



One-pot waterborne superhydrophobic pigment coatings at high solids with improved scratch and water resistance



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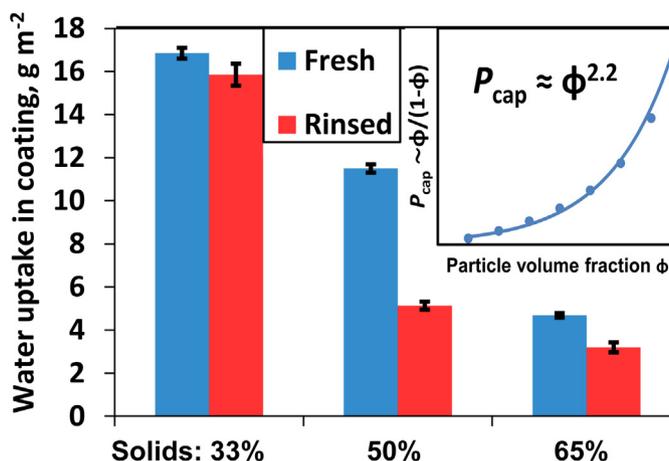
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HIGHLIGHTS

- A one-pot waterborne superhydrophobic coating.
- Sustainable components based on calcium carbonate and fatty acid.
- Improved water and scratch resistance at high solids content.

GRAPHICAL ABSTRACT



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ABSTRACT

A pigment coating was developed to achieve superhydrophobicity in one step from a waterborne formulation containing aragonite calcium carbonate, hydrophobized using sodium oleate, latex binder and cross-linker. Coatings formulated ≤ 50 mass% and applied to polyethylene coated paperboard substrates displayed typical superhydrophobic features: water contact angles $\geq 150^\circ$, low roll-off angle and low stain sizes, but poor scratch and water resistance as well as foaming issues during preparation. Reformulation at higher solids content significantly improved scratch and water resistance properties. Water rinsing of the dried coatings further increased the water barrier capacity due to reduced surfactant-assisted wetting; findings were corroborated by detailed surface chemistry analyses showing the removal of surface-active components after water rinsing of the dried coatings. A plausible cause for the improved durability is the fact that capillary forces increase exponentially with increasing pigment volume fraction (power law exponent of 2.2) leading to efficient binder coverage during the early stage of pigment coating consolidation.

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1. Introduction

Superhydrophobic surfaces are of wide interest in a variety of technological applications, e.g. corrosion protection [1,2], anti-icing coatings [3–5], protection of electrical components [6] and extreme water resistance of papers [7] and fabrics [8]. Demanding applications such as anti-icing may however not be suitable cases for superhydrophobicity because of that the surface features may not retard but instead promote formation of frost [5]. Studies generally report the method of preparation, the superhydrophobic properties together with discussion of the applicability [9,10]. The growing interest of these water repellent surfaces with very high water contact angles, often above 150°, started by studies imaging the surface structure of the lotus leaf [11,12] vis-à-vis its self-cleaning capability, displaying the combination of micro- and nanoscale surface roughness together with a low surface energy wax layer found to be the key to obtain superhydrophobic properties (high water contact angles, low contact angle hysteresis and low roll-off angle). All surfaces having high water contact angles do not necessarily exhibit the lotus effect; surfaces may show high adhesion to water associated with partial penetration of some of the structural features [13].

Two generalized models exist for wetting of rough surfaces. The Wenzel regime [14] describes the situation when the surface is completely wetted by the liquid and is characterized by a large contact angle hysteresis (CAH). A rough surface has a larger solid–liquid interfacial area than its perfectly smooth counterpart, leading to an increase in contact angle. The Cassie–Baxter regime [15] describes when the liquid rests on top of the rough surface features having air trapped underneath. These models give two types of interfaces, viz. a composite air/vapor–liquid–solid or a liquid–solid interface, in which the latter gives higher liquid adhesion. In practice, wetting behavior combining both regimes are common and transitions are encountered by e.g. applying an external pressure or by changing the surface tension of the liquid by adding a wetting agent [16–18].

The mechanism behind interactions between hydrophobic surfaces in aqueous media has received great attention ever since the first measurements displaying interaction forces [19] too long-range to be a result solely of van der Waals forces [20–22]. Cavitation or bridging bubbles due to dissolved gas has become the most widespread explanation [22–27] by observing the similarities to capillary forces between a hydrophilic surface in air as well as by imaging air cavities next to a hydrophobic surface [28–31] and the existence and stability of nanobubbles close to hydrophobic surfaces have been shown in several cases [32–36]. The few studies of measurements of interaction forces between superhydrophobic surfaces [37,38] suggest results to be in line with prediction of the thermodynamical surface free energy of cavity formation [38–40].

Superhydrophobicity is most often prepared in two steps in order to combine surface structure and hydrophobicity. There are numerous approaches for superhydrophobic coatings, far too many to be reviewed here. We focused on one-step waterborne formulations using well-known and sustainable compounds which could be applied in a viable process. One-step approaches using sustainable and renewable components are few, especially examples using waxes or biobased polymers from a supercritical solution [41–43], can suffer from poor mechanical durability [44]. Other approaches are two-step (or multi-step) but from similar compounds as in the present study [45]. A study of a one-step waterborne formulation [46] including hydrophobized clay and starch, describes the importance of the formulation (specifically addition sequence and mixing speed) to achieve good dispersion and avoid foaming to successfully prepare superhydrophobic coatings.

Superhydrophobicity in itself does not impart a moisture barrier, however, depending on the actual coating formulation it can, by an increased diffusion path, give a slight [47] or even substan-

tial [46] decrease in water vapor transmission rate. In accordance, it would be a clear benefit if the superhydrophobic functionality was to be combined with improved moisture and water barrier properties of the coating and display a high mechanical durability.

We report an investigation of waterborne, one-pot superhydrophobic coating from a pigmented formulation containing aragonite calcium carbonate, sodium oleate, latex binder and cross-linker. Foreseen issues on durability were partially overcome by reformulation at higher solids contents and by realizing that wetting, also in the superhydrophobic case, can occur through remaining surface-active components in the coating. At higher solids contents of the formulation, improved scratch resistance was observed by maintained water contact angle after scratching the superhydrophobic coating and the hydrostatic resistance was further improved by water rinsing off remaining surface-active compounds from the dried coatings.

2. Experimental

2.1. Coating formulation

The coating formulation was made similar to many other laboratory pigment coating investigations using experimental protocols based on pigment amounts in parts per hundreds (pph) and laboratory metered rod coating. The pigment used was aggregated acicular aragonite calcium carbonate (Sturcal H, Specialty Minerals) with an apparent density of 0.48–0.61 g cm⁻³ thus very bulky because of the aggregated structure. The BET area was about 5 m² g⁻¹ and the equivalent spherical diameter about 5 μm. Sodium oleate, NaOl (purum, >82% active, Ridel de Haen) was used to hydrophobize the pigment. A carboxylated styrene-butadiene (SB) latex binder (50 mass%, experimental product but similar to commercial DL940 from Dow Chemicals with glass transition temperature of 22 °C) was used and a small amount of a crosslinker (ammonium zirconium carbonate, AZC-R) (32 mass% active, Allinova) was added to the final formulation before coating. The coating substrate was a polyethylene extrusion film coated paperboard of a grammage of 230 g m⁻² aimed for producing paperbased cups.

The following amounts were used: 100 pph pigment, 2–3 pph NaOl, 20–30 pph latex and 0.45 pph AZC-R. The procedure in the first sets of experiments was at room temperature with the exception that NaOl was first dissolved at 40 °C: (1) 150 mL PTFE beaker with 4-blade 50 mm diameter PTFE-coated propeller with NaOl added, (2) add dry pigment, (3) add latex, (4) add x-linker, (5) lab rod coating on paperboards (6, 12, 24 and 40 μm wet film) and (6) dry in heated oven 2 min at 90 °C.

A revised experimental protocol was developed to enable higher solid contents of the formulations. The main difference was that the stirrer unit was placed in a heated water bath and that (step 2) pigment added during 20 min at about 40 °C, mixed 30 min at 100–150 rpm (longer at higher solids), (step 3) latex added during 15 min at 45 °C, ca 350 rpm and (step 4) cross linker added while mixing for a couple of minutes.

Coatings were prepared using a benchtop laboratory metered rod coating (K202 Control Coater, RK Print Coat Instruments Ltd.) with different rod sizes to give different coating weights onto paperboard substrates. Coated samples were dried in a heated oven at 90 °C for 2 min and stored in a climate room (22–23 °C, 45 ± 5% RH).

2.2. Surface characterization

Scanning electron microscopy (SEM) images of samples were recorded using a XL30 ESEM (Philips FEI) after gold sputtering.

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