WHAT FACTORS AFFECT LOTUS EFFECT?

by

Chan-Juan ZHOU, Dan TIAN, and Ji-Huan HE*

National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering,
Soochow University, Suzhou, China

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Lotus effect is the superhydrophobicity property, and widely used for self-cleaning in modern textile engineering. This paper reveals that the lotus effect is a kind of nanoeffect or size effect in nanotechnology, the surface morphology, solution's molecule weight, and temperature are three main factors affecting the lotus effect. Solutions' pH values or ionic liquids are also discussed in this paper. A series of experiments are carried out to measure contact angles for different solutions/liquids on the lotus surface at different temperature.

Key words: *Nelumbo, superhydrophobicity, geometrical potential, nanoeffect, biomimetic design, wetting*

Introduction

The lotus effect [1, 2] is widely used in modern technology, especially in modern textile engineering, due to its self-cleaning property resulting originally from the ultrahydrophobicity of lotus (Nelumbo) leaf. Self-cleaning windows, windshields, utensils, roof tiles, and solar panels are designed with bioinspired superhydrophobic surfaces. Many research has focused on design of lotus-like surface with hierarchical micro/nano structures [3-5], and the measured static water contact angle is always referred to that of pure water. Many plants, however, are damaged by acid rains or muddy water, both cases affect greatly the wetting property of the plant's leaves. Furthermore, acid rains and muddy water enhance erosion of metal structure. Plant leaves have been evolved into special leaf morphologies with necessary wetting properties, impurity of water makes the wetting property changed remarkably. This paper is focused on studying a theoretical model for lotus effect and the effect of impurity of water, ionic liquids, and pH values on the contact angle.

Nanoeffect and lotus effect

Before explaining the lotus effect [1, 2], we give a brief introduction to the nanoeffect (size effect) [6], which causes remarkable improvement of thermal, mechanical, or electronic properties of materials independent of their bulk properties when their sizes are reduced to nanoscales. It can be expressed in the form [6, 7]:

$$\sigma = \sigma_0 + \frac{k_\sigma}{d^\alpha} \tag{1}$$

* Corresponding author, e-mail: hejihuan@suda.edu.cn

where d is the average diameter, σ can be elastic modulus, surface energy, strength, thermal resistance, or other properties, σ_0 – its bulk's property, k_σ – a material constant, and α – a scaling parameter. Nanoeffect arises generally when d tends to hundreds of nanometers.

In eq. (1) d can be the diameter of a fiber, it can also be the diameter of a porous medium with opposite sign of k_σ. For a nanoscale porosity, we write its nanoeffect in the form [6]:

$$\sigma = \sigma_0 - \frac{k_\sigma}{d^\alpha} \tag{2}$$

Figure 1 shows the SEM illustration of lotus surface, showing uniform protrusions on the surface, and among protrusions is the porosity. When the porosity size tends to nanoscales, eq. (2) works.

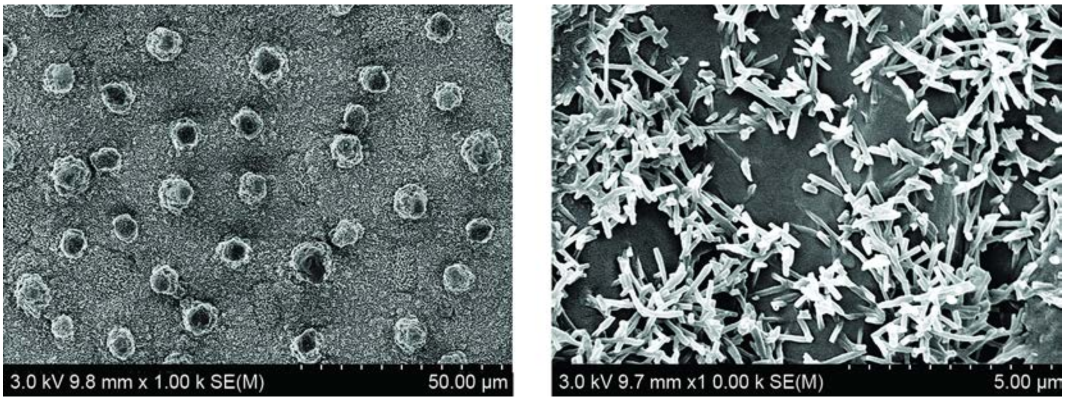

Figure 1. The SEM illustrations of lotus surface

The nanoeffect of nanoscale protrusions on the convex surface is an attraction force, while that of porosity in lotus leaf surface is a repulsion one. The combination of the concave and convex surfaces results in:

$$F = \frac{a}{d^\alpha} - \frac{b}{d^\beta} \tag{3}$$

where F is the equilibrant force between attraction and repulsion, a and b are geometrical parameters associated to convex and concave structures of the surface, respectively, α and β are scaling parameters, according the theory of geometrical potential [8], α and β are the values of fractal dimensions for convex and concave surfaces, respectively, and satisfy:

$$\alpha + \beta = 2 \tag{4}$$

The geometrical parameters, a and b, are associated with the fractal dimensions:

$$a = a(\alpha), \quad b = b(\beta) \tag{5}$$

The contact angle depends mainly upon the interaction between the nanoeffects of protrusion and porosity, change of convex and concave structures will greatly affect attract or repulsion properties, as a results the contact angle will be also changed. When the porosity size increases to a threshold, there is no repulsion, and the contact angle tends to zero.

Water purity and equivalent molecular weight

In order to study the effect of water purity on contact angle, lotus leaves were collected at rivers near the campus of Soochow University, the fresh leaf sees a contact angle of 151.6°, while the dried leaf results in 159.4°. This phenomenon implies that the surface structure does affect the contact angle. Bubble electrospinning can produce lotus-like surface with high hydrophobicity [9, 10].

In our experiment, various sodium bicarbonate solutions were prepared, which are slightly acid. A 2% sodium bicarbonate solution decreases the contact angle from 151.6° to 141.7° on the lotus leaf surface, tab. 1, this is because of the van der Waals bond between H^+ and surface charge. The van der Waals force works only within the ranges of 10-100 nm. Table 2 shows alcohol solution’s contact angle, a 20% ethyl alcohol solution increases the contact angle from 151.6° to 161.9° on the lotus leaf surface, similar phenomenon is seen for 10% acetic acid. Both ethyl alcohol and acetic acid have similar structure to water molecule. The maximal contact angle in literature is as high as 170°, the decrease of the contact angle of the lotus leaf surface implies a possible environmental change. Tables 1-3 show the effect of mass fraction of sodium bicarbonate solution, alcohol solution, and acetic acid solution, respectively, on the contact angle on lotus leaf surface. Figure 2 shows the effect of equivalent molecular weight on the contact angle on lotus leaf surface. The contact angle can be generalized written in the form:

$$\theta = \frac{1}{\sum_{n=0}^{N} a_n W^n} \tag{6}$$

Table 1. The effect of mass fraction of sodium bicarbonate solution on the contact angle on lotus leaf surface

Mass fraction	2%	5%	8%
Molecular weight	19.3	21.3	23.2
Contact angle [°]	141.7	127.8	120.1
pH value	8.30	8.37	8.42

Table 2. The effect of mass fraction of alcohol solution on the contact angle on lotus leaf surface

Mass fraction	5%	20%	40%	60%	80%	98%
Molecular weight	19.4	23.6	29.2	34.8	40.4	45.4
Contact angle [°]	144.8	161.9	132.3	78.4	10.5	≈0
pH value	7.38	7.20	7.15	7.10	7.06	7.04

Table 3. The effect of mass fraction of acetic acid solution on the contact angle on lotus leaf surface

Mass fraction	5%	10%	15%	20%	30%
Molecular weight	20.1	22.2	24.3	26.4	30.6
Contact angle [°]	131.2	141.1	144.9	135.4	132.5
pH value	2.10	1.89	1.67	1.55	1.34

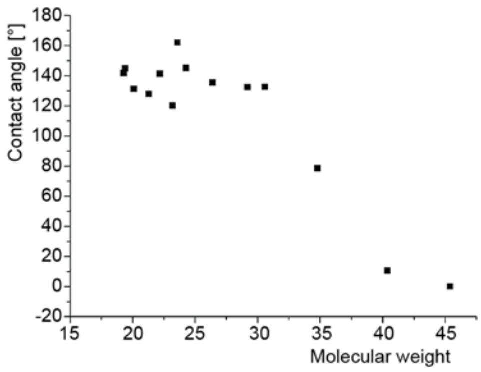

Figure 2. Effect of equivalent molecular weight on the contact angle on lotus leaf surface

where a_n (n = 0 ~ N) are constants which can be determined experimentally, W – the molecular weight.

Effect of temperature on contact angle

As temperature increases, the capillary energy increases, which can be described by the Boltzmann factor in the form:

$$\theta = \frac{1}{\sum_{n=0}^{N} a_n W^n} \exp\left\{-\frac{E}{kT}\right\} \tag{7}$$

where E is the water drop's energy, T [K] – the absolute temperature, and k – the Boltzmann constant, which is a physical constant relating the average kinetic energy of the solution in the water drop. Equation (7) reveals that a higher temperature will results in a lower contact angle, as shown in figs. 3 and 4, and tables 4 and 5.

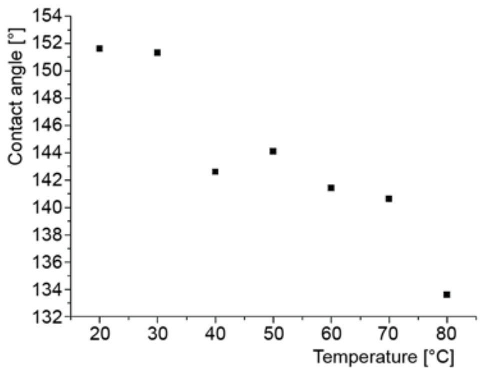

Figure 3. Effect of temperature of deionized water on the contact angle on lotus leaf surface

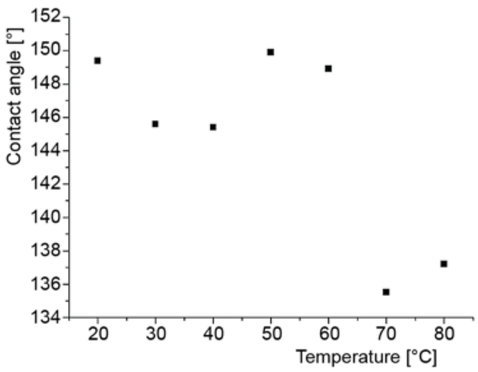

Figure 4. Effect of temperature of sodium chloride solution on the contact angle on lotus leaf surface

Table 4. The effect of temperature of deionized water on the contact angle on lotus leaf surface

Temperature [°C]	20	30	40	50	60	70	80
Contact angle [°]	151.6	151.3	142.6	144.1	141.4	140.6	133.6

Table 5. The effect of temperature of sodium chloride solution on the contact angle on lotus leaf surface

Temperature [°C]	20	30	40	50	60	70	80
Contact angle [°]	149.4	145.6	145.4	149.9	148.9	135.5	137.2

Highly selective repulsion

It is obvious from previous experiment that the contact angle reaches its maximum when the equivalent molecular weight locates between 18 and 25, and it reduces greatly with the increase of equivalent molecular weight, when it reaches larger than 40, the contact angle becomes zero. This phenomenon implies that the lotus leaf surface has a high repulsion capacity and excellent selectivity of water over other molecules solutions with equivalent molecular weight larger than 25. For neutral pH solutions, the equivalent molecular weight may be near to 20. Any non-neutral solutions have van der Waals force acting on the lotus leaf surface, this will affect the contact angle. To verify our theory, we carried out other experiment using oil and water to measure contact angles, see fig. 5.

It is found that water on the lotus leaf surface can form small spheres rolling down and up rapidly, while the oil is agglomerative on the surface.

Figure 5. Comparison of water, oil and starch solution on the contact angle on the lotus leaf surface

Discussion

Equations (6) and (7) can be also written, respectively, in alternative forms:

$$\theta = \frac{\sum_{n=0}^{N} a_n W^n}{\sum_{n=1}^{N+1} b_n W^n} \tag{8}$$

$$\theta = \frac{\sum_{n=0}^{N} a_n W^n}{\sum_{n=1}^{N+1} b_n W^n} \exp\left\{-\frac{E}{kT}\right\} \tag{9}$$

where a_n $(n = 0 \sim N)$ and b_n $(n = 1 \sim N + 1)$ are constants which can be determined experimentally. For simplicity, we consider a simple case:

$$\theta(W) = \frac{a_0 + a_1 W}{b_1 W + b_2 W^2} \tag{10}$$

We assume that the contact angle reaches its maximum for pure water. This requires:

$$\theta(18)=\frac{a_0+18a_1}{18b_1+18^2 b_2}=151.6 \tag{11}$$

and

$$\frac{\mathrm{d}\theta(18)}{\mathrm{d}W}=\left.\frac{a_1(b_1W+b_2W^2)-(a_0+a_1W)(b_1+2b_2W)}{(b_1W+b_2W^2)^2}\right|_{W=18}=0 \tag{12}$$

or

$$-a_0b_1-36a_0b_2-18^2a_1b_2=0 \tag{13}$$

We assume that the contact angle becomes zero when $W = 45.2$, this requires:

$$\theta(45.2)=\frac{a_0+a_1 45.2}{45.2b_1+45.2^2 b_2}=0 \tag{14}$$

From eqs. (11), (13), and (14) we can obtain the needed formula for the relationship between the contact angle and molecule weight.

Conclusion

This paper gives an explanation of the lotus effect and highly selective repulsion of lotus leaves on solutions with molecular weight close to that of water. Impurity of water, non-neutral solutions, and nanoscale surface will greatly affect the wetting properties of the surface. This paper suggests a possible way to design bioinspired surfaces for bioinspired superhydrophobic/superoleophobic surfaces or a face with an extremely high repulsion capacity and remarkably excellent selectivity of some a special solution over others. If we design such a surface with opposite concave-convex structure to that of the lotus leaf surface, *i. e.*, nanoporous membranes [9, 11], we can embody the membranes highly selective absorption of a certain particle over others.

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