Effects of Ozone and Nanocellulose Treatments on the Strength and Optical Properties of Paper Made from Chemical Mechanical Pulp

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This effects of ozone and nanocellulose treatments were studied relative to the optical and strength features of chemical mechanical pulp (CMP) papers. An ozone treatment was performed at room temperature, and then nanocellulose was added. Sixty-gram handmade papers were made, and their physical, mechanical, and morphological properties were studied using X-ray diffraction (XRD) and scanning electron microscopy (SEM). With the ozone treatment, changes in the optical features were not significant at the 95% level; however, the addition of nanocellulose led to significant changes: the tensile strength, burst strength, air resistance, opacity, and brightness increased by 14.1%, 15.9%, 34.8%, 2.8%, and 3.2%, respectively, in comparison with the control sample. The enhancement with nanocellulose reduced the tear strength, coarseness, and yellowness by 15.7%, 12.9%, and 7.6%, respectively, compared with the control sample. The crystallinity of neat nanocellulose was 65.59%, while the crystallinities with the use of 5% to 10% nanocellulose were 72.41% and 62.26%, respectively. The SEM results indicated that using a 10% nanocellulose treatment led to the reduction of the CMP paper's porous character.

Keywords: Ozone treatment; Nanocellulose; Mechanical features; Optical characteristics; X-ray diffraction; SEM

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INTRODUCTION

Mechanical methods, through the use of different refinement processes, or chemical methods, by the means of alkaline treatments, enable manufacturers to produce papers with better quality (Fahey and Bormett 1982). Recycled pulps have different and weaker properties in comparison with paper made from first-generation pulp. For instance, the features of recycled liner paper are not as good as virgin kraft papers that have the same basic weight. Therefore, methods should be effective and selective to produce high quality paper from a cellulose primary material, such as chemical mechanical pulp (CMP).

One of the effective methods for increasing the strength features of paper is by treatment with ozone. In fact, using an ozone treatment at low to medium levels can improve some of the important features of CMP and help to produce papers through minimal energy use and chemical additives, which have a minimal negative effect on the other strength characteristics of the paper. An ozone treatment can increase the relative bonded area (RBA), and some of the strength properties, such as the tensile strength, internal bond (IB), and the compressive strength of the paper (Procter 1973). In addition, ozone treatment can lead to delignification from the pulp's surface, oxidation of pulps, and increase the potential bond creation by increasing the fines amounts. As a result, different gains can be expected, even in the lower concentration percentages of ozone. Zanuttini and McDonough (2002) considered the effect of different levels of ozone with moderate consistency of pulp to improve the specifications of old corrugated container (OCC). Other pulps that are used in the production of liner kraft paper and concora medium papers were considered as well. A comparison was made between the ozone function and the effect of alkaline and refinement treatments, both of which were considered to improve some factors of paper strength. The results showed that proper features of corrugated paper, such as concora medium test (CMT) and IB, increased greatly. Refinement and alkaline processing of OCC can create these results. A higher concentration of alkali affects the level of freeness of pulp, but increases the organic materials in wastewater. The effect of delignification, which is accomplished using ozone, on the bond creation ability can be evaluated by studying the effect of the ozone function and reaction on pulp with higher kappa numbers.

One of the main purposes of using nanocellulose pulp in paper is to improve properties. Nano additives can be used to improve the features of CMP and weaker pulps. The idea of using nanomaterials can include improving the optical features, as well as improving the mechanical and strength characteristics (Ramsden 2004). Adding nanofibers to paper and cardboard can help producers to produce layered and coated products. Bio-based nanomaterials, especially cellulose-based nanomaterials, have great importance because of their specific safety and strength specifications (Hadilam *et al*. 2013). Henriksson *et al.* (2008) used wood cellulose nanopulps to produce porous nanocellulose papers with high toughness. They produced a paper having a tensile strength of 214 MPa. This tensile strength is greater than the tensile strength of cast iron and the same as steel (Henriksson *et al*. 2008). Madani *et al*. (2011) considered delignification and the elimination of long-fiber pulps by means of using nanofiber cellulose (NFC) particles and then studied its effect on the produced paper's tensile strength. The results showed that adding NFC particles without long-fiber pulps increased the tensile strength significantly, in comparison with adding particles without NFC. It follows that artificial boosters can improve the papers’ strength significantly, together with favorable costs of manufacture.

Lakani and Afra (2013) considered the effect of the mixing duration of pulp and nanocellulose on the papers' features. Their results indicated that increasing the time duration to 1 h led to an increase in dewatering time and a reduction of air resistance. Many studies have been conducted about the use of nanocellulose to improve paper properties (Abe *et al.* 2007; Nogi *et al.* 2009; Yousefi *et al.* 2010). The main aim of the present study is to consider the effect of ozone and nanocellulose on the features of chemical mechanical pulp.

EXPERIMENTAL

Materials

Chemical mechanical pulp

Bleached chemical mechanical pulp was prepared from the CMP storage tower of the Mazandaran wood and paper company (Mazandaran, Iran), with a 70% mixture of hornbeam and beech and logs with good quality and a 5% to 15% mixture of long-fiber bleached pulps.

Cationic starch

The cationic starch with a degree of substitution (DS) of 0.035 was obtained from Glucosan® Company (Ghazvin, Iran) and was used at 1% of the paper pulp dry weight. Because some starches are insoluble in cold water, the cationic starch used in this study must be heated to dissolve it. To be soluble in water, a beaker with water and starch at a concentration of 5% was kept for 30 min at 90 °C, and when the starch had been solubilized. The cationic starch properties are presented in Table 1.

Table 1. Cationic Starch Properties

Properties	Value
Moisture	14%
Gelation temperature	70 °C
Cooking temperature	90 °C
pH	6
Viscosity	75.7 (cp)
Degree of substitution	0.035

Nanocellulose

Nanocellulose was acquired from the Nano Novin Polymer Company (Sari, Iran), and was used at three levels, *i.e.*, 0%, 5%, and 10% of the dry weight of pulp. The median diameter of the nanomaterial was less than 50 nm.

Ozone

Because ozone is an unsustainable material and cannot be stored, a generator device SS2 made by the Shamim Sharif Company (Tehran, Iran), was used to produce the ozone. This device can produce 10 g/h of ozone with an air input. In this pilot study the device consisted of an oxygen capsule, an ozone producer generator, and a reflective reactor made of Plexiglas® with a volume of 500 cm^3.

Ozone treatment

A Plexiglas® reactor from the Shamim Sharif Company (Tehran, Iran) was used to treat the ozone at room temperature. After adding the CMP inside the reactor, at three levels of 0%, 0.4%, and 0.8% by dry weight of CMP, the ozone was added. All the treatment were done at 85℃ and for 15 min.

Preparation of handsheet paper

After treating the samples with ozone, nanocellulose was mixed with the CMP at three levels, *i.e.*, 0%, 5%, and 10%, and then the mixture was mixed for 30 min at room temperature. Making handmade paper was done based on the TAPPI T205 sp-02 (2002) regulation using a handsheet maker Labtech Company (USA) device. In the present study, the prepared papers weighed 60 $g.m^{-2}$.

Paper characterization

The mechanical characteristics (tensile strength, burst strength, and tear strength), and the optical characteristics of brightness, opacity, and yellowness were tested on the handmade papers according to TAPPI T494 om-01 (2001), T403 om-02 (2002), T414 om-04 (2004), and T452 om-98 (1998), respectively. To measure the air resistance, the Gurley Densometer device was used. In the given Gurley method, the values represent the air resistance.

X-ray diffraction (XRD)

X-ray diffraction was performed using an X-ray diffraction device (XPert model) manufactured by Philips Co. in the Netherlands. The test was performed with radiation from a cobalt lamp with a wavelength of 1.79 Å, a step size of 0.02 degrees, a speed of 0.3 degrees per second, and an emission angle of 2θ in the range of 1 to 9 degrees. The samples were prepared in plate form with dimensions of $0.1 \times 1 \times 10$ mm^3, and the device generating power adjustments were set to 30 mA and 40 KV.

Crystallinity index (CrI) was evaluated using the following Eq. 1 (Segal *et al*. 1959),

$$\mathrm{CrI} = 100\ (I - I_\beta)/I \tag{1}$$

where I is the diffraction intensity assigned to the 200 reflection of cellulose I_β, which is typically in the range 2θ = 21 to 23°. I_β is the intensity measured at 2θ=18°, where the maximum occurs in a diffractogram for non-crystalline cellulose.

Scanning electron microscope (SEM)

To assess the presence of nanocellulose particles on the surface of the paper and fibers, a scanning electron microscope (AIS2100; Seron Technology Co., Korea) was used.

Data analysis

Data analysis was run completely randomly. Finally, comparison and classification was implemented using the Duncan Multiple Range Test at a 95% confidence level, while SPSS software (IBM Software, Armonk, New York; version 11.5) was used for statistical calculations, as shown by lower-case letters on the bars in each figure.

RESULTS AND DISCUSSION

In the present study, the ozone treatment had three levels, *i.e.*, 0%, 0.4%, and 0.8%. Nanocellulose was applied at three levels, *i.e.*, 0%, 5%, and 10%. The F-value and significance level are shown in Table 2. The addition of nanocellulose was found to significantly affect the coarseness, air resistance, tensile strength, tear strength, burst strength, opacity, brightness, and yellowness, at the 95% level. The addition of ozone was not found to have a significant effect on the coarseness, air resistance, tensile strength, tear strength, and burst strength, at the 95% level; it did significantly affect the opacity, brightness, and yellowness at the 95% level. The interaction between the ozone and the nanocellulose was not significant with respect to the coarseness, air resistance, tensile strength, tear strength, burst strength, opacity, brightness, and yellowness at the 95% level.

Table 2. Variance Analysis (F-Value and Significance Level) of Ozone and Nanocellulose Treatments

Specifications of variable	Coarseness (µm)	Air resistance (S)	Tensile strength (Nm/g)	Tear strength ($mN.m^2/g$)	Burst strength ($kPa.m^2/g$)	Opacity (%)	Brightness (%)	Yellowness (%)
Ozone treatment	0.716 ns	0.837 ns	2.104 ns	1.756 ns	1.798 ns	75.636*	31.175*	36.484*
Nanocellulose	10.324*	106.986*	33.986*	5.159*	9.6*	71.370*	17.930*	47.486*
Ozone* nano-cellulose	1.710 ns	0.269 ns	0.953 ns	0.782 ns	0.687 ns	0.223 ns	0.509 ns	0.099 ns

Significance level: 95%*, ns: non-significant

Figures 1, 2, and 3 show the effects of the ozone and nanocellulose treatments on the physical, mechanical, and optical features of handmade papers.

The Effect of Ozone Treatment

The tensile index is an indicator of the paper tensile potential durability caused by paper utilization level under tensile stress. The most important factor affecting the tensile strength is the number and quality of the pulp's inter-fiber bonds. Increasing inter-fiber bonding favorably affects the tensile strength by the effects of refinement or a wet press. The paper tensile strength is always less than the pulp tensile strength at the same level of refining (Scott 2005). An application of the ozone treatment at 0.8% increased the tensile strength by 3.2% in comparison with the control sample.

Using the ozone treatment at a level of 0.8%, the tear and burst strengths increased by 9.1% and 5.7%, respectively, in comparison with the control treatment. One of the key parameters affecting tear strength is the fiber length. The ozone may be able to increase the accessibility to the hydroxyl groups by affecting the pulp surface and eventually improving the quality of the inter-fiber bonding.

The burst strength is among those strengths that depend on the fiber length and the amount of inter-fiber bonds, of which the inter-fiber bonding is regarded as more important. The burst index is proportional to the square of the average fiber length (Asadpour *et al*. 2008; Akbarpour and Resalati 2011). The control treatment has lower flexibility and weaker inter-fiber bonds. Ozone treatment increased this bonding by making more hydrogen bonds, and therefore, the burst strength increased. Using the ozone treatment at the 0.8% level, the coarseness increased by 2.9%, in comparison with the control treatment. The ozone treatment at the 0.8% level decreased the porous character by 3.4%, compared with the control samples. This treatment also reduced the opacity and yellowness by 3.8% and 6.5%, respectively, and increased the brightness by 4.2%.

The Effect of Nanocellulose

The addition of nanocellulose had a significant effect on the coarseness, air resistance, tensile strength, tear strength, burst strength, opacity, brightness, and yellowness at the 95% level of significance. The specific area of cellulose pulps increases as the particle size shrinks at the nanometer scale. This means that more hydroxyl groups become available at the nanofiber level and are able to create hydrogen bonds with adjacent fiber surfaces, finally creating a network of nano- and regular pulps (Yousefi *et al*. 2011); this increases various paper strengths. Using nanocellulose at a 10% level, the tensile strength was increased by 14.1%, and the tear strength decreased by 15.7%.

Addition of nanocellulose reduced the tear strength; it had a similar effect on the reduction of tear strength in mixing CMP and nanocellulose papers. These findings were again attributed to changes in fiber strength and the hydrogen bonding at the surfaces. To explain tear strength behavior, it should be mentioned that the shortening of fibers reduces the tear strength during refining; on the other hand, enhancement of the bonding level increases the strength. In mixing papers, excessive refining affects the strength reduction more than other factors. Adding NFC and its deployment into the pulp mixture limits the amount of direct bonding between ordinary pulps and reduces the strength of pulp networks under tear stress (Afra *et al*. 2013).

Using nanocellulose at the 10% level increased the burst and air resistance by 15.9% and 34.8%, respectively; and the coarseness decreased by 12.9%. Using nanocellulose at the 10% level also increased the opacity and brightness by 2.8% and 3.2%, respectively, while yellowness decreased by 7.6%.

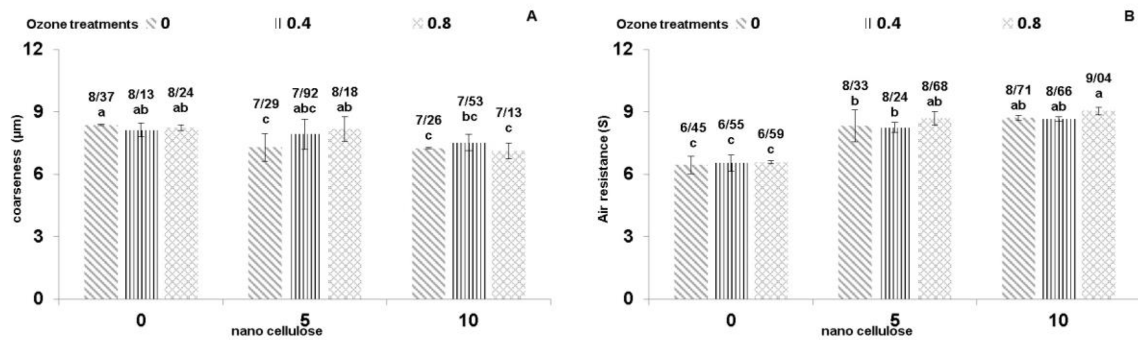


Fig. 1. Effect of nanocellulose and ozone treatments on (a) coarseness and (b) air resistance

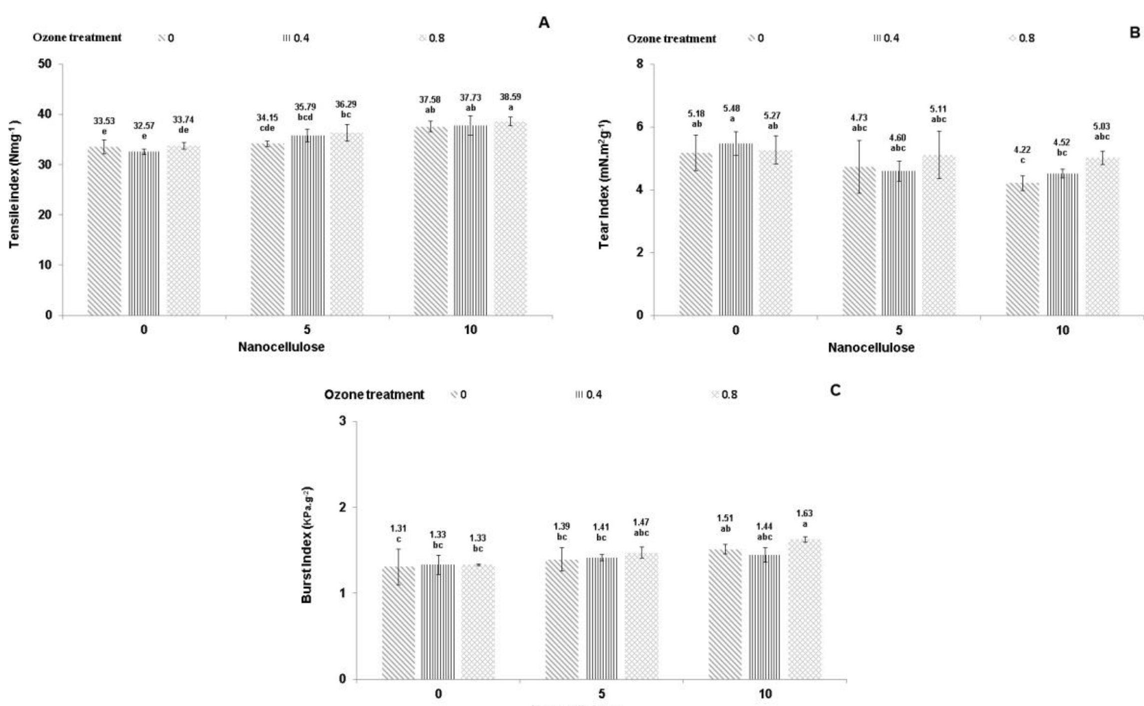


Fig. 2. Effect of nanocellulose and ozone treatments on (a) tensile strength, (b) tear strength, and (c) burst strength

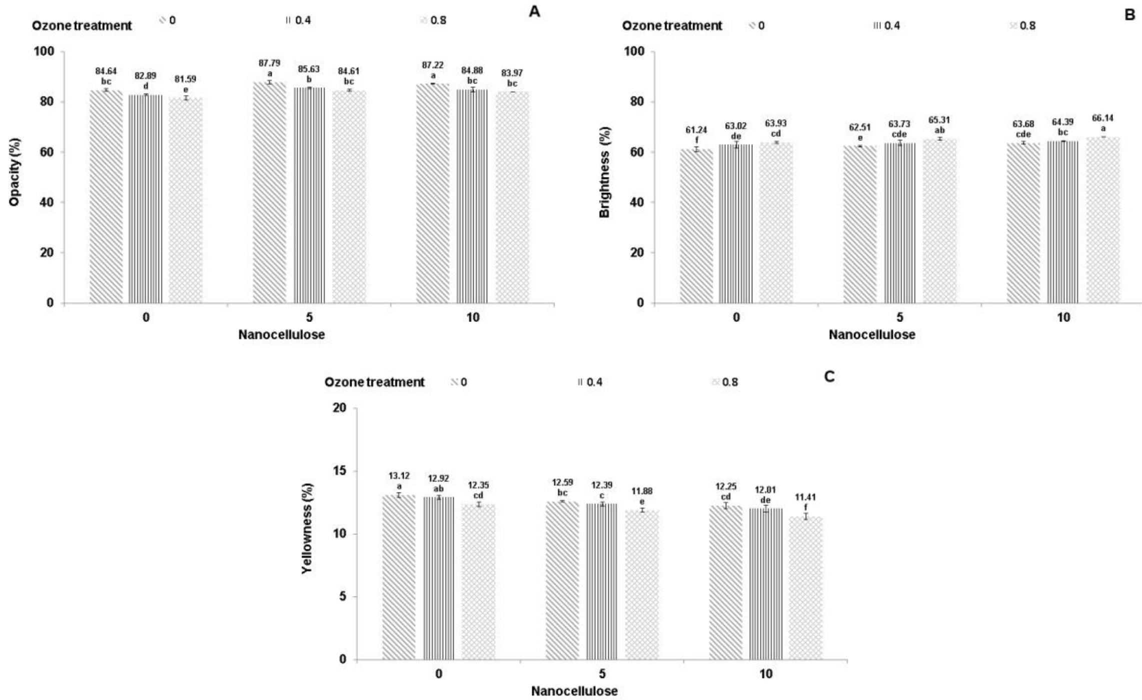
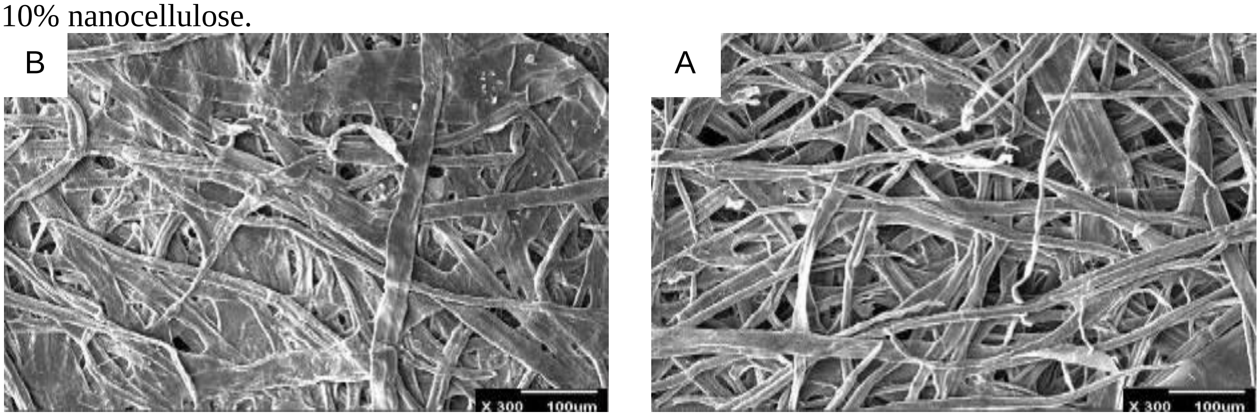


Fig. 3. Effect of nanocellulose and ozone treatments on (a) opacity, (b) brightness, and (c) yellowness

Morphology

Microscopic studies of the paper structure via SEM

Figures 4, 5, and 6 show the surface of treated handmade paper. It is clear that the ozone treatment did not have any effect on the pulp surface. However, the following can reduce the extent of pores: increasing nanocellulose, coating the fiber surface, and using 10% nanocellulose.



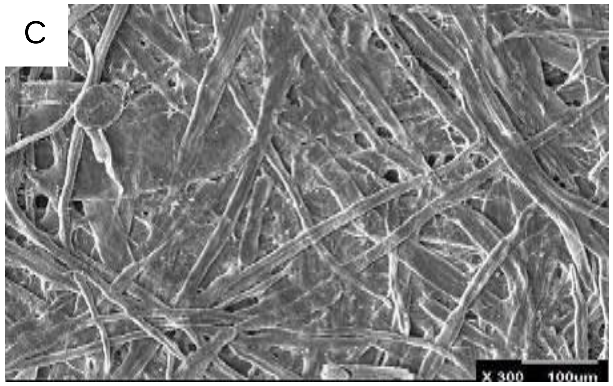


Fig. 4. The surface of paper without ozone treatment with (a) 0% nanocellulose, (b) 5% nanocellulose, and (c) 10% nanocellulose

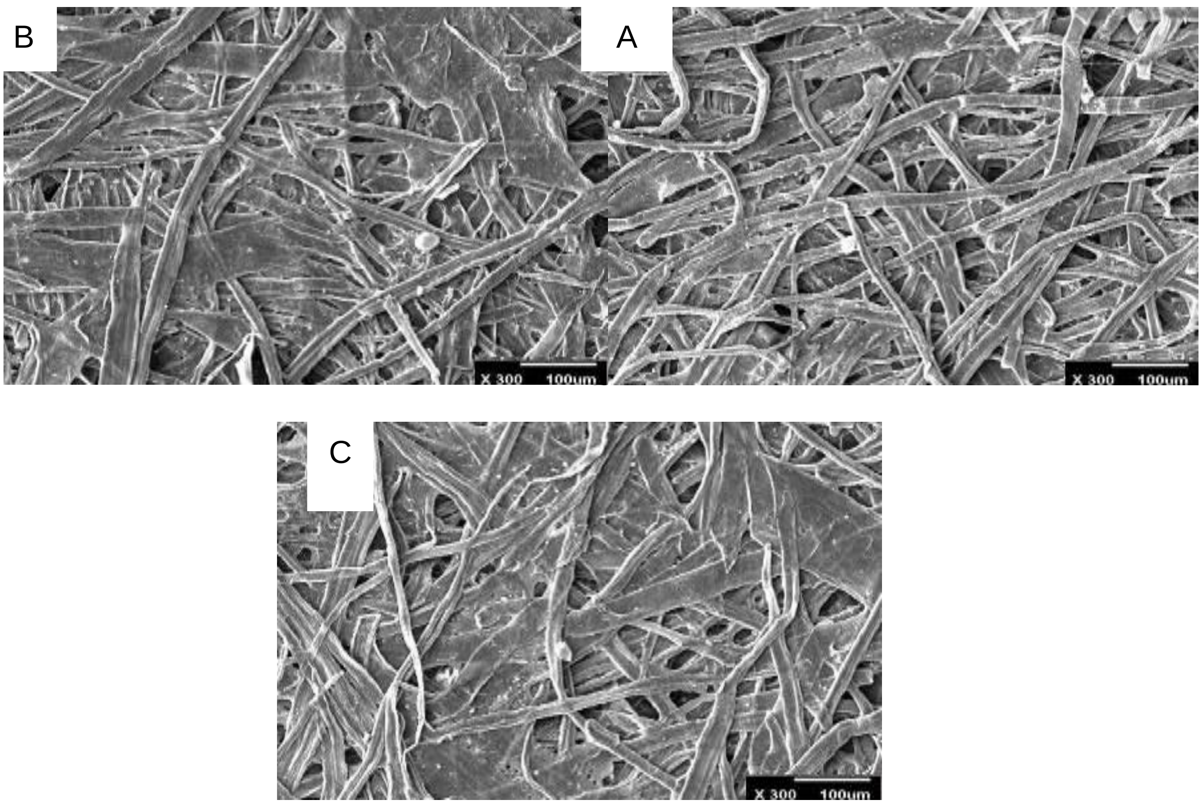


Fig. 5. The surface of paper with 0.4% ozone with (a) 0% nanocellulose, (b) 5% nanocellulose, and (c) 10% nanocellulose

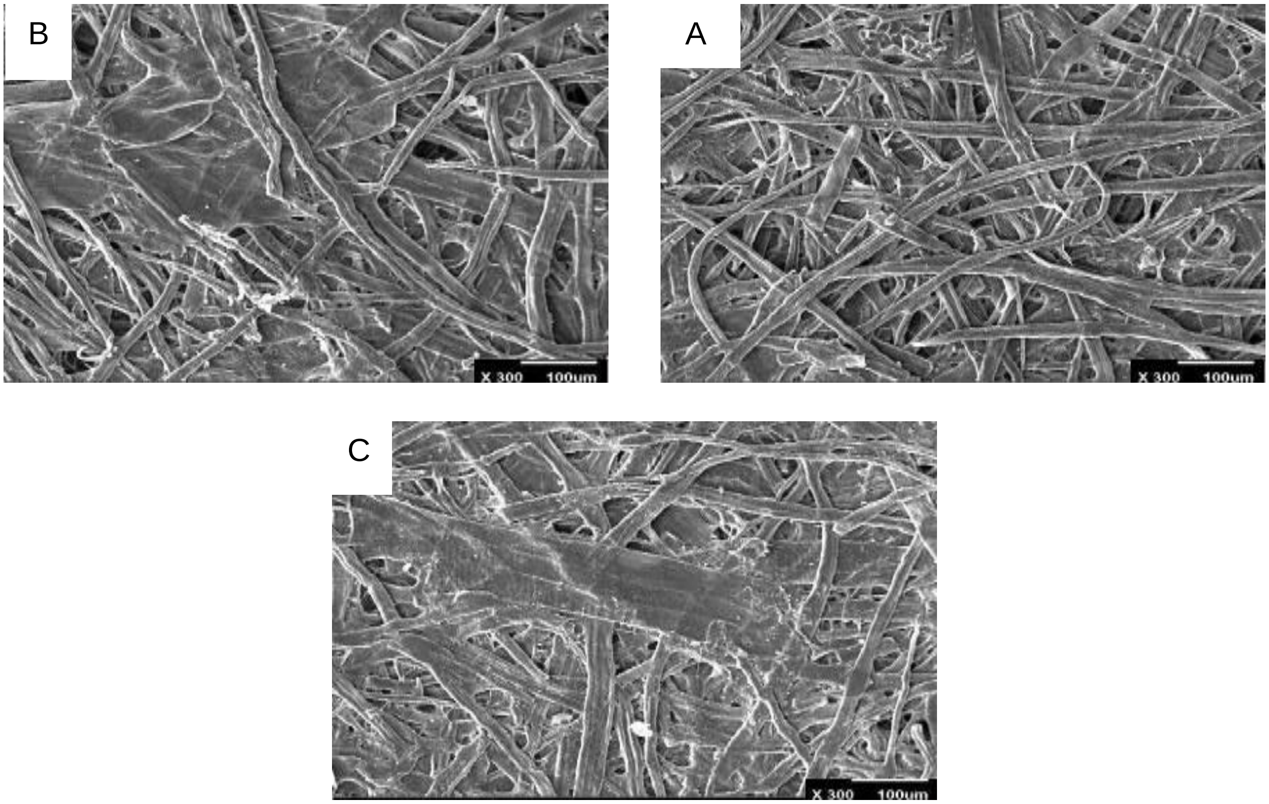


Fig. 6. The surface of paper with 0.8% ozone with (a) 0% nanocellulose, (b) 5% nanocellulose, and (c) 10% nanocellulose

Structural study by X-ray diffraction (XRD)

X-ray diffraction spectra related to papers with 5% and 10% nanocellulose and a pure sample of nanocellulose were obtained at 10° to 40°. As can be seen in Fig. 7, the peak of the neat nanocellulose is relatively wider, and the addition of nanocellulose to the pulp made the X-ray diffraction peak sharper. The crystallinity of the neat nanocellulose was calculated to be 65.59%, while the crystallinities with 5% and 10% of nanocellulose were 72.41% and 69.26%, respectively. As can be seen in the XRD figure, the peak of pure cellulose became relatively wider. The widening of peaks is rooted in the reduction of the crystallinity (Yousefi *et al*. 2011).

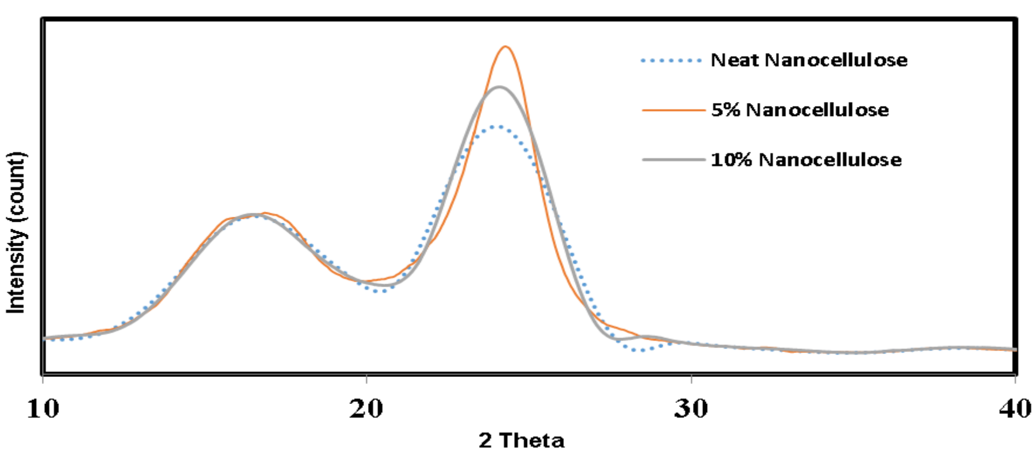


Fig. 7. Spectra of X-ray containing neat nanocellulose and paper with 5% and 10% nanocellulose

CONCLUSIONS

1. Using the ozone treatment increased the tensile strength, tear strength, burst strength, pores, the brightness, and the coarseness by 3.2%, 9.1%, 5.8%, 3.4%, 4.2%, and 2.9%, respectively, with comparison to the control treatment.
2. Using the ozone treatment reduced the opacity and yellowness by 3.8% and 6.5%, respectively.
3. The addition of nanocellulose increased the tensile strength, burst strength, air resistance, opacity, and brightness by 14.1%, 15.9%, 34.8%, 2.8%, and 3.2%, respectively.
4. The addition of nanocellulose decreased the tear strength, coarseness, and yellowness by 15.7%, 12.9%, and 7.6%, respectively.
5. The crystallinity of neat nanocellulose was 65.59%, while the crystallinities with the use of 5% to 10% nanocellulose in paper were 72.41% and 62.26%, respectively.

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