# Micro-Morphologies of Two Typical Leaf Surfaces and the Effects on their Hydrophobicity and Anti-Adhesion

Hui-Na Cao[1], Zhi-Wu Han[1,*], Hui-Ying Guan[2], Zhi-Hui Qian[1] and Jun-Feng Ye[1]

[1]Key Laboratory of Bionics Engineering of Ministry of Education, Jilin University, Changchun 130022, China

[2]Jilin Institute Of Chemical Technology, Jilin 132022, China

**Abstract:** The surface micro-morphologies of two kinds of leaves—folium perillae and corn husk—which have excellent anti-adhesion characteristics at high temperature and wet circumstance, were investigated by scanning electron microscopy (SEM). The hydrophobicity and anti-adhesion characteristics were quantitatively measured meanwhile. Results showed that they all had non-smooth surface morphologies mounted with cilia and demonstrated favorable anti-adhesion features. Folium perillae which showed hydrophilicity, had the surface compactly pieced together by jigsaw-like plates, with stomas embedded. On the other hand, corn husk showing hydrophilicity, had the surface appeared longitudinal undulated ripples with sags and crests, and had grains on secondary microscale.

**Keywords:** Micro-morphology, non-smooth, hydrophobicity, anti-adhesion, stoma, cilia.

## 1. INTRODUCTION

Numerous professional or practical applications, such as minimally invasive surgery instruments, micro/nano electromechanical systems, and building materials, require surfaces with low adhesion and stiction [1, 2]. As the size of these devices decreases and operation condition becoming extremer, the development of non-adhesive and hydrophobic surfaces tends to crucial for many of these emerging applications. The problem of anti-adhesion, water repellency and self-cleaning has been solved by some kinds of plant leaves in nature [3], such as folium perillae and corn husk. These two kinds of leaves always put under buns when steamed and could be revealed fluently without stick when cooked, showing excellent anti-adhesion characteristics at high temperature and wet environment. Bathlott had carried out a series of researches concentrating on the morphology and hydrophobicity of plant surfaces [4]. Shu-jie Wang discussed some concrete indexes of plant surfaces, such as compound morphology and anti-adhesion [5].

In this paper the compound surface morphologies of these two kinds of leaves were observed by scanning electron microscopy (SEM) according to their micro-morphological characteristics. The hydrophobicity and anti-adhesion were further determined respectively by contact angle equipment and electronic universal testing machine [6, 7]. The influence mechanism of surface morphology on hydrophobicity and anti-adhesion was presented subsequently. Such original information may provide an insight into surface machine molding and apparent morphology design for biomimetic engineering.

## 2. MATERIALS AND METHODS

### 2.1. Experimental Materials

The materials of experimental samples were fresh mature folium perillae and corn husk, which were collected in Changchun, Jilin province, P. R. China. The leaves were gently flushed with clean water and dried in the air before experiments.The frontal side of folium perillae and inner side of corn husk were selected in this experiment.

### 2.2. Morphology Observation

Images of the surface morphologies of intact region on all specimens were taken by stereo microscope. The micro- and nano-texture of all specimens' surfaces were observed with Scanning Electron Microscopy (SEM) (EVO18, ZEISS).

### 2.3. Contact Angle Measurement

The equilibrium water contact angles of the prepared surfaces were measured by a contact angle meter (JC2000A, Shanghai Zhongchen Ltd, China). The volume of the applied droplets of distilled water was 3 μL. The mean value was calculated from at least five individual measurements. The states of drops are displayed in Figure **5**.

### 2.4. Surface Adhesion Measurement

An Electronic Universal Testing Machine (EUTM) (INSTRON-5869, Changchun Institute of Applied

*Address correspondence to this author at the Key Laboratory of Bionics Engineering of Ministry of Education, Jilin University, Changchun 130022, China; Tel: 0431−85095760−8405; Fax: 0431−85095760-8402;
E-mail: zhwhan@jlu.edu.cn

E-ISSN: 2311-1755/13 

Chemistry) was used to access the adhesive effects of different surface textures on leaves. The specimens were cut and stuck to double-sided tissue tapes (Maped 752810), of which the other side not torn off. The adhesion regions which were 18×36mm should remain no air bubbles. The extra parts of the tape and leaf were fixed to the bending fixtures of the EUTM. Then the stripping forces were tested with the upper fixture rising 100mm/min and the lower still. The cohesive forces of all experimental leaves were measured 5~10 times respectively. The mean values are listed in Table **1**.

## 3. RESULTS AND DISCUSSION

### 3.1. Micro-Morphologies of Leaf Surfaces

As shown in Figure **1**, under stereo microscope, the frontal surface of folium perillae was characterized by densely and randomly distributed hemispherical papilla. The tapering epicuticular cilia, fulfilled with water, mounted randomly along the leaf veins.

While under the SEM as shown in Figure **2**, the surface was pieced together by jigsaw-like plates with zigzag edge and plump in center. Amazingly, the split joint of the plates was ingenious and compact without gap between two parts, except for a few stomas embedded. The plates' lengths were 50~130μm, and widths 23~50μm approximately. The diameters of the stomas were about 20~25μm. Plates on the leaf veins were strip shaped and longitudinal arranged, separating the piece to several regions.

As shown in Figure **3**, under stereo microscope, the inner surface of corn husk showed regular strips equidistantly arranged in parallel rows. Additionally, there were non-smooth particles densely distributed along the longitudinal direction.

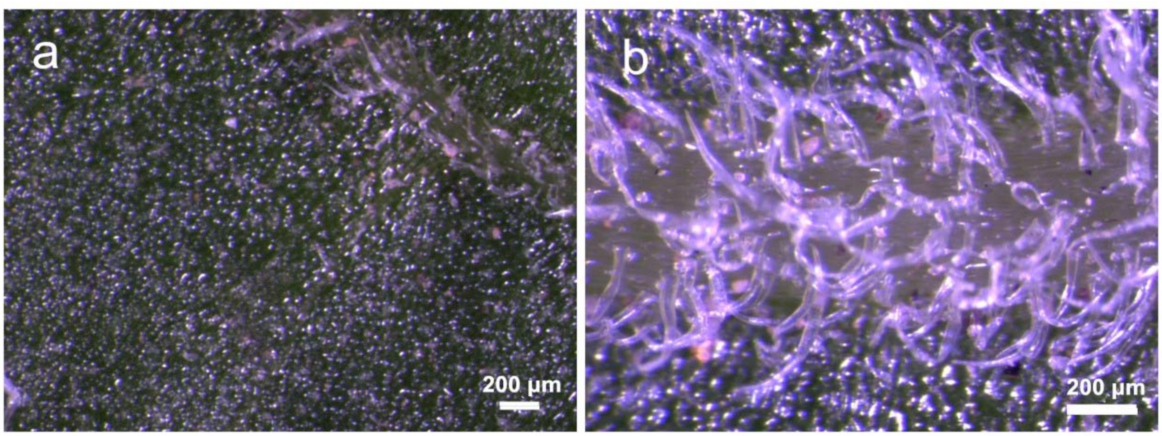


**Figure 1:** Stereo microscope images of frontal surface of folium perillae: (**a**) surface morphology; (**b**) epicuticular cilia distributed on leaf veins.

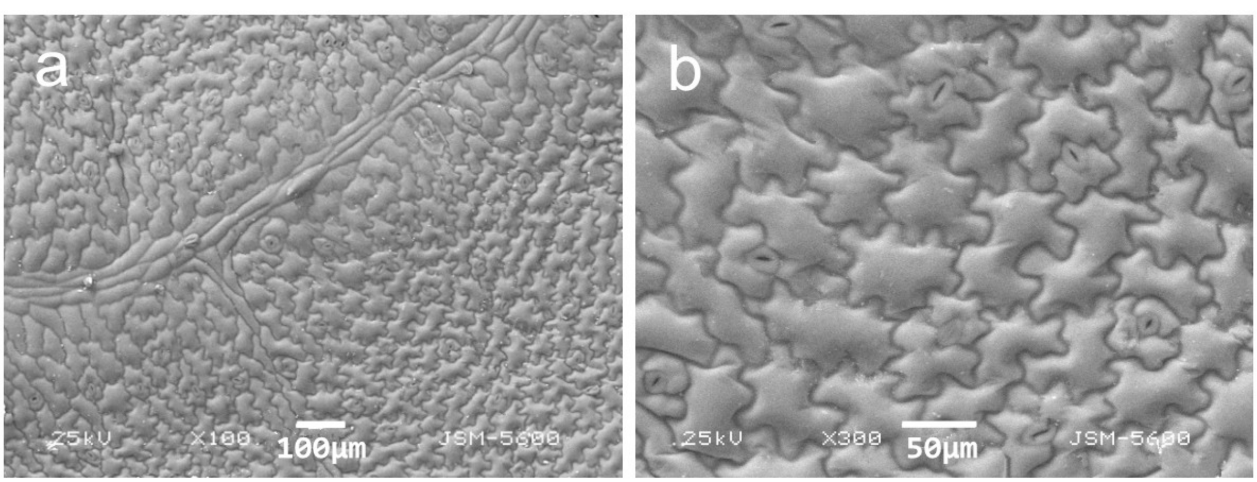


**Figure 2:** SEM images of frontal surface of folium perillae.

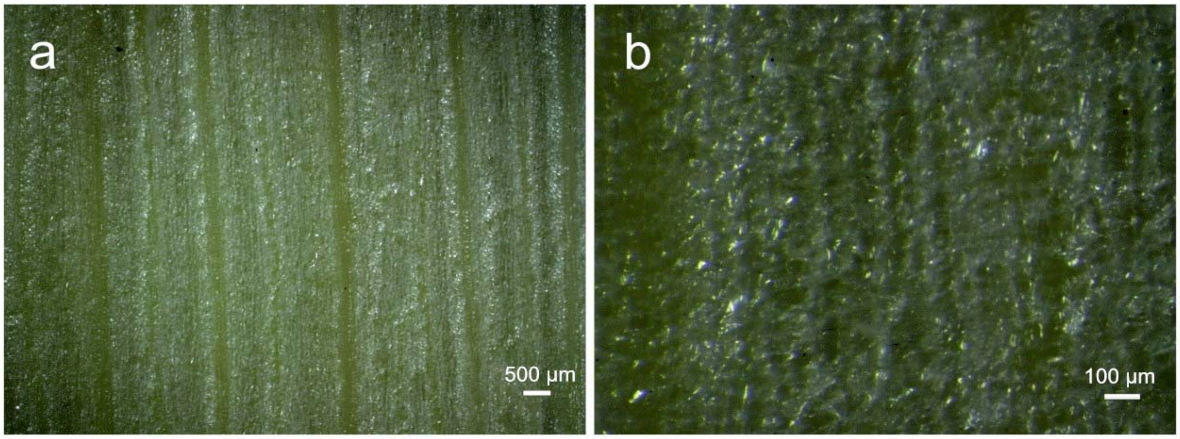


**Figure 3:** Stereo microscope images of inner surface of corn husk.

Under high-resolution electron microscope as Figure **4a**, there were raised ridges and depressed ravines arranged side by side on the surface, where randomly distributed hairs and rare tiny stomas. The ridges could divide into rigid ridges width 200μm and soft ridges arraying between two rigid ridges. In addition, there were rectangular winkles covering on rigid ridges and irregular winkles on soft ridges. Moreover, all the winkles had secondary microscale grains as shown Figure **4b**.

### 3.2. The Hydrophobicity of Leaf Surfaces

The contact angle of folium perillae was only 28.7° on average, showing hydrophilicity to some degree. On the contrary, corn husk had a contact angel of meanly 101.6°, which shows relatively strong hydrophobicity.

Drops can exist in multiple equilibrium states on rough surfaces [8]. It is now known that there are typically two prominent states in which a drop can reside on given rough surfaces (Figure **5**) [9]. The drop either sits on the peaks (Figure **5a**) of the rough surface or it wets the grooves (to be referred to as a wetted contact) (Figure **5b**), depending on how it is formed. The apparent contact angle of the drop that wets the grooves, $\theta_r^w$ is given by Wenzel's formula [10]

$$\cos\theta_r^w = r\cos\theta_e \quad (1)$$

where *r* is the ratio of the actual area of liquid-solid contact to the projected area on the horizontal plane and $\theta_e$ is the equilibrium contact angle (which is typically a value between the advancing and receding contact angles) of the liquid drop on the flat surface. We do not consider the separate cases of advancing and receding angles on a surface. The apparent contact angle of a drop that sits on the roughness peaks, $\theta_r^c$ is given by Cassie's formula [11]

$$\cos\theta_r^c = r_w \varnothing_S \cos\theta_e + \varnothing_S - 1 \quad (2)$$

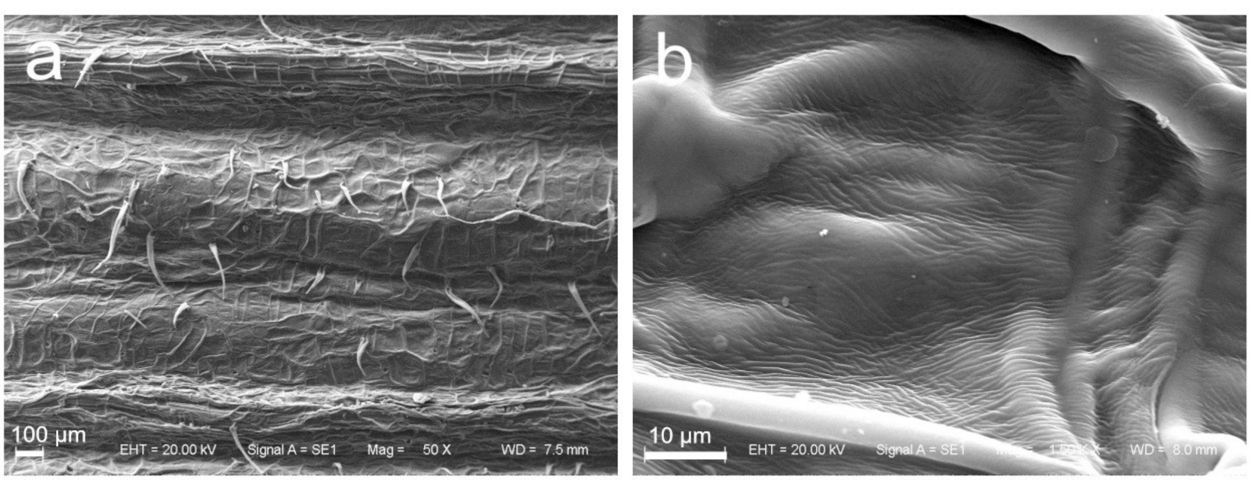


**Figure 4:** SEM images of inner surface of corn husk.

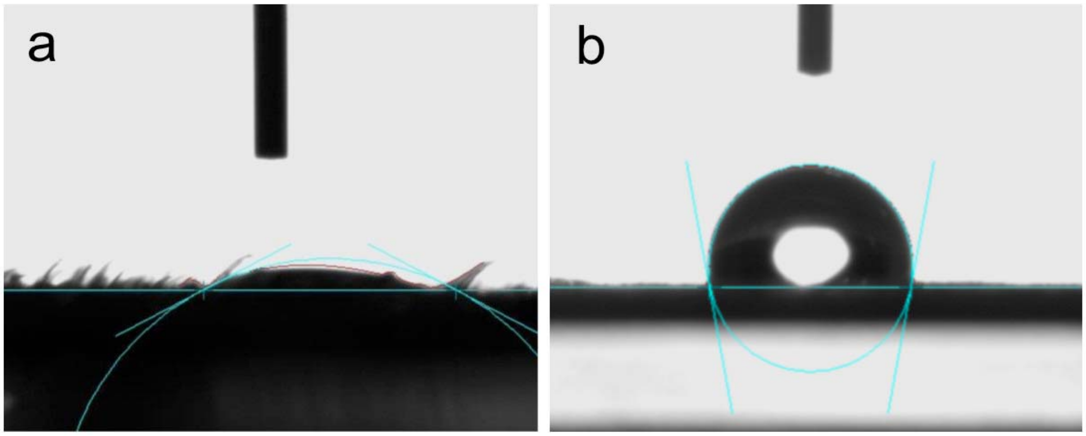


**Figure 5:** Two states of water drops on leaf surfaces: (**a**) a wetted drop on folium perillae; (**b**) a composite drop on corn husk.

where $\varnothing_S$ is the area fraction on the horizontal projected plane of the liquid-solid contact and $r_w$ is the ratio of the actual area to the projected area of liquid-solid contact. This will be referred to as the Cassie or composite drop.

Supposing $\varnothing_S = 1$, we have $r_w = r$, in which case the Cassie formula becomes the Wenzel formula. For non-smooth surface, the value of *r* is greater than 1, that is, the larger the *r*, the rougher the surface. According to Eq. (1), if $\theta_e$ >90°, cos$\theta_e$ <0, then $\theta_r^c$ increases with *r*; whereas, if $\theta_e$ <90°, cos$\theta_e$ >0, then $\theta_r^c$ decreases as *r* increases. Normally, the surface shows strong hydrophobicity if the contact angle lager than 150°. Similarly, the surface with contact angle ranged from 90° to 150° displays a certain degree of hydrophobicity, for example, corn husk. When the contact angle is smaller than 90°, the surface will appear hydrophilic, like folium perillae [12].

The surface tension, polarity, and such other chemical characteristics have influence on the surface wettability and developments of surface chemical bonds. From the comparison as Figure **5**, it obviously proved that the surface morphology, texture and chemical composition of their attachment could affect surface hydrophobicity directly. It is assumed that the contact angle was larger in the case that the surface appeared with multilevel convex-concave winkles and covered by wax, like corn husk. The leaf surface distributed with stomas and relatively smooth on secondary micro scale, like folium perillae, usually performed hydrophilicity.

### 3.3. The Anti-Adhesion of Leaf Surfaces

According to the curves of stripping force showed in Figure **7** and experiment data listed in Table **1**, the cohesive forces of selected leaf surfaces were both

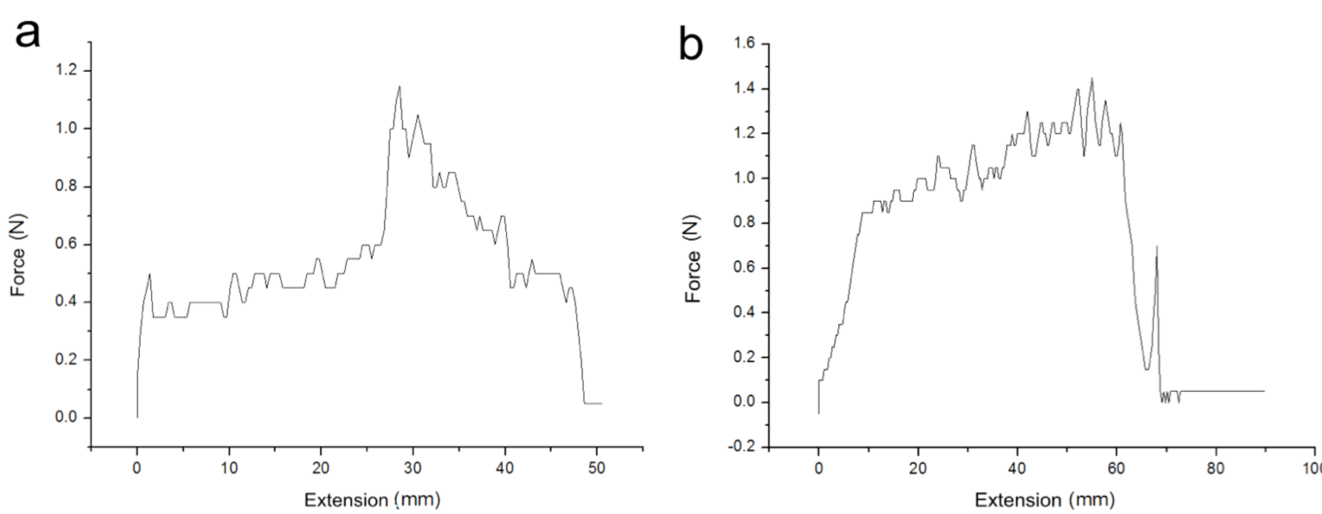


**Figure 6:** Curves of stripping force on leaf surfaces: (**a**) folium perillae; (**b**) corn husk.
The forces increased rapidly at the beginning of the peeling process, then kept relatively stable with small range fluctuating when the peeled extension spread, until two stripes separated and the forces collapsed.

**Table 1: Mean Value of Stripping Forces on Leaf Surfaces**

| | $F_{bL}$ [a] (N) | $\sigma_{\tau bL}$ [b](kN/m) | $F_{bm}$ [c](N) | $\sigma_{\tau bm}$ [d](kN/m) | $\sigma_{\tau m}$ [e](kN/m) |
|---|---|---|---|---|---|
| folium perillae | 0.594 | 0.033 | 1.158 | 0.064 | 0.044 |
| corn husk | 1.017 | 0.056 | 1.617 | 0.090 | 0.073 |

[a]$F_{bL}$—the minimum stripping force, [b]$\sigma_{\tau bL}$—the minimum stripping strength, [c]$F_{bm}$—the max stripping force, [d]$\sigma_{\tau bm}$—the max stripping strength, [e]$\sigma_{\tau m}$—the mean stripping strength.

small. The frontal surface of folium perillae performed minimal mean stripping strength as 0.044 kN/m and better anti-adhesion effect. On the other hand, the stripping strength of corn husk was 0.073kN/m, 1.7 times to that of folium perillae, which demonstrated slightly worse anti-adhesion characteristic relatively. Collectively, the compact plate-joint texture with stomas embedded showed positive influence on anti-adhesion effect.

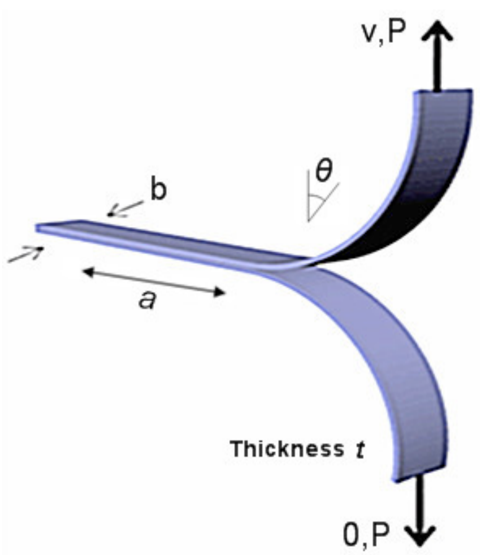


**Figure 7:** Stripping test: the upper film rising at the velocity of *v* and the lower one still, the films' width was *b* and thickness *t*, the extension peeled by force *P* was *a*.

The interface is the contact surface of two kinds of substances that are not compatible or reactive. Generally, the interface includes four types: gas-liquid, gas-solid, liquid-solid, and solid-solid [13]. Adhesion is the force required to separate two surfaces. According to interface thermodynamics, strength of adhesion not only depends on interfacial force, it also depends on condition of the interface and mechanical characteristic of the two substance phases, such as interface tension, surface texture compatibility [14]. Assume that the contact surface as a unit area, then interfacial surface energy, the work *W* required to separate them is defined as [15]

$$W_a = \gamma_A + \gamma_B - \gamma_{AB} \quad (3)$$

where $\gamma_A$ and $\gamma_B$ are surface tension of A and B, and $\gamma_{AB}$ is interface tension.

The stripping test (Figure **7**) is a particularly simple adhesion test for thin adherent films, which gives the force required to peel two thin strips of material [16]. For this configuration

$$U_S = -ab\gamma \quad (4)$$

where $\gamma$ is the interfacial surface energy, $U_S$ is the surface energy.

$$U_P = P(a - a\sin\theta) \quad (5)$$

where *P* is the detaching force applied to the system and *U*p is the potential energy.

The elastic energy $U_E$ of the system is the sum of two terms; the energy $U_B$ stored in the sharp bend in the elastic film and the energy required to stretch the film as it is removed from the still one. Consider an infinite plane of elastic material of Young's modulus *E*.

$$U_E = U_B - \frac{P^2 a}{2btE} \quad (6)$$

The total energy is

$$U_T = U_S + U_P = -ab\gamma + Pa(1-\sin\theta) + U_B + \frac{P^2 a}{2btE} \quad (7)$$

If $U_B$ is constant as peeling proceeds

$$\frac{dU_T}{da} = -b\gamma + P(1-\sin\theta) + + \frac{P^2 a}{2btE} \quad (8)$$

The elastic energy term is usually insignificant when compared with the other components of equation (8) and may be neglected. When

$$\frac{dU_T}{da} = 0 \quad (9)$$

the work done in breaking the joint is exactly compensated by the gain in surface energy of the system. Then

$$P = \frac{b\gamma}{1-\sin\theta} \quad (10)$$

Here the peeling force is largely independent on the surface properties of both the adherent film and the substrate.

As described above, if the adhesion of the interface is desired, the adhesion strength is very considerable. But in fact the adhesion strength is only little portion of the theoretical value, which is result from poor contact conditions among molecules during the contact process. Additionally, the roughness to some extend is beneficial to the surface adhesion, by preventing expand of slit in the interface. However, too much roughness could affect the infiltrate of liquid phase, thus lead to air remaining in the interface. By this token, the epicuticular cilia on leaves increased the surface roughness and stress concentration zone, leading to destroyed interface adhesion. Furthermore, the non-smooth surface textures of these leaves also reduced contact squares and reduced adhesive strength. As for the surface adhesion of folium perillae, the stomas distributed on the surface destroyed the negative pressure of the vacuum caused by the tight contact of leaf and tape. Therefore, the force to reveal the tape was reduced further.

## 4. CONCLUSIONS

The surface morphology of plant leaf is involved with the size of construction units, morphology and distribution of epidermal cells, epicuticular trichomes, and wax, which all have influence on the hydrophobicity and anti-adhesion of leaf surfaces. Folium perillae and corn husk all had non-smooth morphologies and cilia on leaf surfaces, contributing to the anti-adhesion feature. Particularly, corn husk demonstrating hydrophobicity had longitudinal undulated ripples and multilevel winkles. On the other hand, folium perillae's surface which shows hydrophilicity, was pieced together by plates, with a number of stomas embedded, but didn't have a secondary texture.

Although the exact relationship between the surface morphology and its hydrophobicity and anti-adhesion is still not clear, the experimental data suggest that micro-scale geometrical morphology plays an important role on these features. Water-repellent and non-adhesive surfaces are required for many professional or practical applications with the development of society and science. Our discussion contributes to the demands above and helps facilitate biomimetic researches.

## ACKNOWLEDGEMENT

This work was supported by the Natural Science Foundation of China (NO. 51290292).

## REFERENCES

[1] Bhushan B. Tribology issues and opportunities in MEMS. Dordrecht: Kluwer–Academic 1998. http://dx.doi.org/10.1007/978-94-011-5050-7

[2] Bharat B, Yong CJ. Natural and biomimetic artificial surfaces for super hydrophobicity, self-cleaning, low adhesion, and drag reduction. Prog Mater Sci 2011; 56: 1-108. http://dx.doi.org/10.1016/j.pmatsci.2010.04.003

[3] Burton Z, Bhushan B. Surface characterization and adhesion and friction properties of hydrophobic leaf surfaces. Ultramicroscopy 2006; 106: 709-19. http://dx.doi.org/10.1016/j.ultramic.2005.10.007

[4] Bhushan B, Jung YC. Micro and nanoscale characterization of hydrophobic and hydrophilic leaf surface. Nanotechnology 2006; 17: 2758-72. http://dx.doi.org/10.1088/0957-4484/17/11/008

[5] Ren LQ, Wang SJ, Tian XM, *et al*. Non-Smooth morphologies of typical plant leaf surfaces and their anti-adhesion effects. J Bionic Eng 2007; 4: 33-40. http://dx.doi.org/10.1016/S1672-6529(07)60010-9

[6] Jung YC, Bhushan B. Contact angle, adhesion, and friction properties of micro- and nanopetterned polymers for superhydrophobicity. Nanotechnology 2006; 17: 4970-80. http://dx.doi.org/10.1088/0957-4484/17/19/033

[7] Guo ZG, Liu WM, Su BL. Superhydrophobic surfaces: From natural to biomimetic to functional. J Colloid Interface Sci 2011; 353: 335-5. http://dx.doi.org/10.1016/j.jcis.2010.08.047

[8] Johnson RE, Dettre RH. Contact angle hysteresis. Adv Chem 1964; 43: 112-35. http://dx.doi.org/10.1021/ba-1964-0043.ch007

[9] Bormashenko E, Pogreb R, Whyman G. Cassie–Wenzel wetting transition in vibrated drops deposited on the rough surfaces: is dynamic Cassie–Wenzel transition 2D or 1D affair? Langmuir 2007; 23: 1-3. http://pubs.acs.org/doi/pdf/10.1021/la700935x

[10] Wenzel RN. Surface roughness and contact angle. J Phys Colloid Chem 1949; 53: 1466. http://dx.doi.org/10.1021/j150474a015

[11] Cassie ABD. Contact angles. Discuss. Faraday Soc 1948; 3: 11. http://dx.doi.org/10.1039/df9480300011

[12] Johnson RE, Dettre RH. Contact Angle, Wettability, and Adhesion. In: Contact angle hysteresis. Adv Chem Ser 1964; 43: 112-35. http://dx.doi.org/10.1021/ba-1964-0043.ch007

[13] Mittal KL. The role of the interface in adhesion phenomena. Polym Eng Sci 1977; 17: 467-73. http://dx.doi.org/10.1002/pen.760170709

[14] Marshall SJ, Bayne SC, Baier R. A review of adhesion science. Dent Mater 2010; 26: 11-6. http://dx.doi.org/10.1016/j.dental.2009.11.157

[15] Walker G. Adhesion to smooth surfaces by insects-a review. Int J Adhes 1993; 13: 3-7. http://dx.doi.org/10.1016/0143-7496(93)90002-Q

[16] Wei YG, Hutchinson JW. Interface strength, work of adhesion and plasticity in the peel test. Int J Fracture 1998; 93: 315-33. http://dx.doi.org/10.1023/A:1007545200315

Received on 13-11-2013 Accepted on 20-12-2013 Published on 10-02-2014

DOI: http://dx.doi.org/10.12970/2311-1755.2013.01.02.1