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Nanocrystalline Cellulose and Polyvinyl Alcohol Coating Application to Cardboard Packaging Papers and Investigation of the Effects on Paper Properties

Semiha YENİDOĞAN *

Marmara University School of Applied Sciences Department of Printing Technology, 34722, Istanbul, Turkey

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In the packaging sector of the printing industry, different coating applications are tried and investigated in order to increase the surface appearance and performance characteristics of paper and cardboard. The printability, water and ink absorption capacity, frictional resistance, light sensitivity of the visual graphical design that are going to be printed on the packaging papers are some of them. In this study, different types of cardboards that are used as a packaging material were chosen and coated with nanocrystalline cellulose (NCC)/PVA at different rates (%). In order to determine effective and economical usage conditions, the coating solutions, at three different concentrations as 3 wt.%, 5 wt. %, 7 wt.%, were prepared. The coating was applied on the test papers, which were at the same weights (350 g/m^2) and had different surface properties as matte glossy, bright glossy, American Bristol. NCC/PVA existence on the coated paper surface was confirmed with Fourier Transform Infrared Spectroscopy (ATR-FTIR). The impact of the coating, which was prepared at different concentrations, on the packaging materials was studied with respect to thickness, stiffness, water absorbability, contact angle and surface tension.

Keywords: nanocrystalline, nanocellulose, NCC, packaging paper, PVA, coating, cardboard coating.

1. INTRODUCTION

Packaging materials are widely used in various field, mainly cosmetics, food and beverages. These materials can be based on glass, aluminum, plastic and cellulose. The cellulose-based substrates are widely used in various industries such as packaging thanks to their high endurance, flexibility, low-cost and recyclability [1]. In comparison to other materials, the cellulose-based packaging materials have preferable superior properties in terms of their being lightweight, biodegradable, recyclable, eco-friendly and having lower cost [2 – 4].

In order to improve the performance properties of the papers, additives are added into the pulp or coated on the surfaces of paper as a thin film layer [5, 6]. However, as the surface coating materials, non-organic synthetic materials, such as kaolin, aluminum three hydroxide, zeolite, calcium carbonate, titanium oxide are used, along with different binders and chemicals as well as synthetic polymers, such as polyethylene, and materials like fluorocarbon. These materials are not recycled, eco-friendly and bio-degradable [7]. Due to these reasons, the use of eco-friendly and recyclable subtracts by the virtue of decreasing the synthetic coating agents possessed a great importance in terms of green chemistry and material science [8 – 11].

Biopolymers have an advantage of being sustainable, renewable and biodegradable, therefore they also reduce the carbon footprint. Biopolymer materials have relatively stable pricing and these advantages are driving adoption of these natural products [12]. Nanocellulose materials' usage areas are gradually increasing because of their being green and ecological with respect to carbon footprint and providing superior performance properties on the surface where they are applied [13, 14].

As well as the nanocrystalline cellulose is used in the composite materials because of their mechanical properties, they find a usage area in the paper sector with their biocompatibility, biodegradability and modular structure and their usage area is expanding [15, 16]. Ridway et al. showed in their studies that nanocellulose improved the barrier properties of the papers [17]. Baht et al. claim that CNF/Clay blends improve the quality of printability [18]. Some of the recent nanomaterials in the papermaking and coating industry include nanocrystalline cellulose (NCC) [12]. The studies have demonstrated that these nano materials improve various important properties of coated paper, an example for the tensile strength and elastic modulus differences between the paper, polyvinyl alcohol (PVA) film, cellophane and TOCN film [19]. In the recent years, PVA is widely used as the carrier of the nano materials thanks to its fully biodegradable, non-toxic, biocompatible, water-soluble properties [20, 21]. PVA is a linear and thermoplastic polymer. With its water-solubility and perfect chemical resistance, it is biodegradable and does not have any toxic impact on human body [22]. It was reported that PVA was successful in carrying carbon nanotube, chitin and cellulose nanofibers in nanofiller structures [23, 24].

In the recent years, it is endeavored to develop and improve the structure and surface properties of papers with the materials from renewable resources. NCC that can be easily found among this kind of materials draws great attention thanks to its renewability, biodegradability and good mechanical properties as well as the positive properties that it provides for the paper surface, in the recent years [25].

* Corresponding author. Tel.: +902163365770;
E-mail address: *semihayavuz@marmara.edu.tr* (S. Yenidoğan)

In this study, the test papers are covered with NCC/PVA at different percentage rates in order to study the physical, mechanical and printability properties. The water absorbability, tensile strength, surface energy, brightness values, decolorization process of the coated papers were analyzed.

2. EXPERIMENTAL DETALS

2.1. Materials

In this study, three different cardboard packaging paper, namely matte paper, glossy paper and American Bristol at the same weight (350 g/m^2) were used.

Table 1. Properties of test papers

Properties	Test method	Matte paper	Glossy paper	Bristol paper
Basis wt, g/m^2	ISO 536	350	350	350
Thickness, μm	ISO 534	0.30	0.26	0.49
Cobb (g/m^2 60 s)	ISO 535	20	27	18
Stiffness, mNm	ISO 2493	129	105	265
	MD/CD	85	87	137
Gloss, 75°	ISO 8254-1	33.7	65	46.4
Colour L* ± 0.8 %	ISO 5631-2	100.18	99.89	100.58
a* ± 0.6	ISO 5631-2	0.11	– 0.03	0.17
b* ± 1.1	ISO 5631-2	0.37	– 0.09	– 0.52

As the coating material Nanocrystalline Cellulose (NCC) material, provided from Nanolinter company, was used in dust form. The properties of NCC are given in Table 1 and their images in TEM device are shown in Fig. 1.

Table 2. NCC size and analysis properties

Analysis name	Analysis output	Nanocrystalline Cellulose (NCC)
TEM	Average grain size	Length: 223.90 nm Diameter: 35.72 nm
DLS	Average grain size	216.7 nm
XRD	Crystallinity, %	98.98 %

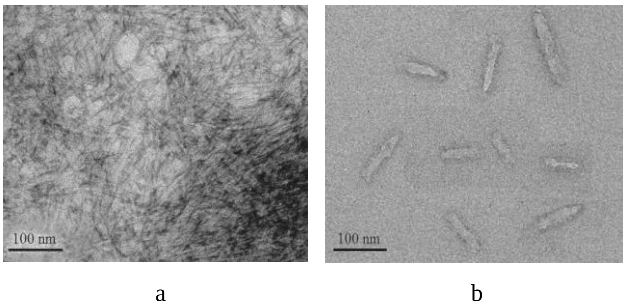

Fig. 1. TEM micrographs showing the morphology of NCC specimens produced from different hydrolysis conditions: a – NCC55; b – NCC60 [15]

As the nanocellulose carrier on the paper Polyvinyl Alcohol (PVA) (Mowiol 20-98) was chosen. PVA polymers' properties are given in Table 3 and Table 4.

Table 3. The properties of the PVA polymer, used in the study

PVA trade name	Abbreviated name	Average M_W, Da	Nominal percent of acetyl groups, %
Mowiol 20-98	PVA-98	125000	2

Table 4. Physical properties of polymer PVA

Polymer	Surface tension, mN/m	Viscosity, ×10^2 Pa·s	Conductivity, μS/cm
PVA-98	60.9 ± 0.3 62.1 ± 0.8 62.6 ± 0.1	14.1 ± 0.1 17.2 ± 0.1 17.8 ± 0.2	17.6 ± 0.4 29.4 ± 0.6 36.7 ± 0.5

2.2. Methods

2.2.1. Preparation of PVA/NCC suspension

Polyvinyl alcohol solutions were prepared. PVA 5 g was dissolved in 80 g distilled water at 90 °C for 60 min under mechanical stirring. Then, the solutions were kept under stirring to reach room temperature NCC dispersions were added to obtain a result NCC content 3, 5, 7 wt.% for coating, while keeping total PVA concentrations constant at 7 wt.%. The obtained mixture was mixed at 80 °C for 120 min in a mechanical mixer. Then, it was cooled down in a refrigerator (12 hours). Afterwards, viscosity and surface tension were determined in room temperature with Brookfield DV-E Viscometer, and conductivity properties with WTW Cond. 3110 SET 3-2CA103. Prepared PVA/NCC mixture's physical properties are given in Table 5.

Table 5. Physical properties of PVA/NCC solutions

Polymer	wt.%	Surface tension, mN/m	Viscosity, ×10^2 Pa·s	Conductivity, μS/cm
PVA/NCC	0	60.9 ± 0.3	14.1 ± 0.1	17.6 ± 0.4
PVA/NCC	3	60.5 ± 0.1	14.5 ± 0.1	27.8 ± 0.4
PVA/NCC	5	59.8 ± 0.4	15.1 ± 0.1	31.6 ± 0.4
PVA/NCC	7	60.4 ± 0.3	15.2 ± 0.1	32.6 ± 0.4

2.2.2. Coating process

The paperboards were coated (Laboratory Type Coating Machine–Atac Machine) using an automatically controlled Mayer rod number 2, pushing the suspension on top of the substrate with a Meyer rod at a fixed speed of 50 mm/s. This coating process was used to apply NCC to one side of the paperboards in single layer, and at three concentrations (3, 5 and 7 wt.%). The samples were finally dried in standard conditions of 23 °C and 50 % humidity for one day.

2.2.3. Characterization

In order to detect the existence of NCCs in Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR- FTIR) NCC/PVA coatings, was used Perkin Elmer Spectrum100 ATR-FTIR spectrophotometer.

2.2.4. Thickness

Thickness measurements of the control paper and coated test papers were made with a Sony brand micrometer with 0.01 – 20 μm sensitivity, according to TAPPI 411 Standard.

2.2.5. Taber stiffness

Taber stiffness values of the coated papers were measured according to DIN 53121 Standard with an equipment (L&W Stiffness Tester).

2.2.6. Cobb test

Water absorption capacity, which represents the amount of absorbed water by unit area of paper in a defined period of time (60 s in this study), was evaluated by Cobb 60 index, according to TAPPI Standard T-441 om-98 method [26].

2.2.7. Paper gloss

Paper gloss of the coated papers was measured with BYK-Gardner GmbH glossmeter, and the results were determined, according to ISO 8252-1:2009 Standard [27]. Coated and uncoated test samples were exposed to thermal aging for lightfastness inside a closed cabin by using Solar box 1500 device under stable Xenon light for 48 hours, according to BS 4321-1969 Standard. After the lightfastness process, the gloss values of the papers were measured and the differences between the first measured values were calculated

2.2.8. Surface energy

Surface energy of the test papers were determined with the contact angle measurements, according to TAPPI T 458 Standard. Depending on time, the measurements were made with Pocket Goniometer Model PG-X, (FIBRO Systems AB, Sweden), program version 3.4. Surface ‘‘free’’ energy was calculated according to ASTM D5946 standard test method depending on the water contact angle.

3. RESULTS

3.1. Fourier transform infrared spectroscopy (FTIR)

In order to determine the characteristic vibrations of NCCs and PVA in NCC/ PVA coatings, the analyses were made with ATR-FTIR. The results are shown in Fig. 2.

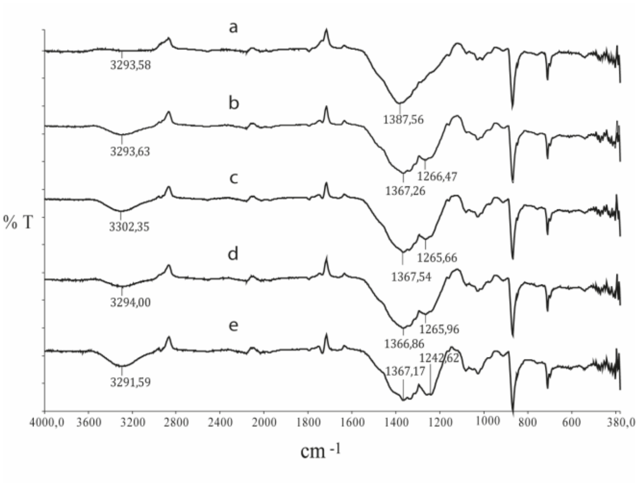

Fig. 2. ATR-FTIR analysis: a – control paper; b – PVA coated paper; c – PVA + 3 wt.% NCC coated paper; d – PVA + 5 wt.% NCC coated paper; e – PVA + 7 wt.% NCC coated paper

In Fig. 2 an indicated a weak the characteristic –OH vibration of cellulose of paper 3293.58 cm^{-1}, about 2900 cm^{-1} aliphatic C–H stretch vibration of methylene, and aromatic C=C stretching vibrations at 1387.56 cm^{-1}, these peaks clearly explain the cellulosic paper chemical structures. Fig. 2 b, showed that the O–H vibration is becoming more prominent because of PVA molecules. It has emerged a peak 1268.47 cm^{-1} because of C–O of alcohol. Fig. 2 b is compatible with PVA sized paper’s chemical structures. Fig. 2 c, d, e exhibited that NCC added PVA coated paper. It is clearly appeared that all paper and PVA peaks already at spectra but the intensity of OH vibration, C=C stretching vibrations C–O vibrations are increased. Also about 1260 cm^{-1} peak growth is from NCC, which is related to the bending vibration of the C–H and C–O bonds in the polysaccharide aromatic rings. It is an expected result for these coatings [24].

3.2. Thickness

The thickness values of the papers, coated with three different concentrations of PVA/NCC mixture, are given in Fig. 3. There was a thickness change to a certain extent in the comparison which was made with the control paper samples on the papers coated with PVA after the coating process. The difference of PVA/NCC concentration did not affect the thickness values of the coated papers. The fact that the thickness values did not change shows that the coating had been stable and made at the same thickness, and these values increase the confidentiality of the results [1].

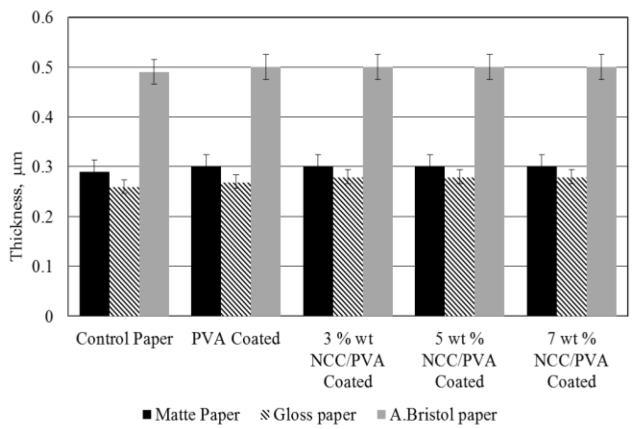

Fig. 3. Thickness properties of NCC/PVA coated papers

3.3. Taber stiffness

The Taber stiffness values of the test papers are showed in Table 6, and a general increase was observed in the values of the papers, coated with PVA/NCC concentration. When the stiffness values are taken into consideration, due to the cellulose structure of the paper, (OH) groups of the molecules of the acetyl structure of the paper, which were between the nanocellulose molecules, and nanocellulose -OH molecules got into reaction and created –H bridges. Depending on the percentile increase of the nanocellulose, they caused an increase in the endurance values by providing the connection of the hydrogen bridges and alcohol groups of PVA on the –OH groups of the paper by the help of the hydrogen connections. Because cross linking occurs on the paper surface as the paper’s hydroxyl groups and PVA’s alcohol interact with one another, an increase was observed in the stiffness values. Due to the binding of NCC on the paper surface, the interaction between paper/nanocellulose, the creation of regular molecule chains and the orientation of the molecules between fibers, the stiffness values increased.

Table 6. Taber stiffness values of MD and CD PVA/NCC coated papers

Coated paper properties	Matte paper (MD/CD)	Glossy paper (MD/CD)	American Bristol paper (MD/CD)
Control	129/85	105/87	265/137
PVA	131/98	105/88	363/325
PVA/NCC (3%)	137/64	154/101	366/285
PVA/NCC (5%)	140/89	132/103	326/192
PVA/NCC (7%)	123/93	138/87	320/293

MD/CD rates are shown, in Table 6. These increase rates in percentages according to different papers types, an increase of 2.3 % was observed when matte coated papers were coated with PVA. While matte coated papers were coated with NCC/PVA mixtures, the best result of Taber stiffness value was 5 % with NCC addition and 8.5 % in MD values, and – 15.2 % in CD values with PVA coating. When 3 % NCC was added to the Taber stiffness values of Glossy coated papers, 46 % increase was observed in MD values, and 17.9 % improvement in CD values with 5 % NCC. In the Taber stiffness values of American Bristol papers, an increase was observed in MD/CD 0 values with NCC addition, while an increase was provided at the rates of 38.1/137.2 % in the Taber stiffness values of the PVA coated American Bristol papers [28].

3.4. Cobb index (water absorption capacity)

The papers' water absorption capacity depends on their properties and coating materials' structures. Fig. 4 shows 3 wt.% nanocrysaline cellulose coating, applied on matte coated paper and American Bristol papers, was the best result. And it is 5 wt.% nanocellulose coating in gloss coated paper. In all of these three paper types 7 wt.% coating results were negative. However, it is related to the increase in the hydrophobic properties of the coated papers, caused by nanocellulose at 7 wt.%. With the PVA coating on the paper, the increase was observed in the values of the cobb index. It is caused by the –H bridges that PVA creates on the paper surface because of being easily solvable [29].

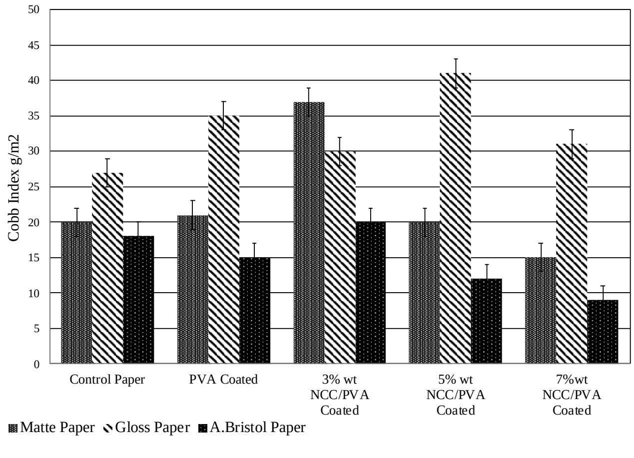

Fig. 4. Cobb index of NCC/PVA coated papers

3.6. Paper gloss

When the test papers were examined in terms of the brightness values, the brightness values of all of the papers increased, compared to the unprocessed control papers. When the values of the papers before and after lightfastness are taken into consideration, it was observed that the heat treatment decreased the brightness values at a certain amount. When the matte paper gloss value changes are examined, it is seen that 3 wt.% PVA/NCC concentration is the most ideal rate in terms of brightness (Fig. 5).

When gloss paper gloss value changes are examined, it is seen in the PVA coated result. When it is taken into consideration in terms of PVA/NCC concentration, 3 wt.% should be preferred in case that more brightness is wanted when 3 wt.% and 5 wt.% rates are convenient (Fig. 6).

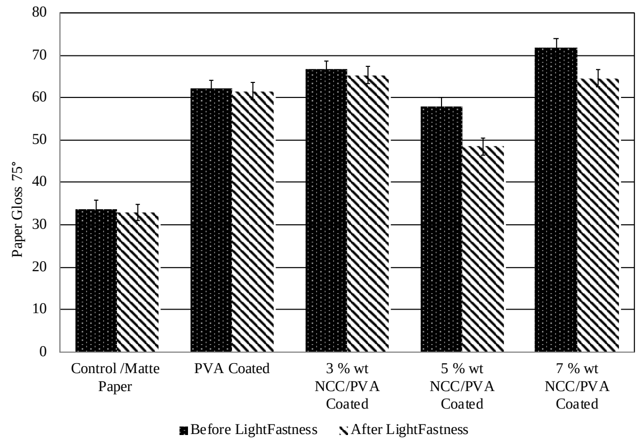

Fig. 5. Matte paper gloss values changes

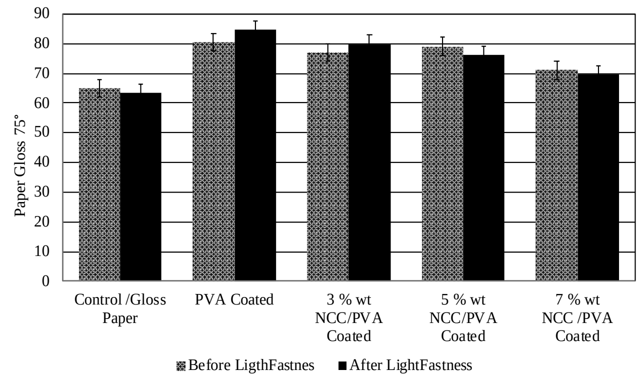

Fig. 6. Gloss paper gloss values changes

When American Bristol Paper gloss value changes was examined, it was the most balanced paper type in terms of before and after light sensitivity. After PVA coating the brightness value increased and then 3 wt.% PVA/NCC concentration gave the most ideal concentration by decreasing a little bit (Fig. 7).

3.5. Surface energy

In general, materials with higher values bond better because good wet-out occurs. Wet-out is an industry term to describe the flow of a liquid over the destination's surface. Good wet-out ensures maximum contact and helps achieve strong bonding [30].

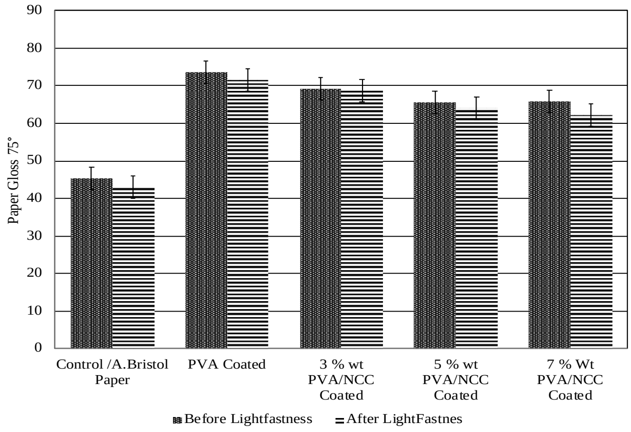

Fig. 7. American Bristol paper gloss values changes

The results of the contact angle measurement of the PVA/NCC coating, applied in different concentrations of 3, 5, 7 wt.% on the American Bristol, matte and gloss coated test papers, were evaluated in comparison with the samples of the control paper, it was found that when their concentrations increased, the contact angle decreased and the absorption properties of the surfaces increased. It can be said that the NCC in the mixture increases the water absorption and decreases the contact angle of all paper types.

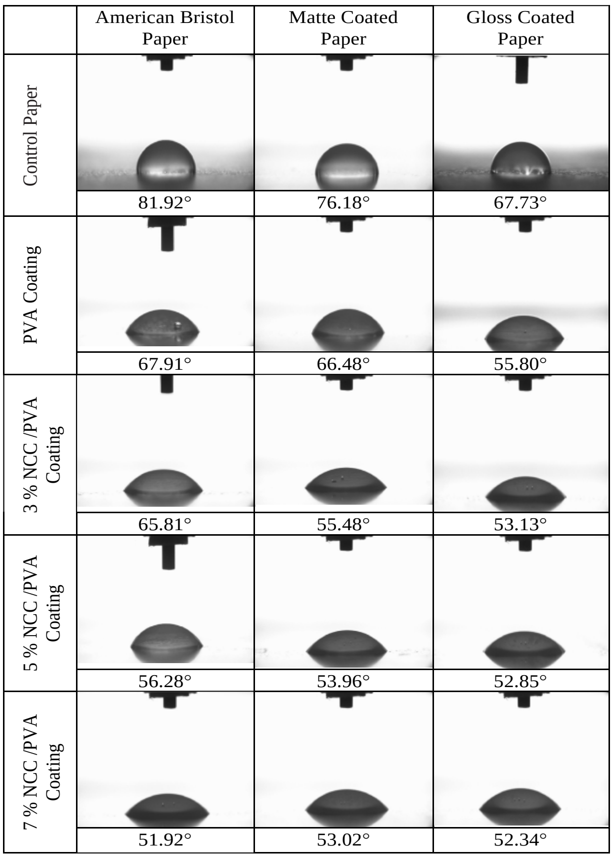

Fig. 8. Test paper contact angle

The contact angle decreased in only the American Bristol and gloss papers, coated with PVA, at 17 % rate and at 12 % at the matte coated paper. As the PVA/NCC concentration increased 3, 5 and 7 wt.%, the contact angle continued to decrease and wettability increased in all of the papers. The decrease occurred in the American Bristol paper with the highest different at 36 % rate, reached the lowest value with 51,92° of contact angle, and it became the lowest value in terms of wettability (Fig. 8).

4. CONCLUSIONS

In this study, NCC/PVA surface coating applications were applied on the cardboard packaging papers, with different weights and properties, at different concentrations. After coating, the performances of the packaging papers' thickness, stiffness, cobb index, surface contact angle and surface tension properties were evaluated. According to this:

1. There was not any change in the thickness of the packaging paper after coating. It was found that the coating on the paper performed an even and uniform distribution.
2. In the stiffness and Cobb Index values, an increase occurred with the impact of –OH links that occurred in the molecules of NCC/PVA surface coatings.
3. There was a general increase in the gloss values of the packaging papers and the most ideal paper gloss properties were achieved with the NCC/PVA coating at 3 wt. % concentration.
4. While an increase was observed in the liquid absorption values depending on the concentration increase of the NCC/PVA surface coatings, a decrease was observed in the values of the contact angles.
5. After the application of the NCC/PVA coatings at different concentrations on different packaging papers, it was seen that they made a positive contribution to the performance properties on the basis of the examined properties.

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