Journal of Colloid and Interface Science 325 (2008) 588–593

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Preparation and physical properties of superhydrophobic papers

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ARTICLE INFO

Article history:
Received 24 April 2008
Accepted 11 June 2008
Available online 20 June 2008

Keywords:
Superhydrophobic
Wood fiber
Silica
Muliti-layer
Humidity

ABSTRACT

In this study, we developed a facile method for preparing a superhydrophobic paper surface using a multi-layer deposition of polydiallyldimethylammonium chloride (polyDADMAC) and silica particles, followed by a fluorination surface treatment with 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS, $CF_3(CF_2)_5CH_2CH_2Si(OC_2H_5)_3$). The superhydrophobic wood fiber products prepared in this study have contact angles of water greater than 150° and sliding angles less than 5°. Besides their high water repelling property, the superhydrophobic paper products kept a high tensile strength at high relative humidity condition. The superhydrophobic paper products also showed high resistance to bacterial contamination.

1. Introduction

Wood fibers are typical hydrophilic natural materials. With biodegradability, renewability, and low cost, wood fibers have been widely used as package materials. One of the problems of using wood fiber material in packaging containers is its hydrophilicity that results in high water and moisture absorptions. The simple approaches for increasing the hydrophobicity of cellulose paper containers include internal and surface sizing or surface barrier coating. Although paper hydrophobicity can be significantly improved, paper sizing alone cannot meet the high water repellent requirement when paper products are used as food and drink packages. For such applications, barrier coating is the most important technique manufacturing high water resistance paper containers. With regard to the barrier coating layer formation, a wide range of candidates are available, such as organic polymers [1,2], inorganic ceramic and metals [3,4], and sol–gel coating layers [5–8], etc. Polymers are the most common coating materials used for improving water resistance of paper packages. However, thick coating layers, usually >50 μm, must be applied to achieve desired water resistant levels. This does not only result in a high coating cost but also poor paper recyclability. In order to reduce the coating cost, the industry widely uses wax as the barrier coating material. However, because of the low melting temperature, the melted wax forms deposition on paper machine and wood fibers when temperature reduces below its melting temperature. Therefore, waxed papers are unrecyclable.

The common way for increasing hydrophobicity is lowering the surface energy. However, even materials with the lowest surface energy (6.7 mJ/m^2 for a surface with regularly aligned closest-hexagonal-packed $-CF_3$ groups) only around 120° of water contact angle can be achieved for a smooth substrate. There have been numerous recent reports regarding successful generation of superhydrophobic surfaces (water contact angle >150°) by developing a roughness on a substrate surface utilizing lithographic patterning [9,10], laser/plasma etching [11–13], vertical alignment of nanotubes/nanofibers [14–17], sol–gel method [18–20], phase separation [21,22], binary colloidal assembly [23], glancing angle deposition [24], and so forth [25–28]. However, to the best of our knowledge, superhydrophobic paper products have not yet been reported. It is well known that wood fibers are hollow and highly hydrophilic materials. The porous substrate of paper provides multi micro- and macro-channels for water penetration. Therefore, it is very interesting to know if such porous materials can be converted to superhydrophobicity. Undoubtedly, low-coast, superhydrophobic, water-repellant, and self-cleaning fibers can bring a large number of benefits to the paper industry, food package industry, medical supplying industry, and military applications. For example, the biodegradable paper can be extremely interesting materials using for self-cleaning paper packages.

Multi-layer assembly technology has been proven to be a simple and inexpensive way to fabricate various kinds of surfaces with tailored chemical deposition and architecture in micro- and nano-scales [29–32]. The assembly technology also enables the deposition of multilayer films on rough surfaces [33–36]. The character of multi-layer deposition technology holds great promise in fabricating superhydrophobic surfaces on large areas in a simple and inexpensive way. This study focuses on developing a simple and inexpensive way to prepare superhydrophobic paper products using multi-layer deposition method, followed by a fluorination treatment. Three types of paper specimens are prepared for the

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0021-9797/$ – see front matter
doi:10.1016/j.jcis.2008.06.034

comparative study: untreated paper (UP), hydrophobic paper (HP) that was treated by POTS, and superhydrophobic paper (SHP) that was prepared by silica particles deposition, followed by POTS treatment. The resistance to both liquid water and moisture was investigated. The resistance of the superhydrophobic paper specimens against bacterial contamination was also studied.

2. Experimental

2.1. Materials

The silica particles with diameters of about 220 nm, 420 nm, 800 nm, and 1 μm were synthesized according to literature reported method [37]. The reagents used for silica particle synthesis, including tetraethyl orthosilicate (TEOS) (98%), ammonium hydroxide (NH_4OH) (28%), and ethanol (99.5%), were all purchased from Sigma–Aldrich. The top layer of commercial linerboard made from unbleached kraft softwood fiber was used as wood-fiber-based substrate. The aqueous solution of poly(diallyldimethylammoniūm chloride) (polyDADMAC, 20 wt% in water), with molecular weight of 100,000–200,000, was purchased from Sigma–Aldrich. 1H,1H,2H,2H-perfluorooctyltriethoxysilane (POTS, 97%) used for surface hydrophobic modification was purchased from Alfa Aesar. Deionized water purified in an ultrapure water system (NANOpure) was used in all the experiments. Escherichia coli-Ampicillin^R was used as model bacteria for antibacterial contamination test. Luria–Bertani (LB) medium used for growing and maintaining bacteria cultures was purchased from Sigma–Aldrich. All chemicals were used as received.

2.2. Synthesis of silica particles

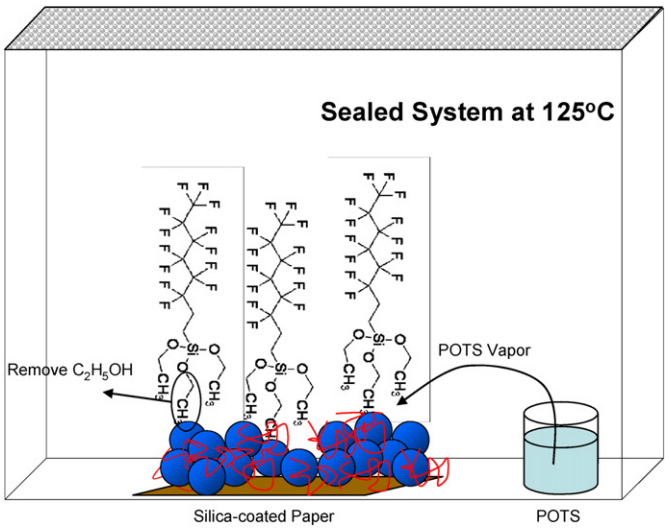
Silica particles were synthesized according to the process described by Stober et al. In the present work, TEOS was hydrolyzed to form silica particles in ethanol with catalyst, NH_4OH at room temperature over a period of two days. Spherical silica particles with a smooth surface were obtained. Silica particles were then dried at room temperature.

2.3. Preparation of silica-coated substrate

Cationic polyDADMAC and anionic silica particles were used for multi-layer self-assembly deposition. PolyDADMAC aqueous solution was prepared by dissolving 1 g of polyDADMAC in 19 g of deionized water, and silica particle suspension was prepared by dispersing 0.2 g of silica particles in 19.8 g of deionized water. The silica suspension was sonicated by ultrasonicator (W-385) for 10 min before use. The negative charged paper substrate was first immersed in polyDADMAC solution for 20 min to render the substrate positively charged, followed by rinsing with deionized water for 1 min. The substrate was then immersed in silica suspension for 10 min, followed by rinsed with deionized water for 1 min. By repeating above steps, a thin film of multilayer polyDADMAC/silica particles was fabricated on the paper surface.

2.4. Surface modification of silica-coated substrate

The surface modification carried out by chemical vapor deposition of POTS was shown in Scheme 1. The silica-coated paper substrate was placed in a sealed vessel, on the bottom of which was dispensed a smaller unsealed vessel within a small amount of POTS. The sealed vessel was then put in an oven at 125 °C to enable the silane groups of POTS vapor to react with the hydroxide groups on the silica surface. After 2.5 h, the paper substrate was removed to another clean sealed vessel and heated to 150 °C for another 2.5 h to volatilize the unreacted POTS molecules on the paper substrate.



Scheme 1. Schematic illustration of the surface modification on silica-coated paper surface.

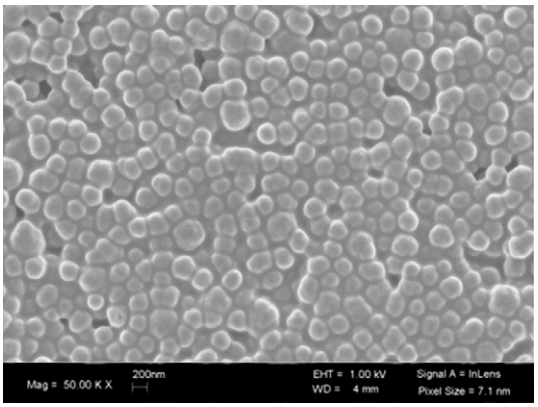


Fig. 1. SEM image of synthesized silica particles with average size of 220 nm.

2.5. Characterization

The surface morphology of the samples was examined with LEO 1530VP field emission scanning electron microscope and Hitachi 800 field emission scanning electron microscope. The specimens were pressed slightly sputter-coated with gold. The water contact angles of the samples were measured by First Ten Angstroms dynamic contact angle analyzer (FTA 200) at ambient temperature with a droplet volume of 0.013 ml. Humidity environment was prepared by a vacuumed oven (VWR 1400E). Lab Master tensile tester (84-91 LTL, Test Machine Inc.) was employed to measure the tensile strength of the samples under different humidity conditions. All the samples were cut into specimens with a dimension of $15 \times 7.25 \times 0.4$ mm^3 before the tension strength measurements.

3. Results and discussion

3.1. SEM Morphology

Fig. 1 showed the SEM micrograph of synthesized silica particles, which had an average diameter of about 220 nm. The silica particles dispersed very well in deionized water after applying ultrasonication. The superhydrophobic surface was fabricated by multi-layer deposition of polyDADMAC and silica particles on linerboard substrate, followed by a fluorination treatment. Fig. 2