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Cellulose nanofibers as binder for fabrication of superhydrophobic paper

Tina Arbatan [a], Liyuan Zhang [b], Xi-Ya Fang [c], Wei Shen [a,*]

[a] Australian Pulp and Paper Institute, Department of Chemical Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia
[b] Center for Material and Fiber Innovation, Institute for Technology Research and Innovation, Deakin University, Geelong, Victoria 3217, Australia
[c] Monash Center for Electron Microscopy, Monash University, Wellington Road, Clayton, Victoria 3800, Australia

HIGHLIGHTS

- Superhydrophobic paper is obtained via a two-step dip-coating method.
- Precipitated Calcium Carbonate (PCC) pigments were used to create a rough coating layer on the surface of paper.
- Cellulose nanofibers were used as binder to form and retain the PCC clusters on the surface of fibers.

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ABSTRACT

This study reports the preparation of superhydrophobic paper via a facile two step dip coating method. In the first step, filter paper samples were dip coated using an aqueous suspension containing Precipitated Calcium Carbonate (PCC) pigments and cellulose nanofibers, to form a highly rough layer on the surface of the filter paper. Subsequently, the coated papers were treated with a solution of alkyl ketene dimer (AKD) in *n*-heptane, which led to the formation of superhydrophobic paper. Contact angle measurements confirmed the superhydrophobic nature of the paper prepared. SEM analysis was also carried out to characterize the surface differences of the coated paper samples with and without the added cellulose nanofibers and to clarify the binding role of cellulose nanofibers. It was observed that cellulose nanofiber is a critical component to the formation of the rough PPC coating layer required for giving superhydrophobicity; it significantly improves the retention of PCC clusters on the surface of the paper and the retained PCC clusters offer the structure of dual scale roughness.

1. Introduction

The phenomenon of superhydrophobicity has attracted a lot of attention in the last two decades. The interest in such highly non-wettable surfaces has led to a great number of studies, ranging in topic from the development of fabrication techniques to the exploration of potential applications [1–11]. Various substrates such as glass, plastic, metal and paper can be rendered superhydrophobic, via routes such as the template method, photolithography and chemical deposition [12]. 'Superhydrophobic paper', in particular, has been the subject of many studies, due to the unique inherent characteristics of paper, such as cost effectiveness, wide availability, versatile bulk and surface properties, flexibility and, most importantly, to the high market requirements in applications such as packaging materials, bioactive paper and lab-on-paper [13]. Superhydrophobic papers have been fabricated via routes such as chemical vapor deposition [14], rapid expansion of supercritical CO_2 solution of AKD [15,16], plasma etching [17,18], ink-jet printing [19], and surface treatments via nano-material deposition [20]. Hu et al. have also utilized commodity papermaking materials to significantly increase the water resistance of paper [21]. Traditionally, improvement of water resistance of paper products in papermaking is achieved via the "internal sizing" process. The internal sizing process typically adds cellulose reactive chemical, such as alkenyl succinic anhydrate (ASA) and alkyl ketene dimer (AKD) to the fiber suspension; the reaction between ASA or AKD with cellulose fibers in the subsequent paper drying process imparts a hydrophobic effect to fibers. This treatment can significantly increase water contact angle with paper (>100°), thus suppressing water wetting of and water penetration in the paper. However, such treatment will not lead to superhydrophobic paper, which is defined by a water contact angle >150° [22]. Shen et al. showed that on AKD-sized paper where water has a contact angle of 124.2°, the fraction of contact between the water drop and the paper surface was 51% [23]. By creating the sufficiently high level of roughness, however, Onda et al. have reported that a thin film of AKD deposited on a glass surface can show extreme water repellency; with water forming a contact angle of 174°, due to the fractal growth of AKD crystal [24]. The fractal growth of the AKD

* Corresponding author. Tel.: +61 3 9905 3447; fax: +61 3 9905 3413.
E-mail address: wei.shen@monash.edu (W. Shen).

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crystal on the glass surface leads to the formation of a highly rough (sub-micro-scale) surface, making such AKD surface superhydrophobic, even though the intrinsic contact angle of a smooth AKD surface was reportedly only 109° [24]. These studies show the possibility of using AKD to achieve superhydrophobicity, provided that the sufficient scale of roughness be formed.

In this study, AKD sizing is used to hydrophobize paper, after PCC pigments have been coated onto the paper to provide a micro- and sub-micro-level of roughness. According to the literature reports, PCC pigments are known to be capable of providing such surface roughness required for superhydrophobicity [21,25]. The challenge is to choose a material which can act as a binder to adhere PCC particles and clusters on the surface of paper fibers, while not occupying much of the inter-particle pores in the PCC clusters so as to minimize the loss of surface roughness due to the presence of the binding material. Under this consideration, cellulose nanofibers were exploited as binder.

Cellulose nanofibers [26–31] have the capacity to be incorporated in sustainable processes such as fabrication of nano-composites and bio polymer coatings. Cellulose nanofibers can be extracted from plants via mechanical, enzymatic, or thermal routes. The most reported engineering application of cellulose nanofibers has so far been in the reinforcement of materials such as composites and polymers, [30,32,33] or as a dry strength agent in the papermaking industry [30]. Cellulose nanofibers have also been used as a binder in making cellulose-graphite nano-composites with potential use in Li-ion batteries [34].

Introducing cellulose nanofibers as a binder, this paper presents a facile two-step dip-coating approach for the surface treatment of filter paper using PCC particles, resulting in the fabrication of superhydrophobic paper upon hydrophobization by AKD.

2. Materials and methods

2.1. Materials

Advantec grade 2 qualitative filter paper (φ = 42.5 mm, made of 100% alpha cotton cellulose according to the manufacturer) was used as the paper substrate. PCC powder (Precarb 100) was obtained from BASF. Our SEM analysis showed that Precarb has a clustered formation of rolling-pin shaped crystallites. AKD wax (WAX 88 KONZ, melting point ≈50 °C) was also obtained from BASF; it was used for paper hydrophobization (sizing) purpose. *n*-Heptane (99.3%) was obtained from Merck; it was used as a non-polar solvent to carry out AKD sizing of paper and coating layer. *n*-Heptane is expected to have the minimal effect on the structure of paper, since it is non-polar and does not cause fiber swelling. Cellulose nanofibers suspension was prepared in situ using the method previously reported in literature [35]. Northern Bleached Softwood Kraft (NIST reference material 8495) was used as the starting material (the average fiber diameter of the obtained cellulose nanofibers was around 47 nm; the estimated aspect ratio was from 109 to146) [35].

2.2. Superhydrophobic paper preparation

As the first step, PCC-cellulose nanofibers coating slurry was prepared and applied onto the filter paper surface via dip coating of the filter paper samples, in order to form micro- and sub-micro-scale of roughness on the paper fibers. Subsequently, AKD sizing was performed to make the coated paper surface superhydrophobic. To check whether variation of cellulose nanofiber content affects the final properties of the prepared superhydrophobic papers, the binder content in the coating slurry was varied while the PCC content was kept constant. The weight ratio of cellulose nanofibers to PCC in the aqueous slurry was varied in the range of 0.01:1–0.05:1 (gram cellulose nanofibers: gram PCC). To prepare the slurry, 1 g of PCC powder was dispersed in 5 ml of distilled water, then the aqueous cellulose nanofibers suspension (1.4 wt.% stock suspension) containing the required amount of cellulose nanofibers (between 0.01 and 0.05 g) was added to the slurry, while the overall volume of the coating slurry was kept constant to 15 ml for all samples. To investigate the effect of binder (cellulose nanofibers) on the wettability of the coated paper and to examine the quality of adhesion between the PCC particles and paper fibers, the same grade of filter paper was dip coated with the slurry containing PCC only (i.e. without cellulose nanofibers as binder) and the as-prepared samples were sized with AKD following the same method described above. Preparation of coating slurry without the cellulose nanofibers was carried out in the same way as those slurries with cellulose nanofibers, except that in this case no cellulose nanofibers was added to the slurry; the paper samples were dip coated using the slurry containing 1 g of PCC dispersed in 15 ml of distilled water.

To dip coat each of the paper samples, 1 ml of the slurry prepared using the above mentioned method was used. The dip coated paper samples were then placed in between two sheets of blotting paper and dried by passing through a drum dryer (Semmer autodryer type MR-3) for 18 min at a set drying temperature of 112 °C.

Subsequently, AKD sizing of the samples was carried out. AKD in *n*-heptane solution (0.6 g/l) was prepared and 1 ml of the solution was used to submerge the samples prior to placing them in an oven at 105 °C for half an hour to cure the sizing. The paper samples were then removed from the oven and cooled to room temperature in a desiccator.

2.3. Coating layer characterization

The surface structure and the wettability of the coated paper samples were analyzed. A JEOL JSM-7001F FEGSEM (2008) scanning electron microscope was used to characterize the following samples: (1) PCC and cellulose nanofiber slurry deposited on a glass slide for observation of the network structure of cellulose nanofibers in PCC layer; (2) PCC coated paper with added cellulose nanofibers as binder, (3) PCC coated paper without added cellulose nanofibers as binder and, (4) AKD sized un-coated paper. An contact angle measurement system (OCA-230, DataPhysics, Germany) was used to measure water contact angles and rolling angles. To measure the water contact angle, a water drop of 5 μl was placed on the sample and the "Ellipse Fitting" method was used to calculate the contact angle. For superhydrophobic PCC coated samples with cellulose nanofibers as binder, rolling angle was also measured. To measure the rolling angle, strips of superhydrophobic paper samples were stuck onto a glass slide, which was then placed on the tilting stage of the instrument. The tilting stage enables fine tuning of the slope of the sample surface. A 5-μl sessile drop of water was then placed on the surface. The slope was changed from 1° to 5° of angle to check and see at what angle the drop starts to roll off the sample surface.

3. Results and discussion

3.1. Water contact angle measurements and SEM images

All the superhydrophobic paper samples, where cellulose nanofibers were used as binder, showed contact angles above 150° (Fig. 1a–c), and rolling angles of less than 5° (Fig. 2). However, changing the cellulose nanofibers content from 0.01:1 to 0.05:1 (gram cellulose nanofibers: gram PCC) had no substantial effect on the wettability of the samples. On the other hand, neither