Supplementary Information

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

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Experimental Details

Preparation of nanocomposite-coated surfaces

For nano-PCC coatings, a known quantity of nano-PCC particles was dispersed in given mass of distilled water, then the aqueous cellulose nano-fibre suspension was added to the slurry, while solid (including PCC and cellulose nano-fibres) content of the nano-PCC coating slurry was kept constant at 5 wt. % for all samples. After dip coating, the samples were then dried for 48 hours at the constant temperature and humidity of 23±1 ℃ and 50±2 %. Paper coated by nano-PCC coating slurry was referred to as NPSH.

In order to investigate the combination effect of nano-PCC particles and nano-MTM particles on the wettability and barrier property of the coated paper, different surface coating methods were developed. The first method was to blend the nano-PCC particles with nano-MTM particles together to prepare the mixing coating slurry. The weight ratio of PCC to MTM in the aqueous slurry was ranged from 0.9:0.1 to 0.5:0.5 (gram PCC: gram MTM), with the other steps the same as described above. Paper made by one step of dip-coating with nano-PCC/nano-MTM slurry was referred to as NPMSH in all sections below. The second method was to separately apply the nano-MTM coating slurry and nano-PCC coating slurry onto the filter paper surface in two steps by first dip-coating the filter paper with nano-MTM coating slurry (the solid content of nano-MTM coating slurry ranging from 1 wt. % to 5 wt. %) followed by dip-coating with nano-PCC coating slurry (the solid content of nano-PCC coating slurry ranging from 1 wt. % to 5 wt. %). Paper made by two steps of dip-coating with separately nano-MTM coating slurry and nano-PCC coating slurry was referred to as NMPSH in all sections below.

For GCC, nano-MTM, and the combination of GCC and nano-MTM coatings, the slurry preparation and drying procedures were the same as those of the nano-PCC coating, and the details was described in the previous work (Zhang et al. 2017). Paper coated by GCC coating slurry was referred to as NGSH; paper coated by nano-MTM coating slurry was referred to as NMSH; paper coated by the combination of GCC and nano-MTM coating slurry was referred to as NGMSH in all sections below.

Modification of nanocomposite-coated surfaces

All the nanocomposite-coated paper (including filter paper and paperboard) samples are treated by AKD, a process known as sizing in papermaking industry. A known quantity of AKD wax is dissolved in n-heptane to form a solution of 1.5 g/l. The coated samples are dipped into the solution to perform solvent-AKD sizing. To cure the sizing effect, the sized samples are put into an oven at 105 ℃ for 0.5

h. The samples are then cooled at room temperature in a desiccator for 48 h to continue the curing of sizing.

Coating layer characterization

Scanning electron microscope (SEM) characterization. The morphological details of the samples are characterized by an FEI NanoSEM 450 field emission scanning electron microscope (SEM). To take the SEM images of nanoparticles, one drop of water/nanoparticles suspension is dropped on a silicon wafer mounted on conductive carbon adhesive tabs to dry in air. For paper samples, they are cut into small pieces and stuck on conductive carbon adhesive tabs directly.

Contact angle measurements. Water contact angles and tilt angles of all paper samples are determined by a contact angle measurement system fitted out a tilting stage (OCA-230, DataPhysics, Germany). The volume of water droplet is 5 μL, unless specifically noted. Five different regions of the paper samples are measured and the average is calculated.

Three-dimensional (3D) surface map. The quantitative information about the morphological structures of the as-prepared surfaces is analysed by a three-dimensional (3D) surface measurement system (Contour GT–I 3D optical profilometer, Bruker, Australia). The measurement details can be found in previous research (Zhang et al. 2017). An area of ~1 mm×1.3 mm of a sample (determined by the analysis software of the profilometer) is chosen to be analysed. The 3D surface profile and the root-mean-square roughness (R_q) of the samples are given to explain the reasons for the difference wetting performance of the as-prepared surfaces.

Performance characterization of as-prepared surfaces

Water vapour permeability. In order to investigate the water vapour-barrier property of the as-prepared surfaces, the water vapour permeability (WVP) of the samples is tested. Water vapour permeability rate (WVPR) of all the samples is determined according to the standard gravimetric method (ASTM E96-10). All paper samples were conditioned at 22±1℃ and 50% RH for 48 h before being tested. The fabricated paper samples were fixed on the top of a vapometer cup containing a hygroscopic salt (calcium chloride). The test assembly was weighed and placed in a condition-controlled chamber (22±1℃ and 50 % RH). WVP is calculated based on the water vapour transmission rate (WVTR) according to the following formula:

$$\mathrm{WVP} = \frac{WVTR*d}{S(R_1-R_2)}$$

where *d* (m) is the thickness of paper sample, *S* is the saturation vapour pressure at the testing temperature, R_1 is the relatively humidity at the test chamber, R_2 is the relative humidity at the vapour sink. The unit of WVP is 10^{-14} kg.m^{-1}. s^{-1}. Pa^{-1}.

Hydrophobic performance under humid conditions. Water vapour-barrier performance of the samples is also tested in harsh humid conditions with 95% relatively humidity (RH) to indicate the super-hydrophobic stability of the samples. If the sample performs poor water vapour-barrier, the water vapour will easily penetrate from one side of the sample to another side which is isolated from the humid conditions; the contact angle of the isolated side will decrease. As shown in Fig. S1, in order to be isolated from the humid atmosphere, one face of the samples was sealed using water-proofing tape onto glass slides, and then the glass slides attached with paper sample were kept in a container which could be completely sealed. A beaker holding 50 ml distilled water was placed into the container to provide the 95 % relatively humidity (RH), and then the sealed container was placed at ambient atmosphere for determined time. The samples were peeled from the glass slides to test the contact angles and tilt angles of the isolated sides at determined exposure time (shown in Fig. S2).

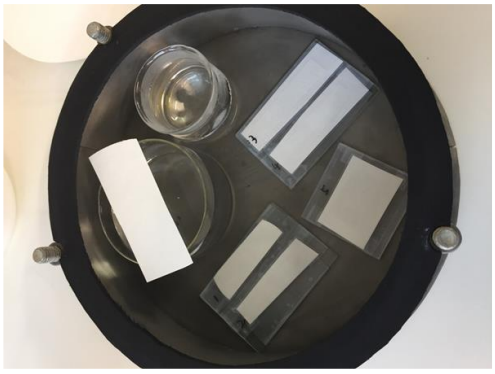

Fig. S1 the test assembly for investigating the water vapour-barrier property of the samples in harsh humid conditions: 20 ℃, 95 % RH (provided by distilled water in the completely sealed container).

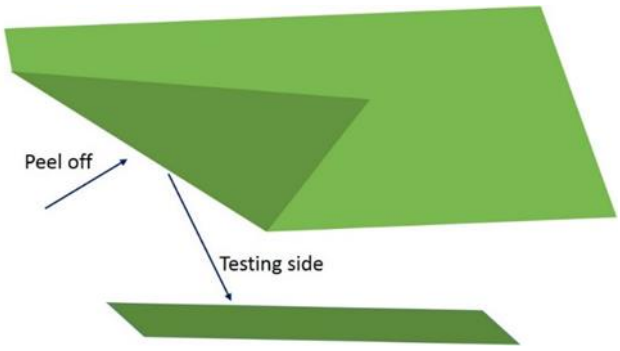

Fig. S2 Schematic illustration of the testing side for the contact angle measurement to indicate the water vapour-barrier property of the samples in harsh humid conditions (20 ℃, 95 % RH).

Evaporation experiments. Before performing the evaporation experiments of water droplets on paper samples, all paper samples are preconditioned under the experimental conditions (22 ±1 ℃ and 40 ± 5 % RH) for 48 h. In an experiment, a water droplet of 9 µL is gently deposited on the sample using a micro pipette, and data acquisition commences immediately after the droplet deposition. The evaporation processes on different samples are monitored by the mass loss of the water droplets using a 4-digits analytical balance which is interfaced by a PC. The side-view profile evolution of the droplet is captured using the contact angle apparatus (OCA-230, DataPhysics, Germany).

Supporting Images and Tables

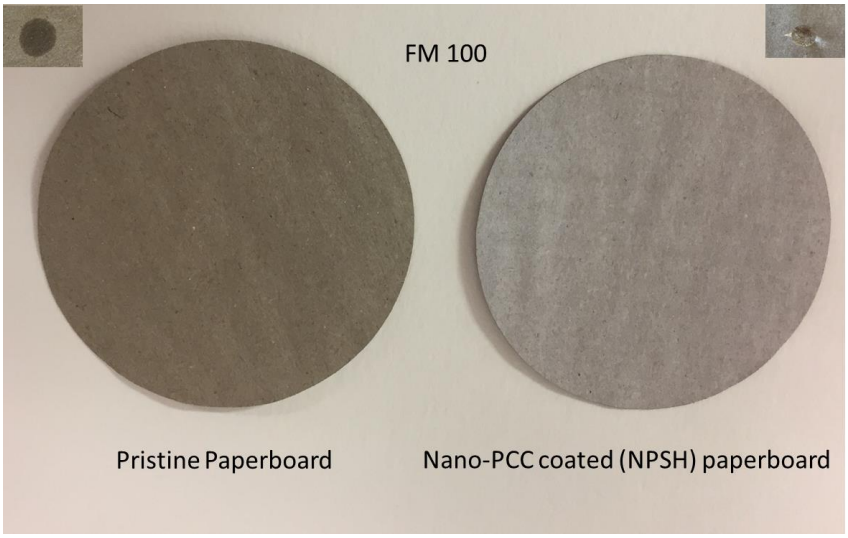

Fig. S3 Images of FM100 paperboard before and after being treated with nano-PCC coating slurry: the inset images showed the wetting property of the samples.

Table S1. Summary the properties of the paperboard samples.

Sample	Basis weight (g/m2)	Starch coating	Calendering	Fillering
SC100	100	Y	SC	Y
FM80	80	N	C	Y
FM100	100	N	C	Y
FM135	135	N	C	Y
FM165	165	N	C	Y

Notes: “Y” stands for “Yes”; “N” stands for “No”; “SC” stands for “Super Calendering”; “C” stands for “Calendering”.

Table S2. Summary of the wetting property of NMPSH samples in different combinations of coating conditions.

Solid content of PCC coating slurry (wt. %) \ Solid content of MTM coating slurry (wt. %)	1	2	3	4	5
1	N	N	N	N	N
2	N	N	N	N	N
3	Y	Y	N	N	N
4	Y	Y	Y	N	N
5	Y	Y	Y	Y	Y

Notes: “N” stands for the corresponding modified filter paper surface without super-hydrophobicity; “Y” stands for the corresponding modified filter paper surface with super-hydrophobicity.

Table S3. The change in the tilt angles with the exposure time for different samples under humid conditions (22±1 ℃, 95 % RH).

exposure time (h)	sample (tilt angle)	
	NMPSH (˚)	NPSH (˚)
0	15.4	<2
12	15.6	11.7
36	16.1	>20
48	17.2	>20
60	17.8	>20
66	18.3	>20
72	18.6	>20

Table S4. Summary of the initial states of water droplets on all the samples at the evaporation experiment.

Samples	Contact angle (˚)	Tilt angle (˚)	Width (mm)	Height (mm)	Evaporation time (min)	Surface property
NPSH	165.7	<2	0.691	1.102	63.04	Roll-off SH
NGMSH	162.4	<2	0.734	1.054	59.74	Roll-off SH
NGSH	156.7	9.8	0.863	0.982	55.78	Sticky SH
NMPSH	151.4	15.4	0.920	0.924	49.18	Sticky SH
NMSH	127.5	>20	1.343	0.679	43.57	H
AKD	115.9	>20	1.421	0.597	38.29	H

Notes: the width and height values refer to the initial states of the water droplets on all kinds of samples; “SH” means super-hydrophobic, “H” means hydrophobic.

Reference

Zhang X, Batchelor W J, Shen W (2017) Building dual-scale roughness using inorganic pigments for fabrication of super-hydrophobic paper. Ind Eng Chem Res 56:3618-3628. https://doi.org/10.1021/acs.iecr.7b00225