Soft Lithography Replication of Bioinspired *G. dalenii* Surface for Condensation, Fog Harvesting and Microfluidic Applications

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In this work we study the condensation and fog harvesting performance on a natural/fixated *G. dalenii* leaf and on its replicated sample. Microstructure surface replication by our soft lithography procedure was found to be remarkable. In addition, both the mechanisms of nucleation and the dynamics of droplet growth showed an excellent agreement (within the standard deviation) when comparing fixated and replicated *G. dalenii*. On other hand, up to 200% greater fog harvesting performance was reported on replicated *G. dalenii* sample when compared to the flat control one. The greater fog harvesting performance on the replicated sample was attributed solely to the inclusion of microstructures opposite to the flat sample. A droplet energy of adhesion analysis supports the better fog harvesting performance of replicated *G. dalenii*. We conclude on the excellent surface structure, condensation mechanism and fog harvesting performance replication by soft lithography.

1. **Introduction**

Bioinspired surfaces have received increasing attention in the past decades due to their unique surface arrangement and functionalities [1, 2]. Their unique structure and wettability confer such surfaces with excellent liquid-repellent, anti-icing, and heat transfer properties. In the case of a lotus leaf, its extraordinary water repellent and self-cleaning performance is owed to the unique micro- and nano-structure arrangement of their epidermis cells [1]. On other hand, the distinctive combination of hydrophilic and hydrophobic wax regions is found to be a key parameter on the great fog harvesting performance of the Namib desert beetle [2]. Besides the unique liquid-solid interactions reported on the abovementioned natural surfaces, the occurrence of dropwise condensation and droplet-jumping on a great variety of bioinspired surfaces has been recently demonstrated [3, 4]. In addition to their excellent condensation and fog harvesting performance, the exclusive functionalities could also be readily applied in micro- and nano-fluidics, hence the interest on the surface replication of such surfaces. In this work we study the mechanisms of condensation and fog harvesting on a natural and on a replicated by soft lithography *G. dalenii* samples. In addition, comparison with a flat smooth control epoxy sample is also provided.

2. **Materials and Methods and Surface Replication**

The leaves of a *G. dalenii* ornamental plant were fixated in order to preserve their original properties following the procedure reported in Ref. 5. Thereafter, replication of the fixated sample was carried out by using PVS as the negative replica and epoxy resin as the positive replicas as in Ref. 6. In addition, a smooth flat epoxy resin sample was prepared as the control sample. To evaluate the surface structure replication, fixated and replicated *G. dalenii* samples were subjected to 3D Optical Laser Scanning Microscopy (3D-OLSM) and to Scanning Electron Microscopy (SEM), presented in Figure 1.

![Figure 1. 3D-OLSM on (a) fixated and (b) replicated *G. dalenii* and SEM on (c) fixated and (d) replicated *G. dalenii*.](image)

From Figure 1, the replication of the microstructure diameter, height and spacing is remarkable and within the standard deviation. Nonetheless, due to the soft nature of our fixated sample, the replication of the nanostructures was less efficient (Fig. 1c & d) [7].

3. **Results and Discussion**

Experimental observations of condensation at the microscale were carried out in an Environmental Scanning Electron Microscope (ESEM) FEI FIB-ESEM Versa 3D. Characteristic ESEM snapshots on the dynamics of condensation on the fixated and replicated *G. dalenii* samples are presented in Figure 2.

![Figure 2. Characteristic ESEM snapshots on (a) fixated and (b) replicated *G. dalenii*. Log-log representation of droplet growth in time on both fixated and replicated *G. dalenii* at (c) the base of the leaf and at (d) the side of the ogive-like microstructures.](image)
Due to the excellent spatial resolution of our ESEM, we could distinguish between droplets growing at the base of the leaf or at the side of the ogive-like microstructures. From Figure 2, the expected exponential droplet growth is confirmed: \( D = A \cdot \mu^t \), where \( D \) is the droplet diameter, \( A \) is a constant, \( t \) is the time and \( \mu \) is the power law exponent ranging between 0 and 1 [8, 9]. At the base of the fixated and the replicated \( G.\) dalenii leaves, \( \mu \) was found to be 0.6 ± 0.2 and 0.9 ± 0.1, respectively. Slightly greater droplet growth rate is reported on the replicated sample due to the more wetting nature of the epoxy resin used for the replication when compared to the more hydrophobic nature of the cuticle on fixed one. The more wetting nature of the replicated surface offers greater surface area for droplet heat transfer [10]. We note here that reported \( \mu \) exponents demonstrate that droplet growth is limited by heat transfer at the droplet interface [9]. Droplet nucleation density was found to be 6 ± 2 x 10⁷ and 5 ± 1 x 10⁸ droplets/m² on fixated and replicated \( G.\) dalenii, respectively, which are well within the standard deviation. Hence, both the mechanisms of nucleation and the dynamics of condensation are well replicated when comparing the two samples.

Next, we evaluate the fog harvesting performance by means of exposing both the fixated and replicated \( G.\) dalenii samples, as well as the control sample, to the fine mist (droplet size: 1 – 5 \( \mu \)m [6]) of an ultrasonic humidifier Bionaire BU1300W-I. The amount of water collected was weighted every 20 minutes as shown in Figure 3:

![Figure 3. Amount of water collected in mL/m² versus time in minutes on (squares) fixated \( G.\) dalenii, (circles) replicated \( G.\) dalenii and (triangles) control sample [6]. Standard deviation of 5 independent measurements is included along.](image)

The superior performance of the fixated \( G.\) dalenii is attributed to the greater hydrophobicity of the cuticle when comparing to the replicated one. Nonetheless, a 200% greater fog harvesting performance is reported on the replicated \( G.\) dalenii when compared to the flat smooth epoxy control sample. Since both replicated \( G.\) dalenii and control samples are fabricated from the same resin epoxy, the enhancement in the water collection performance in the case of replicated \( G.\) dalenii is solely induced by the inclusion of the micro- and nano-structures when compared to the flat smooth sample.

A droplet energy of adhesion analysis is then proposed to demonstrate the greater adhesion of droplets on the control sample when compared to the replicated \( G.\) dalenii one. The energy of adhesion, \( E_{adh} \), can be estimated as [11, 12]:

\[
E_{adh} = \gamma_{sl} \sin \theta_s \cos \theta_R R^2
\]

where \( \gamma_{sl} \) is the solid-liquid surface tension and \( \theta_s \) is the droplet base radius equals: \( \sin \theta_s R \) with \( \theta_s \) and \( R \) as the advancing contact angle function of the surface studied and the droplet radius, respectively. Then, for a similar droplet radius and for their respective advancing contact angles, the ratio energy of adhesion on the replicated \( G.\) dalenii versus the control sample, \( E_{adh,r} / E_{adh,c} \), can be estimated as Equation 2 [6]:

\[
E_{adh,r} / E_{adh,c} = \frac{\gamma_{sl} \sin^2 \theta_s R^2}{\gamma_{sl} \sin^2 \theta_R R^2} \phi
\]

where \( \phi \) is the increase in solid-liquid surface area due to the presence of microstructures. By substituting all known values in Equation 2 and for \( R = R_c \), the ratio \( E_{adh,r} / E_{adh,c} \) is estimated as 0.7. The lower \( E_{adh,c} \) when compared to \( E_{adh,r} \) evidences the easiness for the droplets to shed from the replicated \( G.\) dalenii sample demonstrating its greater fog harvesting performance.

4. Conclusions

The excellent microstructure surface replication of a natural fixated \( G.\) dalenii leaf by means of soft lithography is reported. In addition, the remarkable replication of the nucleation and dynamics of droplet growth mechanisms during condensation phase change when comparing fixated and replicated \( G.\) dalenii samples is also demonstrated. Moreover, a 200% greater water collection performance during fog harvesting experiments is reported on our replicated \( G.\) dalenii surface when compared to the smooth flat sample. The greater performance of the replicated sample is solely due to the inclusion of the micro- and nanostructures. An energy of adhesion surface analysis is then proposed to demonstrate the lower adhesion of the droplets to the replicated \( G.\) dalenii sample.

References