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Tailoring Surface Properties of Paper Using Nanosized Precipitated Calcium Carbonate Particles

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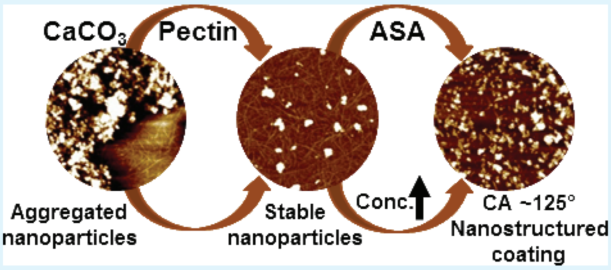

ABSTRACT: Pigment particles used in paper coatings are typically of micrometer size and consequently the thickness of the coatings is, even at its lowest, in micrometer scale. Progress in nanotechnology has given way to the development of nanosized materials to be used in coatings, yet their exploitation has not been studied to a great extent. This study examines utilization of nanosized precipitated calcium carbonate (nanoPCC) particles in nanoscale thin coating layers. In contrast to commonly used coatings, a thin nanoparticle-based coating was targeted to change the substrate surface characteristics via controlled surface structure rather than via high coat weight. A novel approach for stabilizing and modifying the nanoPCC particles with pectin and alkenyl succinic anhydride (ASA) was utilized and a nanoparticle coating with uniform particle distribution was created. The coating applied on paper substrate was hydrophobic, having a water contact angle of 125°. Particle surface modification provided dispersion stability, enabling control of the coating layer structure. The introduced concept provides a new approach to paper coatings utilizing controlled deposition of nanoparticles with extremely low coat weight, yet having high impact on substrate surface properties. Additionally, as paper is an environmentally sound product, the approach to form a controllable nanostructure on a green substrate has potential in applications outside the traditional paper products.

KEYWORDS: precipitated calcium carbonate, nanopigments, surface modification, paper coating, ultrathin coating layer, alkenyl succinic anhydride, hydrophobicity

INTRODUCTION

Nanotechnology has been employed in various applications with hopes of improved and new properties as well as reduced costs. Nanoparticles have unique properties originating from their large surface area compared to volume. However, because of aggregation, they often form micro- rather than nanosized structures and result in only minor improvements.[1] Therefore, to benefit from the properties of individual nanoparticles, avoiding aggregation and maintaining the stability of nanoparticle dispersions need to be emphasized.

In research related to paper applications, nanotechnology is employed in flocculation and retention systems,[2] in pigment and filler applications,[3,4] and in coatings.[5,6] In paper coatings, although grades of nanosized pigment particles exist, literature concerning their utilization is still exiguous. Few examples are available, e.g., utilizing nanosized clays in barrier coatings[7] and development of coating pigment particles with nanostructured surface.[8,9] Coat weight of a typical paper coating prepared using micrometersized particles fluctuates from a few to tens of grams per square meter. Consequently, the thickness of the coatings is, even at its lowest, in micrometer range. Development of nanosized pigments and their controlled utilization in coatings can enable preparation of ultrathin coatings resulting in a substantial decrease in the coat weight and hence, decrease in material consumption. However, when a coating layer is as thin as the diameter of an individual pigment particle, layer uniformity and even particle distribution become important.

Precipitated calcium carbonate (PCC) particles are commonly used as papermaking pigments. Both micrometer and nanoscale products are available. The surface chemistry of calcium carbonate is mainly influenced by Ca^{2+} and CO$_3^{2-}$ ions,[10,11] and the particles tend to be slightly cationic. In order to improve dispersion stability or affinity toward other substances, the particles have to be modified. Surface modification using adsorption has been noted to improve particle disintegration of nanosized calcium carbonate.[12] Depending on the modifying agents used, particle hydrophobicity can be altered,[12,13] and especially modification with fatty acids have been used to improve hydrophobicity.[14,15] Calcium carbonate particles have poor acid resistance and they dissolve in acid conditions. Surface treatment with fluosilicic acid has been noted to improve the acid resistance.[16] Particle modification can also be conducted using substances present during particle precipitation.[17] The challenge with PCC is the low surface charge, which hampers both dispersion stability and surface modification via adsorption. Hence, interactions other than electrostatic could be advantageous for particle surface modification.

Pectin and sodium alginate are natural polyelectrolytes that can form hydrogels with divalent cations, such as calcium.[18−21] Alginate is a polyuronic acid composed of mannuronate and guluronate units whereas pectin is composed of galacturonate units (partially methyl-esterified) interrupted by, e.g., rhamnogalacturonate units.

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The guluronate and galacturonate units of alginate and pectin, respectively, generate the calcium interaction. The calcium interaction could enable utilization of these substances in surface modification of calcium carbonate pigments.

Along with nanosized inorganic pigment particles, organic nanomaterials have lately been a subject of interest in coating applications. Nanofibrillated cellulose (NFC) prepared from wood by disintegration[22−24] has shown potential as a rheology modifier[24] and as an emulsion stabilizer.[25−27] Additionally, it has been reported to possess good barrier properties and has been suggested to promote strength properties of paper alone[5] or combined with polyelectrolytes.[28,29]

In coatings, in addition to even pigment particle layer and surface strength, hydrophobicity is important. A sufficient surface hydrophobicity is beneficial, e.g., in printing to avoid excessive spreading of liquid inks, which causes low quality print. Paper hydrophobicity is typically controlled by paper internal sizing utilizing sizing agents, e.g., alkenyl succinic anhydride (ASA) and alkyl ketene dimer (AKD). In internal sizing, the sizing emulsion is added to the paper furnish prior to paper formation. Also surface sizing, typically with starch, can be used to improve paper's resistance to wetting.[30]

This study explores the utilization of nanosized precipitated calcium carbonate (nanoPCC) particles for light surface treatment of a porous paper substrate. Unlike traditional paper coatings, the nanoparticle coating was targeted to be thin, even as thin as the diameter of an individual pigment particle. With such a thin coating layer uniform particle distribution is of concern. Therefore, besides controlling particle aggregation by controlling dispersion stability, we examined the effect of dispersion stability on thin coating layer uniformity and particle distribution. The cationic nanopigment particles were surface modified with anionic substances, namely, pectin, sodium alginate and polyacrylamide (A-PAM). With pectin and alginate, in addition to electrostatic interactions, the specific interaction with calcium was expected to assist the modification. NFC was also used as a nanoparticle dispersion media. This material has high water binding ability and it forms a gel. The fibril network could function as a matrix binding the nanoparticles within the structure.

Furthermore, the purpose of this study was to control the wetting properties of a porous substrate. This was explored by combining the stabilized nanoPCC particles with ASA. ASA is known to hydrolyze in water and bind calcium ions leading to formation of insoluble substances.[31] Hence, the ability to hinder this reaction via particle stabilization would enable high particle and ASA concentration in a coating dispersion. Such a dispersion would allow tailoring surface properties by preparation of a thin nanoparticle coating layer with high particle coverage and enhanced hydrophobicity.

EXPERIMENTAL SECTION

Chemicals. Precarb nanoPCC was donated by Schaefer Kalk (Diez, Germany) as a ~12% dispersion containing no dispersant; the average particle diameter was 50 nm. Prior to use a 2% stock solution was disintegrated in an ultrasonic bath for 10 min. Stock solutions of 5 g dm^{-3} of pectin from citrus peel (Fluka Chemie GmbH, Steinheim, Germany) with molecular weight of 30 000−100 000 g mol^{-1} (degree of esterification ~60%), low viscosity alginic acid sodium salt from brown algae (Sigma-Aldrich Chemie GmbH, Steinheim, Germany) with molecular weight of 75 000−100 000 g mol^{-1} and A-PAM (Kemira, Espoo, Finland) with molecular weight of 0.5−1 million g mol^{-1} were prepared ~12 h before the experiments. The charge densities of the modifiers were determined by polyelectrolyte titration against Polybrene (2.867 meq dm^{-3}) in 0.1 mM NaCl using a Mütek PCD 03 particle charge detector (Mütek Analytic GmbH, Germany) and ζ-potential values in 1 mM $NaHCO_3$ using a Coulter Delsa 440SX Electrophoretic Light Scattering Analyzer (Coulter Electronic Ltd., USA). These values are presented in Table 1. Prior to use ASA (Hydrores AS 1000, Kemira, Espoo, Finland) was emulsified with water without additives to 1 w-% concentration in a blender for two minutes. NFC was obtained from the Finnish Centre for Nanocellulosic Technologies. The NFC used in the dispersions was prepared from never dried birch pulp by disintegrating the pulp 6 times through a fluidizer (M-110Y, Microfluidics Corp., Newton, MA, USA). Prior to disintegration the pulp was converted to its sodium form and all excess salt was washed away.[32] NFC for model surfaces was manufactured by disintegrating the pulp 20 passes with the fluidizer. Deionized water, further purified using a Millipore synergy UV equipment (Millipore S.A.S, Molsheim, France), was used in all experiments.

Table 1. Charge Density and ζ-Potential Values of the Modifiers

substance	charge density (meq/g)	ζ-potential (mV)
pectin	1.6 ± 0.02	−40 ± 10
sodium alginate	5.2 ± 0.08	−70 ± 10
A-PAM	1.5 ± 0.01	−40 ± 10

Dispersion Preparation. NanoPCC dispersion was modified using pectin, sodium alginate, A-PAM or NFC. Prior to addition of these constituents, the nanoPCC dispersion was sonicated with a Branson sonifier S-450 D (Danbury, USA), for 5 min at 25% amplitude setting. After addition of a modifier, the dispersion was mixed 5 min with a magnetic stirrer and sonicated for 2 min. The total solids content of the dispersions was 1 g dm^{-3}. The amount of modifier needed was determined by measuring the ζ-potential of the dispersion as a function of the modifier concentration to the nanoPCC concentration. A sufficient modifier concentration was considered to be the point where a plateau in ζ-potential was detected.

Modified nanoPCC dispersion was combined with increasing ASA dosage by adding 1, 4, and 16 mL of 1% ASA emulsion to 40 mL of 1 g dm^{-3} modified nanoPCC dispersion. This ASA addition corresponds approximately to 0.25, 1, and 3 g dm^{-3} ASA concentration in the final dispersion. The lowest added amount of ASA was chosen to be relatively small compared to the nanoparticle concentration. The medium and high ASA concentrations were chosen to give insight on how to tune hydrophobicity. The effect of increasing nanoparticle concentration was explored by adding 1 mL of 1% or 2% ASA emulsion (corresponding approximately to 0.25 and 0.5 g dm^{-3} ASA concentration in the final dispersion) to 40 mL of 1, 5, and 10 g dm^{-3} modified nanoPCC dispersion. The resulting dispersions were mixed for 5 min with a magnetic stirrer and sonicated 2 min with the Branson sonifier.

Stability Measurements. Dispersion stability was judged visually and using the Turbiscan Ma 2000 instrument (Formulaction, Toulouse, France), which has a pulsed near-infrared light source (wavelength of 850 nm) and two sensors measuring the transmitted (0° from the incident beam) and backscattered (135° from the incident beam) light flux (in %, relative to external standards) as a function of the sample height. Turbiscan data is reported as a change in transmitted light versus time measured from the middle of the test tube. The turbidity measurement was started directly after dispersion preparation.

Coating of the Nanoparticle Dispersions on NFC and Paper Substrates. The nanoparticle dispersions were applied on NFC model substrates and uncalendered fine base paper substrates (58 g m^{-2}) using spin coater WS-650SX-6NPP/Lite (Laurell Technologies Corporation, North Wales, PA, USA). Commonly the technique is used for preparing thin films on solid substrates by evaporation of spinning solvent[33,34] and hence it is not optimal for coating paper substrates, which eagerly absorb water. Therefore the technique was only used as a way to apply nanoparticles on the topmost layer of paper substrate and to avoid penetration of particles into paper structure. The NFC substrates were prepared by spin coating the NFC dispersion onto 1 cm^2 pieces cut from silicon wafers (Okmetic Oy, Vantaa, Finland) according to procedure described by Ahola et al.,[35] except that poly(vinyl amine) was used as an anchoring polymer. A spinning speed of 3000 rpm and acceleration of 2100 rpms^{-1} was used for both NFC and paper substrates. After spin coating the NFC substrates were stored in a desiccator and the paper samples were dried, under a weight, overnight at room temperature.

Atomic Force Microscope, AFM. The nanoparticle coating layers spin coated on NFC substrates were examined using an atomic force microscope, the Nanoscope IIIa Multimode from Digital Instruments Inc. (Santa Barbara, CA, USA). The images were scanned in tapping mode in air using Si cantilevers (MicroMash) having a resonance frequency of 300−350 Hz. At least three images of each sample were recorded. Heights of particle clusters on a substrate were determined using the Nanoscope Analysis software (version 1.20, Veeco, NY, USA). Substrate coverage by particles was determined from the AFM height images (25 μm^2) using Scanning Probe Image Processor (SPIP) software (version 4.0.6.0, Image Metrology, Lyngby, Denmark) grain analysis with threshold detection method. The coverage values presented are average values of at least three analyzed images.

Contact Angle Measurements, CAM. The static water contact angles of the surfaces were determined using a CAM 200 contact angle measuring device (KSV instruments Ltd., Helsinki, Finland). The measurements were performed in ambient conditions and the drop size was 5 μL. The software delivered with the instrument exploits computer analysis of the drop shape where all points of the drop profile are used to fit the Young−Laplace equation to the shape of the drop. The contact angle values presented (and their standard deviations) are the average of at least three parallel measurements. For clarity the error bars in figures presenting the contact angle as a function of time are included only approximately every 10 s.

■ RESULTS AND DISCUSSION

Nanoparticle Modification. The small size of nanoparticles is considered to be the key to their superior properties compared to micrometer sized particles. On the other hand, the small size increases the tendency of the particles to aggregate, an undesired property in many applications. In addition to nanoscale dimensions, nanoPCC particles have a low surface charge, further reducing their stability. Hence, the ability of anionic substances to improve nanoPCC dispersion stability was examined. A-PAM was chosen as a modifier solely due to its anionic character and its interaction with nanoPCC was expected to be of electrostatic origin. In addition to their anionic character pectin and sodium alginate were chosen as modifiers because of their specific interaction with calcium.[19] NFC was elected due to its ability to form a gel.[23] It is possible that the nanofibrils can stabilize nanoparticles via binding particles inside the fibril network.

The addition of A-PAM, sodium alginate and pectin to the nanoPCC dispersion resulted in a charge reversal indicated as a change in the sign of the ζ-potential from positive to negative (Figure 1a). The dispersion was considered to be saturated with the modifying agent when a plateau in ζ-potential was reached.[36] The amount of a modifier needed to saturate the dispersions was ∼10 mg per gram of nanoparticles in all cases. With this addition the alginate-stabilized particles had the highest ζ-potential value, −23 mV, whereas the pectin-stabilized had the lowest, −14 mV. A high ζ-potential value has been used to indicate dispersions stability and commonly, in the case of pure electrostatic stabilization ζ-potentials higher than ±25 mV are considered sufficient for a stable dispersion. Addition of NFC to the nanoPCC dispersion also caused a charge reversal, changing the ζ-potential from approximately +10 mV to −20 mV. However, the concentration of NFC needed to saturate the dispersion was high; in the saturated dispersion the NFC concentration was equal to the nanoPCC concentration.

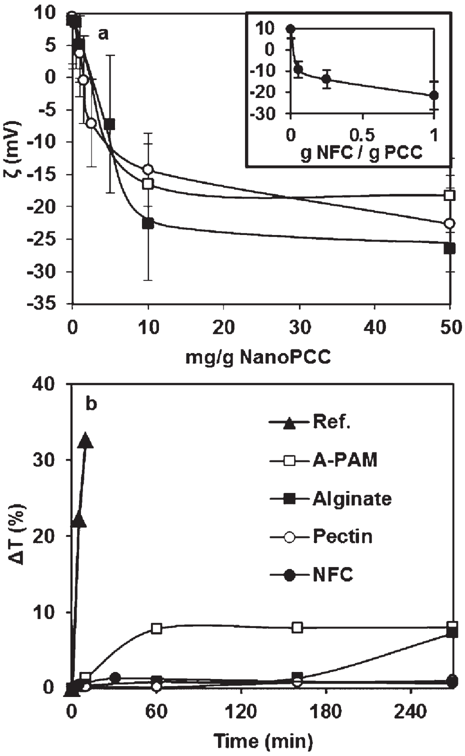

Figure 1. (a) ζ-potential of nanoPCC dispersion as a function of addition of A-PAM (□), alginate (■), pectin (○), and NFC (●) per gram of nanoPCC. (b) Change in light transmission through a sample after addition of A-PAM (□), alginate (■), pectin (○), and NFC (●) to nanoPCC dispersion. The reference is the untreated nanoPCC dispersion (▲).

The stability of the saturated dispersions was judged by measuring the change in turbidity, i.e., light transmitted through a sample. Without modification the nanoPCC dispersion was unstable, seen as a rapid increase in light transmission due to sedimentation of flocculated particles (Figure 1b). Despite the low ζ-potential value, the pectin modified nanoPCC dispersion was stable and no change in turbidity as a function of time was noted. Presumably the adsorbed pectin layer sterically stabilizes the particles. Since the particles are also negatively charged, stabilization is most probably a combination of steric and electrostatic stabilization, often called electrosteric stabilization.[37]

The stability of nanoPCC particles was also improved using A-PAM and alginate; no phase separation was detected, yet a slight increase (∼8%) in light transmission was observed. Possibly A-PAM is not able to fully stabilize the dispersion due to its high molecular weight (0.5 − 1 million g mol^{-1}), enabling bridging between the particles.

With alginate, an increase in turbidity was observed ∼4 h after preparation, indicating that the dispersion is not as stable as with pectin, yet the difference was subtle. Although the guluronate and

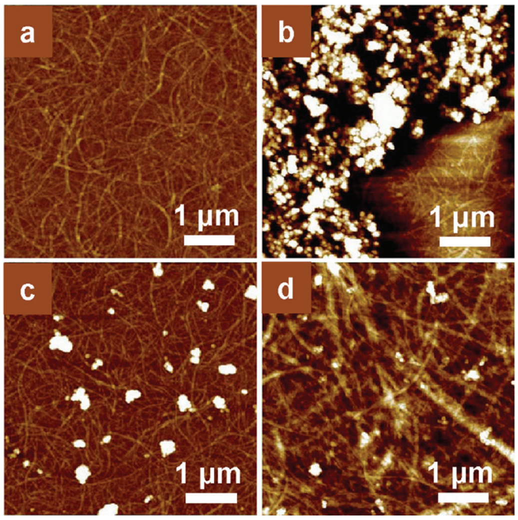

Figure 2. AFM topography images (25 μm^2) of (a) NFC substrate spin coated with (b) unmodified nanoPCC, (c) pectin-modified nanoPCC dispersion, and (d) NFC-modified nanoPCC dispersion.

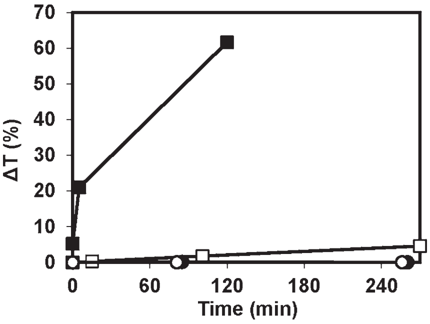

Figure 3. Change in turbidity as a function of time of unmodified nanoPCC dispersion containing 1 g dm^{-3} ASA (■) and pectin-modified nanoPCC dispersion containing 0.25 (□), 1 (●), and 3 g dm^{-3}(○) ASA.

galacturonate units of alginate and pectin, respectively, are structurally near mirror images, differences in their interaction with calcium have been noted.[38] The calcium interaction toward gel formation with alginate is known to be stepwise, including formation of monocomplexes with calcium ions, formation of dimers from the monocomplexes and further association of the dimers into multimers.[21] With low methoxyl pectins only the first two steps and with high methoxyl pectins only the first step have been observed.[19] It is possible that even with the low concentrations used in this study, alginate and pectin show differences in the calcium interaction.

At the saturation point the NFC modified nanoPCC dispersion was stable, remaining in one phase. However, the dispersion appeared to be somewhat grainy. When the ratio of NFC in a dispersion was increased (to 90:10, NFC:nanoPCC) the dispersion became more uniform. Nevertheless, when no shear was applied, small flocs were detectable. With such a constituent ratio, the dispersion is an NFC suspension embedded with nanoPCC particles rather than dispersion of nanoPCC particles modified with NFC.

Cellulose fibrils from bacterial cellulose have been used as a network for carrying inorganic nanoparticles.[39,40] Hence, possibly the stabilization effect of NFC on nanoPCC dispersion can be credited to the fibrils forming a gel-like matrix. It is evident that the interactions between the polymeric substances and nanoPCC particles differ significantly from the nanoPCC-NFC interactions.

As already stated, the development of nanosized pigments and their utilization in coatings can enable a decrease in the coat weight. However, for such thin film, layer uniformity and even particle distribution are of concern. Therefore, in addition to controlling particle aggregation by controlling dispersion stability, we examined the effect of dispersion stability on thin layer uniformity and particle distribution on a substrate.

Nanoparticles are difficult to distinguish on a rough paper surface. Hence unmodified and modified particles were spin coated on an NFC substrate (Figure 2a) serving as a model for the paper substrate. As pectin and NFC were seen to stabilize nanoPCC dispersion, they were used as the modifiers in these experiments. The unmodified nanoPCC dispersion spin coated on NFC substrate formed an uneven layer consisting of large particle aggregates (Figure 2b). Stabilization of nanoPCC particles with pectin significantly enhanced uniform particle distribution and the substrate was covered with small, evenly spread particle clusters (Figure 2c).

A substrate spin coated with the NFC-nanoPCC dispersion contained aggregates observable with a light microscope. Possibly the fibrils entangled in the dispersion form fibril flocs on the substrate during spin coating. AFM imaging revealed uncovered areas on these NFC substrate, resembling the neat NFC substrate, as well as areas covered with NFC accompanied with few nanoPCC particles (Figure 2d). NFC originating from the coating dispersion can be distinguished from the NFC model substrate material by the difference in fibril size as the NFC used in the coating dispersions was prepared by passing the suspension through a fluidizer 6 times while the NFC for the model substrates was prepared using 20 passes (and centrifuged). The low nanoPCC amount on the substrate is due to its low amount in the dispersion, as a ratio of 90:10, NFC:nanoPCC was needed to prevent phase separation.

Combining Nanoparticle Dispersion with ASA. A thin nanoparticle coating was targeted to change the substrate surface characteristics via controlled surface structure. In addition to controllable particle distribution, the possibility to affect substrate wetting properties was explored. This was done by combining nanoPCC particles with ASA, a paper sizing agent. In water, reactive ASA hydrolyses fast and forms dicarboxylic acid.[31] This compound can further dissociate and is then able to bind calcium ions leading to formation of insoluble substances. In papermaking processes this causes deposition problems.[41] Consequently addition of 1 mL of 1% ASA emulsion to a dispersion of unmodified nanoPCC particles caused the mixture formed to aggregate and phase separate observed as a rapid increase in ΔT (Figure 3). No such behavior was seen when pectin modified particles were combined with ASA. Even increasing the ASA concentration to 3 g dm^{-3} did not reduce the stability of the pectin modified nanoPCC dispersion. Clearly the modification of nanoPCC particles with pectin limits the nanoPCC interaction with ASA.

In contrast to the pectin modified nanoPCC dispersion, the NFC-nanoPCC dispersion phase separated when 1 mL of 1% ASA emulsion was added to the dispersion. It is clear that NFC is not able to stabilize the nanoPCC dispersion so that ASA addition would not cause flocculation in the dispersion. However, it was noticed that when ASA and nanoPCC were first

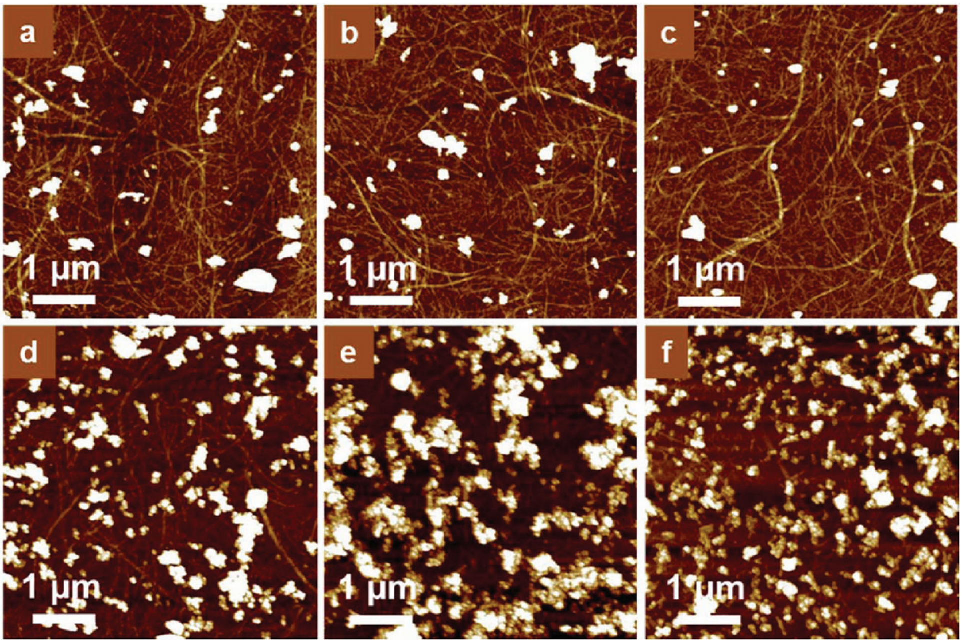

Figure 4. AFM topography images (25 μm^2) of NFC substrate spin-coated with dispersion containing (a) 1 g dm^{-3} pectin-nanoPCC dispersion with 0.25 g dm^{-3} ASA, (b) 1 g dm^{-3} pectin-nanoPCC dispersion with 1 g dm^{-3}ASA, (c) 1 g dm^{-3} pectin-nanoPCC dispersion with 3 g dm^{-3}ASA, (d) 5 g dm^{-3} pectin-nanoPCC dispersion with 0.25 g dm^{-3} ASA, (e) 10 g dm^{-3} pectin-nanoPCC dispersion with 0.25 g dm^{-3}ASA, and (f) 10 g dm^{-3} pectin-nanoPCC dispersion with 0.5 g dm^{-3}ASA.

combined (at a ratio of 35:65, ASA:nanoPCC) and NFC was then immediately added to the ASA-nanoPCC dispersion (at a ratio of 5:1, NFC to ASA-nanoPCC), the resulting mixture was stable. The enhanced stability is due to the presence of NFC as the dispersion containing only ASA and nanoPCC was observed to be unstable (Figure 3). Nevertheless, it is impossible to state if, despite the apparent dispersion stability, ASA and nanoPCC are able to interact. The spin coating of the ASA-nanoPCC/NFC dispersion on the NFC substrate resulted in a structure resembling the surface formed by NFC-nanoPCC dispersion (Figure 2d). The substrate contained uncovered areas and flocs consisting of fibrils and a few nanoPCC particles.

The dispersions of pectin-modified nanoPCC particles combined with ASA spin coated on NFC substrate resulted in evenly distributed particle clusters (Figure 4). The coverage of the substrates (determined with SPIP) coated with the 1 g dm^{-3} pectin-nanoPCC dispersion with varying ASA concentration (Figure 4a-c) was low and somewhat decreased (from ~7% to ~2%) with increasing ASA concentration. The ASA was not visible in the AFM images which resembled the substrate coated with the pectin modified nanoPCC dispersion without ASA (Figure 2c).

Because the coverage of the coating layer was low, we tried increasing the coverage by increasing the nanoPCC dispersion concentration. Nanoparticle dispersion concentration has elsewhere noted to affect the coverage.[42] Only pectin modified particles were used in these experiments. The concentration of modified nanoPCC particles was increased and the dispersions were then combined with ASA (total concentration of 0.25 g dm^{-3}). The increase in the concentration of the modified particles in pectin-nanoPCC/ASA dispersion increased the turbidity of the dispersion, but the ΔT within the observation period (270 min) was less than 2% for 5 and 10 g dm^{-3} dispersions, indicating that the dispersions were stable. Spin coating the pectin-nanoPCC/ASA dispersions containing 5 and 10 g dm^{-3} of the modified particles onto the NFC substrate (Figure 4d and e) resulted in a substrate coverage value of ~19 and ~35%, respectively. These values were considerably higher than that of the substrate spin coated with dispersion containing 1 g dm^{-3} pectin modified particles (Figure 4a). Consequently, we can state that it is possible to increase the pectin-nanoPCC concentration in the dispersion without loss in stability and to increase the particle coverage on a substrate.

The ASA concentration in the 10 g dm^{-3} pectin-nanoPCC dispersion was further increased from 0.25 to 0.5 g dm^{-3}. The dispersion remained stable and spin coating resulted in ~30% coverage of the NFC substrate (Figure 4f). The ability to increase ASA concentration enables tuning of the surface hydrophobicity. The layer did not fully cover the substrate hence being thin compared to common paper coatings. The height of particles on the substrate was approximately 240 ± 70 nm denoting that the layer consisted of groups of few nanoparticles clustered together.

Effect of Nanoparticle Dispersion Coating on Substrate Wetting. The effect of surface treatment with the nanoPCC dispersions on the wetting of a dense and a porous cellulose substrate was evaluated using water contact angle measurements. An NFC film spin-coated on silica was used as the smooth and dense cellulose substrate and fine base paper as the rough and porous substrate. Because of the paper porosity, nanoparticles may migrate into the fiber network. This can affect penetration of water into paper. The NFC film is only ~5 nm thick[35] and hence, the particles cannot fully penetrate this film.

The water contact angle results presented for the paper substrate in Figure 5a were recorded at $t = 25$ s in order to observe changes in water penetration into the structure. Increasing ASA concentration in the pectin-nanoPCC dispersion increased the contact angle on both substrates. With the highest ASA concentration, 3 g dm^{-3}, the water contact angles were 85 ± 7° and 135 ± 5° on NFC and the paper substrate, respectively. Treating

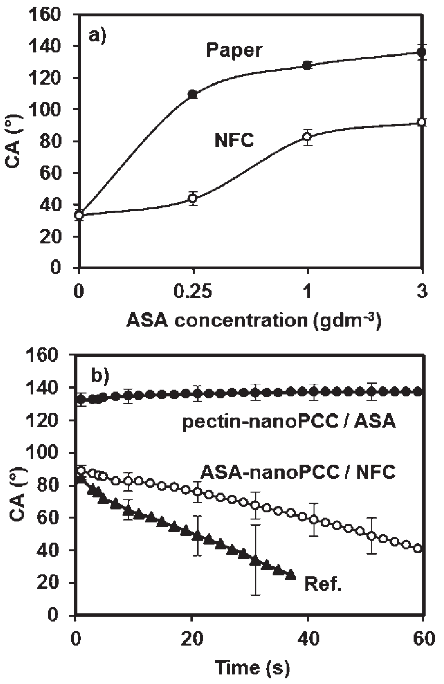

Figure 5. (a) Water contact angle of NFC (○) and paper (●) substrate coated with pectin-nanoPCC/ASA coating as a function of ASA concentration. The contact angle of paper substrates was recorded at *t* = 25 s and of NFC substrates at *t* = 1 s. (b) Water contact angle of paper substrate coated with ASA-nanoPCC/NFC (○) and pectin-nanoPCC/ASA (●) as a function of time. In ASA-nanoPCC/NFC, the ASA concentration was 0.1 g dm^{-3} and in pectin-nanoPCC/ASA the pectin-nanoPCC concentration was 1 g dm^{-3} and ASA 3 g dm^{-3}. The reference (▲) is water-treated fine base paper.

the substrates with a neat 1 g dm^{-3} ASA emulsion resulted in a congruent contact angle level. As this lower ASA concentration was able to produce contact angle on a same level as the dispersion with nanoparticles and higher ASA concentration, it is clear that both hydrophilic pectin-nanoPCC particles and hydrophobic ASA have an effect on the coating wetting properties.

As already stated, in contrast to pectin-stabilized nanoPCC particles, the NFC-modified dispersion lost its stability when ASA was added. A stable dispersion was formed when NFC was added to ASA-nanoPCC dispersion. Because of the strong interaction between ASA and calcium, the ASA concentration could not be increased and the total ASA concentration in this dispersion was approximately 0.1 g dm^{-3}. The lower ASA concentration was seen as considerably lower contact angle value compared to contact angle of pectin-nanoPCC/ASA coating with 3 g dm^{-3} ASA concentration (Figure 5b). In addition to increasing the initial contact angle, coating with pectin-nanoPCC/ASA dispersion decreased water penetration into the paper structure (seen as the unchanged contact angle as a function of time). An equally strong effect was not detected with ASA-nanoPCC/NFC coating, although a decrease in the water penetration rate was observed. Several publications have shown that NFC in coatings can be used for improving barrier properties,[5,43] yet judged solely by the water penetration, such an effect was not observed in this study. Probably a thicker NFC layer is needed.

The pectin-nanoPCC particles are hydrophilic, whereas ASA is a hydrophobic substance. Therefore the hydrophobicity of pectin-nanoPCC particle coated substrates depends on the ASA concentration. This is clearly illustrated in Table 2. Increasing the nanoPCC concentration while maintaining a low ASA concentration leads to a decrease in contact angle, whereas increasing the ASA concentration enhances the contact angle.

Table 2. Water Contact Angle of Pectin-nanoPCC/ASA Coatings with Increasing Nanoparticle or ASA Concentration

coating dispersion	CA (deg) at 1 s, NFC substrate	CA (deg) at 25 s, paper substrate
pectin-nanoPCC 1 g dm^{-3} + ASA 0.25 g dm^{-3}	45 ± 4	110 ± 2
pectin-nanoPCC 5 g dm^{-3} + ASA 0.25 g dm^{-3}	35 ± 1	95 ± 5
pectin-nanoPCC 10 g dm^{-3} + ASA 0.25 g dm^{-3}	30 ± 2	85 ± 7
pectin-nanoPCC 10 g dm^{-3} + ASA 0.5 g dm^{-3}	65 ± 5	125 ± 2

The nanoparticles are too small to induce any structure-based increase in hydrophobicity as has been shown previously.[44] Hence, the ASA concentration is the main factor affecting coating hydrophobicity. Pectin is needed to stabilize the nanoPCC dispersion, to facilitate even particle distribution and to restrict the reaction between ASA and calcium. Evidently with nanoPCC stabilization, it is possible to increase the particle and ASA concentration, enabling tunable particle coverage as well as coating layer hydrophobicity.

Few other studies exist reporting exploitation of nanoparticles in preparing hydrophobic paper coatings,[45] including utilization of fatty acid modified calcium carbonate particles.[12,14,15] However, typically these coatings have microscale roughness or the coatings are exceedingly thicker than the diameter of an individual nanoparticle. On the contrary, we introduce a way to produce an ultrathin coating layer with high impact on substrate surface characteristics.

The proposed procedure, to increase stability of dispersions containing ASA by restricting the interaction with calcium carbonate particles by nanoparticle surface treatment, differs notably from the traditional manner where the ASA emulsion itself is stabilized by polymers[31] and then used, separate from paper pigmentation, for sizing. In the proposed concept, surface treatment with pigment particles and surface sizing of paper are combined rather than applied as separate processes.

The prepared nanostructured coatings as well as the coating dispersions used differ significantly from common procedures to coat paper. Consequently, the traditional coating methods are not necessarily suitable for using such dispersions, as for example, in blade coating force is applied on the coating dispersion inducing penetration of nanoparticles into paper structure. Prior to utilizing the introduced approach in industrial scale coatings, a proper coating technique needs to be developed to complement the avenue to prepare a truly nanoscale coating.

Utilizing a low-cost filler material, PCC, together with a natural polyelectrolyte and a commonly used sizing agent it is possible to significantly change substrate surface properties. Paper is a sustainable product. Hence, considering the variety of calcium carbonate grades available (also used in, e.g., biomedical applications), indeed the application potential of the process described lie beyond use in coated paper products.

CONCLUSIONS

A procedure to prepare a controllable nanostructure on a substrate of biobased material was introduced. Without modification nanoPCC particles aggregate and the particles form large particle clusters on a substrate. Pectin and NFC, both organic materials, can stabilize the nanoPCC dispersion, yet only pectin-stabilized particles retain their stability upon addition of ASA to the dispersion. Pectin adsorbs onto nanoPCC particles both because of electrostatic attraction as well as its specific interaction with calcium. The stabilization is probably a combination of electrostatic and steric stabilization. NFC, on the other hand, forms a fibril network capturing the nanoparticles.

Dispersion stability was noted to be essential to obtain a uniform nanoparticle coating. Stabilization of nanoPCC particles enabled the nanoparticle concentration in the dispersion to be increased accompanied by an increase in hydrophobic substance concentration. The nanoparticle coating increased the water contact angle of a porous paper to 125°, also decreasing the penetration rate of water into the paper structure.

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