Fabrication of Hydrophobic Film Using Plant Leaves from Nature

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ABSTRACT

In this study, we have investigated the feasibility of reproducing the hydrophobic characteristics of plant leaves from nature by replicating the micro/nano features of a leaf surface in UV embossed film. Films were fabricated by means of UV nanoimprint lithography (UV-NIL) technology. By varying UV-NIL processing conditions, we were able to produce hydrophobic films which replicated the micro/nano structure of leaves. The surface topology of those replicated films was observed by scanning electron microscope (SEM) and atomic force microscope (AFM). Also for the purpose of evaluating the hydrophobicity of the replicated film surface, contact angle (CA) was measured. We propose a new measure of replication quality to evaluate how well the film can reproduce the hydrophobic characteristics of natural plant leaves. In terms of these measurements of CA and replication measure (r), we were able to confirm that UV-NIL could be a possible tool to produce a hydrophobic film by replicating surface of plant leaves.

Keywords: UV-nanoimprint lithography, Plant leaf, Hydrophobicity, Contact angle, Replication measure

1 INTRODUCTION

For the past decade, the secret of biological surfaces has been elucidated with the help of scanning electron microscope (SEM). So recently, botanists have investigated hydrophobicity of plant leaves with high CA [1,2]. And hydrophobic films with high contact angle (CA > 150^0) have attracted many researchers' attention for various practical applications [3]. Some researchers developed hydrophobic films by utilizing chemical treatment. And various methods have been reported in the literature to construct hydrophobic surface which have micro and nano structures similar to those in the plant leaves. Conventionally, hydrophobic surfaces are fabricated with the help of chemical treatment by changing surface energy of materials or by modifying the surface roughness, for instance, etching of polypropylene (PP) [4], plasma-enhanced chemical vapor deposition [5], and carbon nano tube aligning [6] etc. Some of these methods produce hydrophobic surfaces by controlling the surface topography through complex chemical processes. These methods mentioned above are generally time-consuming or costly. In contrast to these methods, this article suggests a new and simple method to produce a hydrophobic rough surface based on hydrophobic plant leaves by means of UV-NIL.

2 EXPERIMENTAL

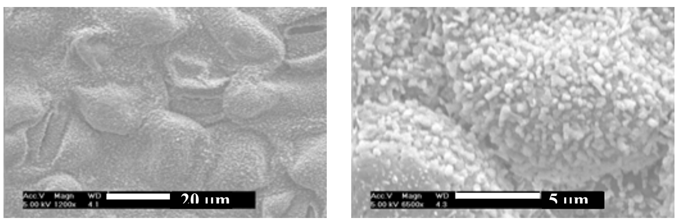
The hydrophobicity of a material is commonly measured by the CA that a water droplet makes with the surface. Before performing imprint experiments, we measured the water contact angles of many plant leaves and selected just four plant leaves for further investigation due to their excellent water repellency in this study: *Bamboo, silver maple tree, love grass, tulip tree*. CA values were measured both on upper-surface and on under-surface in the natural state. The CA measurement equipment used in this study was a Krüss Drop shape Analysis system (Krüss GmbH Germany, model: DSA 10-Mk2). Unfortunately, this contact angle meter was suitable only for measuring equilibrium contact angles, not advancing or receding contact angles. CA values were measured at ten distinct positions using water 5 µl in volume and averaged for each case. Through this measurement, we were able to find that CA of under-surfaces is higher than that of upper-surfaces in general (table 1). Based on this result, we selected the under-surface of leaves rather than the upper-surface in our subsequent imprint experiments.

2.2 SEM Images of Plant Leaves

Figures 1 – 4 show SEM images of green plant leaves at various magnifications. Green plant leaves have a double-structured surface which is the combination of micro- and nanostructures (epicuticular wax crystals [2]). These four kinds of plant leaves had their own surface structure based on combination of micro/nano sized structures: *tulip tree,* 5 µm ~ 15 µm sized hemisphere structure which has nano scale particles on its surface; *silver maple*, 10 µm ~ 20 µm sized small dots and about 100 µm sized veins of leaf which have many nano scale wrinkles; *bamboo,* long veins of leaf and about 5 µm sized protruding pattern on which rose quartz like nanostructure exists; *lovegrass*, caterpillar looking long veins of leaf which has 5 µm ~ 10 µm sized protrusions over which banana looking nano structures are sparsely spread.

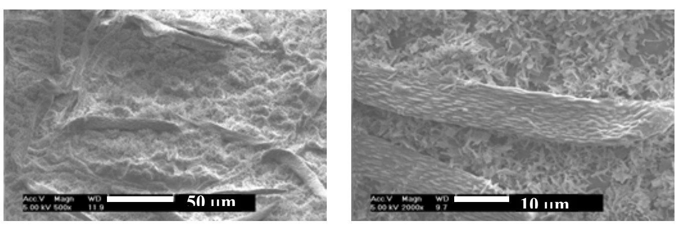
2.3 Replication of Plant Surfaces via UV-NIL Technology

The primary aim of this study is firstly to fabricate a rough surface patterned after hydrophobic plant leaves' under-surface via the UV-NIL technique and secondly to check the hydrophobicity of the replicated surface. So, for this study, our group designed and constructed the UV-NIL equipment as schematically shown in figure 5. This UV-NIL process was carried out in the following sub-processes: setting up the processing sequence via a controller, attaching a plant leaf on a jig, fixing the jig on the vacuum chuck, dispensing the UV curable photopolymer on the slide glass, removing air from a vacuum chamber, applying pressure to the pneumatic cylinder, exposing the photopolymer to UV light and finally detaching the replicated film from the jig. In this UV-NIL experiment, we used *RenShape SL 5180* UV curable photopolymer (Vantico Inc., density: 1.15 × 10^3 kgm^{-3}, viscosity: 240 cps, critical Exposure: 13.3 $mJcm^{-2}$). One should be able to determine the appropriate processing conditions for a successful replication of leaf surface via UV-NIL technology. The present study with the equipment we developed found the most appropriate processing conditions as follows: the UV light exposure time of 600 seconds and the applied pressure of 150 kPa. It may be mentioned that all processes were performed at room temperature. All thin films mentioned in this article were deposited on flat slide glass. After we completed the fabrication process, we kept the replicated films in vacuum desiccator to prevent the film from being exposed to air and dust.



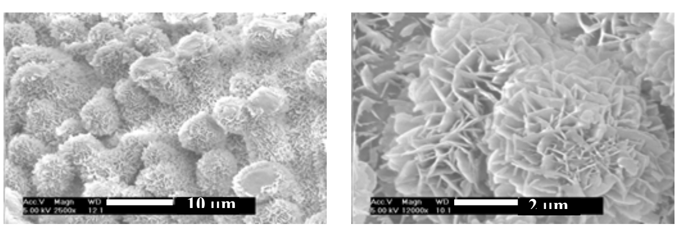
(a) (b)

Figure 1. SEM images of the *tulip tree* leaf under-surface at various magnifications: (a) 1200×, (b) 6500×.



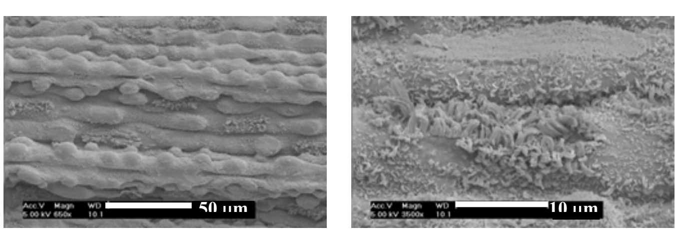
(a) (b)

Figure 2. SEM images of the *silver maple tree* leaf under-surface at various magnifications: (a) 500×, (b) 2000×.



(a) (b)

Figure 3. SEM images of the *bamboo* leaf under-surface at various magnifications: (a) 2500×, (b) 12000×.



(a) (b)

Figure 4. SEM images of the *lovegrass* leaf under-surface at various magnifications: (a) 650×, (b) 3500×.

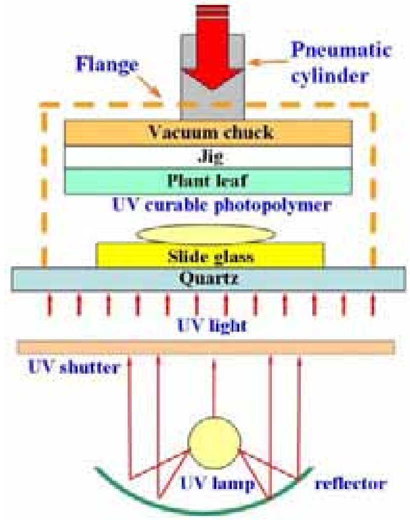
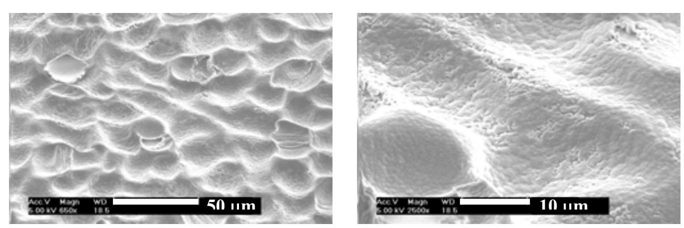


Figure 5. Schematic of UV-NIL equipment.

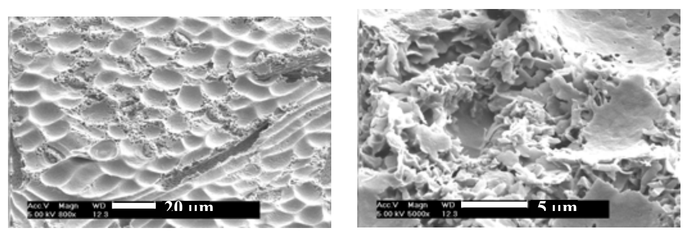
2.4 SEM Images of Replicated Films

Figures 6 - 9 show SEM images of replicated films. Needless to say, since plant leaves had protruding patterns, replicated films naturally had porous and rough surface structures. However, while the microstructure was generally well replicated, those nanostructures were not so well reproduced on the cured polymer film surface. This seemed to have happened because the nanostructure of plant leaf was not rigid enough to endure the pressure applied during the UV-NIL process and thereby might have collapsed or broken, resulting in poorer replication of nanostructures. Another possible reason might be that UV cured photopolymer once infiltrated inside nanoscale holes or indented surface in a liquid state remains in the leaf surface when it is cured and the film is detached from the plant leaf.



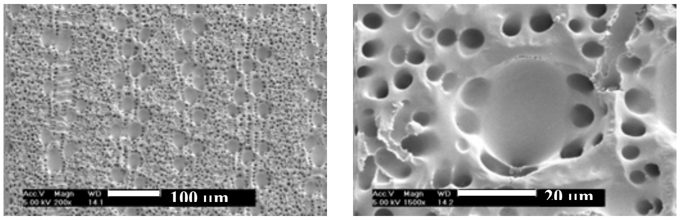
(a) (b)

Figure 6. SEM images of the replicated film surface (*tulip tree*) at various magnifications: (a) 650×, (b) 2500×.



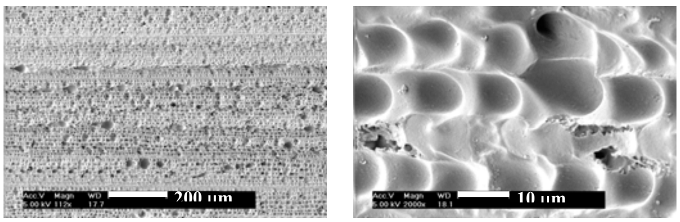
(a) (b)

Figure 7. SEM images of the replicated film surface (*silver maple tree*) at various magnifications: (a) 800×, (b) 5000×.



(a) (b)

Figure 8. SEM images of the replicated film surface (*bamboo*) at various magnifications: (a) 200×, (b) 1500×.



(a) (b)

Figure 9. SEM images of the replicated film surface (*lovegrass*) at various magnifications: (a) 112×, (b) 2000×.

3 ANALYSIS OF REPLICATED FILMS

3.1 Measure of Replication Quality

It might be of interest to find how well the nano/micro combined structure is reproduced in the replicated films. For the purpose of quantifying the replication quality of replicated films, we proposed a new replication measure, r, defined by the surface area ratio, i.e.

$$r = \frac{\text{surface roughness of a replicated film}}{\text{surface roughness of a plant leaf}} = \frac{\text{scanning surface area of a replicated film / projected scanning surface area}}{\text{scanning surface area of a plant leaf / projected scanning surface area}}$$

As schematically depicted in figure 10, a replication measure r represents a kind of degree of replication. We propose to measure the surface area of both the plant leaves and their replicated films with the help of a function of AFM. Scanned AFM images in an observed area topographically represent plant surface, indicating its dimensional feature qualitatively similar to SEM. But the quality of the AFM image may become poorer than SEM due to the limitation of AFM in dealing with very steep surface and the frequent failure of the AFM probe tip during the scanning. However, SEM image does not provide a quantitative measure of three dimensional topography of the surface of interest. In this regard, we propose to use an AFM function to measure the surface area. It may be mentioned that r is larger than zero and smaller than unity. If r approaches to unity (when area of the mold surface is equal to that of the replicated polymer, i.e. $r \approx 1$), it means complete replication quality. And as r decreases, replication quality gets poorer. In the measurement of surface area, we scanned an area of 100 μm × 100 μm in non-contact mode of AFM. We obtained surface areas at 10 different sampling locations for each sample and calculated average and standard deviation of the measured areas. Figure 11 shows typical AFM images of *bamboo* leaf and its replicated film surface. Table 2 summarizes measurement results in terms of the average surface area with standard deviation and replication measure r. Due to the failure of probe tips, unfortunately, we could not obtain AFM images of *silver maple tree* leaf of which the data is thus not included in table 2. r values higher than *0.96* for all cases seem to indicate a satisfactory replication via UV-NIL. Undoubtedly, value of r cannot be regarded as an absolute estimation of replication quality. However, considering the difficulty of quantifying complicated topography of the natural plant leaf surface and their replicated films, the replication measure seems to be a relatively meaningful method to evaluate the replication quality to some extent. From this measurement, we were able to confirm the feasibility of producing replicated films by imprinting plant leaves whose surface is composed of micro and nano combined structures.

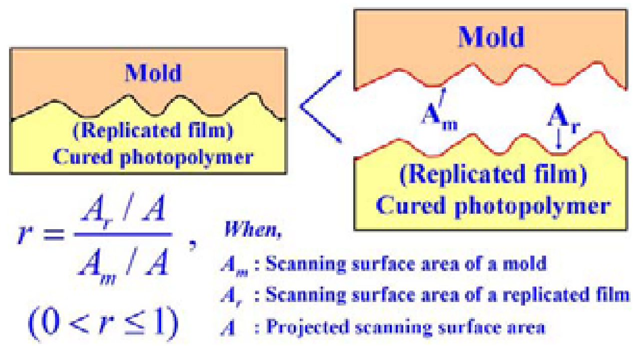
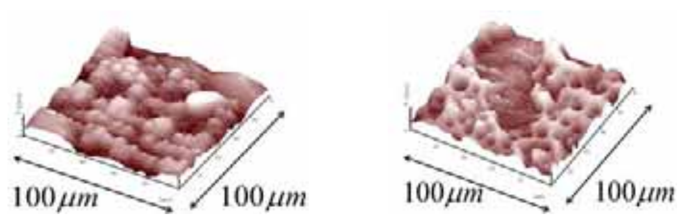


Figure 10. Basic idea of replication quality test.



(a) (b)

Figure 11. AFM images of two samples: (a) under-surface of *bamboo* leaf, (b) its replicated film surface.

3.2 Hydrophobic Characteristics

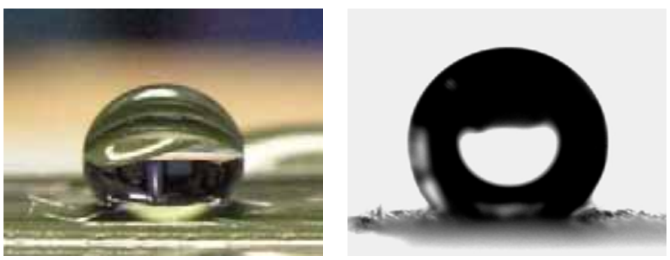
CA could be a measure of hydrophobicity of a replicated film surface. For a reference value to be compared with replicated films, we measured a CA of a flat and smooth surface of UV cured photopolymer materials as follows. For this purpose we fabricated a cured flat polymer surface over a self assembled monolayer (SAM) laid silicon wafer by means of UV-NIL equipment. A SAM was laid on the silicon wafer surface through the vapor evaporation method with 1H,1H,2H,2H-Perfluorodecyltrichlorosilane, $C_{10}H_4C_{13}F_{17}Si$ to help release of the cured photopolymer from the silicon wafer.

	Tulip tree	Silver maple tree	Lovegrass	Bamboo
CA of upper-surface of leaves	123.41 ± 4.50^0	115.07 ± 3.26^0	116.80 ± 3.66^0	102.49 ± 3.39^0
CA of under-surface of leaves	134.74 ± 1.71^0	136.42 ± 2.39^0	142.26 ± 5.77^0	136.25 ± 2.97^0
CA of replicated films	117.28 ± 3.98^0	121.95 ± 3.98^0	131.38 ± 3.79^0	126.71 ± 3.43^0

Table 1. Comparison of CA between green leaves and the replicated films, when a water drop is about 3 mm in diameter and 5 µl in volume

	Tulip tree	Lovegrass	Bamboo
Average surface roughness of a plant leaf	1.11199	1.21503	1.44064
Standard Deviation	0.04569	0.05743	0.10414
Average surface roughness of a replicated film	1.07953	1.17339	1.39929
Standard Deviation	0.01658	0.05728	0.08904
Replication measure	0.97081	0.96551	0.97126

Table 2. Replication measure r of each replicated film when projected scanning area is 10^{10}nm^2.



(a) (b)

Figure 12. Photos of a water drop: (a) on under-surface of lovegrass leaf, (b) on its replicated film surface.

With the help of SAM, the surface of the UV cured photopolymer maintained the smoothness of the silicon wafer surface. CA value of a flat and smooth surface of the UV cured photopolymer was found to be $\theta_Y = 80.46 \pm 0.92^o$.

We have measured CA values for all the replicated films. As a typical illustration, figure 12 shows photos of a water drop on under-surface of lovegrass and on its replicated film. Table 1 summarizes the measured CA values for comparison between leaves and replicated films. And CA value is represented by $\theta = X \pm Y$, with X and Y indicating the average value and standard deviation, respectively. Due to the large water drop size (about 3mm in diameter and 5µl in volume) provided by the contact angle meter used in this study, CA values of plant leaves range between 135^o and 142^o (less than 150^o which is the data reported in literature [1]). CA differences between leaves and replicated films were relatively small (about 13^o in average). In table 1, *lovegrass* leaf and its replicated film had the highest CA. On the other hand, *tulip tree* leaf and its replicated film had the lowest one.

4 CONCLUDING REMARKS

In this study, we investigated the feasibility of making hydrophobic rough films by replicating plant leaves from nature via UV-NIL technology without resorting to any chemical treatments. Appropriate processing condition of UV-NIL enables us to successfully replicate hydrophobic films from four typical plant leaves. Furthermore, to quantify the quality of replicated films we proposed a new replication measure, r. r values obtained in this study were found to be around 0.97, clearly indicating good replication. The measured CA also shows the hydrophobicity of the replicated films. Good quality of replicated films in this study seems to confirm that UV-NIL is a new and simple fabrication method to produce hydrophobic films by simply mimicking nature.

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