Fabrication of highly water-repelling paper by surface coating with stearic acid modified calcium carbonate particles and reactive biopolymers

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ABSTRACT

Cellulose paper is the most attractive green packaging material due to its recyclability, renewability, sustainability and biodegradability. In some applications, paper with a high level of water resistance is desirable to meet specific requirements in modern packaging fields. This research aimed to develop a water-repelling paper with cost-effective and nontoxic materials. Commercial precipitated calcium carbonate (PCC) particles were modified by stearic acid (SA) and incorporated with soybean oil-based binder as a water repelling coating agent. The water-repelling efficiency of the coated paper was highly dependent on the ratio of SA / PCC as well as the binder content in the coating formula. PCC particles modified with 12wt% SA were efficient in increasing the water contact angle (WCA) of the coated paper to 146° at a coating weight of 5 g/m². The binder for the coating was synthesized with acrylated epoxidized soybean oil (AESO) through Michael addition reaction. The triglyceride structure in the polymer chain imparted good bio-degradability to the binder polymer. It was found that surface modification of PCC with stearic acid played an important role in improving the WCA of paper. A super hydrophobic paper with a WCA of 162° was fabricated with a coating formula of 60% SA-modified PCC and 40 wt% AESO-binder.

Keywords: Paper; Biopolymer binder; Modified calcium carbonate particles; Coating; Water-repelling; Water contact angle

1. INTRODUCTION

Controlling the surface wettability of cellulosic substrates is important in paper packaging applications. Paper and paperboard may lose physical and mechanical strength through absorbing water during distribution and storage. Traditional methods such as internal sizing and surface sizing could provide a first barrier for paper against water, but often cannot meet the requirements for modern packaging applications. To date, artificial superhydrophobic surfaces with a water contact angle greater than 150° on top of cellulosic paper substrate have been fabricated based on the selection of appropriate methods to create roughness and/or low surface energy,1,2 such as graft polymerization,3 chemical vapor deposition and nanoparticle coating.4 If environment concerns are taken into consideration, low-cost and biodegradable materials are preferable in making superhydrophobic paper. Stearic acid was proved to be an effective agent in reducing the surface energy of ZnO or TiO2 nanostructures and building superhydrophobic surface after coating.5,6 However, the adhesion of those particles on paper surface often requires the incorporation of organic binder such as organosilane,7 polystyrene/tetrahydrofuran solution8 or polymer latex,9 most of which are non-biodegradable. Acrylated epoxidized soybean oil (AESO) is an interesting macromonomer derived from soybean oil. Studies revealed that polymers prepared from co-polymerizations of AESO with monomers such as vinyl monomers, diamines, or anhydrides have several optimized properties and these polymers can be widely used as surface coating or adhesive agents.10-13 Precipitated calcium carbonate (PCC) is widely used as filler for many paper products to decrease the production cost and improve the optical properties of paper.14 It is considered to be a safe and eco-friendly material.

In this paper, we reported the fabrication of a superhydrophobic paper with commercially available PCC particles, stearic acid and AESO. The obtained paper exhibited high water repelling properties in terms of water contact angle. The superhydrophobic paper was expected to have good biodegradability due to the nature of the raw materials.

2. EXPERIMENTAL

2.1. Materials

PCC particles and stearic acid (SA) were obtained from Sigma Aldrich and used as received. Medium porosity filter paper (Fisherbrand, P5) was used as the substrate for the coating trials. AESO, 3-aminopropytriethoxysilane (APTS), benzoyl peroxide (BPO), absolute ethanol and anhydrous acetone were purchased from Aldrich-Sigma.

2.2. Preparation of Water-repelling Paper

Figure 1 shows the concept of preparing a highly water repelling paper by surface coating of filter paper with SA-modified PCC particles and AESO-binder. The hydrophobic modification of the PCC particles with SA was...
carried out according to the method reported by Wang et al.\textsuperscript{5} The SA/PCC ratio was varied from 3 wt% to 15 wt% as detailed in Table 1. The AESO-binder was prepared by mixing AESO in acetone with 30 wt% of APTS as the co-monomer and 0.4 wt% of BPO as the initiator (based on AESO).

The coating slurry was prepared by mixing the PCC powder (modified or non-modified) with the AESO-binder using a homogenizer. For example, 1 g of PCC powder was dispersed in 5 ml of ethanol, and then AESO-binder dissolved in acetone was mixed with the PCC slurry at a weight ratio varied from 0.3:1 to 0.7:1 to yield a smooth slurry. The slurry was coated on the filter paper with a rod coater (K303, Print Coat Instruments Ltd., UK) at a velocity of 3 m/min. The resultant paper was air-dried in a fume hood to remove the solvent, and then cured in an oven at 80 °C for 30 min. in practice, the solvent may be recovered by evaporation and condensation.

![Figure 1 Schematic of highly water-repelling paper and hydrophobic modification of PCC particles with stearic acid](image1)

**Figure 1** Schematic of highly water-repelling paper and hydrophobic modification of PCC particles with stearic acid

![Figure 2 Proposed reactions in the coating process between the cellulose fiber and the coating components](image2)

**Figure 2** Proposed reactions in the coating process between the cellulose fiber and the coating components

Abrero through a Michael addition reaction and provide reactive silanol groups, which in turn could form covalent bonding between the hydroxyl groups of cellulose fibers and PCC particles. The AESO-binder is predominantly consisted with triglyceride structures and therefore believed to possesses good bio-degradability.\textsuperscript{15,16}

2.3. Characterization of Paper Surface

A JEOL 6400 scanning electron microscope (JEOL Ltd., Japan) was used to characterize the paper surface before and after the coating. The water repelling property of the paper was evaluated a water contact angle. The static contact angles of water droplets (3 μl) on the paper surface were determined using an Optical Tensiometer (Attension Theta, Finland).

3. RESULTS AND DISCUSSION

The surface of the original filter paper was super-hydrophilic with a WCA of close to 0° as shown in Table 1. When the coating formula consisted of only the AESO-binder, the WCA of the filter paper increased to 106° after the coating treatment, which indicated a strong hydrophobicity of the AESO-binder. When PCC particles were introduced into the coating formula, the increased of the WCA of the filter paper due to the coating treatment was much more pronounced. This was particularly true for the PCC modified with SA, with a WCA above 136°. The SA modification could have changed the PCC surface from hydrophilic to hydrophobic, by forming a closely packed monolayer of stearate molecules over the PCC surface to results in a lower surface energy of the PCC particles.

| Sample Description | WCA (°) |
|--------------------|---------|
| Filter paper       | 0       |
| Filter paper +binder* | 106±7   |
| Filter paper +binder+PCC | 125±3   |
| Filter paper +binder+3%SA-PCC | 136±5   |
| Filter paper +binder+6%SA-PCC | 139±6   |
| Filter paper +binder+9%SA-PCC | 141±4   |
| Filter paper +binder+12%SA-PCC | 146±3   |
| Filter paper +binder+15%SA-PCC | 146±2   |

*The solid percentage of the AESO-binder in all coating formulas was 20 wt%.

The results in Table 1 also show that with the increase of the stearic acid concentration in the PCC modification process, the water contact angle of the resultant coated paper increased considerably. When the PCC modified with 12% SA was used for the coating formula, the WCA of the resultant coated paper was as high as 146°. However, further increased in the stearic acid concentration above 12% did not result in additional increase of the water contact angle of the coated paper.
The surface morphology of the filter paper before and after the coating treatment was studied by SEM imaging, as shown in Figure 3. The SEM images show that the SA modified PCC particles were firmly attached to the surface of the paper substrate by partly imbedding in the AESO-binder layer. It is interesting to note that in Figure 3(c) the PCC particles modified with 12% SA (labeled as 12%-SA-PCC) protruded from the fiber surface to form a rough surface with three-dimensional micro/nano patterns, which are believed to be more effective in creating air pockets for the increase of WCA. When an excessive amount of SA was applied in the PCC modification, the PCC particles aggregated into larger particles and embedded deeper in the AESO-binder to yield a less rough surface, as shown in Figure 3(d). The surface morphology change explained why higher SA dosage in the PCC modification did not lead to a higher WCA of the coated paper.

Apart from the influence of the SA/PCC ratio, the concentration of the AESO-binder in the coating formula also had an effect on the WCA result. A suitable concentration of AESO-binder is required to firmly anchor the PCC particles on the paper surfaces to minimize the negative effects of detached particles. Figure 4 shows the effect of the AESO-binder content in the coating formula on the WCA of the coated paper.

When the original PCC was used in the coating, the WCA of the coated paper increased only slightly with the increase of the AESO concentration. This can be explained by the relatively low surface roughness, in which case most of the unmodified PCC particles were engulfed in the hydrophobic AESO-binder. In contrast, when the 12%-SA-PCC was used in the coating formula, the WCA of coated paper were much higher, under otherwise the same conditions. A WCA up to 162° was achieved when the AESO-binder percentage was raised from 20wt% to 40wt% in the coating formula. The rougher surface along with the lower surface energy of the coated paper contributed to the observed high WCA, as in the Cassie–Baxter state both hydrophobic solid and air gaps are favorable for the water droplet to rest upon and display super-hydrophobicity (WCA>150°).

On the other hand, the attachment of stearic acid might significantly reduce the surface energy of PCC particles and consequently change dispersion behaviors of the particles in AESO-binder. If less AESO-binder wrapped around the modified PCC particles, more PCC particles would stay in a separate state rather than aggregated together and/or engulfed by the AESO-binder in the coating layer. A 40 % concentration of AESO in the coating formula proved to be sufficient for the adhesion of the PCC particles to the paper substrate without causing harm to the water contact angle. Further increase the AESO content may lead to the embedment of the PCC particles in the binder and loss of roughness of the coating layer, and consequently a decrease of the water contact angle. Therefore, an overdose of the AESO-binder in the coating formula can have a negative effect on the WCA of the coated paper.

4. CONCLUSIONS

In this study, a highly water-repelling paper was successfully fabricated by surface coating with SA-modified PCC and AESO-binder. The hydrophobicity of the PCC
particles was effectively improved by the modification with stearic acid. The water-repelling efficiency of the coated paper in terms of water contact angle was dependent on the ratio of SA/PCC as well as the AESO-binder content in the coating formula. The PCC particles modified with 12 wt% stearic acid was found to be efficient in creating a water repelling surface on paper. A super-hydrophobic paper with a WCA up to 162° was obtained when filter paper was coated with the SA-modified PCC and 40 wt% AESO-binder in the coating formula.

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