A Comparison of the Special Wetting Property between Locust and Butterfly Wing

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Keywords: Superhydrophobicity, Adhesion, Wettability, Insect, Biomaterial.

Abstract. The microstructure, wettability and chemical composition of butterfly and locust wing surfaces were investigated by a scanning electron microscope (SEM), a contact angle meter and a Fourier transform infrared spectrometer (FT-IR). The hydrophobicity models were established on the basis of Cassie equation. The wetting mechanism was comparatively discussed from the perspective of biological coupling. The butterfly and the locust wing surfaces are composed of naturally hydrophobic materials, but exhibit different complex wettability. The butterfly wing surface is of low adhesion (sliding angle 1~4°) and superhydrophobicity (contact angle 150.5~156.2°), while the locust wing surface is of extremely high adhesion (sliding angle>180°) and superhydrophobicity (contact angle 150.6~154.8°). The complex wettability of the wing surfaces ascribes to coupling effect of hydrophobic material and rough structure. The butterfly and locust wings can be used as bio-templates for design and preparation of biomedical functional surface, intelligent interfacial material and no-loss microfluidic transport channels.

Introduction

In the last few years, the interfacial materials with desirable properties and functions have attracted tremendous interest due to valuable theoretical importance and a wide variety of applications in industrial, military, biomedical and domestic fields [1~3]. After long-term natural evolution and selection, many animals and plants have possessed special surface micro/nanostructures, which endow the creatures with multi-functions. Inspired by the wettability of various bio-surfaces such as lotus leaf, lots of superhydrophobic and self-cleaning materials have been artificially prepared [4~7]. The superhydrophobic material with high adhesion can be used as “mechanical hand” in the field of no-loss microfluidic transport. As one of the most complicated three-dimensional periodical substrates in nature, the insect wing has become a popular biomimetic fabrication template because of the superior characteristics [8]. In this work we investigated the chemical composition, microstructure, hydrophobicity and adhesion of butterfly and locust wing surfaces, found different complex wettability. The wetting mechanism was discussed comparatively from the perspective of biological coupling. The results may bring inspiration for bionic design and fabrication of smart biomedical materials.
Materials and Methods

Materials

The specimens of locust (five species in Arcypteredae) and butterfly (five species in Pieridae) were collected in Changchun City, Jilin City, Harbin City and Dalian City of northeast China. The wings were cleaned, desiccated and flattened, then cut into 5 mm × 5 mm pieces from discal cell (butterfly) and remigium (locust). The distilled water for contact angle (CA) and sliding angle (SA) measurements was purchased from Tianjin Pharmaceuticals Group Co. Ltd., China. The volume of water droplets was 5 μl.

Methods

After gold coating by an ion sputter coater (Hitachi E-1045, Japan), the wing pieces were observed and photographed by a SEM (Hitachi SU8010, Japan). A video-based CA measuring system (DataPhysics OCA20, Germany) was used to measure the CA of water droplet on the wing surface via sessile drop method at ambient conditions of 25±1°C. The SA of water droplets was measured in the direction from the wing basal to the wing terminal end. The chemical composition of the wing surface was analyzed by a FT-IR (Nicolet FT-IR200, USA). The hydrophobicity models were established on the basis of Cassie equation.

Results and Discussion

The Superhydrophobicity of the Wing Surfaces

The wing surfaces of the five butterfly species and the five locust species display superhydrophobicity. The CA on the butterfly wing ranges from 150.5° to 156.2°, the average is 154.1°. The CA on the locust wing ranges from 150.6° to 154.8°, the average is 153.1° (Table 1).

<table>
<thead>
<tr>
<th>Species</th>
<th>Measured CA</th>
<th>Predicted CA</th>
<th>SA (°)</th>
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<tbody>
<tr>
<td><strong>Butterfly</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthocharis cardamines</td>
<td>156.2</td>
<td>157.8</td>
<td>2</td>
</tr>
<tr>
<td>Aporia hippia</td>
<td>150.5</td>
<td>153.2</td>
<td>4</td>
</tr>
<tr>
<td>Colias erate</td>
<td>153.3</td>
<td>155.6</td>
<td>3</td>
</tr>
<tr>
<td>Colias heos</td>
<td>155.4</td>
<td>157.3</td>
<td>1</td>
</tr>
<tr>
<td>Leptidea morsei</td>
<td>154.9</td>
<td>152.7</td>
<td>3</td>
</tr>
<tr>
<td>Average</td>
<td>154.1</td>
<td>155.3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Locust</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Podismopsis amplipennis</td>
<td>154.8</td>
<td>155.0</td>
<td>&gt;180</td>
</tr>
<tr>
<td>Podismopsis augustipennis</td>
<td>150.6</td>
<td>153.7</td>
<td>&gt;180</td>
</tr>
<tr>
<td>Podismopsis dolichocerca</td>
<td>152.4</td>
<td>152.1</td>
<td>&gt;180</td>
</tr>
<tr>
<td>Podismopsis maximpennis</td>
<td>153.6</td>
<td>155.3</td>
<td>&gt;180</td>
</tr>
<tr>
<td>Podismopsis viridis</td>
<td>154.2</td>
<td>155.8</td>
<td>&gt;180</td>
</tr>
<tr>
<td>Average</td>
<td>153.1</td>
<td>154.4</td>
<td>&gt;180</td>
</tr>
</tbody>
</table>

The Adhesion of the Wing Surfaces

The water droplet displays low adhesion on the butterfly wing surfaces, the water SA is extremely small (1~4°) (Table 1). As a contrast, the water droplet displays high adhesion on the locust wing surface. The droplet does not leave the locust wing surface at any angle of inclination, even verticalized or inverted (Fig. 1).
The Wetting Mechanism of the Wing Surfaces

Butterfly and locust are typical flying insects. The wings require higher hydrophobicity to reduce flying drag, lighten body burden, and improve movement efficiency. According to the FT-IR spectra, the butterfly and locust wing surfaces are composed of naturally hydrophobic materials. The main composition of the butterfly wing surface is chitin, protein and fat. The locust wing surface is covered with a waxy layer. The hydrophobic material alone, however, can not make the butterfly and locust wing surfaces achieve superhydrophobicity.

The wing surfaces of locust and butterfly show high adhesive superhydrophobicity and low adhesive superhydrophobicity, respectively, which results from the different surface microstructures. Both the butterfly and locust wing surfaces exhibits multiple-dimensional micro/nano structures. On the butterfly wing surface, the micrometric scales like overlapping tiles constitute the primary microstructure [Fig. 2(a)], the submicrometric vertical ribs and horizontal bridges on the scales constitute the secondary microstructure [Fig. 2(b)], the nano protuberances on the vertical ribs and horizontal bridges constitute the tertiary microstructure [Fig. 2(c)]. On the locust wing surface, the vein grids constitute the primary microstructure [Fig. 2(d)], the micrometric pillar gibbosities constitute the secondary microstructure [Fig. 2(e)], the nano corrugations between the pillar gibbosities constitute the tertiary microstructure [Fig. 2(f)].

The spacing between the micrometric gibbosities on the locust wing surface (averagely 14.37 μm) is 7.1 times of that on the butterfly wing surface (averagely 2.02 μm). The density of the micrometric gibbosity on the locust wing surface is far smaller than that on the butterfly wing surface. On the locust wing surface, the air fraction (the percentage of liquid/vapor contact area) of water droplet is 0.536. The micrometric structure of the locust wing surface can be partially wetted by a water droplet. Relatively less air is trapped and sealed between water droplet and the locust wing surface. Two types of air pockets (open/close) are formed. As the water droplet is removed from the locust wing surface, negative pressure is produced due to the exchange of confined air, so high adhesive force is induced [9]. On the butterfly wing surface, the air fraction of water droplet is over 0.892, which is much bigger than that on the locust wing surface [10]. The water droplet stands on the tips of the micrometric gibbosities, much air is left under the droplet. The solid-liquid-gas triple contact lines (TCL) are expected to be contorted and extremely unstable. The butterfly wing surface, on which a water droplet can roll off effortlessly and readily, displays low adhesive superhydrophobicity.
Figure 2. The hierarchical microstructure of butterfly and locust wing surfaces under SEM
(a) Primary structure (butterfly); (b) Secondary structure (butterfly); (c) Tertiary structure (butterfly); (d) Primary structure (locust); (e) Secondary structure (locust); (f) Tertiary structure (locust).

The Hydrophobicity Models of the Wing Surfaces

The butterfly and locust wing surfaces are relatively rough with superhydrophobicity and heterogeneity. A composite contact is formed between the droplet and the surface. Thus, the contact behavior can be expressed by the Cassie-Baxter equation:

$$\cos \theta_c = \phi_s \cos \theta_e + \phi_f - 1$$

(1)

where $\theta_c$ is the apparent CA of a droplet on a heterogeneous composite surface, $\phi_s$ is the area fraction of solid on a composite surface ($0<\phi_s<1$), $\theta_e$ is the intrinsic CA of a droplet on an ideal flat surface (approximately $95^\circ$ and $105^\circ$ on the butterfly and locust wing, respectively). For butterfly wing, the contact state of a water droplet on the micro/nano structure is shown in Fig. 3(a).

Figure 3. The microstructural models for hydrophobicity on the wing surface
(a) butterfly; (b) locust.

In this case, Eq. (1) can be modified for the theoretical (predicted) CA ($\theta_t$) as follows:

$$\cos \theta_t = \frac{4 l^2}{e^2} + 1 * \frac{b e}{c f} * \cos \theta_e + \frac{b e}{c f} - 1$$

(2)

where the parameters $b, c$ represent the width and the spacing of the scale, respectively; $l, e, f$ represent the height, width and spacing of the longitudinal ridge, respectively [Fig. 3(a)].
For locust wing, the parameters $r$, $h$, and $d$ represent the radius, height and spacing of the pillar gibbosity, respectively [Fig. 3(b)]. Thus:

$$\phi_s = \frac{\pi r^2}{d^2}$$  \hspace{1cm} (3)

Based on Eqs. (1), (2) and (3), the predicted CAs on the butterfly and locust wing surfaces were calculated (Table 1). Taking predicted CAs as independent variable $y^*$, measured CAs as dependent variable $y$, the degree of fitting was judged by:

$$Q=\sum(y-y^*)^2$$  \hspace{1cm} (4)

$$R_{New}=1-(\frac{Q}{\sum y^2})^{1/2}$$  \hspace{1cm} (5)

where $Q$ is the sum of square of deviations, $R_{New}$ is the coefficient of determination in nonlinear regression equation. The calculated $R_{New}$ values are 0.937~0.956 for the five butterfly species, and 0.930~0.961 for the five locust species. There is no significant difference between the measured CAs and the predicted CAs, demonstrating the hydrophobicity models are in good accord with the Cassie equation.

**Summary**

The butterfly and locust wing surfaces are composed of naturally hydrophobic materials, and possess complicated micro/nano structures, including primary structure, secondary structure and tertiary structure. The butterfly wing surface is of low adhesive superhydrophobicity (SA 1~4°, CA 150.5~156.2°), while the locust wing surface is of high adhesive superhydrophobicity (SA>180°, CA 150.6~154.8°). The distinct complex wettability of the butterfly and locust wing surfaces results from the different microstructures. The coupling effect of hydrophobic material and rough microstructure contributes to the special wettability of the butterfly and locust wing surfaces. The hydrophobicity models accord well with the Cassie equation. This work promotes our understanding of wetting mechanism of bio-surfaces, and may bring interesting insights for biomimetic preparation of novel interfacial material with biomedical functions.

**Acknowledgement**

This work was financially supported by the National Natural Science Foundation of China (Grant No. 31671010), the Natural Science Foundation of Jilin Province, China (Grant No. 201115162) and the Innovative Program for Postgraduate Students of Changchun Normal University (Grant No. cscxy2015007, cscxy2017003, cscxy2017006). Dr. Prof. Gang Sun is the corresponding author of this paper.

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