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Artificial Leaves via Reproduction of Hierarchical Structures by a Fast Molding and Curing Process

Sungjune Park, Patrick van Rijn, Alexander Böker*

In this work, we have developed a practical approach for the replication of hierarchical structures on a native leaf surface via a fast two-step molding process combining both the fast curability to prevent shrinkage of cells and the strong resistance to chemical compounds for further applications. The negative replica of the leaf was produced from perfluoropolyether (PFPE) by precise molding followed by a fast curing with UV. A liquid ceramic precursor material (polyvinylsilazane, PVSZ) was used to fabricate the positive leaf structure through the same process as applied for the negative imprint of the surface yielding a highly detailed replica of the native leaf surface structure. Static water contact angle measurements show that the biomimetic surfaces exhibit a wettability similar to the native leaves.

In recent years, a variety of plant surfaces have been used for the development of artificial biomimetic materials.^[1–4] One of the most prominent properties of such surfaces is their extraordinary wetting behavior, which mainly depends on the surface morphology. The superhydrophobic and self-cleaning properties are closely related to the presence of hierarchical structures with multiscale roughness, consisting of cells, and micro-/nanostructured wax crystals on the cell surface.^[5–7] This hierarchy prevents the water droplets on the leaf surface from wetting the surface, retaining air underneath them, resulting in extremely high contact angles above 150° and a small contact angle hysteresis of less than 10°.^[6] The water droplets easily roll off the surface carrying dust and dirt particles, leaving behind a clean surface.^[3,8] Such hierarchical structures are of great interest for various technological applications, including self-cleaning surfaces, construction materials, and textiles. In the past, artificial leaves with hierarchical

surface structures have gained much attention and several methods have been devised for their fabrication based on lithographic processes,^[9,10] electro-depositions,^[11] and colloidal systems.^[12] However, the above-mentioned methods constitute complex and time-consuming fabrication processes. In contrast, molding methods are simple and cost effective to transfer and replicate surface structures even on the nanoscale,^[13,14] however, they encounter problems with artifacts from shrinkage of cells in fresh leaves due to loss of water. Additionally, the softness of the superimposed wax crystals on the leaf surface could be destroyed or could collapse.^[15,16] To circumvent these problems, an effective fast molding process to reduce the loss of water is required. Fast replication processes were successfully demonstrated in the past,^[17,18] however, to form the wax crystals, additional thermal evaporation of wax had to be applied to create hierarchical structures.

Therefore, in this work a two-step molding process was used to replicate the leaf structures via a fast curing and molding process to prevent shrinkage of the cells and realize the multiscale roughness with hierarchical structures without any additional self-assembly processes. In previous reports, mostly a polydimethylsiloxane (PDMS) has been used for replicating the leaf surface.

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Figure 1. Schematic illustration showing the fabrication process of PVSZ artificial leaf structures.

However, as a fresh leaf surface typically contains water, the long curing times and elevated temperatures required for curing PDMS caused shrinkage of cells due to loss of water during the molding process.^[16,19] Therefore, in this work, PDMS has been replaced by the photocurable perfluoropolyether (PFPE) polymer. The PFPE, which is elastomeric, UV sensitive, and resistant to organic solvents is used for the negative mold.^[20–22] The positive structure was fabricated using a ceramic precursor, polyvinylsilazane (PVSZ), with a high mechanical strength and organic solvent resistance as well.^[23] The resistance of the fabricated surfaces toward various contaminants, organic solvents, and corrosive aqueous solutions of various pH values would allow for the development of novel applications in the field of self-cleaning materials.

Figure 1 illustrates the procedure used to fabricate the artificial leaf with hierarchical structures. Fresh Genus *Lonicera* leaves were selected as a biological hydrophobic model surface. To remove adhering particles, the leaves were rinsed with water. Functionalized PFPE was synthesized as previously described^[21,22,24] and used for the negative leaf imprints. 1 wt% of photoinitiator (Darocur 1173, Ciba, Japan) was added to the polymer and homogeneously mixed. To create the PFPE negative structures from the leaf, the polymer with photoinitiator was dropped onto a fresh leaf and immediately a glass slide was pressed on the polymer with extremely low pressure (0.68 g cm^{-2}) and irradiated with UV light (Panacol UV-F 400 F, 450 W, $\lambda = 325\text{--}380 \text{ nm}$) for 5 min at a distance of 10 cm to cure the PFPE. During the treatment with UV light, the maximum sample temperature was approximately 34°C , which does not constitute a significant local heating, thus preventing loss of water. After UV irradiation, the native leaf was carefully peeled off from the substrate leaving behind the cured PFPE negative structures. Subsequently, PVSZ (HTT 1800; KiON Corp., USA) was used to produce the positive leaf structures. 1 wt% of photoinitiator (Irgacure 500, Ciba specialty, Japan) and 0.5 wt% of thermal initiator (Dicumylperoxide, Aldrich) were added to the polymer and homogeneously mixed by stirring for 10 min to enhance the UV and thermal curing kinetics.^[23] To fabricate the positive leaf surface, the negative PFPE structure was applied for molding onto the PVSZ. Prior

to that, the negative PFPE was treated with 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane ($\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SiCl}_3$) under vacuum for 1 h at room temperature to generate a releasing layer to prevent adhesion between the PFPE stamp and the PVSZ. Then, the PVSZ was dropped onto a silicon wafer and the PFPE negative stamp was smoothly placed on it without pressure. UV irradiation was applied for 15 min to solidify the PVSZ structures. Peeling the PFPE stamp from the developed solid, PVSZ revealed the positive structures, which were then postcured at 150°C for 3 h. The synthesis and photo-curing mechanism of the polymers are given in Scheme 1 (see Supporting Information).^[21–23]

Figure 2 shows FE-SEM images of the native Genus *Lonicera* leaf surface and PVSZ-derived artificial leaf. The native leaf surface exhibits hierarchical structures consisting of microstructures and randomly oriented nano-hair-like structures as shown in Figure 2 a–c. Both surface features are built from convex epidermal cells and three-dimensional epicuticular waxes.^[25] Figure 2d–f displays the artificial structures replicated by the above-described a two-step molding process. On a large level, micron-sized surface undulations can be seen. On a smaller level, randomly distributed sub-micron wax hairs with variable sizes are detected on the surface. Short hairs were replicated nicely whereas longer hairs of about $150 \mu\text{m}$ in

Figure 2. Hierarchical structures on the surface: (a–c) FE-SEM images of the native leaf surface; (d–f) PVSZ-derived artificial leaf surface obtained from a two-step molding process. Insets in (a) and (d) represent magnified views of the long hairs and arrows indicate native (a) and artificial structures (d) at their highest ends.

length appear truncated at a certain length most likely caused by the removal of the PVSZ replica from the PFPE negative stamp (Figure 2d).^[26] However, the submicron hair structures having diameters of around 200 nm and varying length between 500 and 1000 nm were successfully replicated into the cured PVSZ structures, as shown in Figure 2 f. Therefore, the method presented here demonstrates that the hierarchical structures can be replicated in great detail using a fast and reliable replication process without any additional self-assembly step.

In the following, we compare the surfaces of a flat PVSZ film, the PVSZ-derived artificial leaf and a PVSZ film modified with the perfluorosilane used in the second molding step. Figure S1 (see Supporting Information) shows the detailed chemical composition of the surfaces investigated by X-ray photoelectron spectroscopy (XPS). As seen in Figure S1b, the PVSZ-derived artificial leaf surface obtained from a molding process using a perfluorosilane-modified PFPE stamp exhibits O1s, C1s, Si2p signals, and an additional F1s-peak compared with that of the flat cured PVSZ film (Figure S1a, Supporting Information). In the XPS spectra of the PVSZ artificial leaf (Figure S1b, Supporting Information) and the perfluorosilane-modified PVSZ surface (Figure S1c, Supporting Information), the peaks generated from the samples exactly correspond to each other. As the surface of PFPE has no binding site for covalent bonding such as an $-NH-$ or silanol-group, which can react with a fluorosilane,^[27,28] one can draw the conclusion that the fluorosilane layer on the surface of the negative PFPE structures partially reacted with the PVSZ and therefore was transferred to the positive PVSZ surface during the molding process.

In order to investigate the effect of the hierarchical structures on the surface wettability, we measured static water contact angles with a contact angle goniometer. A water droplet of 1 μ L in volume was gently deposited on the surface with a microsyringe and the contact angle was monitored with a camera. All measurements were repeated five times to deduce a mean value and a standard deviation. From Figure 3, one can observe that the PVSZ artificial leaf surface is highly hydrophobic with a water contact angle of $\approx 112.5^\circ$. The value is significantly higher than that of the flat perfluorosilane-modified PVSZ film ($\approx 99.8^\circ$), which is slightly higher than the $\approx 94.0^\circ$ of the cured flat PVSZ film without surface treatment,^[23] which demonstrates that the wettability of the replica predominantly arises from the surface structure and not from the chemical nature of the surface. In addition, the contact angle of the replica is very close to that of the native leave surface, which amounts to $\approx 115.0^\circ$. According to these results, it is clear that the replication method presented here not only replicates the hierarchical structures of a natural leaf in great detail but also generates an

Figure 3. Static contact angles of water drops on the surfaces of the fresh native leaf, the PVSZ-derived artificial leaf, and the perfluorosilane-modified PVSZ film.

artificial surface with hydrophobicity similar to the original leaf surface.

To summarize, we have demonstrated the successful replication of the hierarchical structures of a natural leaf surface by a simple and fast two-step molding process. First, PFPE negative structures were generated through a fast UV curing to avoid shrinkage of the cells from loss of water. Subsequently, hierarchical artificial leaf surface structures were produced with high fidelity by UV- and thermal-curing of a PVSZ mold. The replicated surfaces showed a static water contact angle similar to the native leaves and higher than that of a fluorinated planar thin film of PVSZ. As the presented fabrication method is straightforward, it should be possible to extend it to other leaves surfaces.

Supporting Information

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

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