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## 6.2 - Superhydrophobic paper coating containing non-conventional clay

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### ABSTRACT

Hydrophobic clay fillers have not been extensively used in dispersion coatings for paperboard due to the difficulty of dispersing them in water. The objective of this work was to investigate whether hydrophobic clay can be utilized as filler in latex-starch based barrier dispersion coatings. Hydrophobic clay filler was compared with conventional clay in terms of coating respect to water absorption, water vapor transmission rate and water contact angles. The results show that a coating containing hydrophobic clay provides a superhydrophobic character to paper; *i.e.* a high water contact angle (150°) and relatively low water absorption. Raman mapping of clay or hydrophobic clay and that the distribution of hydrophobic clay tends to be more uniform. This indicates that hydrophobic clay conventionally used in the plastics industry may be used as a coating additive to create superhydrophobic surfaces and improve water barrier properties of paper products.

### INTRODUCTION

Barrier dispersion coatings were first invented to provide paper or paperboard with properties required for packaging applications; e.g. barriers against water, water vapor, grease, oil etc. These coatings normally consists of mineral pigments, such as clay and talc, contained in a major components have an important role to play in dispersion coatings, the latex to form a film and the pigment to improve barrier properties and to assist with printability, gluability and to help interest in new materials as alternatives for non-environmentally friendly materials such as wax and polyethylene is continuously increasing within the paper coating field [2-6].

In recent years there has also been a growing interest in developing superhydrophobic surfaces [7, 8]. A precise definition of the term ‘superhydrophobic’ is still a subject of much discussion although it is fairly commonly suggested that the water droplet contact angle needs to be equal to or above 150° [9, 10]. The specific requirement to achieve a superhydrophobic surface is so-called Lotus effect [7].

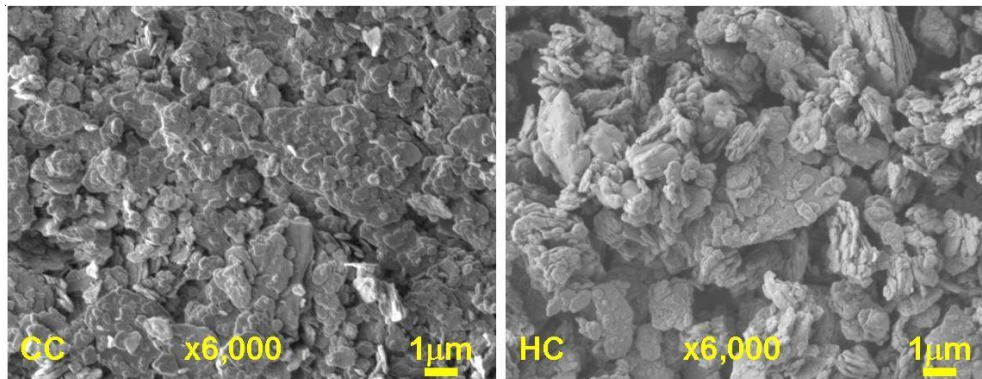
The choice of a certain type of pigment is often governed by specific coating properties or combinations of final coating properties and its runnability on coating equipment. The utilization of new mineral fillers has also recently gained increased attention for their potential to enhance ommonly used to improve barrier performance and strength in a wide range of polymer systems for plastics such as polyethylene and polyesters. These fillers have not been extensively used in dispersion coatings for paper or linerboard due to their hydrophobic nature and the difficulty of

The objective of this work was to investigate whether HC can be used as filler in latex-starch based barrier dispersion coatings. HC filler was compared with conventional clay (CC) filler. To avoid any contraction of the coated surface all coatings were applied to linerboard sheets which were made without internal or surface sizing of the top layer using a laboratory dynamic sheet former. The coated linerboards were examined using scanning electron microscopy and Raman spectroscopy. Further, the coated linerboards were characterized with respect to water absorption, water vapor transmission rate and water contact angles.

## MATERIALS

### *Clay*

Conventional clay and hydrophobic clay are two different commercial kaolin clays supplied by BASF Catalysts LLC, USA, and utilized in this study. According to the manufacturer, the conventional clay (CC) is a standard grade clay used for paper coating that has good coverage, high brightness and a Sedigraph particle size of 92% < 2  $\mu\text{m}$ . The hydrophobic clay (HC), diameter (ESD) of 1.5  $\mu\text{m}$  designed to improve performance and strength in a wide range of calcined) and a chemical treatment that anchored an amino functional-additive to the mineral surface, thus providing a hydrophobic character. Beside the differences in chemical properties, the morphologies of these clays were also dissimilar; the CC exhibiting a flatter particle shape with a higher aspect ratio, as shown in Figure 1.



**Figure 1.** SEM images of conventional (CC) and hydrophobic (HC) clay powder.

### *Binder and co-binder*

The binder was a styrene-butadiene latex (DL629) from Dow Chemical Company (USA) commonly used in dispersion coatings. A hydrophobic waxy corn starch from National Starch (USA) was used as a co-binder and dispersing aid for the clay. This non-ionic starch has been modified to adjust viscosity and then treated with a very large hydrophobic group to give better surface orientation. Latex and starch characteristics as provided by the supplier are given in Table 1.

**Table 1.** Latex and starch characteristics

Latex characteristics		Starch characteristics	
$T_g^1$ (°C)	2	Type/Form	Waxy hybrid maize/ White powder
MFFT <sup>2</sup> (°C)	9	Starch Base	100% Amylopectin
Solids content (%)	50	Bulk density (kg/m <sup>3</sup> )	416 - 512
pH	6	pH [20% solid slurry in water]	5.5 - 7.5
Specific gravity	1	Brookfield Viscosity, (cP) [9% solid, 55°C]	18 cP
Particle size (nm)	-	Molecular weight (MDa)	324

<sup>1</sup> Glass transition temperature

<sup>2</sup> Minimum film formation temperature

### ***Substrate***

The substrate used was a two-layer linerboard which was made on a laboratory dynamic sheet former to a total grammage of 160 g/m<sup>2</sup>. The pulps used to make the base (90 g/m<sup>2</sup>) and the top (70 g/m<sup>2</sup>) layer of the linerboard were commercial kraft pulps obtained from a local paper mill from New Zealand. The only difference between the pulps was that the top layer had a lower kappa number which means that the top layer was bleached to a higher degree.

## **METHODS**

### ***Sheet Forming Procedure***

Laboratory linerboard was formed in three steps: i) forming of the base layer (90 g/m<sup>2</sup>), ii) forming of the top layer (70 g/m<sup>2</sup>) layer and iii) couching of the base and top layer together. The forming procedure of the base and top layer was the same. The consistency of the stock was 0.03% and pH was 7. The wire speed of the dynamic sheet former was 1010 m/min and the pressure of the nozzle was 280 kPa with a flow speed of 4 L/min. Dewatering of the linerboard hours at standard ISO conditions (T = 2 °C and RH = 50%) before they were used for testing and coating trials.

### ***Preparation of coating formulations***

The latex-starch based coatings were prepared in three steps: i) preparation of aqueous starch solution, ii) the addition of clay and iii) the addition of latex and additives. An aqueous solution additional 45 minutes at 600-800 rpm with a high shear mixer (propeller-type impeller). The solid ratio of the film-forming latex binder to the starch co-binder was set to 60/40 and the total binder to mineral solid ratio was 0.85 (54% clay in total solids and 46% binder in total solids). The final solids content was 35 wt-%.

The pigment volume concentration (PVC) of the coatings based on CC and HC was estimated to 34% and 33%, respectively, based on the following densities of the pure main components in the °C) using a Brookfield Dial Reading Viscometer (spindle number 4 at 100 rpm).

### ***Laboratory Coating***

All coatings were applied to linerboards at room temperature (23°C) by using a bench coater (K 105 °C). The dry weight of the coating layers was determined gravimetrically. Six linerboard samples (290 × 190 mm) were coated for each coating formulation.

### ***Grammage, WVTR, Cobb<sub>120</sub> and surface roughness***

Linerboard grammage (g/m<sup>2</sup>) was determined according to TAPPI standard test method T410 om-98. Water vapor transmission rate (WVTR) was measured at 23 °C and 50% R.H. adopting the TAPPI WVTR test method T464 om-01 by using dry CaCl<sub>2</sub> pellets as desiccant. The Cobb<sub>120</sub>-value gives a measurement of the water absorption capacity of the paper given chromatic aberration onto the sample. The reflected light is passed into a spectrophotometer and in-built software is used to select the wavelength of maximum intensity. This wavelength is focused on the surface point being analysed and used to determine the relative height of that point.

### ***Contact angle***

A CAM 200 contact angle goniometer (KSV Instruments Ltd., Helsinki, Finland) was used for determination of contact angles. The contact angles of water on the coatings were measured in air between 0.1 – 10 s after first contact with the surface. The contact angles were calculated using a Laplace contour fit model within the instrument's software. The volume of the droplets (pumped volume) was approximately 6 µL. The results are given as a mean of three measurements.

(grey level variance resulting either from changes in topography or from material differences) to be interpreted as the height for the plot giving a visual interpretation of the surface topography [23, 24].

## **RESULTS AND DISCUSSION**

The coating color viscosity, coat weight and surface roughness are presented in Table 2. The viscosity is roughly the same for both clay coatings without wax, while it increases after addition of a small amount of wax. For the HC-containing coating colors the viscosity increases four times by adding a small amount of wax to the coating, even though the solids content is fairly low (35%). This drastic increase of viscosity indicates a strong interaction between the particles in the HC-containing coating color. However, this thickening effect provides a coating that is suitable for industrial blade or rod coating techniques rather than air-knife applications. The coat weights were roughly the same for all coatings (9 – 12 g/m<sup>2</sup>)

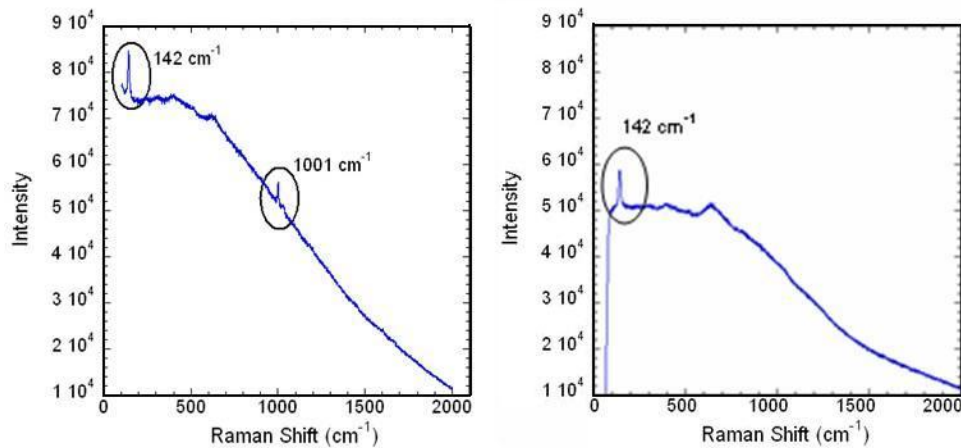
**Table 2.** Coating color viscosity, coat weight and surface roughness of coated paper.

	CC	CC-Wax	HC	HC-Wax
Viscosity, (mPa.s) Mean $\pm$ s.d.	220 $\pm$ 4	258 $\pm$ 2	195 $\pm$ 3	847 $\pm$ 15
Coat weight, (g/m <sup>2</sup> ) Mean $\pm$ s.d.	12 $\pm$ 1	9 $\pm$ 1	11 $\pm$ 3	11 $\pm$ 1
Roughness, Ra ( $\mu$ m) Mean $\pm$ s.d.	3.20 $\pm$ 0.10	3.37 $\pm$ 0.37	3.55 $\pm$ 0.07	3.84 $\pm$ 0.80

Surface roughness is slightly higher for HC than for CC coatings and it generally increases after addition of wax. As the roughness of the HC-Wax coating is slightly higher than the roughness of the other coatings it is suggested that the superhydrophobic surface is created by both surface roughness and chemistry effects. As the variations of surface roughness expressed as standard deviation (s.d.) is higher for HC than for CC, an opportunity exists to improve the superhydrophobicity by fine-tuning the nano/micro-roughness.

#### *Confocal raman spectroscopy examination*

Results from Raman spectroscopy examination of the coated linerboards are presented in Figure 2, 3 & 4. The strongest and sharpest peaks of styrene at a Raman shift of 1000 and 1001  $\text{cm}^{-1}$  as shown in Figure 2 have been used to create the latex intensity maps displayed in Figure 3.



**Figure 2.** Left: Raman spectral analysis of a coating cross-section indicating clay peak at  $142 \text{ cm}^{-1}$  and styrene peak at  $1001 \text{ cm}^{-1}$ . Right: Raman spectral analysis of HC only.

Raman mapping of cross-sections reveals that the latex distribution is uniform in the presence of either CC or HC (Figure 3). The slightly stronger signal (the brighter area) obtained with HC further information a more detailed Raman study on conventional paper coatings is presented elsewhere [25].

Viscosity is one important process parameter in production of barrier coatings and it cannot be excluded that the viscosity differences between the coating colors affected the coverage and the number of coating defects and thus also affected the gas barrier properties. Future work should investigate the impact of a second layer in order to minimize the influence of coating defects such as pinholes.

## CONCLUSIONS

It has been shown that non-conventional hydrophobic clay used in the plastics industry can be utilized as a filler in water-based dispersion coatings for paperboard. A simple one-step dispersion coating creating a superhydrophobic surface has been achieved by combining this non-conventional hydrophobic clay with a low dose of wax additives. The surface roughness and chemistry effects governed the fast initial water spreading on hydrophobic surfaces such as HC-W. Raman mapping of cross-sections reveals that the latex distribution is uniform in the presence of either conventional clay or hydrophobic clay and that the distribution of hydrophobic clay tends to be more uniform than conventional clay, which may reflect good mixing and consolidation of hydrophobic clay.

This provides an alternative coating option for the paper industry to create superhydrophobic surfaces using existing coating technologies such as air-knife or blade coating. A coating with improved water repellency may find new paper based products and applications. This in combination with tailored layers of moisture barriers has the potential to create a product of broader use.

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