

Functional surfaces produced by foam coating

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ABSTRACT: This paper reports experiments on silica coating formulations that are suitable for application as a thin pigment layer with foam coating technique on a paper web. To understand the foaming properties of nanosilica dispersions, the critical micelle concentration, foam half-life time, and foam bubble size stability were determined with three different foaming agents. The results indicate that the bubble stability measurement is a useful characterization method for foam coating purposes. Pilot foam coating trials were done and the effects of the chosen foaming agents were studied on the properties of the nanosilica-coated paper. The surface hydrophilicity of silica coated paper was related not only to silica pigment, but also to the chemical nature of the foaming agent. Standard paper properties were not affected by the thin silica coating.

Application: Foam half-life time and bubble size growth determination are useful tools when creating stable foam for foam coating. Mills can adjust properties of foam coated surfaces through selection of the coating compound and the properties of the foaming agent.

Foam coating is a classic technique that is used for wet-coating woven and nonwoven fabric webs [1]. Advantages of this technique include robustness, relatively simple equipment, and continuous operation in industrial scale. The foam is generated by mixing pressurized air with the coating solution, which includes the coating compound, a foaming agent, carrier, and other additives [2]. Because of the viscoelastic nature of the foam, a large variety of coating materials can be added on a web with various foam application techniques. In this work, water-based foam was fed through a slot die and killed with absorption and infrared (IR) drying. The bubbles collapse mainly because of absorption and leave the coating material on the web surface [3].

Only a few examples of foam coating can be found in the European paper industry. Compositions containing microcapsules with natural foaming agents, gelatin, casein, and soybean extract have been applied as a foam to a paper web [2,4] by Wiggins Teape Ltd. (Hampshire, England). In contrast to conventional coating of paper, the foam technique allows small amounts of chemicals to be applied on a paper or board web in an economically viable way. To create antimicrobial properties of the paper, we previously applied cellulose nanofibrils (CNF) functionalized by titanium dioxide/zinc oxide on paper with foam coating [5,6].

One aim of this work was to find a suitable method to test whether the foamed formulation is suitable for foam coating purposes. In most foam coating applications, the foaming agent is a surfactant additive to the coating formulation; thus, the amount of it is usually minimal. The critical micelle con-

centration (CMC) is defined as the surface active agent concentration above which micelles start to form. At the CMC, the surface becomes saturated; above the CMC an increase of the surface active agent concentration does not further reduce the surface tension. Lowering the amount of surfactant reduces the overall costs, so the CMC for a particular coating composition and the effects of coating material on it should be known. The most commonly used method for the foam stability characterization is measurement of a foam half-life. We chose that method and also used a light transmission method to measure the relative bubble size growth.

EXPERIMENTAL

Materials

The foam properties of silica dispersion with three different foaming agents were studied. The silica was Bindzil 40 NH3/80 (AkzoNobel; Amsterdam, The Netherlands), a water-based, anionic, colloidal dispersion of amorphous silicon dioxide, with an average particle size of 40 nm. Two of the selected foaming agents were molecular surfactants: anionic sodium dodecyl sulfate (SDS) (active content 90%, Sigma-Aldrich; St. Louis, MO, USA) and nonionic octyl/decyl (C8/C10) glucoside AG 6210 (active content 61%, AkzoNobel). The active content of SDS and glucoside given by the producers were taken into account when the surfactant concentrations were calculated. On the basis of studies of surfactant/fiber systems, these two surfactants were classified as fast foaming agents [7]. The third foaming agent, polyvinyl alcohol (PVOH) Mowiol 40-88 (Kuraray; Kurashiki, Japan) is a typical binder polymer in silica pigment coatings that easily foams as an aqueous

solution. Polyvinyl alcohol water solution (5.4 wt%) was prepared by dissolving polymer granules in tap water according to the instructions of the polymer manufacturer [8]. The effect of polyethylene glycol (PEG) (average Mn 400, Sigma-Aldrich) as a stabilizer of SDS foam was included in the study.

Surface tension measurements for CMC determination

The surface tension of silica water dispersions at various foaming agent concentrations was measured at room temperature 23°C with the ring method using a Sigma 70 Tensiometer (KSV Instruments Ltd.; Helsinki, Finland). Solutions of silica foaming agent were prepared in a beaker by carefully mixing the ingredients in tap water with a conductivity of about 15 mS/m. The aqueous solutions were stored at room temperature for 1 day before the surface tension measurement was taken. The practice, reported by Lin, of keeping SDS solutions standing between 12 and 36 h after the solutions were made was adopted to minimize the error from the hydrolysis of SDS molecules to lauryl alcohol [9]. In all determinations, the surface tension was followed by recording at least 20 successive values to reduce random variation in the surface tension value. The result of the surface tension value is the average of the three separate determinations. The silica concentration of the studied dispersions was between 8.4 wt% and 10.0 wt%.

Foam making and foam characterization measurement

In the laboratory scale studies, foams were manufactured with a Hansa-Mixer Pico foam generator (Hansa Industrie-Mixer GmbH&Co. KG; Stuhr, Germany). In the pilot foam coating trial, the foam was produced with a Top-Mix 60 foam generator (Hansa Industrie-Mixer GmbH&Co. KG). The density of the produced foam was 100 g/L in all foam studies.

Foam was characterized by a foam half-life time measurement and a foam bubble size measurement. In the half-life time determination, a 1-L measuring vessel was filled with freshly prepared foam and the separation of the liquid phase from the foam phase was followed visually. The time needed for the separation of half of the original liquid volume was recorded as the foam half-life time. Foam bubble size determination as a function of time was done with TurbiScan Lab (Formulation SA; L'Union, France), which uses multiple light scattering to measure an average bubble size. The bubble size was recorded for 300 s just after the preparation of the foam.

Pilot foam coating and characterization of foam-coated paper samples

In the pilot trial run, a thin nanosilica layer was coated onto a moving fine paper web with foam coating technique using the previously mentioned foaming agents. Surface properties of the silica-coated paper were determined and the effects of the surfactant on these properties were estimated.

The foam coating trial was done at VTT's pilot-scale surface treatment line. The silica foam was pumped from a generator

to a Magnojet slot-type applicator (J. Zimmer; Klagenfurt, Austria) to apply foam onto the moving paper web. After the foam application, the foam bubbles collapse as the water is absorbed into the base paper and the nanosilica pigments attach on the base paper. Drying after the silica foam coating was performed with IR and air drying units. The base paper was a fine paper (78 g/m²) with calcium carbonate filler pigment.

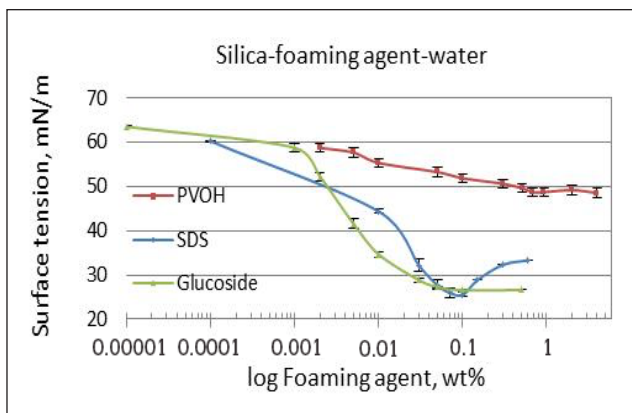
In the silica dispersions, the silica concentration was 10 wt% and foaming agent concentration was 0.2 wt%. Silica dispersions were anionic, having zeta potential between -22 mV and -28 mV and pH between 9.2 and 9.4. In the foam coating trials, the pumping speed of the foam was varied from 15 L/h to 21 L/h and the coating speed was 35 m/min. The calculated silica coat weight was 2 g/m² at the pumping speed of 15 L/h and 3 g/m² at the pumping speed of 21 L/h.

To describe the quality of the paper, the standard paper properties (roughness, gloss, and air permeance) were measured from the coated and dried paper samples and compared with the uncoated fine paper. Air permeance was measured with Parker-Print Surf using 20 kPa pressure. The static contact angle of water on the paper surface was measured using a drop size of 2 µL with a CAM 200 device (KSV Instruments). Elemental distribution of silicon over the silica-coated paper was studied using a scanning electron microscope (SEM) and a Noran System Six energy dispersive x-ray (EDX) spectrometer (Thermo Scientific; Waltham, MA, USA). The acceleration voltage was 10 kV. EDX mapping is a qualitative technique in which the intensity of the x-ray energy characteristic of the emitter element is measured relative to its lateral position on the sample [10]. A more detailed surface analysis of the silica pigment coating on paper surface was carried out using a Merlin high-resolution scanning electron microscope (HR-SEM) (Carl Zeiss AG; Oberkochen, Germany) with a secondary electron (SE) detector and 30000x magnification. The accelerating voltage was 3 kV and the paper surface was treated with platinum sputtering before the imaging.

RESULTS AND DISCUSSION

To obtain the minimum concentration of the surface active agent for silica foam manufacturing, the CMC of the silica dispersions was determined. The surface tension values of the silica dispersions with three foaming agents are shown in **Figure 1**. It can be seen that the silica dispersion with the nonionic C8/C10 glucoside surfactant reaches the constant surface tension value of about 27 mN/m at the lowest surfactant concentration, around 0.04 wt%.

The surface tension curve of silica dispersion with SDS has a minimum surface tension of 26 mN/m at SDS concentration 0.1 wt%, but then the surface tension goes up at increasing surfactant concentration to reach a constant value of about 33 mN/m at concentration 0.3 wt%. This surface tension drop around CMC is associated with the presence of dodecanol (lauryl alcohol) impurity in the SDS solution [7,9]. PVOH as a polymer foaming agent reduces the surface tension of silica dispersion less than the glucoside or SDS (Fig. 1). Polymer



1. Surface tension of dispersions of nanosilica foaming agent and water dispersions at different foaming agent concentrations. (PVOH = polyvinyl alcohol; SDS = sodium dodecyl sulfate.)

foaming agent causes foam stability mainly through electric and steric repulsion, which is controlled by the extent of unfolding and conformational structure of the polymer [11]. It also increases the viscosity of the fluid, which stabilizes the foam. The CMC of PVOH determined in silica dispersion is 0.7 wt% to reach surface tension value of about 49 mN/m. The surface tension value at a low surfactant concentration (0.00001 wt%) shows the mere silica dispersion surface tension of 63 mN/m.

The properties of the silica foams around CMC were characterized by determining the foam half-life time and the bubble size of the foam as a function of time. Of the three foaming agents, PVOH had the longest half-life time, 17 min, obtained at CMC concentration (**Table I**).

With the anionic surfactant SDS, the foam half-life time is almost the same at CMC and at concentrations two and four

times higher than CMC. With nonionic C8/C10 glucoside, however, the foam stability is clearly improved when the surfactant concentration is two times higher than CMC. These results show that the foam properties can significantly change above CMC and the foam stability is not predictable on the basis of the surface tension measurement, as is also found in other studies [12,13]. With PVOH, the foam half-life time is already at a good level below CMC. In this foam coating work, a foam half-life of 4 min or longer was targeted for pilot foam coating trials. Polyethylene glycol is able to further stabilize foams [14], but according to our results, it did not improve the foam half-life of the silica foam with SDS.

The speed of bubble growth was measured using the TurbiScan Lab device. The bubble growth is related to the elastic modulus of the foam bubble [15] and is thus a more relevant parameter for the breakage of bubbles during the foam coating. The results are shown in **Fig. 2**. The results of two different glucoside concentrations are shown to indicate the repeatability of the measurement. There is a measurable difference in bubble growth between the pure SDS and SDS combined with PEG.

The ability of PEG to stabilize the foam is known from the literature [14], and we have also observed this in our foam coating trials. When using high web speeds, the foam bubbles start to break in the space between the applicator slot and the web. This occurs if only SDS is used with silica particles. By adding PEG, fewer bubbles break. Because the half-life test did not find any difference between these two cases but the TurbiScan Lab measurement did, we believe that the bubble growth measurement might thus be usable for the characterization of the foam for the foam coating.

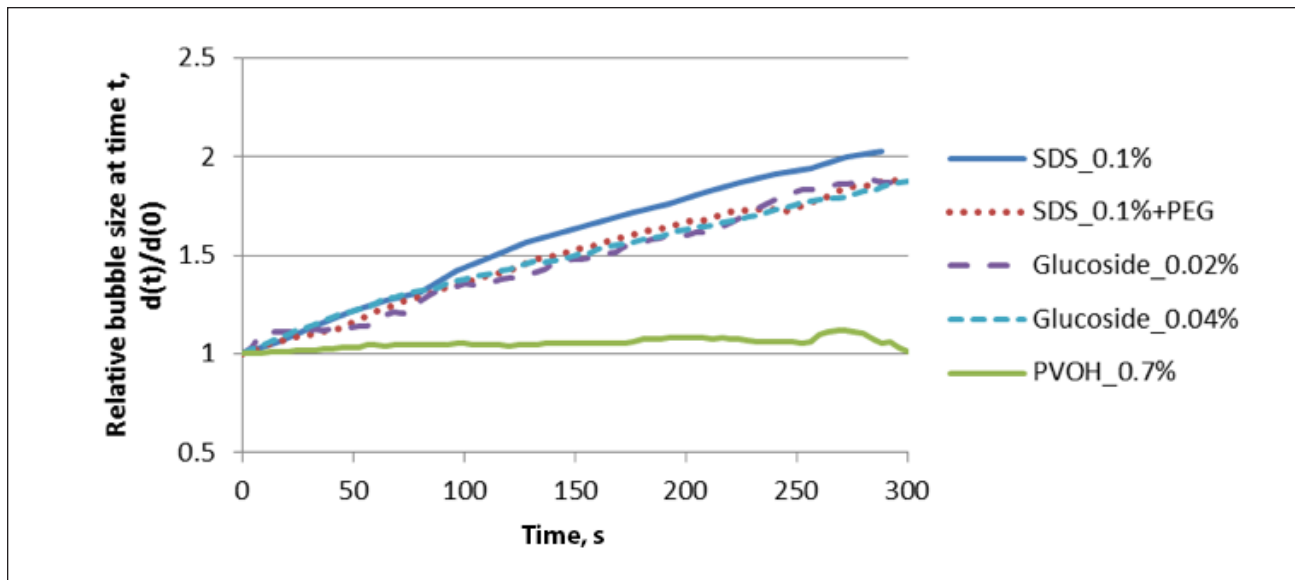
In the pilot foam coating trials, thin silica coatings of a coat weight from 2 g/m² to 3 g/m² were produced. The foaming

	Foaming Agent Concentration, wt%	Half-life Time, min	Silica Concentration, wt%
SDS	0.1*	4.0	9.9
SDS	0.2	4.0	9.8
SDS	0.4	4.5	9.6
SDS + PEG 400 (3 wt%)	0.1	4.0	7.0
C8/C10 Glucoside	0.02	2.2	10
C8/C10 Glucoside	0.04*	3.2	10
C8/C10 Glucoside	0.08	4.2	10
PVOH	0.2	9.8	9.6
PVOH	0.7*	17	8.7
PVOH	0.9	19	8.3

* Critical micelle concentration determined.

SDS = sodium dodecyl sulfate; PEG = polyethylene glycol; PVOH = polyvinyl alcohol.

I. Half-life time of silica foams at concentrations around critical micelle concentration determined for silica dispersions.



2. Relative bubble size as a function of time of dispersions of nanosilica foaming agent and water.

	Roughness, μm	Air Permeance, $\mu\text{m}/\text{Pas}$	Gloss, %	Contact Angle, Water (23°C), 0.5 s, °
Base Paper	5.2 (0.1)	4.3 (0.1)	5.1 (0.3)	29.7 (1.8)
Silica + SDS	5.8 (0.1)	4.0 (0.1)	4.5 (0.3)	16.9 (1.3)
Silica + Glucoside	6.0 (0.1)	3.7 (0.1)	4.2 (0.1)	14.9 (1.0)
Silica + PVOH	6.0 (0.1)	3.7 (0.1)	4.1 (0.2)	52.9 (4.6)

SDS = sodium dodecyl sulfate; PVOH = polyvinyl alcohol.

II. Standard paper properties, average value, and standard deviation (in parentheses).

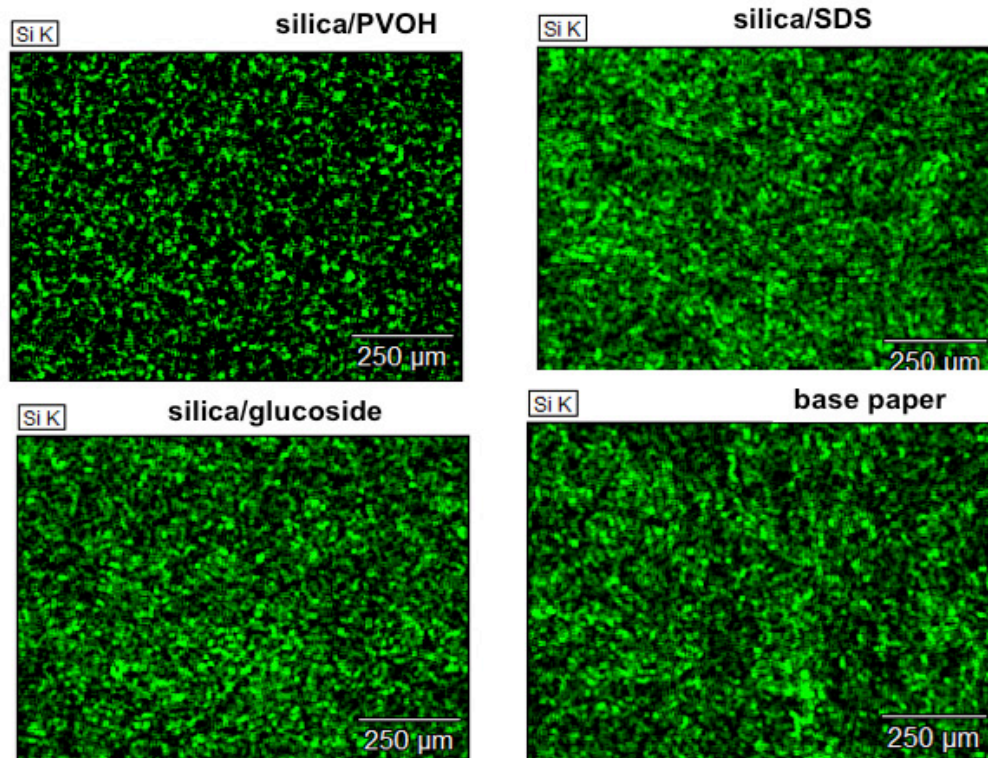
agent concentration of 0.2 wt% in the silica dispersion was chosen. On the basis of the laboratory studies, this concentration was known to give stable foams with all three surfactants studied.

The foam coating process worked well with three surfactants. **Table II** shows the results of paper roughness, gloss, air permeability, and water contact angle of silica-coated paper compared with an uncoated base paper. Thin silica coating slightly reduces paper gloss, and roughness is somewhat higher. The air permeance results indicate that a thin silica layer reduces only slightly the air permeance of the whole paper; however, the silica coating clearly changes the surface hydrophilicity. The silica pigment is hydrophilic, and the silica-coated samples with a molecular foaming agent had a lower contact angle with water than the uncoated fine paper. The silica coating with PVOH as a foaming agent induced a higher water contact angle than the uncoated reference. The partially hydrolyzed PVOH has acetyl groups, which made the surface more hydrophobic. The results indicate that the surface hydrophilicity was related not only to the silica pigment, but also to the chemical nature of the

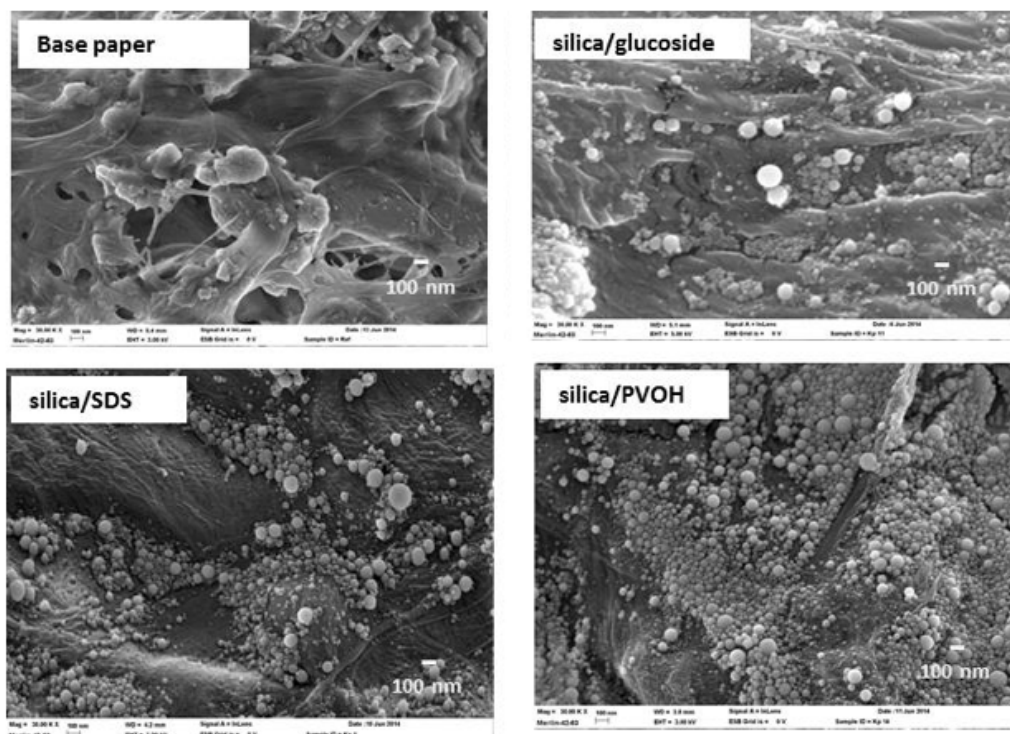
foaming agent. Surface properties such as hydrophilicity, which affects the water absorption and the ink setting of the water-based inks on pigment coating, can be affected by appropriate selection of the foaming agent.

The distribution of the silica pigment on the surface of a paper was studied with SEM-EDX silicon-element mapping analysis. In the image, higher color intensity represents surface areas with higher amounts of silica. The silicon map of the base paper has weak signs of silicon, which originate mainly from the background noise of the EDX detector. Silicon maps of the coated paper surface show that the silica pigment is evenly distributed and the pigment distribution is similar for the surfaces coated with different foaming agents (**Fig. 3**).

A more detailed analysis of the silica pigment location on the surface of the paper was done with HR-SEM-SE images, which give topographic information of the silica coating on the base paper. The SE images with a magnification of 30000x in **Fig. 4** show that the silica particles do not cover the base paper. Instead, the silica particles form clusters on the fiber network. The silica clusters look similar on the three silica-coated surfaces produced with different foaming agents.



3. Silicon (Si) element maps of the base paper and the silica foam-coated paper samples.



4. High-resolution scanning electron microscope–secondary electron images at 30000x magnification of the base paper and the silica foam-coated paper surfaces.

CONCLUSION

In this work, CMC of silica dispersions and the stability of the foamed silica dispersions with three different foaming agents were studied. Polyvinyl alcohol as a polymer foaming agent reduced the surface tension of the silica dispersion less than the molecular surface active agent glucoside and SDS but produced the most stable foam. The surface tension does not predict the foam stability. The increased foam stability obtained with PEG can be detected from the bubble growth but not from the half-life time of foam.

The hydrophilicity of the thin silica-coated paper surfaces was related not only to the silica pigment but also to the chemical nature of the foaming agent. This offers possibilities to adjust, for example, absorption of water-based chemicals or inks on paper surface with a thin pigment layer. Foam coating is a promising and economically viable technique for imparting functionality (e.g., hydrophobicity) on paper, board, nonwoven, and textile webs. Our earlier work to apply functionalized CNF on paper has shown that the foam coating technique can be used to create antimicrobial properties on the paper. The technique is also well suited for various sheet-formed products, such as cosmetics, hygiene, and household wipes. **TJ**

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ABOUT THE AUTHORS

Foam coating technique offers possibilities to apply a large variety of materials on paper, board, and nonwoven webs. Suitable methods are needed to characterize foaming properties of different materials for foam coating purposes. Information is also needed about the effects of surface active agents on the surface properties of foam coatings. These developments would enhance the usability of the technique.

We have supplemented the existing knowledge and practical applications with results on foam properties of nanosilica dispersions. We have also studied the effect of foaming agents on the properties of foam coated surface. The large variety of foaming agents offers numerous possibilities to choose compositions of coating material and surface active agent for foam coating purposes. In this research, we based the selection of foaming agent on our earlier studies on various surfactant/fiber systems.

The results showed that the bubble growth measurement and foam half-life time determination are both useful characterization methods for the purpose of foam coating trials. It is also a very interesting finding that the surface properties of the coating can be affected by the selection of coating compound and the properties of the foaming agent.

Foam half-life time and bubble size growth measurements are useful tools when studying performance of foaming agent to create stable foam for the foam coating process. The results and knowledge we have gained while studying silica dispersions will be used for adding new functionalities to web materials with the foam coating technique.

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