Nanofibrillated cellulose as a coating agent to improve print quality of synthetic fiber sheets

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ABSTRACT: To determine the potential of nanofibrillated cellulose (NFC) for use as a coating material, we studied the characteristics of several NFC-coated samples on a synthetic fiber sheet. We used two water-based printing methods to characterize the change in print quality and prepared two types of NFC by two different physical treatment methods. Various coat weights were applied onto synthetic fiber sheets, and the printability of the coated sheets was evaluated by ink absorption rates and print density. Ink pigment penetration was characterized with a confocal laser scanning microscope and a scanning electron microscope, with chemical analysis of samples using focused ion beam. The contact angle and the ink penetration rates decreased with increased coat weight of NFC. This result is the opposite of what the Lucas-Washburn equation would predict. For pigment-based flexographic inks, ink pigments were captured at the NFC layer. For dye-based inks, the ink components penetrated and moved through the NFC-coated layer. For ink-jet printing, the print quality improved with the NFC coating.

Application: Synthetic fiber sheets coated with NFC can improve printing resolution and ink density, especially for pigment-type inks.

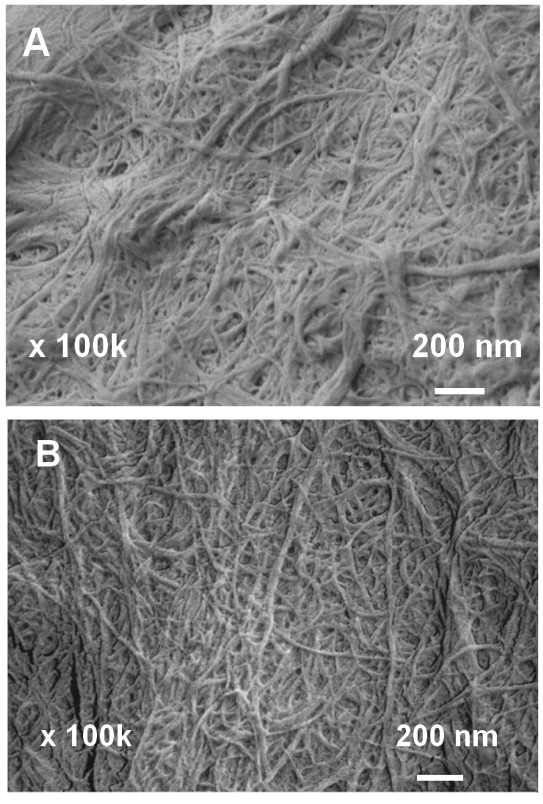
Nanotechnology has been advancing rapidly in recent years. Although most nano-scale products use expensive chemicals and difficult processing techniques, the possibility has been explored of using natural and renewable materials such as cellulose nano-fibers that have the potential to be environmentally friendly with a wide range of applications. A recent review of articles demonstrated the interest in using nano-scale cellulose to generate new materials such as composites with novel properties [1].

Various preparation methods to produce cellulose nanofibers have been reported. Chemical methods use a pure source, such as microcrystalline cellulose hydrolyzed with sulfuric acid treatment, to give uniform cellulose "whiskers" that are around 10 nm in width and 100 nm in length [2]. Another method, using wood fibers, is TEMPO-mediated oxidation [3, 4] that produces excellent-quality samples composed of stable fibers. Clear films could be made with this material, but the chemical costs might be high if the chemicals cannot be recycled. Various mechanical methods have been described, such as crushing pulps using a ball mill and adding organic solvents [5] or forcing fibers through a constriction in a homogenizer with high pressure to generate a distribution of small-length fibers [6]. These mechanical methods produced nano-scale fibers at low cost, but the fibers had a wide size distribution and were not well dispersed. In the literature, these fibers have had various names, such as micro-fibrillated cellulose (MFC), nanofibrillated cellulose (NFC), cellulose nano-crystals, and cellulose nanofibers. The applications of cellulose nano-fibers in various fields have been reported, especially as a reinforcing agent in a composite structure [1, 7–8], but their use in coatings for paper or other substrates has not been well reported in the literature.

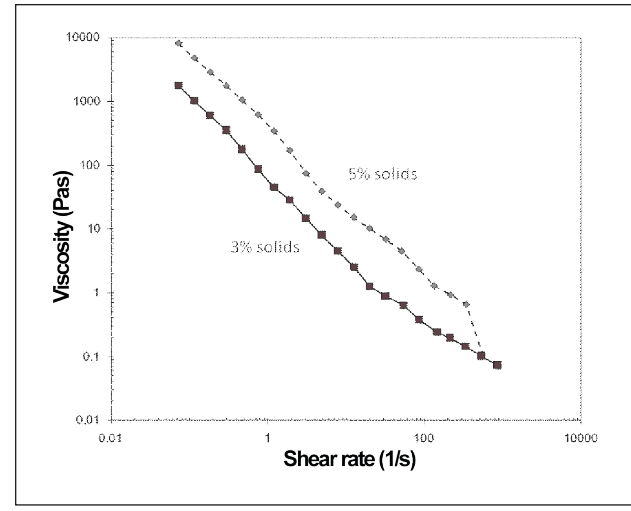
Recently, coated and uncoated papers, as well as nonwoven fabrics and synthetic fiber papers, have been used as materials for high-quality printing. We report on the ink absorption and printing characteristics of nanofibrillated cellulose as a coating on synthetic fiber sheets. The coating layer of interest is a layer that would upgrade uncoated synthetic fiber sheets for water-based printing applications, such as flexographic and ink-jet printing.

MATERIALS AND METHODS

Nanofibrillated cellulose (NFC) was prepared by two methods that both use mechanical energy and shear to disrupt wood fibers into smaller structural elements. With one method, the NFC was prepared by pretreating cellulose fiber sheets with a magnesium chloride ($MgCl_2$) solution, processing them with a dispersion mill (Kady International, Scarborough, ME, USA), and finishing with three passes through a homogenizer (Mini DeBEE, BEE International, South Easton, MA, USA). For the second method, the NFC was prepared by pretreating cellulose fiber sheets with an enzyme and processing them with a pilot-scale refiner. Both NFCs were made in the Process Development Center of the University of Maine. The pretreatments helped reduce the energy demand, but NFC can be produced without them. In general, both mechanical methods produced a similar material when viewed and poured from a beaker.



1. FE-SEM images of NFC: (A) prepared with a homogenizer (NFC1) and (B) prepared by a refiner (NFC2).



2. Steady shear viscosity of NFC2 at 3% and 5% solids.

The solids content of the NFC suspensions for both methods was around 3%. Even at this solids level, the suspension was viscous and demonstrated a high level of shear thinning. NFC suspensions were coated onto a synthetic fiber sheet with various wire-wound rods. A hydrophilic nonwoven sheet made from polyvinyl alcohol (PVA) fibers (12 g/m², BFN No.1, Hirose Paper Mfg., Kochi, Japan) was produced by a wet process. Three target levels of coat weight, 0.5, 1.5, and 3.0 g/m², were prepared by using different rods.

The contact angle of the samples, coated with a pigment-type flexographic ink (T&K TOKA, Tokyo, Japan), was measured. Images were collected using a microscope lens systems and a charge coupled device (CCD) camera. Image analysis determined the contact angle for different times right after the drops were placed on the substrate.

The absorption rates of a water-based ink into coated sheets were characterized with a Bristow absorption wheel. A known volume of ink was added to the trough. The viscosity of the ink was nearly equal to that of water, and the area of the trace left on the substrate was measured. The contact time between the ink and the substrate was varied by changing the speed of the wheel. We calculated the volume absorbed per unit area.

The coated samples were printed by a flexographic printing tester (K-Lox Proofer, R K Print Coat Instruments, Royston, UK) using the pigment-type red ink (T&K TOKA) and the dye-type red ink. The ink-jet printing was applied on the samples using the pigment-type black ink on an ink-jet printer (LEXMARK 9300 series). The print densities were measured by a print density tester (Quick Dens 100, X-Rite, Grand Rapids, MI, USA) and the printed images were observed using a confocal laser scanning microscope (CLSM) (TCS-SP2, Leica Microsystems, Wetzlar, Germany). The ink penetration behavior was also characterized using a field emission scanning electron microscope (FE-SEM) equipped with a focused ion beam (FIB) device to prepare cross sections and an energy dispersive X-ray analyzer for chemical analysis (NVision 40, Carl Zeiss AG, Oberkochen, Germany).

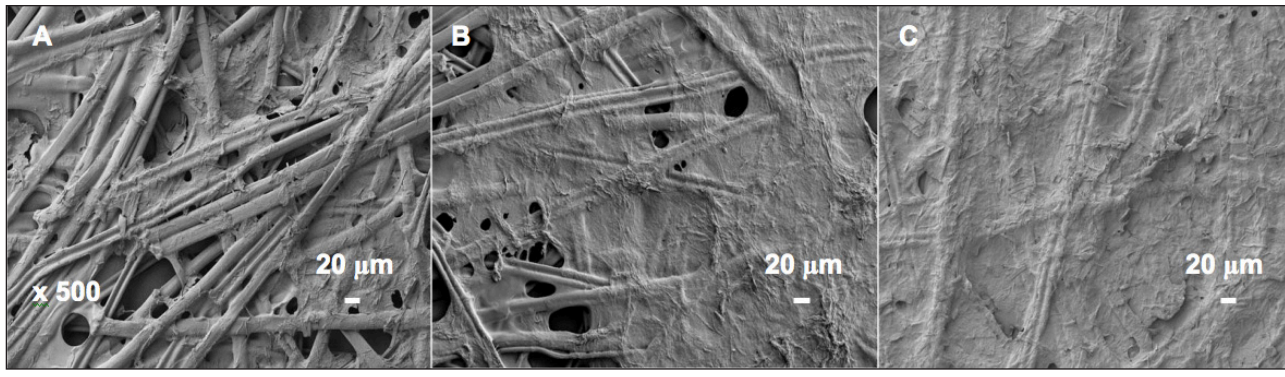
RESULTS AND DISCUSSION

NFC samples

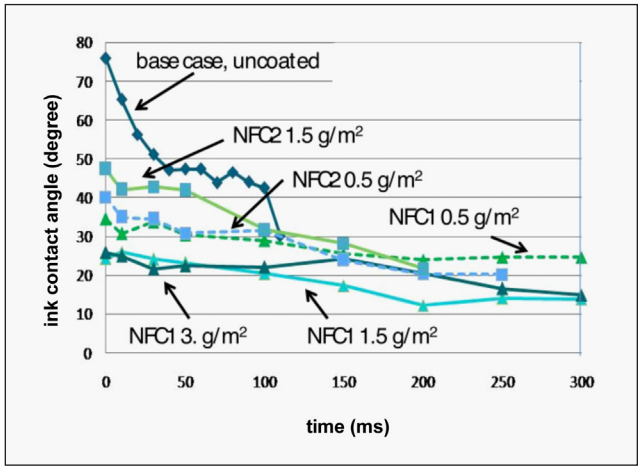
Figure 1 shows the images of NFC at high magnification. The NFC produced by the refiner (NFC2) was more individually separated than the NFC by the homogenizer (NFC1), but the differences were not large. The process with the refiner would be expected to result in more mechanical action for each fiber element, but some material may not have high shear zones. The width of an individual fiber was around 20 nm, although larger fiber dimensions were seen. The length of the fibers was hard to characterize because the ends of the fibers extended beyond the image or disappeared under other fibers. However, most of the fibers seen were well over a micron in length. **Figure 2** shows the steady shear viscosity of 3% and 5% solids suspensions. As noted earlier, even at the lower solids, the material was thick and had the consistency of yogurt, but shear thinning occurred to a great extent. There were no difficulties applying the NFC suspensions smoothly to the substrates.

Characteristics of the coated sheets

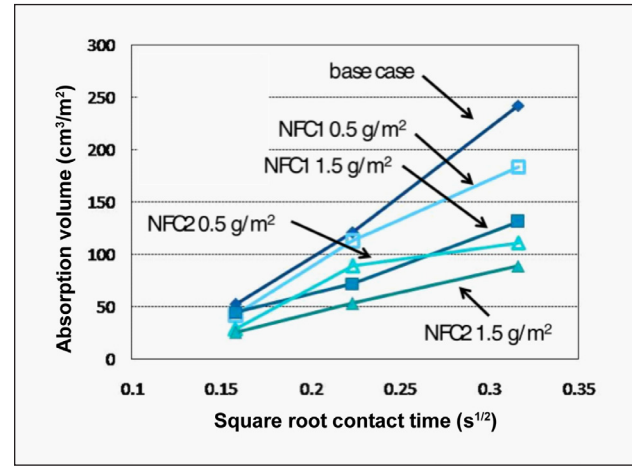
Figure 3 compares the FE-SEM images of the NFC-coated surfaces at different coat weights at a lower magnification than Fig. 1. The NFC covered the entire surface for the high-weight coating (3.0 g/m²). However, for the low-weight coat-



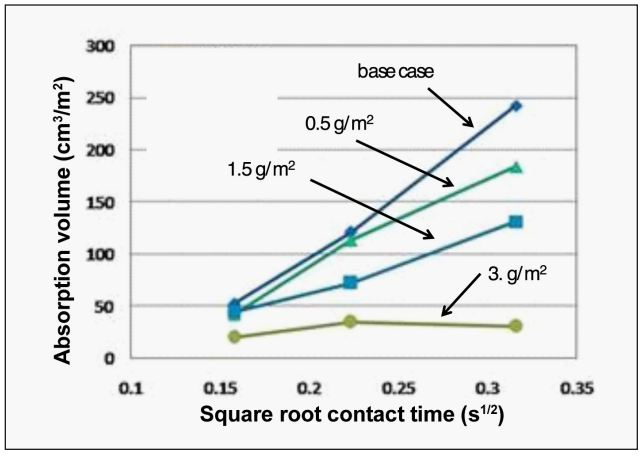
3. FE-SEM images of the NFC-coated surface: (A) 0.5 g/m² coat weight, (B) 1.5 g/m² coat weight, and (C) 3.0 g/m² coat weight.



4. Ink contact angle of the NFC coated sheets at various coat weights: NFC1 produced by a homogenizer, and NFC2 produced by a refiner.



6. Ink absorption volume at different contact times for NFC1 and NFC2 at 0.5 and 1.5 g/m² as noted.



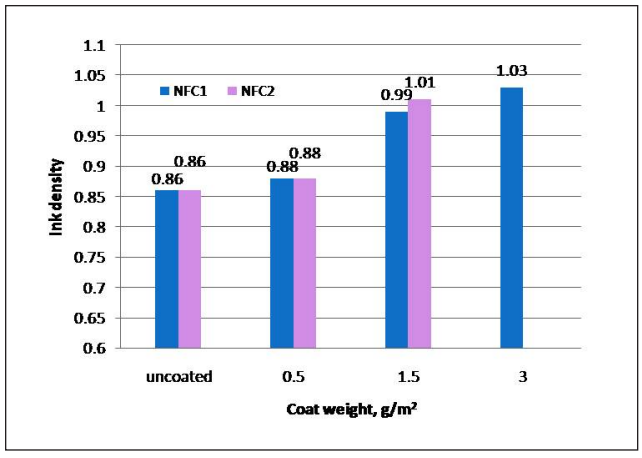
5. Ink absorption volume at different contact times on NFC1-coated sheets at three coat weights.

ing (0.5 g/m²), the NFC covered unevenly and left uncoated areas and some large-pore regions. The middle-weight coating (1.5 g/m²) still had significant holes that would allow an easy path for absorption. The fine and thin fibers were tangled and covered the base sheets. The left image of Fig. 3 shows that the base sheet had uniform fibers of around 20 µm.

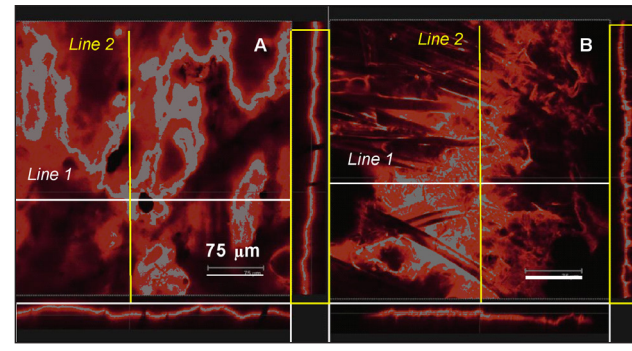
Figure 4 presents the ink contact angle of the coated sheets. The initial contact angle decreased with increasing coat weight of NFC, which was expected because the NFC was more hydrophilic than the PVA fiber. The contact angle on the NFC produced with a homogenizer (NFC1) was lower than those produced by the refiner (NFC2). For all samples, the contact angle decreased as time increased, which was likely related to ink absorption into the substrate. Within resolution of the camera, the drops did not spread in the radial direction. By looking at the rate of decrease, the rate of absorption decreased even for the low-weight sample.

Ink absorption rates

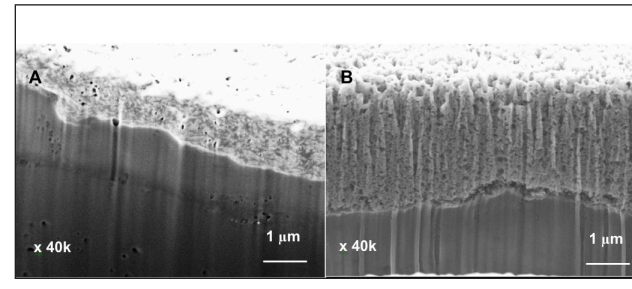
Figures 5 and **6** show ink absorption measured using the red-pigment ink for flexographic printing. We reported the total liquid volume absorbed per unit area for different coat weights as a function of contact time. The rate of absorption decreased as the NFC coat weight increased. This result is the opposite of what the Lucas-Washburn equation would predict for a decrease in contact angle; that is, a decrease of contact angle increases the capillary pressure and the absorption rate. The amount of NFC added to the system was quite small and should not have influenced the pore volume of the substrate.



7. Ink density on the printed samples: NFC1 produced by a homogenizer, and NFC2 produced by a refiner.



8. Reconstructed images of the orthogonal projections for the printed samples with 3 g/m² coat weight observed by CLSM: pigment-type ink (left) and dye-type ink (right).



9. Cross section images of the printed area prepared by FIB: (A) flexographic printing with the pigment-type ink, and (B) ink-jet printing with the pigment-type ink.

However, this decrease in absorption rate could be explained by low permeability of the NFC layer and the surface becoming covered with NFC. In addition, the ink pigments may be captured by the NFC layer near the surface, thus increasing the resistance to penetration. The ink pigment imaged in the FE-SEM was found to have a long side of 200 nm and a short side of 50 nm, which was larger than the width of an individual fiber of NFC (20 nm) and likely would have been caught by the NFC layer shown in Fig. 1. The NFC produced with the homogenizer (NFC1) showed a higher absorption rate than the NFC by a refiner (NFC2), which can be explained by contact angles in Fig. 3. The difference in pretreatment methods also may have led to a change in the average surface properties of the fibers.

Ink density and ink pigment penetration behavior

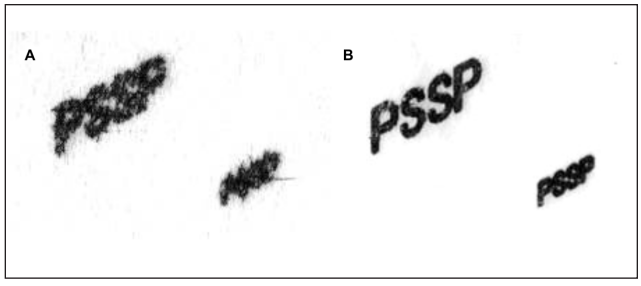
The ink density on the samples printed with the flexographic printing tester increased with increasing NFC coat weights, as shown in **Figure 7**. The NFC produced with a refiner (NFC2) showed slightly higher density than the NFC made by a homogenizer (NFC1). The flexographic printing tester supplied the same amounts of ink with an engraved roll to a rubber surface that contacted the sample. Therefore, the amount of ink presented to the substrate would be the same for all samples. Although the higher absorption rates of the uncoated samples may be able to influence ink transfer and increase the print density, the opposite result was seen. This result suggests that ink pigments were fixed near the surface on the samples with high coat weights but were able to penetrate into the uncoated samples.

CLSM images show the distribution of ink pigments on the surfaces; the cross sections are shown in **Figure 8**. The center of the figure is XY-plane stacked images, the bottom image is an XZ-plane that is sectioned optically along line 1, and the right image is a YZ-plane that is sectioned along line 2. The red-ink pigment emitted a strong fluorescence at the excitation wavelength of 514 nm and was shown as gold-red. The fibers did not emit any fluorescence at this wavelength. The XZ- and YZ-plane images show that the pigments in the pigment-type ink mostly distributed on the surfaces. The dyes in the dye-type ink penetrated through the NFC coated layer, as shown in the right-side inset cross section in Fig. 8.

Figure 9 shows the cross-section images produced by FIB on the printed samples with the pigment-type flexographic ink. The images show that the ink pigments distributed on the NFC layer and did not penetrate through it. The results of elemental analysis by EDX showed that the top layer included barium, chloride, and sulfur derived from the pigments of the ink; the second layer included chloride from magnesium chloride ($MgCl_2$) added to the NFC during preparation; and the bottom layer had none of these elements. This result also demonstrated that the ink pigments were captured on the NFC layer and did not penetrate through the coated layer, which led to high print density on the surface of NFC-coated samples.

Ink-jet printing

For results that involved ink-jet printing, the print quality improved by coating with NFC on the synthetic fiber sheets, as **Figure 10** shows. The pigment in the ink-jet ink was much smaller than the pigment in flexographic ink. However, the diameter of the ink-jet black pigment, around 35 nm, was larger than the width of an individual fiber of NFC, 20 nm. The coated samples still were far from a high-



10. Images of the ink-jet printed samples: (A) on the uncoated synthetic fiber sheet, and (B) on the coated sheet of NFC with 3 g/m².

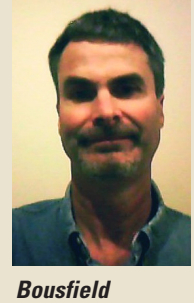
quality media intended for ink-jet printing. The edges of the letters had some feathering issues and some solid regions still had white showing through. These defects possibly could be eliminated by an even higher coat weight, above the 3 g/m² reported here. The cross-section images prepared by FIB in Fig. 9 show that the pigment layer distributed on the NFC layer and the pigments in ink did not penetrate through the NFC layer. However, for the dye-based color inks, the improvement was minimal and the dyes were able to penetrate through the NFC layer.

ABOUT THE AUTHORS

Our objective was to use nanofibrillated cellulose to improve the printing properties of synthetic fiber sheets. Although there has been research on ink-paper interactions, the use of NFC is a new area of study. We found that we had to make adjustments while spreading NFC on the sheets because of its viscosity. An interesting finding was the amount of NFC that was needed before we saw improvements in paper properties.

Mills may be able to produce NFC onsite at low cost and use it as a coating agent to improve print quality of synthetic fiber sheets. Our next step is to test NFC application methods at higher solids.

Hamada



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CONCLUSIONS

NFC helps to capture ink pigments near the surface and causes an increase in ink density and print quality for both pigmented flexographic and ink-jet prints. The individual fibers of NFC are sufficiently small to capture even the small pigment used for ink-jet inks. NFC has the potential to be a low-cost surface treatment that results in porous hydrophilic surfaces that can capture ink pigments near the surface and prevent the pigments from penetrating into the sheet. Synthetic fiber sheets coated with NFC demonstrated improved printing resolution and ink density, especially for pigment-type inks. **TJ**

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