Reproducing Superhydrophobic Leaves as Coatings by Micromolding Surface-Initiated Polymerization

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Micromolding surface-initiated polymerization enables the fabrication of polymer coatings that reproduce the microscale surface topography of superhydrophobic leaves onto solid supports. Here, the surfaces of superhydrophobic leaves from *Trifolium repens* and *Aristolochia esperanzae* are molded and reproduced as the topography of a partially fluorinated polymer coating through the surface-initiated ring-opening metathesis polymerization of 5-(perfluoroctyl)norbornene (NBF8). The polymer coatings have thicknesses exceeding 100 μm, which can be tailored by the amount of monomer added to the mold. These coatings are robustly bound to the substrate, contain compositions not found in nature, and achieve superhydrophobicity that is comparable to the actual leaf.

1. Introduction

In recent years, nature and its remarkably optimized designs acquired through millions of years of evolution have provided endless sources of inspiration for researchers who seek ideas to address specific challenges.[1] Some examples of nature-inspired approaches include the efficient collection of water from dry environments,[2] the minimization of the damage caused by solid particle erosion in mechanical components,[3] the improvement of the efficiency and land area reduction of heliostat fields,[4] and the design of liquid-repellent surfaces that use a microtextured substrate to lock-in a lubricating liquid to achieve omniphobicity, self-repair, and performance at high pressures.[5] Moreover, the superhydrophobic character and self-cleaning capability demonstrated by a large number of plant leaves and other living organisms are the driving forces behind numerous attempts of using these biological structures as templates for the fabrication of superhydrophobic surfaces.[6] Superhydrophobic surfaces have potential applications as self-cleaning surfaces,[2a,3] water-repellent textiles,[3] and ice-resistant coatings,[6] as well as surfaces to promote interfacial slip[5] and drag reduction.[6] Methods to mimic these surfaces include soft lithography,[2b] microlithography,[2a] UV-nanoimprint lithography,[7] etching,[8] membrane casting,[9] and two-beam laser interference.[2c] While efforts to replicate nature’s superhydrophobic and self-cleaning surfaces have been largely successful by other groups,[2b,7,10] the resulting products are often hand-held, peel-away materials, and not surface-bound coatings, as are targeted here.

In this Communication, we fabricate polymer coatings that reproduce the surface topography of superhydrophobic leaves through a process called micromolding surface-initiated polymerization (μMSIP),[11] which combines soft lithographic molding with a surface-initiated polymerization (SIP). We have recently introduced μMSIP as a versatile process to fabricate surface coatings with microscale topographies that replicate artificial masters.[11]
Here, we employ this technique to not only reproduce the highly evolved and functional surface architectures optimized by nature but also provide tremendously greater versatility in chemical composition, as the building blocks of nature are limited to hydrocarbons. Accordingly, the resulting bioreplicated, surface-bound polymer coatings are obtained by means of the mold-confined, surface-initiated ring-opening metathesis polymerization (SI-ROMP) of 5-(perfluorooctyl)norbornene (NBF8), which exhibits a critical surface tension of 9 mN m\(^{-1}\).\(^{[12]}\) The reproduction of nature’s engineered, microscopically rough, and highly functional surfaces onto a solid substrate through an SIP technique provides chemically anchored polymer coatings with the capability to withstand external chemical and physical conditions that may diminish the integrity or performance of the natural masters.\(^{[13]}\)

2. Results and Discussion

Scheme 1 illustrates the different steps of μMSIP to create polymer coatings that reproduce the structures and topography of the master substrates. In this case, Trifolium repens (white clover) and Aristolochia esperanzae (Dutchman’s pipe) were chosen because they provide both high equilibrium water contact angles and different complex surface topographies. Briefly, each master leaf was molded by soft lithography with an elastomeric composite comprising hard-PDMS (h-PDMS) and Sylgard 184 PDMS to produce a negative replica exhibiting the corresponding inverted structures of the surface of the leaf (see Supporting Information for details). Initiator species were added into the mold by depositing a dilute solution of Grubbs catalyst in diethyl ether and letting the solvent evaporate. Immediately afterward, the mold was filled with pure NBF8, and subsequently pressed against the activated surface of the substrate from which the textured film would grow. A gold-coated silicon substrate was activated in advance by anchoring initiator species onto the surface (see Supporting Information for details). As the polymerization progresses, both the surface-tethered growing polymer chains and those grown from the mold start filling the inverted structures, thereby reproducing the corresponding surface features. After 20 min, the composite mold bearing the textured pattern was removed, and as a result, a surface-bound pNBF8 film displaying the surface relief of the respective master was obtained. As shown in Scheme 1, one of the advantages of μMSIP is that the fabrication of polymer coatings is a fast, straightforward process once the reusable composite mold has been prepared.

Figure 1 shows the morphological characteristics of the fixed Trifolium repens leaf (a,c,e) and a pNBF8 film (b,d,f) at different magnifications and angles of inclination. Figure 1a,b shows a low magnification, tilted view of the fixed leaf and coating, respectively. The epidermal surface of the leaf displays a structured relief comprised of dome-shaped convex epidermal cells. Likewise, the

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**Scheme 1.** The μMSIP process used to produce microtextured pNBF8 films that mimic the surface topography of superhydrophobic leaves.
topography of the pNBF8 film obtained by means of μMSIP shows a microrelief consisting of dome-shaped structures over large areas without observable defects. Figure 1c,d shows a top view, magnified image of the leaf and the resulting polymer coating, respectively. Figure 1c reveals a closer inspection of the epidermal cells of the leaf and the stomata (pores on the epidermis of the leaf that control gas exchange), represented by the dark-colored structures appearing in between some of the epidermal cells. The polymer structures that dominate the surface of the coating (Figure 1d), exhibit similar shapes and sizes as compared with those present on the leaf. Quantitative measurements, performed by means of image analysis of Figure 1c,d, reveal that the average length and width of the larger surface structures on both the leaf and the coating are, within error, the same. For example, the length and width of the natural structures (epidermal cells) are 28 ± 3 and 19 ± 2 μm, respectively; those of the coating are 30 ± 3 and 20 ± 3 μm, respectively. Stomata features on the coating are on average 30% wider and 10% lengthier than those on the leaf. Further comparison between the morphology of the leaf and that of the coating shows that
the features on the coating appear to be connected by polymeric strands at the base, whereas the boundaries of each epidermal cell on the leaf are well defined and disconnected. This may be a consequence of the h-PDMS mix not being able to entirely penetrate through the space separating the epidermal structures. In general, the only structures that exhibit orientation on the leaf surface are those epidermal cells close to or that form the veins of the leaf; the rest are randomly oriented. In Figure 1c, the epidermal cells running diagonally from the bottom left to the top right, and those on the top left and bottom right are examples of the former and the latter, respectively. Polymer structures in Figure 1d do not show any orientation in particular as the imaged area of the coatings is not near the veins. Figure 1e,f shows zoomed-in tilted images of the leaf and coating, respectively. Figure 1f shows that the tips of some structures have defects or craters, that we attribute to areas in the composite mold lacking a uniform layer of fluorinated silane that was employed to prevent adherence between the mold and the leaf.

Figure 2 shows the morphological characteristics of the Aristolochia esperanzae leaf and its corresponding pNBF8 textured film. Tilted images (a,b,e,f) were taken at 45° with respect to the surface parallel.
coating at different magnifications and angles of inclination. By contrast to the epidermal relief of Trifolium repens, the individual epidermal cells present on the surface of the Aristolochia esperanzae leaf are larger and exhibit a more heterogeneous geometry (Figure 2a). The Y-shaped structures that appear in Figure 2a (leaf) and 2b (polymer coating) correspond to veins in the leaf. Figure 2c,d shows a top view, magnified image of the leaf and the resulting polymer film, respectively. Figure 2c reveals epidermal cells exhibiting irregular, randomly oriented shapes. Interestingly, star-like features are formed when one sloped-end of several (usually six) epidermal cells come together. These shapes can be seen at the middle, bottom middle, top right, and top left of Figure 2c. These features also appear in the polymer coating, and can be discerned at the middle left and bottom right of Figure 2d. Although the surface structures present both on the leaf and the coating do not exhibit well-defined dimensions, a quantitative approximation of their length and width, done by image analysis of Figure 2c,d, reveals that these have similar ranges in both the leaf and the coating. For example, the scale of the length and width of the epidermal cells ranges from 36 to 57 and 15 to 33 μm, respectively; those of the coating range from 36 to 81 and 16 to 32 μm, respectively. Figure 2e shows a magnified image of the surface of the leaf and reveals that short epicuticular waxes (white hair-like structures) dominate the surface of most epidermal cells. The fact that some areas of the surface lack these structures may be explained as a consequence of the fixing and sputtering procedures. Reports by Neinhuis and Barthlott[14] show that epicuticular waxes are fragile structures that can be easily altered by external factors. By contrast to the fixed leaf, the surface of the features present on the polymer coating (Figure 2f) has few of these structures. A plausible explanation for this is that during the separation of the composite mold from the leaf, the epicuticular waxes may become detached and remain embedded into the composite mold. Consequently, submicroscale recesses in the composite mold become clogged, preventing any growth of polymer inside them. A small percentage of these features are not clogged as evidenced by some sporadic polymer growth atop features as shown in Figure 2d,f.

Figure 3. a) Profilometry line profiles of pNBF8 coatings that reproduce the surface topography of fixed Aristolochia esperanzae and Trifolium repens leaves. After curing, the composite molds were cut smaller than their original size in order to discard the corresponding thickness of the leaf. The nearly vertical lines represent cuts through the coating to the substrate, which is set at 0 μm on the y-axis. The line profile for the Aristolochia esperanzae coating was measured in the middle of the coating, whereas that for the Trifolium repens coating was measured at the edge. b) Profilometry line profiles of a Trifolium repens fixed leaf and pNBF8 coating.

Table 1 summarizes the advancing \( \theta_a \) and receding \( \theta_r \) water contact angles for the Trifolium repens and Aristolochia esperanzae leaves, and those of their respective coatings. The values for the width are in good agreement with those obtained from image analysis of Figure 1. Measurements obtained from the line profile indicate that the films reproducing the surface topography of the Aristolochia esperanzae and Trifolium repens leaves exhibit in some parts of the surface, peak-to-valley heights as large as ~40 μm. Figure 3b shows zoomed-in line profiles for the Trifolium repens leaf and a pNBF8 coating. Profilometry measurements show that the width and height of the epidermal cells on the surface of the leaf are 19 ± 6 and 2.7 ± 1.0 μm, respectively; those of the polymer features on the coating are 19 ± 6 and 2.9 ± 1.0 μm, respectively. The values for the width are in good agreement with those obtained from image analysis of Figure 1.
corresponding polymer coatings. The *Trifolium repens* leaf exhibits higher advancing and receding contact angles than those exhibited by the *Aristolochia esperanzae* leaf. The *Trifolium repens* meets the requirements to be considered as superhydrophobic, i.e., $\theta_a > 150^\circ$ and hysteresis $< 10^\circ$, whereas the *Aristolochia esperanzae* leaf falls slightly short of this definition (hysteresis $= 11^\circ$), despite having a high $\theta_a$ angle. The polymer coatings formed by $\mu$MSIP also exhibit a low wettability toward water, as evidenced by the high $\theta_a$ and $\theta_w$ water contact angles that are, within the measured errors, the same as those of the leaf. Despite some differences between the leaf and coating (most notably, the absence of hair-like surface features for the reproduced coating of *Aristolochia esperanzae* and observable defects in the coating for *Trifolium repens*), these results indicate that $\mu$MSIP enables the preparation of surface-bound polymer coatings exhibiting sufficient microscopic roughness to achieve the superhydrophobic wetting state. This level of performance may be explained from a chemical composition perspective; the fluorinated nature of the coating, with its lower surface energy than a hydrocarbon, compensates for the lack of perfection in the reproduction. The low contact angle hysteresis for the reproduced coating of *Aristolochia esperanzae* illustrates that roughness on the scale of tens of microns without submicron scale features is sufficient to achieve the superhydrophobic wetting state.

### 3. Conclusions

We have demonstrated that $\mu$MSIP is a versatile and fast route to fabricate textured coatings that reproduce the microscale surface topography of superhydrophobic leaves onto solid supports. Overall, the surface morphology of the polymer coatings based on the size and height of the reproduced epidermal cells is in excellent agreement with that of the reproduced leaves as evidenced by SEM and corresponding quantitative image analysis. Profilometry measurements showed that the polymer micromorphological relief rests upon a thick, robust coating whose thickness may be controlled, in principle, by the amount of monomer added to the mold. Contact angle measurements on the resulting pNB8F coatings confirmed the achievement of a superhydrophobic wetting behavior and the influence of a combination of chemical composition and microroughness on wettability (*Aristolochia esperanzae* case). This proof-of-concept work opens the door to the possibility of reproducing a great number of other biologically optimized surfaces available in nature as surface coatings.

### Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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