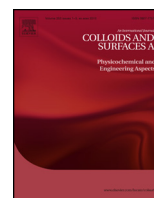




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Fabrication of artificial super-hydrophobic lotus-leaf-like bamboo surfaces through soft lithography

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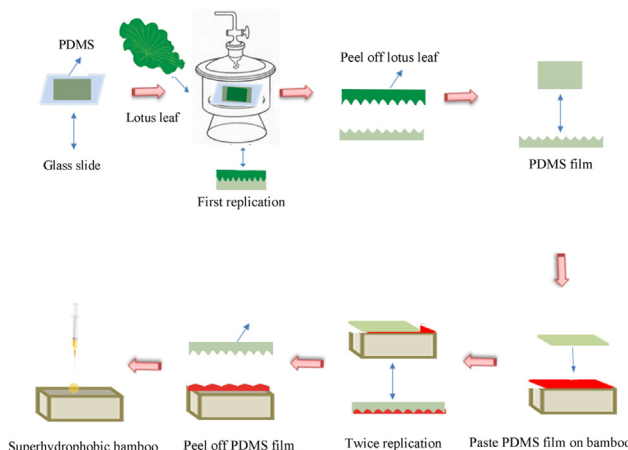
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HIGHLIGHTS

- Lotus-leaf-like microstructure surfaces were built on bamboo surfaces using soft lithography.
- Soft lithography is a kind of effective and widely used method to fabricate micro/nano superhydrophobic structures.
- The lotus-leaf like bamboo can effectively prevent moisture to invasion of bamboo, and improve the dimensional stability.
- It opens up a new way for the researches of functional bamboos and will broaden the application prospects of bamboo.
- It can prolong the bamboos' service life, and alleviate the contradiction between the supply and the demand of timber.

GRAPHICAL ABSTRACT

A lotus-leaf-like rough surface was biomimetically prepared on bamboo surfaces by transfer technology of soft lithography. The fresh lotus leaf and PDMS were as a template and seal. The bamboo could have a hydrophobic and low adhesion ability similar to lotus leaves after twice replications and transcriptions.



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ABSTRACT

The surfaces of plants represent multifunctional interfaces between the organisms and the environment. The paper reports an experimental method to improve the bamboo properties, in terms of hydrophobicity, and resistance to water absorption. The soft lithography technique was used to modify the bamboo surface, transferring over it a lotus-leaf-like topography, based on a micro/nano hierarchical structure using fresh lotus leaves as the template and polydimethylsiloxane (PDMS) for seal. Results describe a characterization based on topographical, chemical and water contact angle analysis. The super-hydrophobicity of lotus-like bamboo surfaces were analyzed by virtue of WCA and the microstructures observed by means of SEM, showing a WCA of 156.5° close to that of the lotus leaf's 160.5°, and rough surface structures with micro-nano papillate hills on bamboo surfaces. Water droplets could easily roll down on such bamboo surfaces, exhibiting super-hydrophobic and low adhesion properties. The successful fabrication of lotus-leaf-like bamboos provided a new direction for researches on the water corrosion resistance of bamboos, which could effectively prevent the damage of moisture to bamboos.

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1. Introduction

Bamboo, an abundant and inexpensive natural resource in China [1], has been reliably used to replace woods in alleviating the con-

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tradition between the supply and the demand of timber [2,3]. The unique structure of bamboo endows it a high strength and tenacity, and its short growth cycle makes a young bamboo grow into an adult tree in only one year [4]. However, as a lignocellulosic material, bamboo has plenty of hydrophilic groups and porous structures, which almost has no resistance to moisture. When stored or used under the circumstance of moisture, bamboo is easy to appear the phenomena of mildew, decay, out of shape and cracking, etc. Therefore, it is imperative to find a way to effectively prevent the damage to bamboos caused by moisture, which provides a good way for the research of hydrophobic bamboos [5,6].

Wettability is a characteristic property of material surfaces, and basically depends on both surface energies and surface structures [7–9]. Many studies have reported that the combination of hierarchical roughness, with a low surface free energy material caused the fabrication of hydrophobic surfaces [10–12]. Many living organism surface structures in nature have evolved over several billion years of evolution [13,14]. In addition, evolutionary processes have given lots of functional plant surfaces exhibiting unusual wetting characteristics [15], such as superhydrophobicity [16,17], superhydrophilicity [18,19], self-cleaning [20,21] and low adhesion [22,23]. The best known example of a superhydrophobic surface is the lotus leaf (*Nelumbo nucifera*) [24–26]. It was reported that observed under the SEM, the surface of lotus leaves showed protruding nubs of 20–40 μm apart each covered with a tinier size scale rough of epicuticular wax crystalloids, including $-\text{CH}_2-$ from paraffinic wax crystals which are the origin of the hydrophobicity property [10,12,26]. Besides, the WCA of lotus leaves is higher than 150° , and sliding angle (SA) is lower than 10° , showing the superhydrophobic and self-cleaning effects [9,10,26]. Guo et al. [10] believed the special hierarchical surface structures and the hydrophobic wax-like material were the reason for the superhydrophobicity, and its WCA was around 162° . Guo et al. [9] reported that they found water droplets could not wet the surface of the lotus leaf and formed nearly spherical shapes with a WCA of about $161 \pm 2^\circ$ and a low SA of about 3° .

Bio-inspired the lotus effect [27], the field about surfaces with superhydrophobic and low surface energy has gained a rapid progress in recent years. Therefore, it could make bamboo surfaces shift from hydrophilicity to hydrophobicity by building a lotus-leaf-like [28] microstructure surface, which might effectively prevent bamboos from the damage of moisture. The key to fabricate such surfaces is only to have the rough surface topography and low surface chemical energy like lotus surfaces. The traditional methods to synthesize lotus-leaf-like surfaces are as follows: the solution method [29], the sol gel method [30], solidification of alkylketene dimer [31], and the plasma fluorination method [32], etc. Jin et al. [6] fabricated a superamphiphobic bamboo surface by solution method combining the control of the ZnO nanostructures and fluoropolymer (FAS) deposition, and the WCA of bamboo was 156° . Li et al. [33] fabricated a superhydrophobic bamboo based on an anatase TiO_2 film modified with octadecyltrichlorosilane (OTS), and got a maximal water contact angle of 154° . Herein, a kind of effective and widely used method to fabricate micron and nanometer structures was introduced to prepare a hydrophobic surface. Soft lithography [34–36], first present by Whitesides in 1983, is especially suitable for replicating micro-nano structures of plant leaf surfaces [37]. It is based on the elastomer mold or seal as the core, such as polydimethylsiloxane (PDMS) [38]. PDMS is a low surface energy material containing $-\text{CH}_3$ groups, which has the intrinsic deformability and hydrophobic properties [26]. Recently many researches based on the method of soft lithography have reported to make hydrophobic PDMS surfaces [26,39]. Khorasani et al. [40] treated a porosity and chain ordering PDMS surface with a WCA of 175° using a CO_2 -pulsed laser as an excitation source. Jin et al. [41] used a laser etching method to make a rough PDMS surface

with WCA higher than 160° and sliding angle lower than 5° . However, the researches on simulating the micro-nano structures of lotus leaves on bamboo surfaces via soft lithography almost have not been proposed.

The paper reports an experimental method to prepare a lotus-leaf-like bamboo surface to improve the bamboo properties, in terms of hydrophobicity, and resistance to water absorption using soft lithography with a fresh lotus leaf and PDMS as a template and seal. The soft lithography technique was used to modify the bamboo surface, transferring over it a lotus leaf-like topography, based on a micro/nano hierarchical structure. Results describe a characterization based on topographical, chemical and water contact angle analysis, and the lotus-leaf like bamboos can effectively prevent moisture to invasion of bamboos. So the dimensional stability of bamboos can be improved, and will also prolong the service life of bamboos. The successful fabrication of lotus-leaf-like bamboos can open up a new way for the researches of functional bamboos, and broadens the application prospects of bamboos.

2. Materials and methods

2.1. Materials

Moso bamboo (*Phyllostachys pubescens*) slices of (Length) 10 mm \times (Width) 10 mm \times (Height) 3 mm purchased from Anji County of Hangzhou City, Zhejiang Province in China, were ultrasonically rinsed in deionized water and then acetone for 60 min, and then they were dried in the oven at 60°C for 24 h. Polyvinyl butyral (PVB, Mw 40,000–70,000), and Anhydrous ethanol (AE) were purchased from Aladdin Industrial Corporation. PDMS and curing agent: 184 silicone elastomer base, were purchased from DOW Corning Corporation of the United States. All chemicals were used as received.

2.2. Preparation of hydrophobic bamboos with lotus-leaf-like surface structures

PDMS and curing agent were fully mixed based on the mass ratio 10:1, and picked up the suction until no bubbles existed in the mixture. The fresh lotus leaf were put flatly in Petri dishes, and then the mixture of PDMS and curing agent was poured into these Petri dishes containing fresh lotus leaves. Put them into vacuum container to be evacuated, discharging the bubbles under the leaf blades. Then the above samples were transferred to 60°C oven curing 1 h. At last, the cured mixture films of PDMS and curing agent were separated from lotus leaves, so the templates with opposite structures of lotus leaf surfaces could be prepared. The films were the first time replicated products.

PVB was dissolved in AE to configure a 15 wt.% PVB/AE solution. The solution was coated on bamboo surfaces, and the first time replicated films were used as seal templates to be pressed on these bamboo surfaces for a second replication, which experimental process was same to the first replication. The samples of bamboos with lotus-leaf-like surface structures could be successfully obtained after stripping the second replicating films. Fig. 1 was the flow chart of the biomimetic preparation of bamboo surfaces with lotus-leaf-like surface structures.

2.3. Characterizations

The surface morphology of the samples was characterized by the scanning electron microscopy (SEM, FEI, Quanta 200). The chemical compositions of the samples were measured by energy dispersive spectroscopy (EDS). Fourier transform infrared spectroscopy (FTIR) spectra for the bamboo samples were recorded via

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