Wet Self-Cleaning of Biologically Inspired Elastomer Mushroom Shaped Microfibrillar Adhesives

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We report that hydrophilic polyurethane mushroom shaped microfiber arrays possess wet self-cleaning ability using the lotus effect as biologically inspired synthetic fibrillar adhesives. In comparison with a flat surface made of the same polyurethane, the fiber array exhibited almost 100% wet self-cleaning without any degradation of adhesive strength. We attribute this cleaning ability to the mushroom shaped tip ending geometry of the fiber array, which causes the fiber array to be apparently hydrophobic even though the fiber material is hydrophilic. These results suggest that tip ending shape is one of the significant design parameters for developing contamination-resistant polymer fibrillar adhesives.

The adhesion ability of fibrillar structures in nature has motivated many researchers to study the principles behind this adhesion and develop synthetic fibrillar adhesives inspired by these biological fibrillar structures. In addition to the adhesion ability, self-cleaning ability is also one of the attractive properties of the biological fibrillar adhesives, which has been studied for gecko foot hairs by Hansen and Autumn. They showed that geckos were able to clean their dirt-contaminated feet by stepping on clean dry surfaces. This cleaning by contacting on clean surfaces can be defined as contact self-cleaning. The leaves of the lotus plant exhibit another naturally occurring example of self-cleaning. Micro/nanoscale roughness as observed on these leaves can make a surface (super)hydrophobic, and dirt particles on them can then be removed by water droplets, which capture the dirt particles as they roll off the surface. This water droplet based surface cleaning is known as the lotus effect. Several researchers have demonstrated these two types of self-cleaning with synthetic fibrillar adhesives which were made of photore sist, parylene, carbon nanotubes (CNTs), and polypropylene. Particularly, Lee and Fearing demonstrated contact self-cleaning on hard polymer (Young’s modulus > 1.5 GPa) nanoﬁber arrays, whereas Sethi et al. showed wet self-cleaning on CNTs using water droplets. In contrast with self-cleaning studies with hard material fiber arrays, there is a lack of works on self-cleaning of soft elastomer fibrillar adhesives. In this work, we demonstrate that mushroom shaped microﬁber arrays (re-entrant textured surface) made of a hydrophilic soft elastomer are also able to possess wet self-cleaning using the lotus effect as biologically inspired fibrillar adhesives. It is worth noting that simple cylindrical structures with hydrophobic materials can also show super-hydrophobicity and wet self-cleaning.

Elastomer mushroom shaped microfiber arrays with a 300 µm thick backing layer were fabricated with polyurethane (BJB Enterprises, ST-1060) using methods that we demonstrated previously. After a negative silicon template for the fiber array was fabricated using deep reactive ion etch and the notching effect, the liquid precursor mixture of the polyurethane was poured into the template. The polyurethane precursor was cured at room temperature for 1 day, and the fiber array was released by removing the silicon template with XeF2. It is worth noting that the mushroom shaped tips of the fibers were exposed to XeF2.

during the fiber array releasing step, resulting in a change of tip surface material properties by surface fluorination. A flat elastomer surface sample with 300 μm thickness was also prepared by exposing the surface to XeF₂ for the same amount of time used to release the fiber array to ensure a fair comparison between the flat surface and the fiber array. A scanning electron microscopy (SEM) image of the fabricated fiber array in Figure 1 shows every single fiber has a mushroom shaped (re-entrant shape) tip ending although the sidewall of the tip is locally rough due to the notch effect.

To characterize wet self-cleaning using the lotus effect on the flat surface and the fiber array, the static contact angle and contact angle hysteresis (difference between advancing and receding contact angles) of the two samples were measured by placing a deionized (DI) water droplet on the samples. The static apparent contact angle (θ_{app}) of a water droplet on the fiber array was 128°, and the static equilibrium contact angle (θ) of a water droplet on the flat surface was 82°. Contact angle hysteresis was 87° for the fiber array and 97.5° for the flat surface. Due to the contact angle and contact angle hysteresis differences between the two samples, a 60 μL water droplet was necessary to free flow on the flat surface, whereas a 20 μL water droplet was enough to free roll off the fiber array when the samples were tilted to a 90° angle. As contaminating elements, 5–30 μm diameter silica spherical particles (Duke Scientific Corporation, Spherical Glass Materials (Dry)) were used. If these particles are transferred to the fiber array by pressing hard onto a surface, very small particles (especially the ones with a diameter smaller than the fiber stem diameter) could be embedded inside the fiber array, which could degrade the fiber array adhesion repeatability and magnitude. Therefore, we gently dropped the particles by gravity on the flat surface and the fiber array, and we selected the smallest particle diameter as 5 μm to minimize particle embedding during pressing onto a given substrate during adhesion testing. Then, 60 and 20 μL water droplets were placed on flat and fiber array samples, respectively. The two samples were tilted to a 90° angle to cause the water droplets to move across the samples for washing. Before and after this washing, the number of particles in a predefined area (a 0.9 mm by 0.7 mm rectangle) was counted through optical microscope images and their wet self-cleaning abilities were compared. In addition, pull-off forces of the fiber array were measured before contamination and after contamination and washing to inspect any possible adhesion degradation by wet self-cleaning. For pull-off force measurements, we used a glass hemisphere instead of a flat glass surface as the test contact surface to minimize alignment errors during the experiments.

A 6 mm diameter smooth glass hemisphere (ISP Optics, QU-HS-6) attached to a load cell (Transducer Techniques, GSO-25) was mounted vertically by a motorized stage (Newport, MFA-CC) with 100 nm resolution. The hemisphere was pushed into the sample surface with a preload force and retracted at a slow speed of 1 μm/s. During retracting, the maximum tensile force was measured as the pull-off force.

Figure 2 shows that, after washing, the particles still remained on the flat surface and tended to congregate whereas all particles were removed by washing the fiber array. It was observed that a free-flowing water droplet left tiny droplets on the flat surface and then the tiny droplets wet particles locally and congregated them during drying. This observation is consistent with the fact that the flat polyurethane surface is natively hydrophilic (θ < 90°). However, due to apparent hydrophobicity (θ_{app} > 90°), a water droplet rolled off the fiber array was able to capture the particles during rolling in the same way as the lotus effect. These experiments were repeated six times at different locations, and the number of cleaned particles from the two samples was counted in each experiment. Pull-off forces for the fiber array were also measured six times at different locations during these experiments. Wet self-cleaning ability with percentage bars for two samples and pull-off forces of the fiber array for different preloads are illustrated in Figure 3. In contrast to the flat surface, the fiber array exhibited almost 100% wet self-cleaning (Figure 3a). During the measurements, we observed negligible adhesion from the contaminated fiber array. To simply quantify it, we conducted three additional pull-off force measurements with the contaminated fiber array for a 20 mN preload. The results showed 0.12, 0.07, and 1.58 mN pull-off forces.

Figure 4a, b shows profile views of water droplets on the flat surface and the fiber array, respectively. The fiber array is apparently hydrophobic (θ_{app} = 128°), while the flat surface is apparently hydrophilic (θ_{app} = 90°).
hydrophilic ($\theta = 82^\circ$). Studies show that a predefined rough surface with gradually decreasing surface energy or increasing equilibrium contact angle ($\theta$), which is measured on a flat surface, creates a transition between two contact interfaces.\textsuperscript{31,36-38} One is a fully wet interface that conforms to the Wenzel model,\textsuperscript{39} and the other is a solid–air composite interface that conforms to the Cassie model.\textsuperscript{40} The large contact area between the liquid and solid in the Wenzel state leads to high contact angle hysteresis, which does not allow water droplets to readily roll off of the rough surface. By contrast, a composite interface of the Cassie state facilitates both nonwetting (high apparent contact angle) as well as easy water droplet roll-off because of the small total contact area between the water droplet and the solid substrate.\textsuperscript{31} These models predict the apparent contact angle ($\theta_{\text{app}}$) of a water droplet on the rough surface for a particular $\theta$ value. Once the topography of a rough surface is defined, a critical contact angle ($\theta_c$) for the transition can be obtained by equating the Wenzel and Cassie equations. When $\theta$ is above $\theta_c$, the composite interface has lower overall free energy and the composite interface is in a stable state. When $\theta$ is below $\theta_c$, the fully wet interface is in a stable state. Based on the topography of our microfiber array, the lines of the two models were drawn to predict a stable interface between the water droplet and the fiber array for a particular $\theta$ of the flat surface. The two lines are illustrated in Figure 4c simultaneously with the critical contact angle ($\theta_c = 101^\circ$) and a point determined by the cosines of $\theta$ and $\theta_{\text{app}}$, which are measured on two samples. Since $\theta$ is smaller than $\theta_c$, the interface between the water droplet and the fiber array is predicted to be stable as a fully wet interface. Interestingly, $\theta_{\text{app}}$ is 128°. This observation suggests that the water droplet on the fiber array is not in a stable state but rather in a metastable state\textsuperscript{31,36-38} of the composite interface on the fiber array. This metastable composite solid–liquid–air interface is consistent with the Cassie model and corresponds to a local minimum in the free energy, even though the fully wetted Wenzel state corresponds to a global minimum in the free energy.\textsuperscript{31} It was reported that this metastable state is possible when a rough surface is a re-entrant textured surface; that is, the surface topography cannot be described by a simple univalued function $z = h(x,y)$, and a vector projected normal to the $x$–$y$ plane intersects the texture more than once.\textsuperscript{37} Since every fiber has a mushroom shaped tip, ultimately the fiber array can be a re-entrant textured surface.

To demonstrate this approach qualitatively, we fabricated two other polyurethane (ST-1060) fiber arrays using methods described by Aksak et al.\textsuperscript{14,17} which are called type 1 and type 2 herein. Type 1 is a 50 $\mu$m diameter, 100 $\mu$m length, and 120 $\mu$m center-to-center spacing cylindrical fiber array in a square packing arrangement. Type 2 has the same dimensions as type 1 other than mushroom tip endings 100 $\mu$m in diameter (Figure 4d,e). When a 20 $\mu$L DI water droplet was deposited onto both samples, a droplet on type 1 was easily wet into surface unless it was placed on the fiber array very carefully whereas a droplet was very stably deposited on type 2. Although Jung and Bhushan previously showed that this difference in stability could be attributed to the enlarged tip area, their structures were natively hydrophobic.\textsuperscript{34} In Figure 4d,e, it is shown that the net traction at solid–liquid–air interfaces can depend on the fiber tip shape, particularly when the fiber material is hydrophilic ($\theta < 90^\circ$). In a simple cylindrical fiber array (type 1) case, the downward net traction leads to a fully wetted interface (Figure 4d). The edge of the fiber tip serves to pin the water interface, allowing for apparent superhydrophobicity, but any disturbance that causes the water to push past the edge of the fiber onto the sides results in wetting as observed in the experiments. However, in a mushroom shaped fiber array (type 2) case, the upward net traction can support sagged water unless the solid–liquid interface reaches the cylinder surface under the tip (Figure 4e). Thus, stable water droplet deposition on type 2 can be

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\textsuperscript{(38)} Quere, D.; Lafauma, A.; Bico, J. Nanotechnology 2003, 14, 1109.


attributed to not only the enlarged tip area but also the re-entrant shape\textsuperscript{31} of the mushroom tips. Consequently, even though the fiber material is natively hydrophilic, our microfiber array with mushroom shaped tip endings can be apparently hydrophobic enough to possess stable wet self-cleaning.

In summary, elastomer microfiber arrays with mushroom shaped tip endings exhibit wet self-cleaning seen in lotus leaves in nature, while providing dry adhesion. Almost 100\% of 5–50 \( \mu m \) diameter silica particles on the fiber array were cleaned using the lotus effect even though the material is natively hydrophilic. Moreover, contaminated and then wet self-cleaned fiber arrays exhibited almost 100\% adhesion recovery. This remarkable wet self-cleaning ability results from fibrillar structuring with mushroom shaped tip endings, which causes the switch from a hydrophilic flat surface to an apparently hydrophobic solid–air composite surface. Thus, it is demonstrated that tip ending shape design of fiber arrays is one of the important parameters for developing contamination-resistant fibrillar adhesives.