Superhydrophobic surfaces with dual-scale roughness and water vapor-barrier property for sustainable liquid packaging applications

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Abstract There is an ongoing unmet global need to manufacture novel sustainable liquid packaging materials, that are not based on plastic film or aluminum foil. Superhydrophobic coating technologies have been proposed for developing more sustainable packaging materials. In this study, the underlying engineering principles for fabricating superhydrophobic surfaces proposed for liquid packaging are investigated, including but not limited to the substrates used and engineering properties of the surfaces. Specifically, to improve the engineering performance of superhydrophobic paper for use in packaging, the feasibility of combining platy montmorillonite (MMT, for its barrier properties) and nano-rolling-pin-shaped precipitated calcium carbonate (PCC, for its superhydrophobicity) into multifunctional coating layers is investigated. Water droplet evaporation experiments are performed to identify how subtle changes in the morphological structures of as-prepared superhydrophobic paper samples can produce a useful roughness structure for packaging applications. Paperboard, which is widely utilized in packaging, is chosen as a substrate to study the challenges of fabricating superhydrophobic paperboards for use in packaging. The results of this study provide engineering principles for using sustainable paper-based materials with a dual-scale roughness structure and barrier properties in liquid packaging applications.

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Introduction

Paper-based materials made of natural cellulosic fibers, such as paper, paper cartons and paper boards, have essential application value in the packaging field because of renewability, biodegradability, processability, flexibility, etc. (Khwaldia et al. 2014; Aloui and Khwaldia 2017; Dal et al. 2020). However, untreated paper packaging has poor barrier properties and easily loses mechanical strength due to the porous structure of cellulosic fibers (Zhu et al. 2018). To overcome these issues, original paper is generally treated by surface coating (Zhang et al. 2021).

Superhydrophobic surfaces with an apparent contact angle equal to or larger than 150° and various adhesive properties, as defined by contact angle hysteresis, have received renewed attention from both the research community and industry (Zhang et al. 2014; Aloui and Khwaldia 2017; Dal et al. 2020). However, untreated paper packaging has poor barrier properties and easily loses mechanical strength due to the porous structure of cellulosic fibers (Zhu et al. 2018). To overcome these issues, original paper is generally treated by surface coating (Zhang et al. 2021).

Demonstrations of water droplets being repelled by superhydrophobic surfaces have been stunning to the public and appealing to the traditional paper industry, which has led to the proposal of developing superhydrophobic surface coatings for use in liquid packaging based on sustainable paper-based functional materials.

Pigment coatings are generally utilized to improve the application performance of paper (Sand et al. 2009). A coating layer must satisfy the following requirements for paper packaging to perform well under humid conditions. First, liquid water must not penetrate into the fiber structures, and second, water vapor must be prevented from entering the paper structure (Rhim 2010; Li et al. 2019a, b; Qin et al. 2020). However, a porous and rough surface structure is required to produce superhydrophobic property (Zhang et al. 2008), whereas a compact and smooth structure is needed to meet the latter requirement (Youm et al. 2020). Thus, it is unlikely that a coating layer based on pigments with a single functionality can resolve this contradiction. Therefore, a dual-functional coating layer with both superhydrophobic and water vapor-barrier properties has been demonstrated to have promising potential for considerable improving outcomes (Hu et al. 2009; Li et al. 2019a, b).
Few researchers have studied the barrier properties of superhydrophobic paper-based materials. Therefore, multifunctional coating layers are fabricated in this study to design a novel sustainable liquid packaging material with superhydrophobic property, as well as the barrier property of paper and paperboard surfaces. Different methods have been reported for fabricating paperboards with superhydrophobic surfaces (Khanjani et al. 2018; Cordt et al. 2020; Jiao et al. 2020; Li et al. 2021a, b). However, these methods involve the use of expensive reagents, harsh chemical conditions, and complex steps, and cannot achieve the barrier property also required for liquid packaging materials. Therefore, it is highly desirable to develop a novel simple and cost-effective method to prepare paper-based materials with superhydrophobic and barrier properties for sustainable liquid packaging applications.

This work addresses water-resistant paper by using common papermaking coating pigments to create a dual-functional coating layer with superhydrophobic and barrier properties. Two kinds of eco-friendly nanoparticles with synergistic effects were utilized to fabricate superhydrophobic paper with high barrier properties: nano-platy montmorillonite (nano-MMT) and nano-rolling-pin-shaped precipitated calcium carbonate (nano-PCC) particles. Water droplet evaporation experiments were performed to identify subtle differences in the surface morphological structures of the as-prepared superhydrophobic paper and thereby select promising morphological structures for liquid packaging applications. Finally, the developed nanoparticle-based superhydrophobic coating was applied to different commercial paperboard samples. In this study, a simple but effective multifunctional coating method has been developed to produce superhydrophobic paperboards with good performance in terms of barrier and superhydrophobic properties as a potential solution for sustainable liquid packaging in the traditional paper industry.

### Materials and experimental method

#### Materials and chemicals

Whatman Grade 4 qualitative filter paper (made of 100% alpha cotton cellulose according to the supplier) and paperboard samples (the properties of which are summarized in Table S1) were obtained from Visy Industries, Australia, and used as substrates. Carboxyl methyl cellulose (CMC) and normal-heptane (99.3%) were purchased from Sigma-Aldrich and used without further purification. AKD wax (WAX 88 KONZ, melting point ≈ 50 °C) was obtained from BASF in the form of pellets. PCC powder (Precarb 200) was obtained from BASF. Ground calcium carbonate (GCC, Imercarb 10) powder was obtained from Imerys Australia. Montmorillonite (MMT) was provided by Rockwood Pigments and Trading Pty Ltd, Australia. The preparation and characterization of cellulose nanofibres have been detailed elsewhere (Zhang et al. 2017). Commercial juice packages (juice boxes) made of six layers of materials, including paper, polyethylene, and aluminum foil were used. Disposable double-wall paper cups were purchased from Kent Paper, Australia.

#### Experimental method

Different morphological structures are constructed on paper surfaces: six kinds of nanoparticle/cellulose nanofiber coating slurries are prepared and applied to filter paper via a dip-coating process. The labels of the prepared samples are presented in Table 1. A nano-PCC coating slurry is also applied

| Table 1 | Labels of the samples investigated in this study |
|----------|-------------------------------------------------|
| Abbreviation | Treatment of paper sample |  |
| NPSH | Paper coated with a nano-PCC coating slurry |  |
| NPMSH | Paper coated by one-step dip-coating with a nano-PCC/nano-MMT slurry |  |
| NMPSH | Paper coated by two-step dip-coating with separate nano-PCC and nano-MMT coating slurries |  |
| NGSH | Paper coated with a GCC coating slurry |  |
| NGMSS | Paper coated with a combination of GCC and nano-MMT coating slurries |  |
| NMSH | Paper coated with a nano-MMT coating slurry |  |
to the paperboard, and the properties of the paperboard samples are summarized in Table S1. NPSH and NMPSH paperboards are prepared by treating commercial paperboard samples with nano-PCC and nano-PCC/nano-MMT nanocomposite coating slurries, respectively, using a modified surface coating method, the Mayer rod coating method, as detailed below. The preparation procedure of the nanoparticles and as fabricated samples for SEM analysis has been detailed in a previously report (Arbatan et al. 2012; Zhang et al. 2017).

Then, the water vapor-barrier property of the NPSH, NGSH, NMSH, and NGMSH filter paper samples is determined under humid conditions (22 ± 1 °C, 95% RH). The details of the experiments performed to measure the sample hydrophobic performance under humid conditions can be found in the Supplementary Information.

Filter paper has a simple composition and can be easily treated by dip-coating, and is therefore chosen as the substrate to study the synergistic effects of the two groups of papermaking pigments. Two methods of surface dip-coating are developed: the first method consists of applying nano-PCC and nano-MMT to the filter paper surface by one-step dip coating (to produce the NPMSH sample), and the second method consists of applying nano-PCC and nano-MMT separately onto the filter paper surface by two-step dip coating (to produce the NMPMSH sample). Further experimental details for the preparation of the nanocomposite-coated surfaced can be found in the Supplementary Information. The water vapor-barrier performance of the NMPSH and NPSH samples is studied by measuring the average water vapor permeability (WVP) of the samples. The details of the experiment performed to determine the water vapor permeability can be found in the Supplementary Information. Noncontact 3D optical profilometer is applied to quantitatively characterize the random roughness structures of NPSH, NMPSH and NPMSH. Details of the experimental procedure for obtaining a three-dimensional (3D) surface map can be found in the Supplementary Information.

The evaporation behavior of a sessile water droplet on the superhydrophobic samples, including NPSH, NGSH, NGMSH, and NMPSH, is analyzed to characterize subtle differences in the morphological structures of the as-prepared superhydrophobic papers. A video-frame sequence of the side profile of the sessile test droplet during the evaporation process is recorded, with the corresponding evaporation times (min) noted below the successive images. The initial width and height of the test droplets on all the samples are measured by ImageJ and summarized in Table S5. Details of the Evaporation experiments can be found in the Supplementary Information.

**Results and discussion**

**Properties of the two groups of papermaking pigments**

The morphological structures of ground calcium carbonate (GCC) are shown in Fig. 1a, where the GCC size varies from micro- to nano-scale. SEM analysis shows that the PCC powder consists of relatively uniform clusters of rolling-pin-shaped crystallites (as shown in Fig. 1b). The morphological structures of nanoscale dimensions of MMT are shown in Fig. 1c. Figure 2 shows that a water contact angle of 165.7° ± 2.6° for the NPSH filter paper; however, the tilt angle of the NPSH sample is very difficult to measure because a water droplet easily rolls off the surface for the slightest tilt of the NPSH sample. The contact angle of the nano-PCC modified filter paper (NPSH) is higher than those of the NGSH, NMSH, and NGMSH samples, in agreement with previously reported results (Arbatan et al. 2012; Zhang et al. 2017). The differences in the contact angles of the samples are most likely caused by the different dimensions and morphological structures of the nanoparticles. As shown in Fig. 1, the rolling-pin-shaped PCC particles have of microscale lengths and nanoscale widths; the blocky GCC particles have micro-scale sizes, and the platy MMT particles have nano-scale sizes. Figure 1b shows microscale clusters of PCC and nanoscale needle points of the rolling-pin-shaped PCC particles resulting in a dual-scale roughness structure for the NPSH sample, that exhibits the best superhydrophobic performance among the investigated samples.

Table 2 shows the water vapor-barrier performance of the NPSH, NGSH, NMSH, and NGMSH filter paper samples: the water vapor resistance is poor for the nano-PCC and satisfactory for the GCC and nano-MMT coating layers. The water vapor-barrier performance of the GCC coating layer is
improved by the addition of nano-MMT particles (as in the NGMSH sample). A material structure needs to be layered and densely packed to achieve satisfactory barrier performance, while being dual-scale and porous to exhibit superhydrophobicity. These diverse requirements place restrictions on the superhydrophobic surfaces applied in packaging. Therefore, the barrier potential of superhydrophobic paper-based packaging needs to be increased to enhance performance. Our results show that a microscale structure in the nano-PCC coating layer is provided by PCC clusters, whereas the spatial organization and orientation of the needle points of the nano-PCC particles provide a nanoscale structure. Therefore, the dual-scale structure of the porous nano-PCC coating layer results in superhydrophobic property (shown in Fig. 2). As expected, the porous structure has poor water vapor-barrier performance. By contrast, MMT particles have an inherently layered nanoscale structure with a high

Fig. 1 SEM images of a micro-GCC particles, b nano-PCC particles and c nano-MMT particles. Scale bars are given in the images

Fig. 2 SEM images of the NPSH filter paper surface consisting of 0.03:1 g cellulose nanofibres: gram nano-PCC: the inset in the left corner shows the contact angle between a water droplet and the NPSH surface; the inset in the right corner is a magnified SEM image
aspect ratio. MMT has a strong tendency to form a densely packed and flat layer during the coating process, increasing the barrier performance against water vapor, liquid water, and gas penetration (Krook et al. 2002; Aloui and Khwaldia 2017; Zhang et al. 2017; Sato et al. 2020).

The porous and dual-scale structure of the nano-PCC coating layer results in superior superhydrophobicity to that of other types of nanoparticles used in this study, and the nano-MMT particles exhibit the highest barrier performance. Therefore, nano-PCC and nano-MMT are selected as copigments in a dual-functional coating layer. In the following section, the synergistic effect of nano-PCC and nano-MMT on forming a coating surface with superhydrophobic and barrier properties is investigated.

### Table 2 Contact angle measurement before and after being exposed in humid conditions for 3 days

|                  | NGMSH (NF:GCC:MMT = 0.03:0.8:0.2) | NPSH (NF:PCC = 0.03:0.1) | NGSH (NF:GCC = 0.03:0.1) | NMSH (NF:MMT = 0.03:0.1) | AKD sized only |
|------------------|----------------------------------|--------------------------|--------------------------|--------------------------|-----------------|
|                  | Before | After | Before | After | Before | After | Before | After | Before | After | Before | After |
| CA               | 162°   | 151°   | 167°   | 144°   | 156°   | 136°   | 127°   | 125°   | 110°   | 63°    |
| TA               | <5°    | ~20°   | <5°    | >20°   | 14.3°  | >20°   | >20°   | >20°   | >20°   | >20°   |

**Fig. 3** SEM images of a the NPMSH surface with 0.8:0.2:0.03 (grams PCC: grams MMT: grams cellulose nanofibers), where the inset in the left corner shows the contact angle between a water droplet and the NPMSH surface; b the NMPSH surface with a 1% solids content of the MMT coating slurry and 3% solids content of the PCC coating slurry, where the inset in the left corner shows the contact angle between a water droplet and the NMPSH surface; magnified SEM images of the c NPMSH and d NMPSH surfaces.
A simple process for fabricating superhydrophobic surfaces with dual-scale roughness and water vapor-barrier property

None of the NPMSH samples (papers coated by one-step dip-coating with the nano-PCC/nano-MMT slurry) are superhydrophobic. All the contact angles on the NPMSH samples are approximately 130°; although the highest contact angle is only 139°, all the NPMSH samples show a pinning effect (the tilt angles are larger than 20°). We previously reported (Zhang et al. 2017) that nano-MMT particles could be built-up onto micro-GCC particles to create an NGMSH surface with dual-scale roughness; however, a similar result cannot be obtained for the NPMSH sample. Figure 3a, c show that the nano-MMT particles tend to assemble into microscale MMT clusters rather than form a layer over nano-PCC particles in the NPMSH coating layer. Even worse, the microscale MMT clusters fill the voids formed by nano-PCC particles and cover the nanoscale needle points of the nano-PCC particles, impairing the dual-scale roughness structures and eliminating the superhydrophobicity of the NPMSH sample. The main reason for this result is that the similarity of the length scales of the structures in the two pigments precludes the formation of a dual-scale roughness structure. Furthermore, mixing these two pigments in the coating formulation disrupts the PCC surface structure, such that the mixed formulation cannot provide the required superhydrophobicity.

A structurally optimized coating layer keeps liquid water out and provides a barrier to water vapor. The outer PCC and inner MMT layers may form such a suitable configuration. This engineering strategy exploits the functionality of each pigment layers, without subjecting the individual pigments to conditions that would deteriorate their properties. Therefore, a simple two-step coating fabrication process is proposed to reduce interference from nano-MMT particles to the dual-scale roughness structures, while exploiting the barrier properties of these particles. Figure 4 is a schematic showing the application of the nano-MMT coating slurry to the filter paper surface to provide a barrier property, followed by application of the nano-PCC coating slurry onto the nano-MMT coated surface to provide superhydrophobicity. The wetting property of the NMPDH samples obtained using different combinations of coating strategies are summarized in Table S2. The optimal coating is identified as a 1 wt% solids content of the nano-MMT coating slurry and a 3 wt% solids content of the nano-PCC coating slurry and used for further study. The nano-MMT particles in the NPMSH sample easily self-aggregate into microscale MMT clusters. By contrast, nano-MMT particles form a densely packed and flat layer beneath the nano-PCC coating layer in the NMPDH sample. Therefore, the dual-scale roughness structure provided by the nano-PCC particles is slightly impaired by coating with the nano-MMT particles. Figure 3b, d show no discernible surface defects caused by coating the microscale MMT clusters onto the NMPDH surface.

The NMPDH sample prepared under the optimal conditions is superhydrophobic with a contact angle of 152.1° ± 3.3°, which is lower than that of the NPSH sample (165.7° ± 2.6°, as shown in Fig. 2). This result can be attributed to the different morphological structures formed on the surfaces on the NPSH, NMPDH and NPMSH samples. A noncontact 3D optical profilometer is used to quantitatively characterize the random roughness structures of the samples (the 3D surface profiles and Rq values are shown in Fig. 5). The 3D surface profile of the NPSH sample shown in Fig. 5a indicates abundant microscale and nanoscale structures with a relatively even distribution of small pits (the areas shown in light and dark blue), where the highest and lowest points are 15,503.412 nm and 54,702.711 nm, respectively (as determined by the...
software). The 3D surface profile of the NMPSH sample shown in Fig. 5b is relatively smoother than that of the NPSH sample, and the difference between the highest and lowest points of the NMPSH sample is smaller than that of the NPSH sample. The 3D surface profile of the NPMSH sample shown in Fig. 5c appears to be considerably smoother than that of the NMPSH surface. The 3D surface profile results are consistent with the measured contact angles on the NPSH, NMPSH and NPMSH samples. The largest contact angle and lowest hysteresis are obtained for the NPSH sample with a dual-scale structure and the

Fig. 5. Three dimensional surface profiles of the prepared surfaces: a the NPSH surface with a 5 wt% solid content (consisting of PCC and cellulose nanofibers); b the NMPSH surface with a 1 wt% solid content of the nano-MMT coating slurry and 3 wt% solid content of the nano-PCC coating slurry; c the NPMSH surface with 0.8:0.2:0.03 (grams PCC: grams MMT: grams cellulose nanofibers, for which the water contact angle ~ 139°). $R_q$ notes the root-mean-square roughness.
 roughest surface, whereas the smallest contact angle and highest hysteresis are obtained for the NPMSH sample with the smoothest surface. Considering the overall requirements of liquid packaging, the NMPSH sample is acceptable as a superhydrophobic substrate with barrier properties, although its superhydrophobicity is weaker than that of the NPSH sample. A simple two-step dip-coating process for fabricating superhydrophobic paper surfaces with barrier properties using nano-PCC/nano-MMT has thus been developed.

The water vapor-barrier performance of the NMPSH and NPSH samples is evaluated in terms of testing the average water vapor permeability (WVP) of the samples. The WVP reflects the ability of a film to resist water vapor penetration under specified relative humidity and temperature conditions (22 ± 1 °C, 95% RH). A lower WVP indicates a high water vapor-barrier performance. In Fig. 6, the control sample is a pristine filter paper, and a juice package and disposable cup are also tested to indicate the performance of commercial packaging materials. Commercial packaging materials consist of uniform layers of aluminum foil and polyethylene, which provide good moisture penetration resistance. The WVP of the control sample is almost ten times that of the disposable cup and twenty times that of the juice packaging. The WVPs of the commercial packaging materials are considerably smaller than those of the NMPSH and NPSH samples. In Fig. 6, the WVP of the NPSH sample is lower than that of the control, which indicates that the nano-PCC coating layer provides some resistance to water vapor penetration. Therefore, the nano-PCC coating layer both confers superhydrophobicity to the filter paper and improves the water vapor-barrier performance of the paperboard. The WVP of the NMPSH sample is lower than that of the NPSH sample, indicating that the water vapor-barrier performance of NMPSH is superior to that of the NPSH sample. The difference between the two corresponding WVPs is not substantial but provides direction on how to improve the barrier performance of the NPSH sample. In the future, we will treat nano-MMT particles to prevent swelling to improve their barrier performance.

Synergistic effects between water vapor-barrier performance and superhydrophobic durability

The relationship between the water vapor-barrier performance and the hydrophobic stability of the NPSH and NMPSH surfaces is investigated by observing the change in the contact angle under humid conditions (22 ± 1 °C, 95% RH). Figure 7 shows the changes in the contact angles of the NPSH and NMPSH surfaces while being exposed to humidity. The contact angle of the NPSH sample is initially considerably larger than that of the NMPSH sample but gradually

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Fig. 6 Average water vapor permeability (×10⁻¹⁴ kg m⁻¹ s⁻¹ Pa⁻¹) for various surfaces

Fig. 7 The apparent contact angles of different samples as a function of the exposure time under humid conditions (22 ± 1 °C, 95% RH)
decreases with the exposure time. By contrast, the contact angle of the NMPH sample changes little with the exposure time. After being exposed to humid conditions for 72 h, the NPSH sample loses its superhydrophobicity (the contact angle ~ 144°), whereas the NMPH sample remains superhydrophobic with a contact angle of ~ 151°. The contact angles of the NPSH and NMPH samples gradually stabilize after a certain exposure time. The main reason for the decrease in the contact angle of the NMPH samples is that the surface morphological structure of the superhydrophobic samples gradually changes due to the swelling of the cellulose fiber in the base paper. The surface morphological structure only changes slightly after hygroscopic equilibrium is achieved. Accordingly, the contact angle stabilizes. Table S3 summarizes the tilt angles of the NPSH and NMPH samples with increasing exposure time. That is, with increasing exposure time, the tilt angles increase for the NPSH sample and only change slightly for the NMPH sample. These results indicate that the swelling of the paper fiber is inhibited by the water vapor-barrier provided by the nano-MMT coating layer. This barrier also prevents damage to the dual-scale structure of the nano-PCC coating layer and maintains the superhydrophobicity. We therefore conclude that the use of nano-MMT and nano-PCC in a nano-composite coating layer results in synergy between the water vapor-barrier performance and the superhydrophobic durability for the NMPH sample.

Relating the dynamic wetting performance to subtle differences in the morphological structures of superhydrophobic surfaces

It is well-known that the interaction between water and packaging materials involves dynamic contact; therefore, it is important to determine the dynamic wetting performance of packaging materials. Superhydrophobic surfaces with different morphological structures exhibit different contact angle hysteresis, and the contact angle hysteresis affects the dynamic wetting performance of superhydrophobic surfaces. Many researchers have found evaporation studies to be a practical means of studying the dynamic wetting phenomenon (Fernandes et al. 2015; Zhang et al. 2016; Aldhaleai et al. 2020; Han et al. 2020). In this section, the evaporation behavior of a sessile water droplet

![Fig. 8](Images of the evaporation of a 9 μL water droplet on various surfaces. The corresponding evaporation time (min) is noted below the successive video frames obtained by the contact angle measurement system and processed using ImageJ)
on the superhydrophobic samples, including NPSH, NGSH, NGMSH, and NMPSH, is analyzed to relate the dynamic wetting performance with subtle differences in the morphological structures of the surfaces.

Figure 8 shows the video-frame sequence of the side profile of a sessile test droplet taken during the evaporation process, where the corresponding evaporation times (min) are noted below the successive images. Table S4 shows the initial width and height of test droplets on all the samples measured by ImageJ. The NPSH surface is used as an example to characterized the evolution of the evaporation of a test droplet on a sample. The evolution is slow and consists of three stages. Initially, the contact angle remains constant, while both the drop height and contact radius with the NPSH surface decrease. After a small contact radius has been reached, both the drop height and contact angle decrease concomitantly, thus maintaining an essentially constant contact radius. Finally, the contact angle, height, and radius all decrease as the drop volume tends to zero. The drop on the NPSH surface maintains a nearly constant contact angle (CCA) over much of the evaporation period, and a dynamic wetting transition from a constant contact angle to a constant contact radius occurs at approximately 50 min. The onset time for this transition during the evaporation process varies across samples: ~40 min for NGMSH; ~30 min for NGSH; ~15 min for NMPSH. This variation is attributed to the pinning of the triple contact line of the test droplet on the sample surface. Once pinning occurs, the contact mode transitions from a suspended state to a collapsed state. The onset of pinning is related to subtle differences in the morphological structures of the superhydrophobic surfaces. Moreover, constant contact radius (CCR) is observed for the sessile droplet on the two hydrophobic samples, NMSH and AKD sized samples during the entire evaporation period. This result is also attributed to the pinning of the triple contact line due to water collapsing into the fine structures of the NMSH and AKD sized samples at the beginning of evaporation process.

Fabrication of a nano-(PCC/MMT) nanocomposite coating layer on paperboard

Commercial paperboard samples are treated by nano-PCC and nano-PCC/nano-MMT nanocomposite coating slurries to prepare NPSH and NMPSH paperboards, respectively. The paperboard samples have quite different surface properties (hygroscopicity, composition, and morphological structure) from those of filter papers and therefore cannot be effectively treated using the dip-coating method. The Mayer-rod coating method is attempted to treat paperboard samples with a nanoparticle coating slurry, the viscosity of which is adjusted utilizing carboxymethylcellulose (CMC). A nano-PCC coating slurry is taken as an example to investigate the effect of CMC on the coating structure formed by the nanoparticle slurry.

Different average molecular weights and dosages of CMC are added to the nano-PCC coating slurry. First, CMC with three average molecular weights, ~700,000, ~250,000, and ~90,000, are used to adjust the viscosity of the nano-PCC coating slurry. The CMC with the highest average molecular weight (~700,000) easily forms a sticky film on the paperboard surface and impairs the dual-scale roughness structure provided by the nano-PCC particles, whereas an excessively high dosage of the CMC with the lowest average molecular weight (~90,000) is required to achieve an acceptable viscosity. Therefore, the CMC with the medium average molecular weight (~250,000) is chosen for further study. Second, the effect of using the CMC with the average molecular weight of ~250,000 at the dosages of 1.0 wt%, 0.5 wt%, and 0.1 wt% is studied. A sticky film is formed on the modified surface that interferes with the dual-scale roughness structure at a dosage of 1.0 wt% (based on the weight of the total coating slurry), whereas the viscosity of the coating slurry at a dosage of 0.1 wt% (based on the weight of the total coating slurry) does not satisfy that required for the Mayer-rod coating process. Therefore, a CMC dosage 0.5 wt% (based on the weight of the total coating slurry) is used.

Figure 9 shows the superhydrophobic paperboard surfaces prepared under different conditions. Figure 9a shows the superhydrophobic paperboard surface prepared using 0.5 wt% of the CMC with an average molecular weight of ~250,000; the dual-scale roughness structure provided by the nano-PCC particles is not impaired by CMC addition, and the contact angle is 161° ± 3.1°. Figure 9b shows the superhydrophobic paperboard surface prepared using 1.0 wt% CMC. The microscale cluster of nano-PCC particles is clearly covered by a sticky film, and the water
Fig. 9 SEM images of the paperboard treated with the nano-PCC coating slurry and a CMC dosage of a 0.5 wt% and b 1.0 wt%. The CMC average molecular weight is ~ 250,000.

Fig. 10 The average water vapor permeability ($\times 10^{-14}$ kg m$^{-1}$ s$^{-1}$ Pa$^{-1}$) of the paperboard samples before and after treatment with nanoparticle coating slurries.

The contact angle of the surface is only $127.0^\circ \pm 2.8^\circ$. Fig S3 shows images of an FM100 paperboard (where FM denotes the product code, and 100 denotes the basis weight of the paperboard in g/m$^2$, which is the nomenclature used for the other paperboard samples), before and after being treated with the nano-PCC coating slurry under the optimal. The contact angle on the NMPSH paperboard under the optimal CMC dosage (0.5 wt%; ~250,000) is $153.2^\circ \pm 2.9^\circ$.

The effect of the nanoparticle coating layers on water vapor-barrier performance of the treated paperboard samples is investigated by determining the average water vapor permeability (WVP) of the NPSH and the NMPSH paperboards. Figure 10 shows the WVP of the paperboard samples (Table S2 summarizes the properties of the pristine paperboard samples). The WVPs of both paperboards are reduced after being treated with the nano-PCC and the nano-(PCC/MMT) coatings. The WVPs of the NPSH paperboard samples are always lower than those of NMPSH paperboard samples, which indicates that the nano-MMT coating has an important effect on the barrier properties of the samples. The WVP percentage reduction is defined as follows:

$$\text{Percentage reduction} = \frac{\text{WVP of pristine sample} - \text{WVP of modified sample}}{\text{WVP of pristine sample}}$$

Taking the NPSH paperboard samples as examples, the WVP percentage reduction is 14% for the NPSH-SC100 sample and 30% for the NPSH-FM100 sample. The starch coating of FM100 results in a higher moisture sensitivity than SC100. These results indicate that nanoparticle coating treatment can improve the water vapor-barrier performance of moisture-sensitive samples.

Conclusion

In this study, a dual-functional coating surface with both water vapor-barrier and superhydrophobic
properties is obtained by utilizing the synergistic effect of nano-MMT and nano-PCC particles; the results of a moisture exposure experiment show that the nano-MMT coating layer both enhances the barrier performance and stabilizes the superhydrophobicity of the NMPSH sample. Evaporation studies show that the dynamic wetting of the superhydrophobic surface depends strongly on the surface morphological structures, and subtle differences in these structures can affect the onset of the pinning of the three-phase contact line. Finally, superhydrophobic paperboard samples with different barrier potentials are fabricated by a simple surface coating method. Paper samples with superhydrophobic and low-adhesive dynamic wetting properties (low contact angle hysteresis) do not exhibit high barrier performance, whereas superhydrophobic paper with hierarchical roughness structures and modified barrier properties has high application potential for paper-based packaging.

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Author contribution XZ wrote the manuscript and conducted all the fabrication and characterization of the superhydrophobic paper samples. HJ-Z helped with his expertise in 3D optical profilometer and knowledge about properties of cellulotic fibers. YC performed the SEM measurements. WS and LY-Z planned and supervised the whole project and are responsible for all correspondence. All authors contributed to the writing of the manuscript.

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Availability of data and material Additional information, including materials and chemicals used in this study, experiment details, and supporting figures and tables mentioned in the text, is available in the supplementary information.

Declarations

Conflict of interest The authors have no conflicts of interest to declare that are relevant to the content of this article.

Human and animal rights This is not research involving Human participants and Animals.

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