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Fabrication of superhydrophobic paper surface via wax mixture coating

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HIGHLIGHTS

- The paper surface was rendered superhydrophobic via the phase separation of green-based waxes.
- The key steps consisted of emulsifying, coating and annealing, which could be readily accomplished.
- The entire process for superhydrophobic modification was free of organic solvent and fluorochemicals.
- The wax coating layer showed good transparency and mechanical durability.

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ABSTRACT

Nowadays researches endeavour to prepare superhydrophobic paper surface without using fluorderivates which are harmful to both environments and humans. This research aimed at building microstructure using green-based waxes to prepare superhydrophobic paper surface. There were two main processes. First, wax mixture (beeswax/carnauba wax) was emulsified and coated on paper surface. Then the coated paper was annealed at various temperatures. The surface energy of wax mixture increased slightly as the weight ratio of carnauba wax increased. The further heat treatment rendered wax coated paper from hydrophobic or superhydrophobic to "Lotus" state, because submicrometer structure was produced on the base of micrometer spherical wax particles. The wax coating layer also showed good transparency and stability properties.

1. Introduction

Superhydrophobic surface, defined as high water contact angle (CA > 150°), has attracted much attention due to its unique properties like self-cleaning, anti-contamination, anti-sticking, etc. [1,2]. It is well known that in "Lotus Effect" [3], both of low-energy surface composition and certain roughness are essential to form superhydrophobic surface. Therefore, the principle of technology in fabrication of superhydrophobic surfaces is widely accepted as either roughening the low-surface-energy material surface or reducing surface energy by chemical modification, or combining both. A great number of methods for preparing superhydrophobic surfaces have been proposed over the past decades [4–11]. Apart from the above principle, methods for preparing superhydrophobic surfaces are also designed based on the specific physical and chemical properties of the substrates, such as wet chemical reaction for metal substrates [7–9], electrospinning for polymer solutions [10,11]. Unlike materials such as glass, metal and textiles, cellulose-based paper is relatively weak in physical strength and chemical stability. Therefore, various special treatments have been designed and applied to the preparation of superhydrophobic paper. For example, fluorizated SiO_2 nanoparticles [12], long-chain fluoro-containing SiO_2 nanoparticles [13,14], have been used for coating on paper surface to impart superhydrophobicity. The nano-sized structure could also be obtained by direct reaction on fibre surface via atom transfer radical polymerization (ATRP) of GMA and then post-fluorination [15], or plasma etching followed by fluorocarbon film deposition [16,17]. Unfortunately, those fabrication processes involved more or less fluorine containing chemicals or organic solvents that are dangerous for human health and environment.

It is well known that fluoride treatment can effectively reduce the surface energy which is particularly necessary for some hydrophilic surface. However, fluorderivates are not always indispensable materials to produce superhydrophobic surface. Cassie and Baxter developed a model [18] to describe a wetting state on a rough solid surface where the liquid droplet is actually situated on a solid–air–liquid composite surface instead of penetrating into

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the rough grooves, and the apparent contact angle (θ_c) is the sum of two contributions of a liquid–solid interface and a liquid vapor interface as described below:

$$\cos\theta_c = f\cos\theta + f - 1 \quad (1)$$

where f is the fractional area of solid surface with an intrinsic contact angle θ. According to this equation, the influence of these two factors, f and θ, on the apparent contact angle, is intuitively shown in Fig. 1. The apparent contact angle correlates positively with intrinsic contact angle but negatively with the fraction of water–solid interface area. Based on the above prediction model, any hydrophobic material has a potential to become superhydrophobic through reducing the solid–liquid contact area. More than that, it also shows that the surface roughness is more important in superhydrophobicity at low f levels. For example, when the f value is reduced to 0.01, the difference of hydrophobicity in the original materials seems to be inessential to affect the final apparent contact angle. In some reports when the apparent contact angles of modified surface are larger than 170°, the difference among the surface energies of different functional groups became so trival that it was even regarded as measurement error [19]. Another typical example is the lotus leaf which exhibits a superhydrophobic surface with CA of 161 ± 2.7° and CA hysteresis of 2°. However, the epicuticular wax on the lotus surface only has a contact angle of 110°, which indicates a higher surface energy than most fluorides. The hierarchical micro-/nano-structure play a more important role than the wax hydrophobicity do in the superhydrophobicity of lotus leaf.

In fact, recently some researchers have attempted to render paper substrates superhydrophobic through building mass of micro/nano-structure on normally hydrophobic substrates, endeavouring to avoid using fluorochemicals. Li et al. [20] improved plasma deposition of diamond-like-carbon (DLC) onto paper surface from acetylene precursor instead of pentafluoroethane precursor [16,17]. Ogihara et al. [21] produced superhydrophobic paper surface through spay-coating of dodecyltrichlorosilane modified SiO_2–ethanol suspension. Huet al. [22] used fatty acid to form a thin layer at the surface of precipitated calcium carbonate (PCC) which possessed a hierarchical structure, to lower its surface energy and then coated the suspension of PCC with a polymer latex at paper surface. The coated paper still needed an additional dipping treatment of fatty acid to become superhydrophobic. Soon they improved the PCC modification treatment with hexane instead of water as solvent and the surface with almost zero hysteresis and sliding angle was obtained [23]. The surface energy of PCC could also be reduced by alkyl ketene dimer (AKD) sizing, such that the PCC-cellulose nanofibres coated paper turned superhydrophobic features [24]. AKD, with a low surface energy, could also be able to impart paper superhydrophobic in a condition of enough roughness at the surface. Quan and Werner et al. [25,26] processed the rapid expansion of supercritical solution (RESS) of AKD to produce nanoparticle coating at paper surface which showed extremely high hydrophobicity with a water contact angle up to 173°. The mechanism of fabrication of nanoparticles in RESS could be expanded to removing solvent at extremely high temperature, named as liquid flame spray process (LFS). Stepien and colleagues [27] used LFS to deposit TiO_x and SiO_x nanoparticles on paperboard to control wetting properties. It was found that superhydrophobic surface was obtained with TiO_x while superhydrophilic surface with SiO_x.

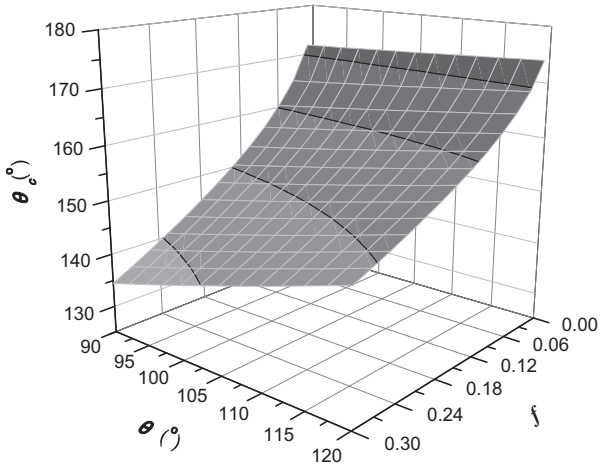

Fig. 1. The theoretical relationship between apparent contact angle (θ_c) and its two factors: intrinsic contact angle (θ) and fraction of water–solid interface area (f).

We committed to develop a low cost and simple procedure to prepare superhydrophobic paper surface that is acceptable for paper making industry. Preliminary studies showed that micrometer wax particles could be produced through emulsifying process, which greatly increases the hydrophobicity of paper after coating on the surface. However, such roughness of wax latex coated paper is not large enough to render the surface superhydrophobic. Another discovery was that at proper temperature different wax phases could be separated from the wax mixture, where the wax with higher melting point kept its solid state and the one with lower melting point melted to flow out. This phase separation process would likely lead to a change of surface morphology. In this study, wax mixture, composed of beeswax and carnauba wax, were firstly emulsified to form wax mixture latex, and then the latex was coated on paper surface. After drying at room temperature, the coated paper was heat-treated for 12 h. In such a way, superhydrophobic paper was prepared simply and cost-effectively. The key advantage of this method is no fluorochemicals and organic solvent involved in the preparation process, which facilitates the industrial application and meet the needs of sustainable development due to green-based materials.

2. Materials and methods

2.1. Materials

Beeswax, carnauba wax and cetytrimethyl ammonium bromide (CTAB) were purchased from Aldrich. A4 copy paper was obtained from Xerox Corporation in a grammage of 75 g/m^2.

2.2. Emulsion preparation

40 mL of 1.25 g/L CTAB solution was added into 10 g of the mixture of molten waxes with different weight ratio of beeswax/carnauba wax in a narrow neck flask in water bath at 90 °C. After a preliminary stirring using a magnetic stirrer for 5 min, the mixture was strongly homogenized (Power Tool X120, Ingenieurbüro CAT, Germany) at a speed of 28,000 rpm for 3 min. Then the hot wax latex was quickly cooled to room temperature in an ice-bath.

2.3. Coating and annealing

A4 copy paper was coated with the above wax mixture latex using a K303 Multicoater (RK Print Coat Instruments Ltd., U.K.) with a bar coating speed of 10 m/min. The coating weight was chosen as 10 g/m^2, which was determined by the diameter of the wire on the bar. After wet coating, the papers were dried at room temperature for an hour. The coated paper was further annealed at different temperatures for 12 h so that minor structure of wax coating layer was produced during the phase separation process.