# RESEARCH ON EDIBLE SUPERHYDROPHOBIC COATINGS FOR FOOD PACKAGING MATERIAL

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*Using FDA-approved edible materials, a simple, fast, and low-cost method was proposed to produce coatings with super-hydrophobic properties. The superhydrophobic coating prepared by wax-ethanol hydrothermal spraying showed superhydrophobic properties, and the water contact Angle (WCA) was greater than 150°. In order to improve the hydrophobicity, firmness, flexibility and durability of the coating, polypropylene (PP) was used as binder. This method can be applied to the inner packaging of liquid food in daily life, greatly reducing the residue of liquid food on the packaging.*

**Keywords:** Edible; Superhydrophobic; Sugar cane wax; Food packaging

## 1. Introduction

Water droplets can roll freely on the surface of the lotus leaf with few residues, which is called the "lotus leaf effect" [1]. This phenomenon is attributed to the large number of nano-scale papillary structures [2-3], forming a super-hydrophobic surface. Materials with a water contact angle greater than 150° and a rolling angle less than 10° are called superhydrophobic materials [4]. In recent years, the superhydrophobic materials have been applied in many fields, such as anti-icing [5], anti-fouling [6,7], anti-corrosion [8,9], anti-fog [10], self-cleaning [11-14], etc. The superhydrophobic materials could be used to solve the problem of liquid food remaining in containers. In daily life, liquid food can produce up to 15% residue in containers [15], resulting in a large amount of waste, such as orange juice, milk, yogurt, honey, etc. Therefore, in order to reduce production cost and waste of resources, superhydrophobic coatings can be applied to food inner packaging.

At present, most of the superhydrophobic materials were fabricated by using fluorocarbon materials [16]. Jiang et al. prepared superhydrophobic coating with perfluorooctyltriethoxysilane on steel mesh for oil-water separation [17].

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Patil et al. synthesized a durable superhydrophobic cotton surface based on ZnO nanoparticles and hexadecyltrimethoxysilane [18]. However, the fluorocarbon compounds, classified as contaminants [19], are not suitable for food packaging coatings to reduce residues adhered on inner surface.

The superhydrophobic coating applied to food containers should be non-toxic. Zhang et al. prepared liquid-repellent coatings by mixing beeswax and carnauba wax on the paper surface. The paper was annealed at various temperatures to complete the preparation [20]. Torun et al. fabricated water-repellent surfaces from biocompatible carnauba wax and polydimethylsiloxane [21]. Zhao et al. obtained a superhydrophobic coating with paraffin wax [22]. The wax extracted from plant is environmentally friendly without toxic chemicals and unapproved additives, which is an ideal material for fabrication of superhydrophobic coating [23]. These methods have promoted the application of superhydrophobic materials in food packaging. However, the raw materials used are not easy to prepare and the operation process is not simple and fast. Sugarcane wax extracted from pure natural sugarcane has the advantages of edible, low cost and safety without pollution. Sugarcane wax is composed of esters, free acids, alcohols and hydrocarbons [24], which is as an ideal material for preparing edible superhydrophobic coating. In this study, a low-cost and simple means of fabricating superhydrophobic coating was conducted with a wax suspension in ethanol. The prepared edible coating was expected to exhibiting excellent liquid repelling properties against a variety of viscous low fat content food liquids on different food packaging materials (glass, cardboard, ceramics, etc.). Apparently, the superhydrophobic coating with sugarcane wax could be effectively used to reduce low fat content liquid food residues adhering to different substrates.

## 2. Experiment

### 2.1. Material

Sugarcane wax (food grade material) was purchased from Cangzhou Fengyuan Wax Industry Co., Ltd. Polypropylene (PP) was provided by Dongguan Solid Adhesive Co., Ltd. Anhydrous ethanol was purchased from Tianjin Xingxing Chemical Reagent Manufacturing Co., Ltd. Glass slides (25.4 x 76.2mm) were provided by Galleon Brand. Yogurt, milk, honey, orange juice and cola were obtained from local supermarkets in Xinxiang, China. Plastic board, cardboard, tin foil, ceramics and other substrates were purchased from the local market in Xinxiang, China.

### 2.2 The preparation of superhydrophobic coating

The preparation process of superhydrophobic coating was shown in Fig. 1. The sugarcane wax suspension was obtained by mixing 1 g of wax with 50 mL ethanol solution followed by heating at 75°C for 3 min. The hot suspension was sprayed onto the surface of glass a distance of 50 cm with PP as a binder to improve its robustness. The coated surface was dried at room temperature to realize the superhydrophobic properties.

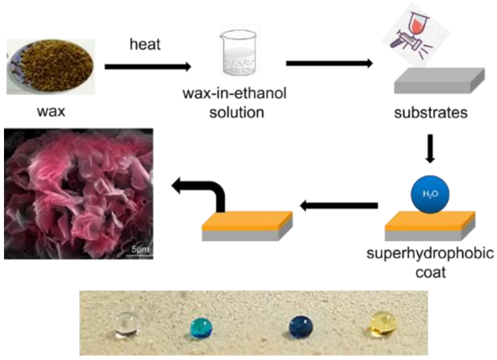


Fig. 1. Schematic illustration of the procedure for solution preparation and coating treatment

### 2.3. The robustness, flexibility, durability and adhesion performance of the coating

The firmness of the coating was tested by water dropping with a height of 30 cm (Fig. 2a). The flexibility of the coating was studied by spraying the coating onto aluminum foil. Aluminum foil which had good flexibility was often used as food packaging material. As shown in Fig.2b, the aluminum foil was bent back and forth which was defined as one cycle. The coating was also pressed with a finger forth and back (one cycle) as shown in Fig. 2c. In order to test the wear resistance of the coating, the coated glass was placed face down to a sandpaper under along a ruler for a distance of 10 cm forth and back, which was defined as one cycle (Fig. 2d).

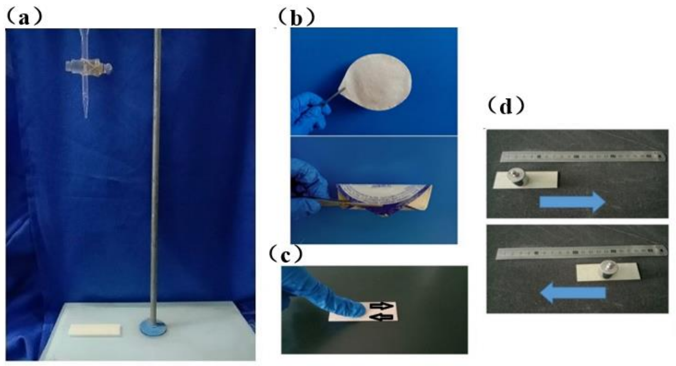


Fig. 2. (a) The device for impact resistance test; (b) A folded shape to emphasize the flexibility of the coating; (c) One finger pressing cycly; (d) One abrasion cycle

Furthermore, yogurt container purchased from the market was coated with sugarcane wax to test the practicality of the superhydrophobic coating. The container was filled with various viscous liquid food, including honey, juice, chocolate milk and coca-coke. The liquid was poured out from the container to test its adhesion performance.

### 2.4. Apparatus

The surface structure was investigated by GTK-16-0300 Brook white light interferometer (BRKR, Billerica, Massachusetts, USA) and a Quanta 200 SEM (FEI, Hillsboro, OR, USA). The superhydrophobic properties was analyzed by an optical contact angle measuring instrument (Shenzhen testing equipment CO., LTD, Shenzhen, China, TST-200H).

### 2.5. Surface density measurement

The weight change of the substrate before and after spraying and solvent evaporation was measured by an electronic balance. The surface density is obtained by the ratio of the weight change to the surface area.

$$\rho_A = (M_2 - M_1)/S_A$$

Where $M_1$ is the weight of the substrate before coating, $M_2$ is the weight of the substrate after spraying and solvent evaporation, $S_A$ is the surface area.

## 3. Results and discussion

### 3.1. The influence of surface density

The WCA on the superhydrophobic surface with the change of surface density $\rho_A$ was showed in Fig. 3a. When the water drop reached the surface of pristine glass with the $\rho_A$ of 0, the spherical shape of the water drop could not maintain. As the surface density $\rho_A$ increased, the hydrophobicity of the coating changed significantly. When $\rho_A$ increased to 0.4~0.6 mg/cm$^2$, the surface turned to be superhydrophobic. Then, the WCA continued to increase with the surface density until the maximum value of 159° was reached. As shown in Fig. 3b, the surface of pristine glass exhibited a smooth surface. However, a lamellar micro-nano roughness structure was formed on the superhydrophbic coating.

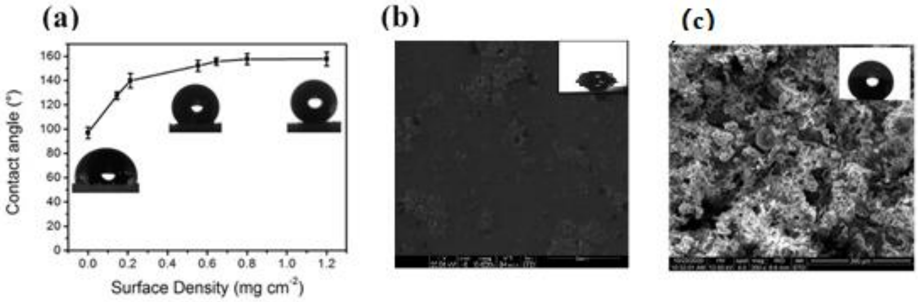


Fig. 3. (a) Variation curve of hydrophobic angle with surface density; (b) SEM image of pristine glass; (c) SEM image of superhydrophic surface with ρA of 0.965 mg/cm$^2$

### 3.2. Morphology of the sugarcane wax coating

As shown in Fig. 4, the convex hulls with micron fluctuation structure distributed uniformly on the surface, which facilitated its superhydrophobic characteristics. Fig. 5a showed that the coated surface was made up of a nanoscale waxy crystals, which was like a flower at higher magnification (Fig. 5b). The micro-nano roughness structure distributed tightly and neatly, resulting in the superhydrophobic properties. The flower-like roughness structure was formed during the rapid volatilization of the ethanol solvent.

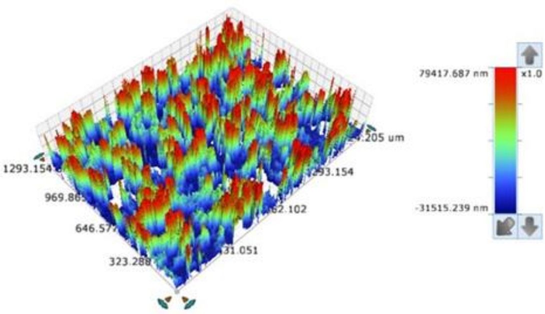


Fig. 4. The roughness of the coating analyzed by white light interferometer

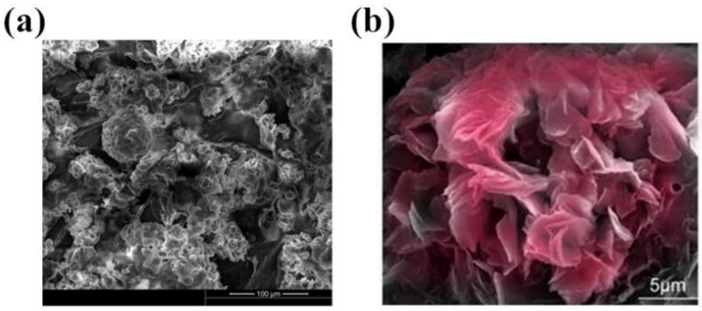


Fig. 5. (a) SEM image of sugarcane wax coating surface; (b) at higher magnification of colored

### 3.3. Contact angle test

The coating prepared from sugarcane wax was sprayed on different substrates and the contact angle of liquid food on the coating was measured. Coatings with sugarcane wax could be applied to different substrates on both soft and hard surfaces (Fig. 6a). The droplets could maintain its spherical shape on different substrate. The WCAs of water, honey, cola and black tea droplets on the surface of the coated glass were measured (Fig. 6b). The WCA of different liquid food on coated glass were all greater than 150°. The results showed that sugarcane wax coating had good superhydrophobic properties to virious liquid food. Moreover, it could be applied to different packaging materials common in life.

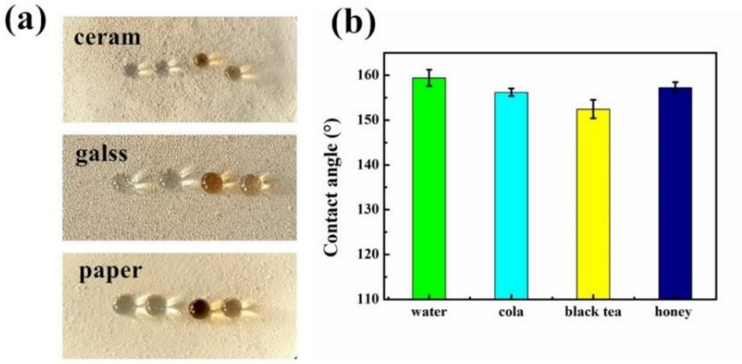


Fig. 6. (a) Photographs of water, honey, cola, andblack tea; (b) The WCA of liquids on coated glass

### 3.4. Heat resistance

The heat resistance of the superhydrophobic coating was investigated because the melting point of sugarcane wax is 70~84℃. To determine whether the sugarcane wax coating withstood the test at this temperature, water at different temperatures was applied to the surface of the coating and the contact angle was measured. As shown in Fig. 7, under the condition of direct contact between sugarcane wax coating and hot water, the contact angle decreases continuously with the increase of temperature. When the water droplets were at room temperature of 20°, they showed a good spherical standing on the coating surface, and the WCA was 161°. When the temperature of water droplets reaches 80°, the contact angle of water droplets on the coating surface decreases greatly. This phenomenon was attributed to the sugarcane wax on the surface of the coating was melted by the hot water droplets, and parts of the rough structure were destroyed. Wax is a superhydrophobic coating made of material, and its temperature resistance should be considered in practical applications. However, the coating made of sugarcane wax can maintain good superhydrophobicity at room temperature and has a good application prospect.

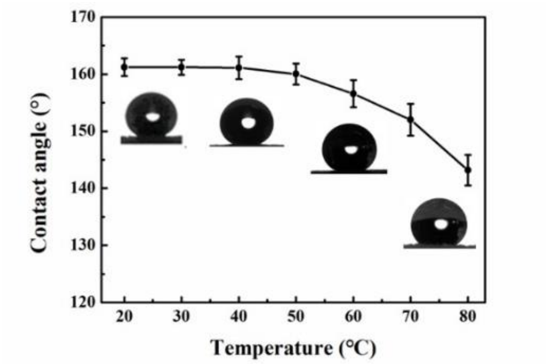


Fig. 7. The change of WCA with hot water temperatures

### 3.5. Robustness

For any research on superhydrophobicity, the firmness of superhydrophobic coatings is an important indicator. If the coating could not adhere tightly, the substrate will lose its superhydrophobic performance easliy. The change of WCA and SA after water impact was measured, which was shown in Fig. 8. The coating exhibited excellent water repellency even after 100 drops with the WCA higher than 150°, proving the firmness of the superhyphobic coating.

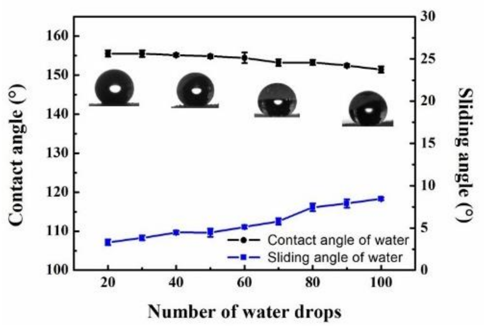


Fig. 8. The WCA and SA of the coating with water droplets

### 3.6. Flexibility

The aluminum foil was bent back and forth as one cycle to test its flexibility. The coating did not come off after the aluminum foil was folded. Fig. 9 showed the change of WCA and SA with folding cycles. After 1000 cycles, the coating remained in good state and kept superhydrophobic, proving its strong resistance to multiple foldings.

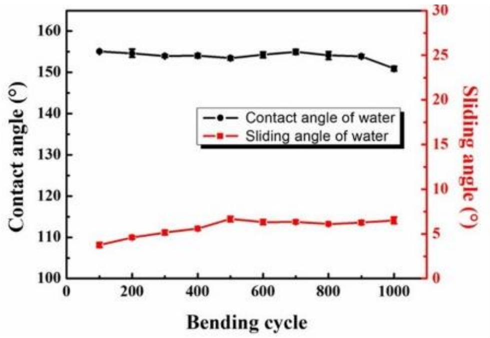

Fig. 9. The change of WCA and SA with bending cycles

### 3.7. Durability

The service life of superhydrophobic coating was determined by its durability. The micron scale roughness structure of the surface resulted in its superhydrophobic property. The physical damages of the coating is a major challenge for its application. The durability was tested by pressing the coating with a finger forth and back (one cycle) as shown in Fig. 2b. After 30 cycles of the pressing, the coating still exhibited excellent superhydrophobic performance (Fig. 10).

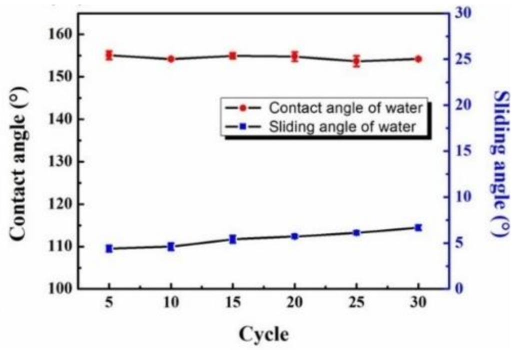

Fig. 10. The change of WCA and SA with pressing cycles

In addition, in order to test the wear resistance of the coating, the coated glass was subjected to abrasion with sandpaper as shown in Fig. 2d. Fig. 11 showed the change of WCA and SA with abrasion cycles. With the cycles of abrasion, the WCA of the coating decreased gradually and the SA increased. After 9 cycles, the coating was still superhydrophobic. Then, the WCA decreased to less than 150°. suffered severe friction damage, but it withstood the test. The coated glass after 0 and 9 cycles was immersed in yogurt as shown in Fig. 12 a-d. The yogurt flowed down easily without adhereing to its surface even after 9 cycles. The photographs of droplets of black tea, honey, yogurt and orange juice on coated surface after o and 9 cycles were also showed in Fig. 12 e and f. After 9 cycles, different kinds of droplets could still maintain spherical shape standing on the coated surface.

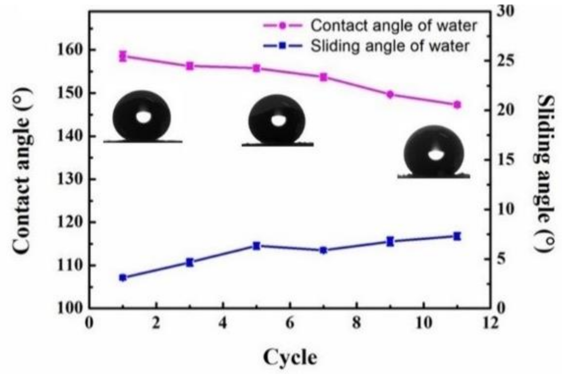


Fig. 11. The change of WCA and SA with abrasion cycles

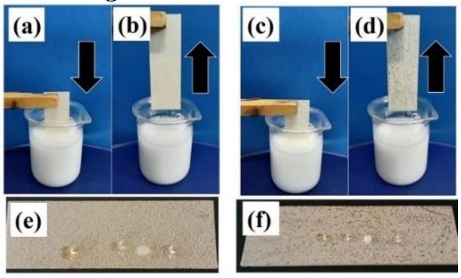


Fig. 12. The coated glass after immersion into yogurt after (a, b) 0 and (c, d) 9 cycles of abrasion; Photographs of droplets of black tea, honey, yogurt and orange juice on coated surface after (e) 0 and (f) 9 cycles of abrasion

### 3.8. Practical application test

The inside of yogurt container was coated with sugarcane wax to test its adhesion performance. Fig. 13 showed the photographs the remaining liquid (honey, juice, chocolate milk and coca-cola) after pouring. The viscous liquid in the sugarcane wax treated container came out easily with a little residue. The liquid residue in the superhydrophobic container was significantly reduced compared to the container without the superhydrophobic coating. The superhydrophobic coating made of sugarcane wax could effectively repel viscous fluids to solve the adhesion problem.

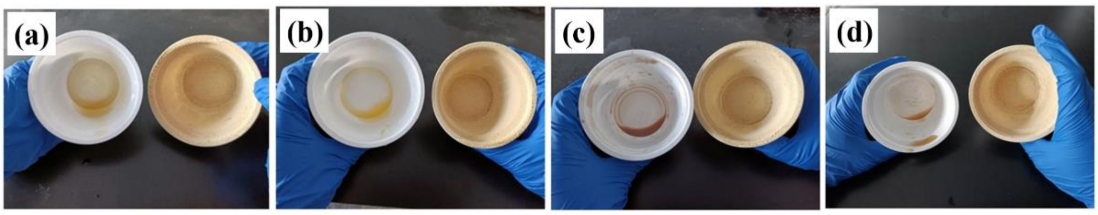


Fig. 13. Photographs of the residue in original cup (left) and sugarcane wax coated cup (right): (a) honey; (b) juice; (c) chocolate milk and (d) coca-cola

### 3.9. Comparison of different wax coatings

It has been reported that paraffin, beeswax, microcrystalline wax and carnauba wax have been used as raw materials for superhydrophobic coatings. Among them, paraffin is a kind of petroleum processing products, belongs to mineral wax. Microcrystalline wax is refined from the residue of petroleum fraction. Beeswax, Carnauba wax is a renewable wax extracted from natural plants and animals. Different types of wax have different chemical compositions, resulting in different properties of the coating. The contact angles and rolling properties of the superhydrophobic coatings prepared by sugarcane wax, paraffin wax, beeswax, microcrystalline wax and carnauba wax angle were compared.

*Table 1*

**The contact angle and sliding angle of the superhydrophobic coatings with different waxes**

| Waxes | Contact angle (°) | Sliding angle (°) |
|---|---|---|
| Sugarcane wax | 158±3 | 7±2 |
| Paraffin wax [29] | 158±3 | 7±1 |
| Beeswax [29] | 162±1 | 7±1 |
| Microcrystalline wax [29] | 161±2 | 5±1 |
| Carnauba wax [29] | 150±2 | 22±1 |

In conclusion, the application of cane wax is more suitable for the concept of sustainable development, because cane wax comes from the cane stem and the raw material is widely distributed in the world. Sugarcane wax, as a pure natural raw material for superhydrophobic coating, is a renewable product, which could increase the added value of sugarcane.

## 4. Conclusion

In this experiment, the edible sugarcane wax was used for superhydrophobic fabrication without adding fluorocarbon materials and silicone resin. The sugarcane wax coating showed the advantages of high surface microstructure strength, long service life and wear resistance. In addition, it is edible and harmless to human body. The coating could be used to reduce low fat liquid food residues on the packaging material, promoting the green and sustainable development. The preparation method of the superhydrophobic coating was easy to operate, fast to produce, low cost, and suitable for large-scale popularization and application.

**Funding:**

This work was supported financially by funding from the Key Scientific and Technological Project of Henan Province (No. 202102210024, No. 152102210099), Key Scientific Research Project of Henan Provincial Education Department (No. 20A150018), High-Level Talent Start-Up Research Project of Henan Institute of Science and Technology (No. 2017043).

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