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Cellulose nanocrystals coating – A novel paper coating for use in the graphic industry

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Abstract:

The rising concern about the impact of printing material on the environment is pushing the graphic industry to turn towards the use of materials derived from abundant, renewable resources. The end-result of this process would be a replacement of conventional printing materials that are often derived from unsustainable resources. The aim of this study was the application of cellulose nanocrystals (CNC) coating as a novel type of sustainable coating that might eliminate use of synthetic coatings. The selected coating was prepared from cellulose nanocrystals suspension that was derived from cellulose fibrils on the laboratory scale. The coating formulation examined in this paper was not yet used on the industrial scale. Experimental research was carried out in the form of preliminary laboratory tests for offset printing application using IGT test methods of ink transfer and set-off. Paper coated with cellulose nanocrystals was used as a printing substrate, while vegetable oil-based ink was used as a printing ink in order to stay in line with environmentally preferred choice of printing materials. The results indicated an increase in surface gloss on paper coated with cellulose nanocrystals, as well as in print gloss on printed paper coated with cellulose nanocrystals. The downside of cellulose nanocrystals coating was the prolonged drying time of ink. Further research should be dedicated to improving cellulose nanocrystals coating as the formulation used in this study caused undesirable cockling and waviness on selected paper grade.

Keywords:

Cellulose nanocrystals (CNC), paper coating, vegetable oil, printing ink, printability tests

1. Introduction

Sustainable development in the graphic industry is promoted by the “green” printing initiative that uses bio-based materials derived from renewable resources and/or with low environmental impact to develop novel, environmentally friendly

solutions for the printing technologies. The contemporary tendency of the industry is to replace synthetic additives and coatings in the paper and board production with alternative bio-based materials that show the same or similar properties as

conventionally used polymer emulsions. Properties that materials should have for a successful implementation are good moisture barrier properties, heat sealability, stiffness and tensile strength, as well as adequate visual appearance and printability properties (Holik, 2006, Khwaldia, Arab-Tehrany and Desobry, 2010).

Cellulose is the most abundant natural organic polymer worldwide and almost an inexhaustible source of renewable raw material (Habibi, 2010). It is structured from cellulose fibres, whose dimensions and chemical composition differ depending on cellulose origin. Cellulose is a polysaccharide, a linear polymer $(C_6H_{10}O_5)_n$ bound together by hydrogen bonds into a strong matted structure. Hydrogen bonding is determined by the close proximity of hydroxyl groups, three of which are present on each monomer. The ability to form hydrogen bonds plays a major role in defining the physical properties of cellulose (John and Thomas, 2008, Cintin, Lovely and Sabu, 2014).

When cellulose is modified on a nanoscale, a novel type of sustainable material is obtained – the nanocellulose. Interest which the graphic industry and paper and board industry showed in nanocellulose is due to increased functionality, improved mechanical properties, interesting optical properties (transparent material that can provide colour without colorants) and enhanced barrier properties (Klemm, et al., 2011, Lavoine, et al., 2012). Above all, the advantage of using nanocellulose is that it is in line with green printing initiative due to its natural origin and chemical components that are the same as the source material, cellulose. Nanocellulose could be used as a strengthening agent in paper due to its high tensile strength; it could be used for surface sizing and coating application. The latter is especially interesting in food packaging industry due to its good oxygen transfer control, water vapour control and oil control (Klemm, et al., 2011, Duran, Lemes and Seabra, 2012).

Nanocellulose is prepared from cellulose fibrils, which are mechanically disintegrated from the plant cell walls in the pulp manufacturing process. The nanocellulose fibrils have a diameter from 2 – 20 nm and a few micrometres in length (Klemm, et al., 2011). The extraction of nanocellulose can be done by a process of acid hydrolysis or enzymatic hydrolysis of kraft pulp cellulose, oxidation processes, electrospinning, high-pressure homogenization or steam explosion (Duran, Lemes

and Seabra, 2012). Various natural sources of cellulose are used for the isolation of nanocellulose, such as wood, agricultural by-products (cotton, wheat straw, sugar beet pulp, hemp, flax, potato tubers, sisal and banana rachis), tunicates, algae and bacteria (Habibi, 2010, Hubbe, 2008, Klemm et al., 2011). The most commonly used source for the extraction of cellulosic fibrils is wood (Hubbe, 2008, Lavoine, et al., 2012). Depending on the preparation and source of origin, there are different grades of nanocellulose: microfibrillated or nanofibrillated cellulose (MFC/NFC), cellulose nanocrystals (CNC) and bacterial nanocellulose (BNC).

Cellulose nanocrystals suspension is most commonly prepared in a chemical process from natural cellulose by acid hydrolysis using sulphuric acid as a hydrolysing agent (Duran, Lemes and Seabra, 2012). In an acid treatment that hydrolyses cellulose and removes microfibrils, cellulose rod-like nanocrystals are produced and formed into liquid-crystalline suspensions (Habibi, 2010). In some literature cellulose nanocrystals are called whiskers or nanorods (Hubbe, 2008, Klemm, et al., 2011). Typical diameter of nanocellulose crystals is considered to be 5 - 70 nm, while the length depends on the cellulose origin: 100 – 250 nm if extruded from plant celluloses and 100 nm to several micrometres if extruded from celluloses of tunicates, algae and bacteria (Klemm, et al., 2011). Cellulose nanocrystals from wood cellulose have a diameter of 3 – 5 nm and length in a range of 100 – 200 nm (Habibi, 2010).

Microfibrillated or nanofibrillated cellulose suspension has gel-like characteristics and it is produced from wood delamination by mechanical pressure before and/or after chemical or enzymatic treatment. MFC/NFC has long fibrils, diameter from 5 - 60 nm and a length of several micrometres (Klemm et. al, 2011, Siro and Placket, 2010). Bacterial nanocellulose is formed as a polymer and nanomaterial by biological self-assembly processes from carbon sources of low molecular weight. It has a diameter of 20 – 100 nm and length $> 1 \mu\text{m}$ (Siro and Placket, 2010).

Laboratory prepared cellulose nanocrystals (CNC) coating and vegetable oil-based ink present selected biodegradable printing materials, under the umbrella of green printing initiative. The goal of our study was to investigate if the novel type of coating could enhance the visual appearance and improve printability properties of

the printing substrate. Experimental part of the research was carried out on laboratory scale in the form of preliminary printability tests for offset application using IGT test methods of ink transfer and set-off.

2. Materials and methods

Printing materials and equipment were conditioned during 24 h in the standard atmosphere, (23 ± 1.0)°C and (50 ± 2.0)%rh, prior to printing.

2.1. MATERIALS

Paper substrate used as a base paper for coating and as a reference paper during printing was uncoated bleached kraft paper K75, 60 g/m² manufactured by Papierfabriek Doetinchem B.V. Felt side of the paper was calendered.

Cellulose nanocrystals coating used in this research was extracted from wood cellulose with solid content of approximately 7 wt% and with no extra additives in the coating solution. It was produced at laboratory scale at the Maine University, USA. The coating was applied in an amount of 1.5 g/m² dry weight to the wire side of the base paper by a laboratory rod coater at PTS institute, Munich, Germany. The coating formulation examined in this paper was not yet used on the industrial scale.

Printing substrates were printed by vegetable oil-based ink, F960 Vision Plus Bio cyan ink from Flint Group, having a bio-renewable content of 65 – 75%. Viscosity of F960 Vision Plus Bio cyan ink at (23 ± 0.1)°C was 52.96 Pas.

2.1.1. PRINTING SUBSTRATES USED IN THE INK TRANSFER METHOD

Prints were made on CNC coated K75 paper samples, machine direction, wire (coated) side, 55 x 275 mm and uncoated K75 paper samples, machine direction, wire side, 55 x 275 mm. Prior to printing, surface gloss was measured on unprinted paper samples of CNC coated K75 paper, machine direction, wire side, uncoated K75 paper samples, machine direction, wire side and uncoated K75 paper, machine direction, felt side.

2.1.2. PRINTING SUBSTRATES USED IN SET-OFF METHOD

Prints were made on CNC coated K75 paper samples, machine direction, wire (coated) side, 55 x 380 mm and uncoated K75 paper samples, machine direction, wire side, 55 x 380 mm. Standard set-off paper, IGT art paper, code KA, 55 mm width was used as a paper in contact.

2.2. METHODS

2.2.1. INK TRANSFER

During the printing process, a fast and uniform ink transfer from the printing disc to the printing substrate is required. Measured by the ink film thickness on paper, ink transfer presents the amount of ink transferred from the printing disc to the paper. Ink transfer is influenced by several factors such as ink viscosity, amount of ink, printing speed and printing force, absorption ability of substrate, and smoothness of the substrate (Thompson, 2004, Todd, 1994).

The method was implemented according to the IGT information leaflet W80. The ink was applied in an amount of 0.20 cm³ of ink with the IGT ink pipette on an inking unit of IGT Printability tester CT-1 and was evenly distributed for 60 s. The printing disc with coated rubber, 65 Shore A, 55 mm was inked for 30 s. Printing force of the IGT Printability tester Orange proofer was adjusted to 600 N with a constant speed of 2.0 m/s.

Printing disc was weighed with precision scale Mettler AE200, of 0.1 mg reading accuracy before the print and after the print to calculate the amount of ink transferred to the paper substrate with the following formula:

$$\text{Ink transfer} = (10\,000 / L \times W) \times \Delta G$$

Where:

L = length of the print (cm),

W = width of the print (cm),

ΔG = weight difference of inked printing disc before and after print (g).

The density of dried prints was measured at 10 spots across the length of a print with Techkon Spectrodens to calculate the average value. Density calibration was on the paper white and measurements were made with D50 illuminant/2°

observer angle. Surface gloss and print gloss were measured at 10 spots across the length of a printing substrate with IGT Gloss Meter G75, at 75° to calculate average value.

2.2.2. SET-OFF

Ink properties for offset printing also depend on the ink drying process. Most common related problems regarding ink setting in the offset process are set-off, smearing and rubbing of ink caused by too slow absorption, or reduced colour strength caused by too fast vehicle absorption (Thompson, 2004, Todd, 1994). The speed of ink drying on paper is measured as the amount of non-absorbed ink on the print that is translated to the standard set-off paper in contact. Density of smeared, translated ink was used to express the absorption rate. Different contact interval times were used in this research: direct contact (0.1 s) and 3 s interval.

The set-off method was conducted according to the IGT information leaflet W48. The ink was applied in an amount of 0.20 cm³ with the IGT ink pipette on the IGT High Speed Inking Unit 4 and was evenly distributed for 60 s, while the inking of aluminium printing disc, 50 mm was carried out for 30 s. The printing force of IGT printability tester Amsterdam 5 was adjusted to 1000 N with a constant speed of 0.7 m/s. After a defined interval time, printed strips were brought into contact with a blank strip of standard set-off paper, attached to the aluminium printing disc.

The density of dried prints was measured at 10 spots across the length of a print with Techkon Spectrodens to calculate average value. Density calibration was on the paper white and measurements were made with D50 illuminant/2° observer angle.

3. Results and discussion

3.1. INK TRANSFER

Comparing the first two prints from a batch made on CNC coated paper and uncoated paper, it was noted that 12.2 % more ink was transferred to uncoated paper to achieve the same density as on the CNC coated paper (see Figure 1). CNC coated samples showed steady ink transfer during

printing of five samples while uncoated samples had more variations, noting ink thickness reduction from the third print onwards, but without a drop in density reproduction.

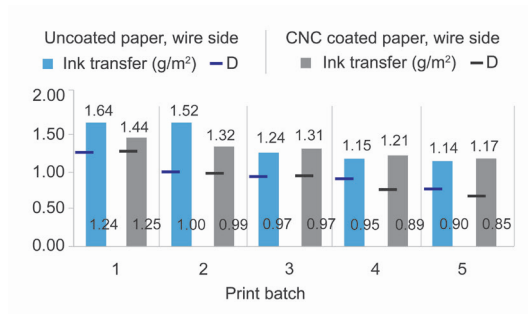


Figure 1 Ink transfer and density of printed CNC coated and uncoated paper samples

Measured gloss units (GU) of printed and unprinted, CNC coated and uncoated papers are shown in Figure 2. CNC coating enhanced surface gloss up to two times, both on unprinted and printed paper samples, giving a pearly gloss effect on the paper surface. It was suggested from a similar study (Bulota, 2013) that the surface gloss enhances as the CNC coat weight increases. However, the felt side of K75 paper, calendared with the Yankee cylinder, showed a significantly higher gloss in comparison to the CNC coated paper, wire side. Still, the application of CNC coating on the wire side has an advantage, according to the study that showed actual decreasing of the gloss when applying nanocellulose coating on the initially higher gloss paper (Nygards, 2011).

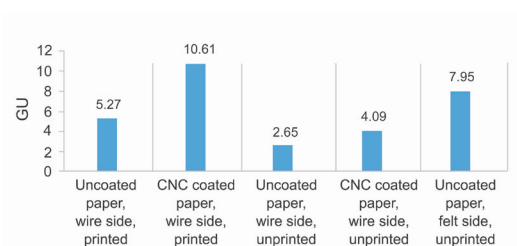


Figure 2 Surface and print gloss of unprinted and printed CNC coated and uncoated paper samples

CNC coated papers showed cockling and waviness caused by the high water content in the coating, as shown in Figure 3. Coating formulation, coating process and correlation between the amount of coating and paper thickness should be addressed in further research to avoid the undesirable side effect of cellulose nanocrystals coating

on paper.



Figure 3 K75 paper sheet, wire side before coating (above) and CNC coated K75 paper sheet, wire side (below)

3.2. SET-OFF

The drying time of ink on printed substrates was longer on CNC coated paper than on uncoated paper. More ink (i.e. $\Delta D=0.14$) was transferred to the set-off paper at a direct contact from prints made on CNC coated paper, as shown in Figure 4. After a 3 s interval, the density of smeared ink on set-off paper was lower from both paper substrates; however, more ink (i.e. $\Delta D=0.09$) was still translated to set-off paper from printed CNC coated papers. The density of printed-only area is higher on CNC coated paper for $\Delta D=0.14$ than on uncoated paper suggesting a higher density reproduction on CNC coated paper from the same amount of ink applied.

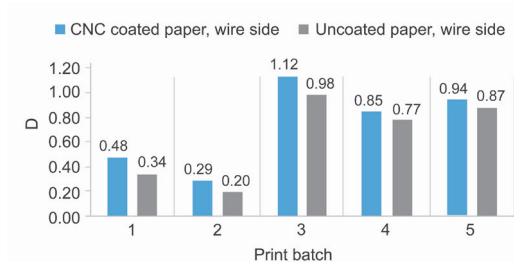


Figure 4 Density of set-off prints with 3 s interval, two fields; 1 - Set-off paper, 1st contact; 2 - Set-off paper, 3 s interval; 3 - Test paper, printed only; 4 - Test paper, 1st contact; 5 - Test paper, 3 s interval
CNC coated paper, wire side and uncoated

paper, wire side are not suitable for printing with aluminium printing disc as it caused mottling, i.e. uneven print appearance on printed substrates. Mottling could have been prevented by using flexible rubber blanked disc instead of an aluminium printing disc. Figure 5 shows the difference in the amount of ink transferred to the set-off paper that was in contact with printed CNC coated and uncoated paper.

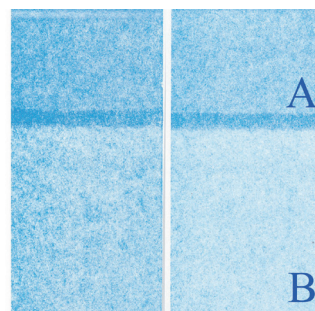


Figure 5 Set-off paper that was in contact with printed CNC coated paper (left) and printed uncoated paper (right); A = direct contact, B = interval of 3 s

4. CONCLUSIONS

Cellulose nanocrystals coating affects the increase in surface gloss and print gloss. However, surface gloss of CNC coating on the K75 paper, wire side is lower than the surface gloss of calendered K75 paper, felt side. The drying time of ink was longer on CNC coated paper than on uncoated paper. Steady ink transfer and less ink needed to achieve target density at the beginning of a print batch is showing an economical advantage of CNC coating application. Formulation of CNC coating used in this research should be further improved due to appeared cockling and waviness of the coated substrate. This undesirable appearance was caused by the high water content of cellulose nanocrystals coating applied on the relatively low grammage paper grade. It is important to address the coating formulation, coating process and correlation between amount of coating and paper thickness of base paper prior to future applications of CNC coating for printing purposes.

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6. References

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