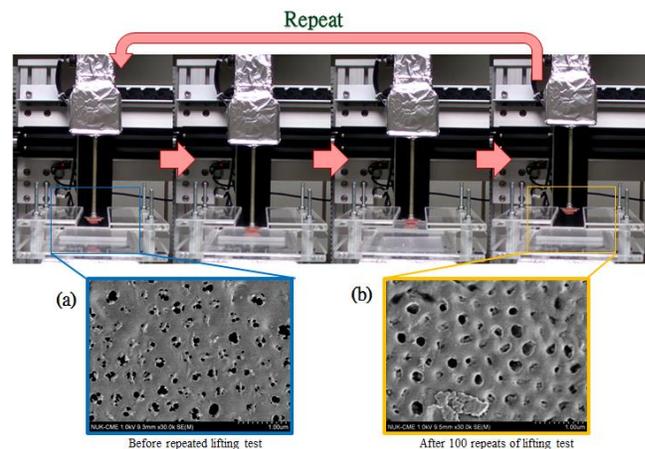


Figure 5. Repeated lifting of a 72 g PMMA slab 120 times. The final measured maximum normal force was 18 N/cm².

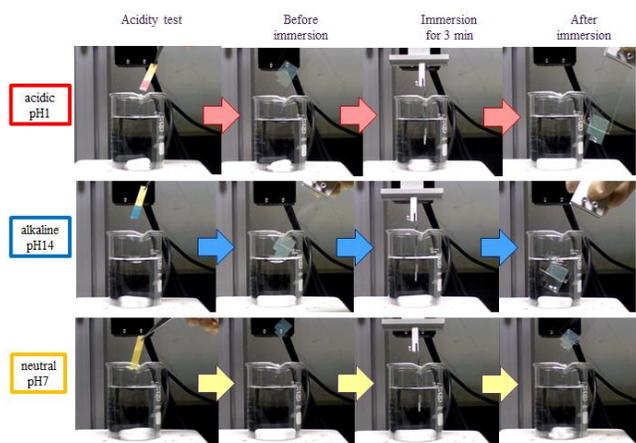


Figure 6. Adhesion tests for immersion in acidic, alkaline, and neutral aqueous solution. (test time: 3 min)

4 CONCLUSION

We produced a biomimetic dry adhesive via UV imprinting a UV resin laminated with a pre-assembly of PS nanospheres. The dry adhesive was given 6×10^8 /cm² nanosuckers, like a octopus' tentacle, to display high physical adhesion toward flat substrate. We can apply a slight normal weight on the top of the dry adhesive to generate high average shear force (about 50 N/cm²) and normal pull-off force (about 54 N/cm²), which as far as we know is the world record among commercial dry adhesives. The UV imprint technique combined with self-assembly of nanospheres can be employed to produce octopus-inspired dry adhesives for further applications.

REFERENCES

- [1] K. Autumn, Y. A. Liang, S. T. Hsieh, W. Zesch, W. P. Chan, T. W. Kenny, R. Fearing and R. J. Full, "Adhesive force of a single gecko foot-hair," *Nature*, 405, 681, 2000.
- [2] K. Autumn and A. M. Peattie, "Mechanisms of adhesion in geckos," *Integr. Comp. Biol.* 42, 1081, 2002.
- [3] R. J. Full, R. S. Fearing, T. Kenny and K. Autumn "Adhesive microstructure and method of forming same." U.S. Patent No. 6,737,160. 18 May 2004.
- [4] H. Ko, Z. Zhang, Y.-L. Chueh, J. C. Ho, J. Lee, R. S. Fearing and A. Javey, "Wet and dry adhesion properties of self-selective nanowire connectors," *Adv. Func. Mater.* 19, 3098, 2009.
- [5] M. T. Northen and K. L Turner, "A batch fabricated biomimetic dry adhesive," *Nanotech.* 16, 1159, 2005.
- [6] H. E. Jeong, K. Y. Suh, "Nanohairs and nanotubes: efficient structural elements for gecko-inspired artificial dry adhesives," *Nano Today* 4, 335, 2009.
- [7] S. Hu, Z. Xia and X. Gao, "Strong adhesion and friction coupling in hierarchical carbon nanotube

arrays for dry adhesive applications," *ACS Appl. Mater. Interf.* 4, 1972, 2012.

- [8] S. Hu, Z. Xia and L. Dai, "Advanced gecko-foot-mimetic dry adhesives based on carbon nanotubes," *Nanoscale* 5, 475, 2013.
- [9] H. E. Jeong, J.-K. Lee, H. N. Kim, S. H. Moon and K. Y. Suh, "A nontransferring dry adhesive with hierarchical polymer nanohairs." *Proc. Nat'l. Acad. Sci.* 106, 5639, 2009.
- [10] H. E. Jeong, S. H. Lee, P. Kim and K. Y. Suh, "Stretched polymer nanohairs by nanodrawing," *Nano Lett.* 6, 1508, 2006.
- [11] M. K. Kwak, H.-E. Jeong, T. Kim, H. Yoon and K. Y. Suh, "Bio-inspired slanted polymer nanohairs for anisotropic wetting and directional dry adhesion," *Soft Matt.* 6, 1849, 2010.
- [12] M. D. Bartlett, A. B. Croll, D. R. King, B. M. Paret, D. J. Irschick. And A. J. Crosby, "Looking beyond fibrillar features to scale gecko-like adhesion," *Adv. Mater.* 24, 1078, 2012.
- [13] M. D. Bartlett, A. B. Croll and A. J. Crosby, "Designing bio-inspired adhesives for Shear loading: from simple structures to complex patterns," *Adv. Func. Mater.* 22, 4985, 2012.
- [14] M. D. Bartlett and A. J. Crosby, "High capacity, easy release adhesives from renewable materials," *Adv. Mater.* 26, 3405, 2014.
- [15] W.-Y. Chang, Y. Wu, Y.-C. Chung, "Facile fabrication of ordered nanostructures from protruding nanoballs to recessional nanosuckers via solvent treatment on covered nanosphere assembled monolayers," *Nano Lett.* 14, 1546, 2014.
- [16] W.-Y. Chang, Y. Wu, Y.-C. Chung, "Bio-inspired nanobowl/nanoball structures fabricated via solvent etching/swelling on nanosphere assembly patterns," *Thin Solid Films*, 570, 527, 2014.