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FUNCTIONAL MATERIALS

Leaf-mimicking polymers for hydrophobicity and high transmission haze

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Abstract. Gifted with unique optical and hydrophobic properties, the plant leaves have been recently considered as micro/nanostructure prototypes for functional surface engineering. Imprinting bio-inspired structures onto surfaces can yield in similar functional properties than in the nature. In this article, we report on a simple and effective method to copy leaf surface structures onto poly-(methyl methacrylate) sheets. The replicated surface structures reduce optical reflectance and enhance optical haze. Besides, the artificial polymer sheets exhibit good hydrophobic properties. Correlation between optical haze and hydrophobicity was studied.

Key words: bionic leaf replication, hydrophobicity, optical haze, contact angle.

1. INTRODUCTION

During the ages of evolution, nature has developed unique characteristics for living creatures. Learning from these structures may provide an effective way to solve problems encountered by human beings. Plant leaves produce most of the oxygen and organic matter on earth through photosynthesis. Typically, dedicated micro/nanostructures are developed on leaf surfaces to apt for different natural ambiences, for example lotus leaves show a structure of nano bumps on conical papillae [1–4]. The typical size of such hierarchical structure is comparable to the wavelength of visible light, which offers particular optical properties to the plant leaves. There have been plenty of researches focusing on mimicking the leaves and applying them as optical functional films. For example, inspired by photosynthesis, the artificial films were used in photovoltaics to reduce the high reflection of bare silicon solar cells [5,6]. In recent studies both, experimental and theoretical results demonstrated that the bio-mimicked structures have good optical transparency and haze ratio [7,8] leading to efficiency increase when applied to photovoltaics. On the other hand, leaves of both, aquatic and terrestrial plant species, exhibit hydrophobic properties [9,10]. Large contact angles against water make it easy to remove raindrops and dust from the leaf surfaces [11]. Such hydrophobic properties are attributed to the surface energy and surface roughness [12]. The latter, i.e. micro/nanostructures on the surface, is the key factor for superhydrophobicity [13].

Despite individual research progresses [7], systematic studies on the correlation between the optical and hydrophobic properties are insufficient. In the application of anti-reflection films on solar cells, the hydrophobicity should be also taken into account. A hydrophobic surface can easily be kept uncontaminated from the rain and dust to reduce photon loss, leading to a highly efficient light harvesting process. Moreover, the leaf surface structures contribute to both, optical and hydrophobic properties, so

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that certain relevance may exist between these two aspects. Therefore, efforts should be devoted to figuring out such relationships for possible leaf candidates. Hydrophobic surfaces with optically transparent properties may facilitate to find a variety of applications.

In this work, we imprinted 32 kinds of leaf structures onto poly-(methyl methacrylate) (PMMA), of which we mainly studied the sugarcane, maize and lotus leaf replicas. All the bio-mimicked PMMA sheets show high optical haze ratio (up to 80%), while the transmittance varies depending on the morphologies. Computational simulations were also performed to clarify the interaction between light and leaf structures. Bionic PMMA sheets were found to have higher contact angles than the smooth ones. Based on this, the relationship between hydrophobicity and optical haze has been studied.

2. METHODS

A two-phase fabrication process was used to replicate the sugarcane, maize and lotus leaves. Firstly, a fresh and clean leaf was fixed at the bottom of a container, then polydimethylsiloxane (PDMS) was deposited on the leaf surface. This process produced the negative structure of the original leaf. Then PMMA was poured onto the negative PDMS film. After polymerization, degasification and annealing in a vacuum oven, the PMMA was detached from the PDMS mold and it would copy all the fine structures of the leaf surface. The morphologies of the bionic PMMA sheets were characterized through field emission scanning electron microscope (FESEM) and surface profilometer. Optical properties were measured by a transmittance and haze tester (WGT-S, Shanghai Physical Optics Instrument Co., Ltd). Hydrophobic properties were measured by a wetting apparatus. Numerical simulation of light scattering was carried out by the finite-differential-time-domain (FDTD) method with the software of Lumerical Solutions Inc.

3. RESULTS AND DISCUSSION

Morphologies of the replicated sugarcane, maize and lotus leaves exhibit distinct microstructures. The sugarcane leaf surface (Fig. 1a) is composed of long concave strips (~20 μm width) with small randomly dispersed elliptical pits. The major axis of those pits lies parallel to the strips. The maize leaves (Fig. 1b) have similar concave strips, but with elliptical stomata arranged on both sides. There are also linear bumps filling the gaps of adjacent protrusions. The lotus leaf (Fig. 1c) is typically a flat surface, decorated with plenty of hierarchical protrusions, that is, nano bumps (see the inset) on top of conical papillae (5–10 μm). Fig. 1d–f show the surface profile of leaf structures in Fig. 1a–c. It is possible to obtain the height profile according to the colour scale. The sugarcane and maize leaves have much higher microstructures than lotus leaves.

Based on the surface profile information, we established 3D models for the sugarcane, maize and lotus leaves (Fig. 2a–c). The nanoscale structures (Fig. 1c) were ignored in the models. They are supposed

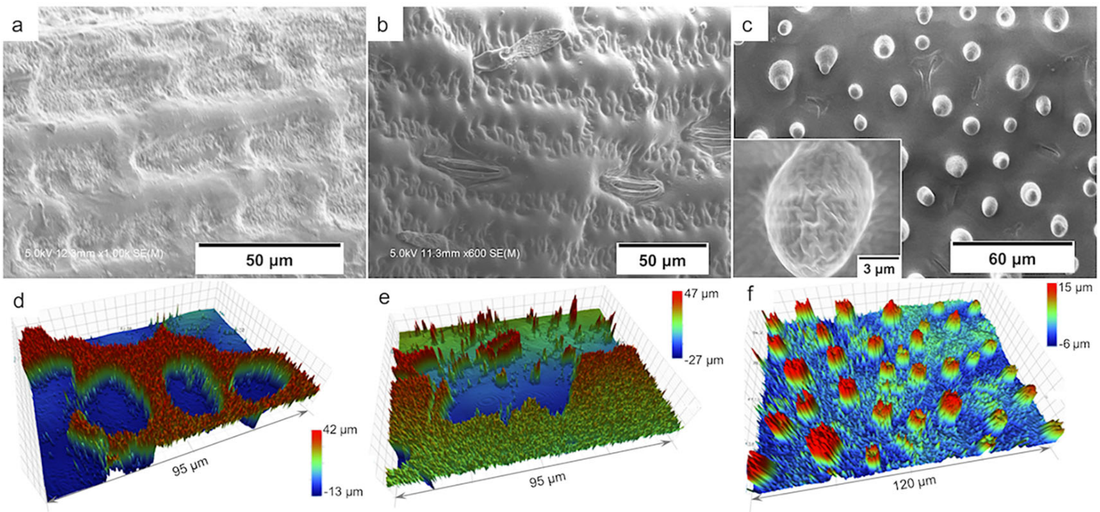

Fig. 1. SEM images and surface profile of replicated sugarcane, maize and lotus leaf structures. (a), (d) sugarcane; (b), (e) maize; (c), (f) lotus. The inset shows a zoomed-in image on lotus leaf. The surface profiles of randomly selected square regions (panel d, e, f) were taken on the replicated leaves but at different positions from SEM images, and the side lengths were marked in each panel.

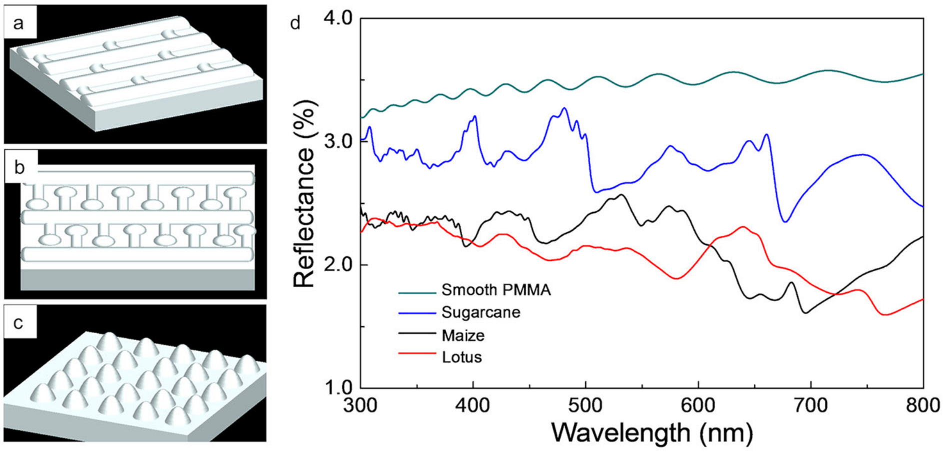

Fig. 2. Numerical simulation of light interference with the leaf models: (a) sugarcane model; (b) maize model; (c) lotus model; (d) simulation results of optical reflectance in the range of visible light.

to play an important role in hydrophobic behaviours [12]. However, computational work reveals a limited influence on the reflectance [8]. The simulated reflectance keeps nearly unchanged after introducing nanostructures into a microscale hemisphere model. We calculated the optical reflectance of the leaf structures as well as the smooth PMMA sheet. There is no obvious peak for all the models, suggesting that the models have similar reflective ability in the whole range of visible light. On the other hand, all the reflectances are extremely low. Plant leaves will benefit from such low reflectance property, which lets more photons to be involved in the photosynthesis. Also, it shows that the leaf surface microstructures on the PMMA sheets reduced the reflectance in comparison with the smooth one (< 3% for leaf structures and ~3.5% for smooth PMMA sheet). It is noteworthy that not all the bio-mimicked structures are in favour of anti-reflection. Different from patterns on plant leaves, specific naturally occurring nanostructures (e.g. butterfly wings) could induce high reflectance (varying from 65% to 98% with different incident angles) in visible light range [14]. Surface structures of plant leaves help to reduce the reflectance and promote the light harvesting, while structures on butterfly wings interfere strongly with visible light, producing distinct colours for the purpose of pairing or camouflaging.

When light irradiates on the above PMMA sheets, it will be reflected, absorbed and the rest will pass through. Lower reflectance will let more photons to get into the leaves, but it would be also beneficial to get a larger absorption area. The transmitted light will be scattered by the microstructures before it penetrates the leaves. Such wide angle scattering makes the transmitted optical spot larger than the incident beam. That means, when the sheets with a larger haze ratio are coated on silicon solar cells, more silicon area will be involved in the photovoltaic process, leading to higher photovoltaic efficiency. Fig. 3a shows the transmission haze for mimicked maize leaf. The laser beam with a diameter of 3 mm produced a ~20 cm spot after travelling through the PMMA. Fig. 3b illustrates the light scattering mechanism on the microstructure patterned surfaces. A maximum open-angle of 41° was found for the bionic maize leaf.

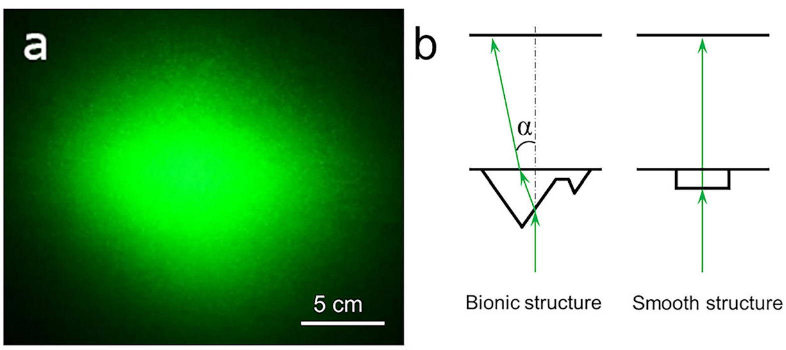

Fig. 3. Measurements of optical transmission haze. (a) Incident laser beam scattered by bionic maize leaf; (b) schematic diagram of light scattering.

The experimental results of transmittance and optical haze ratio are well consistent with the expectation. Smooth PMMA sheet is highly transparent to the incident light, but the haze ratio is extremely low (5.2%). The microstructures on the bionic sheets greatly enhanced the haze ratio along with a reduced transmittance. Among the three leaf structures, maize leaf shows the highest haze ratio while lotus leaf has the best transmittance. Sugarcane leaf has poor transmittance, which would differ its application from the other two. The trend line in Fig. 4 shows relationships between optical transmittance and haze ratio for PMMA sheets with different surface structures, it suggests that the transmittance decreases with the increase of optical haze.

Water contact angle measurements have confirmed that all three bionic PMMA structures are hydrophobic (see Fig. 5). It suggests that the fabrication method is a general route to integrate optical and hydrophobic

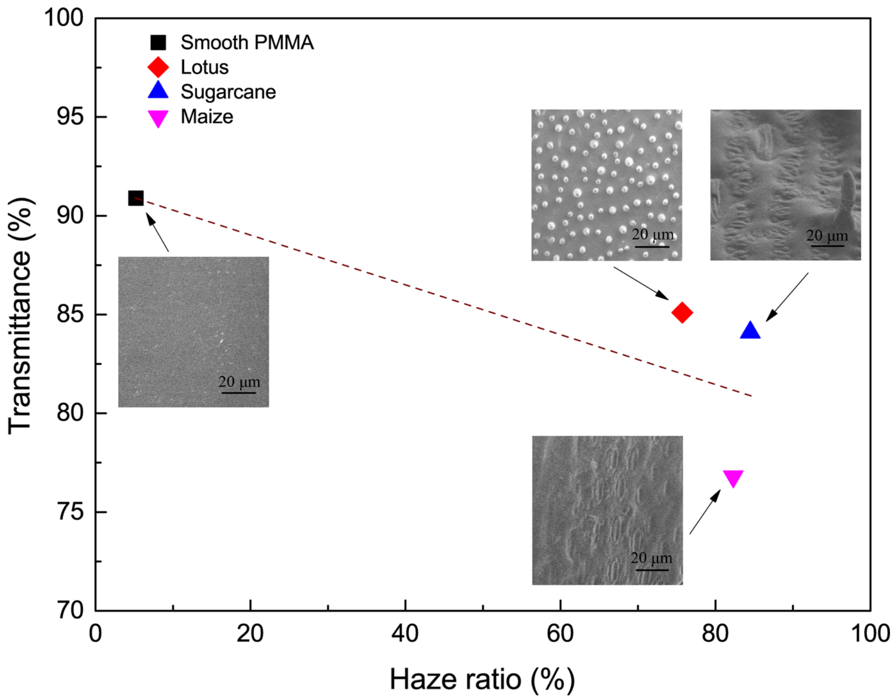

Fig. 4. Relationships between optical transmittance and haze ratio for PMMA sheets with different surface structures.

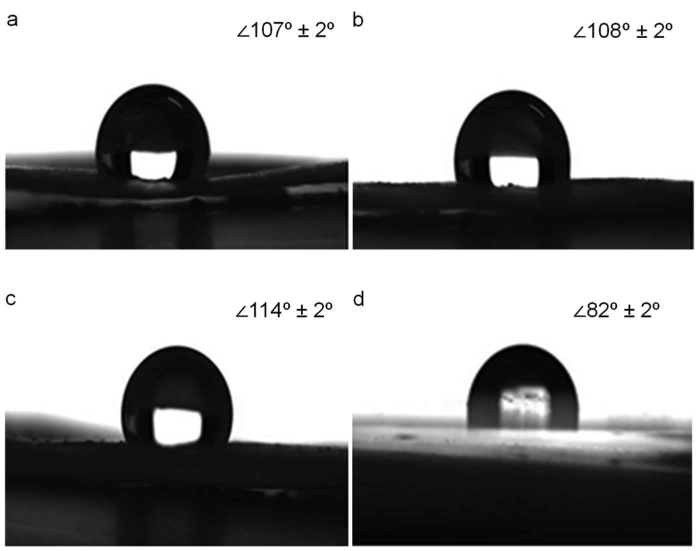

Fig. 5. Contact angle measurements of four PMMA sheets with different surfaces. Bionic structures replicated from sugarcane (a), maize (b) and lotus (c) leaves. Smooth PMMA was also measured as reference (d).

properties together. Though the PMMA is composed of organic molecules, the smooth surface does not exhibit good hydrophobicity (Fig. 5d). When the water droplets meet surfaces with micro- or nanostructures, the contact area is limited. Based on Cassie's model [15], the droplets only contact the top of those spikes, bumps and papillae, with air trapped in the interspace. Smaller contact area leads to a decreased free energy for the interface, providing a driving force to repel the droplets [16]. The shape, size and arrangement of the micro-structures contribute to the hydrophobicity, leading to distinct contact angles on different bionic PMMA surfaces. Compared to sugarcane (Fig. 5a) and maize leaves (Fig. 5b), lotus leaf shows better hydrophobic property (Fig. 5c). As shown in Fig. 1f, the papillae were closely and neatly dispersed. Those nano bumps on the papillae further reduced the contact area. Besides the large static contact angle, droplets on such surface also show a small sliding angle and thus can be easily removed. It is worth noting that the contact angle on bionic lotus surface is slightly smaller than previous results directly measured on lotus leaves [17]. From the structure point of view, some of the nanoscale fiber-like features were missed during the replication process and this probably affected the hydrophobicity. Also, the PMMA may have distinct ability to repel water from the waxy epidermis of lotus leaves.

Besides the aforementioned bio-mimicked leaves, another set of 28 plant leaves were replicated. Most bionic PMMA sheets have enhanced optical haze ratio ranging from 55–85%, while the hydrophobic properties are of great difference (see Fig. 6). There are 13 PMMA sheets which are hydrophilic, including the smooth PMMA. Lotus, sugarcane and maize leaves exhibit better ability to repel water than the others. Remarkably, these three leaves also have relatively high optical haze. They are therefore promising candidates for anti-reflection films, e.g. transparent coating on photovoltaic cells. The one with the highest contact angle (130º) is *photinia serrulata* leaf, but the mediocre optical haze may make it unsuitable in many occasions. Study with all replicated leaves shows that there is no strict correlation between hydrophobic ability and optical haze. A particular micro/nanostructure may have strong interaction with light of certain wavelength. Though it may not be an ideal architecture for trapping air when contacting water droplets, it can act as a hosting matrix for nano-porous complexes to enhance surface wettability through other materials engineering routes, such as screen-printing technique and solvothermal method [18,19].

4. CONCLUSIONS

In summary, bionic PMMA sheets of sugarcane, maize and lotus leaves were replicated via an efficient and low-cost method. Simulation and experimental results reveal that the PMMA sheets with leaf surface structures have extremely low reflectance and relatively high transmission for visible light. Except for the replicated maize leaf, sugarcane and lotus leaf replicas possess good optical transmittance and haze ratio. We also propose that distinct microstructures are required in order to repel water droplets and scatter light. This study also provides a clue that properly optimized surface structures could have better performance in both aspects.

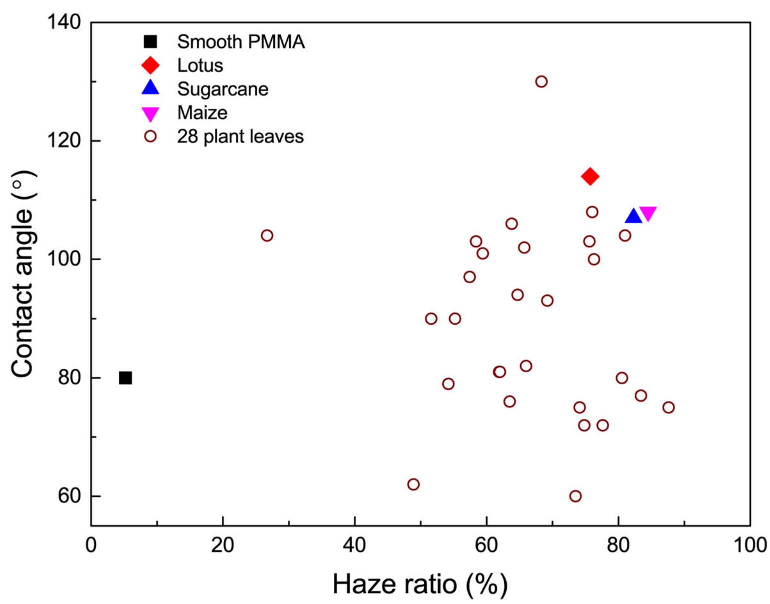

Fig. 6. Relationships between contact angle and haze ratio for PMMA sheets with different leaf surfaces.

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Kopeeritud lehepinna struktuur hüdrofoobsuse ja suure läbipaistvushajususe saamiseks polümeeridel

Zhongjia Huang, Congcong Cai, Xinying Shi, Taohai Li, Marko Huttula ja Wei Cao

Tänu unikaalsetele optilistele omadustele ja hüdrofoobsusele on hakatud taimede lehti pidama sobivateks eeskujudeks funktsionaalsete mikro- ning nanostruktuursete pindade valmistamisel. Artiklis on kirjedatud lihtsat ja efektiivset meetodit taimelehe pinnastruktuuri kopeerimiseks polümetüülmetakrülaadi kihtidesse. Kopeeriti suhkruroo-, maisi- ja lootoselehtede struktuuri. Tulemusena vähenes valguse peegeldus polümeerikihilt ja suurenes kihti läbinud valguse hajumine. Samuti suurenes pinna hüdrofoobsus. Tehti kindlaks korrelatsioon valguse hajumise ja hüdrofoobsuse vahel.