Comparison of the Internal Functionalization and Surface Modification Methods of Chemi-mechanical Pulp Handsheets Using Nanocellulose, Chitosan, and DTPA

Eisa Rezazadeh, Ramin Vaysi,* Mojtaba Soltani, Abdollah Najafi, and Seyed Eshagh Ebadi

The optical and mechanical properties of paper sheets were compared following treatment with biopolymers using two different methods, *i.e.*, internal functionalization and surface modification. Industrial chemi-mechanical pulp was provided, and two groups of paper handsheets were made. The first group of paper sheet samples were prepared with incorporated chitosan in a mixed-in-pulp slurry (at three treatment levels, *i.e.*, 0%, 1%, and 2%), and in the second group, untreated handsheets were spray-coated with either 2% chitosan, 2% nanocellulose, 0.5% DTPA, or a mixed solution (0.5% DTPA + 2% chitosan + 2% nanocellulose). Then, the optical and mechanical properties of the prepared paper sheets were analyzed. The brightness, opacity, and greenness/redness of the samples were measured spectrophotometrically using the CIELab system. Additional properties of the paper, *i.e.*, the water absorption, air permeability, and tear, tensile, and burst resistance, of the treated samples were also measured. The results indicated that the treatments had a considerable effect on the relative mechanical and optical parameters, which resulted in an increase in the mechanical properties, especially when the nano-particles were applied to the mixed-in-slurry process. Inversely, results from the spray-coating method indicated better results for the optical specifications.

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Keywords: Internal functionalization; Surface modification; Nanocellulose; Chitosan; DTPA; Optical and mechanical properties

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INTRODUCTION

Today, with the increase in population, increasing demand for paper, as well as greater restrictions on raw materials, the production of pulp from high-yield pulps and mechanical pulps has found a special place. These pulps have a high efficiency, *i.e.*, greater than 85% utilization, but due to the presence of lignin, extractives, and metal ions, their use is limited to short-term applications, as in the long run they suffer from brightness reversion and photo-yellowing.

Cellulose nanoparticles are made from cellulose, which is the most abundant organic raw material in nature. They have a high potential for strengthening the paper network. The fibrils within mechanically produced cellulose nanoparticles have diameters of approximately 1 to 100 nm and they are able to improve the strength properties of paper (Henriksson *et al*. 2008; Asadi *et al.* 2016).

Chitin, on the other hand, is the second most plentiful natural biopolymer after the components of lignocellulose. It can be obtained from renewable sources, *e.g.*, marine crustaceans. It is structurally similar to cellulose, except that chitin has acetamide (-$NHCOCH_3$) groups at the C2 position. The deacetylated derivative of chitin is a substance called chitosan. Chitosan is a biodegradable, biocompatible, antibacterial, and antifungal agent. The similarity of chitosan and cellulose has made it highly compatible with pulp fibers. The difference between these two biopolymers is in the replacement of the NH_2 functional group with the hydroxyl group in the second carbon of chitosan (as shown in Fig. 1) (Steckel and Mindermann-Nogly 2003; Rahmaninia *et al*. 2015). However, unlike plant fiber, chitosan possesses positive ionic charges, which give it the ability to chemically bind with negatively charged materials.

Previous research has shown that chitosan aminopolysaccharide is an excellent linker for cellulosic fiber structures and can be up to 40% more efficient than starch. Chitosan causes stronger bonds and the production of more resistant paper due to its positive and negative charges of cellulosic materials (Pariser and Lombardi 1998; Vanerek *et al*. 2006).

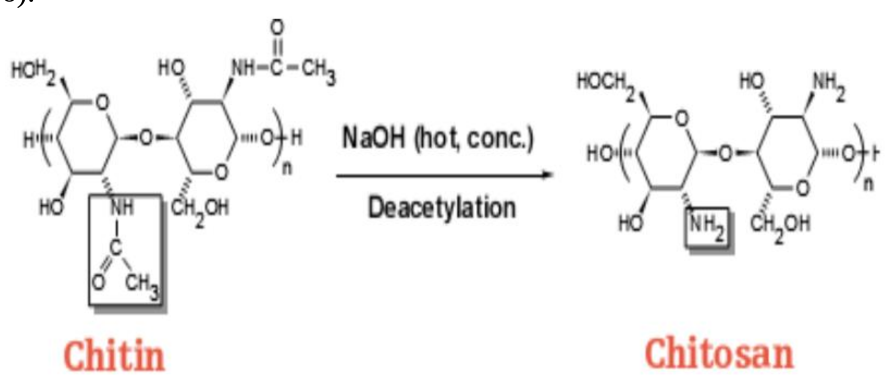

Fig. 1. Conversion of chitin to chitosan *via* deacetylation (Rahmaninia *et al*. 2015)

Diethylene triamine penta-acetic acid (DTPA) is a metal complexing (chelating) compound part of the aminocarboxylic acid (ethy-lenediamine-based) group. In the structure of DTPA, there are five carboxyl (COOH) groups (as shown in Fig. 2). These chelating agents are used to bind multivalent ions and have been used in a wide variety of industrial applications for many years. In addition, diethylene tetraamine pentaacetic acid (DTPA) is used to remove or reduce metal ions. The metal ions in the pulp decompose the hydrogen peroxide and accelerate the clear return of the paper (Yoon and Deng 2006).

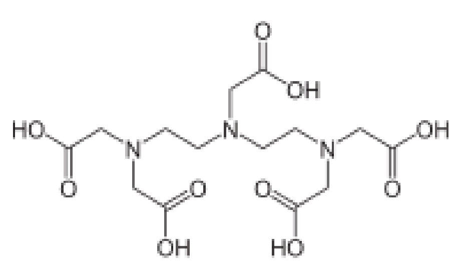

Fig. 2. The chemical structure of DTPA

However, DTPA causes the pulp fibers to stick together and can possibly be a problem in the paper machine. Therefore, DTPA consumption is limited to approximately 0.3% to 0.5%. The pulp is pretreated before its decolorization with hydrogen peroxide. However, it was found that using DTPA in the form of spraying could be a good solution and has a considerable effect on improving the stability of brightness (Vaysi and Kord 2013).

A considerable improvement in the tensile strength and air permeability of CMP paper was reported when cellulose nanofibers were applied as an additive (Aliniyay Lakani *et al.* 2016). In addition, reports about the cationization of additives on the performance of CMP paper showed that mixing long cationic fibers in CMP paper pulp increased the strength and the retention of fines (Rashidi Jouybari *et al*. 2015).

Rahmaninia *et al*. (2015) investigated effects of pH on the performance of chitosan-bentonite additives in CMP paper and found that a 1.25% chitosan treatment at a constant level of 0.3% bentonite at an alkaline pH had the best paper strength. Tavakoli *et al.* (2014) investigated the effect of chitosan-nanosilica layers on cotton fibers and the properties of the prepared paper and reported that the tensile strength increased by approximately 16%, while the paper formation coefficient decreased. However, other investigators have found that the strength of paper decreases after using molecular chitosan coating (Dodangeh *et al.* 2016)

Chitosan can also act as a dry paper strength enhancer, which could result from the ability of chitosan to form three types of bonds, *i.e.*, hydrogen, ionic, and covalent bonds (Hedayati *et al*. 2012).

Ghasemian and Ghaffari (2019) conducted a study to investigate an experimental system for coating nanofiber cellulose/chitosan on printing and writing papers to improve their mechanical properties. They reported that the treatments improved the properties. In addition, they found that the use of the spray method for coating had considerable advantages over the rod coating method, *e.g.*, a uniform distribution of the coating solution, lower cost, and lower consumption of coating materials.

Vaysi and Kord (2013) stated that spraying DTPA on the surface of handmade paper increased the brightness, opacity, and yellowness. In addition, DTPA was effective in increasing the brightness stability and the durability of the paper against photo-degradation.

The present research aimed to investigate the effects of internal functionalization (mixing-in-slurry) and surface modification (spray-coating) of chitosan, nanocellulose, and DTPA on the properties of CMP Paper.

EXPERIMENTAL

Materials

Never-dried-bleached CMP pulp was obtained from a pulp and paper mill in Mazandaran (Mazandaran Wood and Paper Industries), Iran. Homogeneous handsheets with a target basis weight of 60 g/m^2 were prepared from the blended fiber slurry, according to TAPPI Test Method T205 om-88 (TAPPI Test Methods 1996). Two groups of samples were made. The first was a group of samples prepared by mixing the additives in the pulp-slurry before the making handsheets. The other group of samples was prepared by spraying the materials after making the handsheets. The paper sheets were then conditioned for 24 h at a temperature of 23 °C and a relative humidity (RH) of 50%. The handsheet specifications are described in Table 1.

Table 1. Handsheet Specifications

Grammage	Bleaching	Pulp Refining (CSF)	Pulp Species	Pulp manufacturer	Standard
60 g/m^2	Bleached CMP	300	Mixed hardwood	Mazandaran Wood and Paper Industries, Iran	TAPPI T 205 om-88

The nano-fibrillated cellulose (NFC) was purchased from Nano Novin Polymer Co. (Sari, Iran), which was prepared from softwood alpha cellulose pulp with an average fiber diameter of 32 nm (as shown in Fig. 3). The NFC was loaded at 2% by spraying onto papersheets (Luiss and Jackson 2002; Tajik 2015). The nano-fibrillated cellulose (NFC) specifications are described in Fig. 3 and Table 2.

Table 2. Properties of the Nano-fibrillated Cellulose (NFC)

Type	A.P.S (nm)	Purity (%)	Dryness (%)	Brand	M.P (%)
Cellulose, (nano-fibrillated)	35	99	3.5	Nano Novin Polymer Co.	0, 1, 2
Note: A.P.S is average particle size; S.S.A is specific surface area; and M.P is mix proportion					

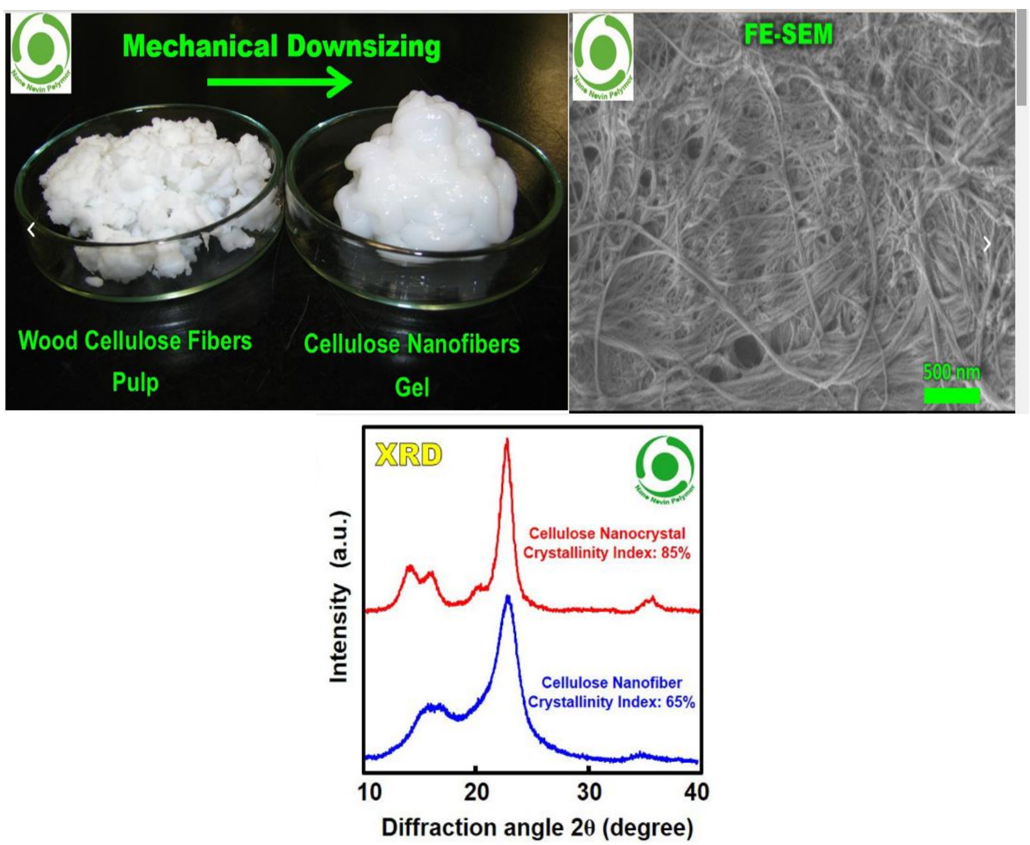

Fig. 3. The FE-SEM, XRD, and specification table of the cellulose nanofiber (Nano Novin Polymer Co.)

Chitosan was purchased from ("Seafresh", Thailand), which was prepared from exoskeletons of crustaceans. The material was described as nanochitosan, and the powder had an average diameter of 40 to 60 nm. The specifications are described in Table 3. For preparation, the required amount of chitosan was dissolved in a 1% acetic acid, and the mixture was stirred at room temperature for 2 hrs. Chitosan was loaded at 1 and 2% of the dry pulp weight.

Table 3. Properties of the Chitosan

Type	Molecular Weight (kDa)	Deacetylation Weight (%)	A.P.S (nm)	Brand	M.P (%)
Chitosan	270	85 to 90	40 to 60	Seafresh, (Thailand)	0, 1, 2
Note: A.P.S is average particle size; M.P is mix proportion					

Diethylene triamine penta acetic acid (DTPA) was prepared from DIPER-Samchun (South Korea), with a 50% solid content and 25 cps viscosity. To spray the DTPA onto the paper surface, 0.5% DTPA was prepared (Vaysi and Kord 2013). The DTPA specifications are described in Table 4.

Table 4. Properties of the DTPA

Type	Solid content (%)	pH	Viscosity (cps)	Density (20 °C)	Brand
DTPA	50	11 to 12	25	1.27 to 1.31	DIPER-Samchun (South Korea)

Methods

The pulp quantity was calculated to provide paper sheets with a basis weight of 60 g/m^2 with the addition of the additives by decreasing the quantity of added pulp. Then the prepared chitosan was internally functionalized by adding it to the suspension in amounts of 1 wt.% and 2 wt.%. Then it was mixed mechanically for 30 min at 800 rpm to 1000 rpm in order to assure good dispersion of all the substances (Ashoori *et al*. 2005; Nicu *et al*. 2010). This treatment was named "mixed-in-slurry".

To prepare samples for the surface modification, paper sheets with a basis weight of 60 g/m^2 were made. Then, 0.5% DTPA, 2% chitosan, and 2% nanocellulose were sprayed separately on the paper sheets. In addition, another treatment named mixed-solution (containing 0.5 % DTPA + 2% chitosan + 2% nanocellulose) was sprayed onto the handsheets. The spraying time and distance were 20 s and 20 cm, respectively, and the treatment process was named "spray-coated" (Ghasemian and Ghaffari 2019). The seven treatment groups are listed in Table 5.

Table 5. Treatment Groups

Testing Groups	Treatments						
	Mixed-in-slurry		Spray-coated				
	Chitosan (%)		Chitosan (%)	Nanocellulose (%)	DTPA (%)	Mixed-solution (%)
	1	2	2	2	0.5	0.5 % DTPA + 2% chitosan + 2% nanocellulose
C	---	---	---	---	---	---
M-Ch-1	√	---	---	---	---	---
M-Ch-2	---	√	---	---	---	---
S-Ch-2	---	---	√	---	---	---
S-Ce-2	---	---	---	√	---	---
S-D-0.5	---	---	---	---	√	---
S-Mix	---	---	---	---	---	√

Note: C is un-treated; M-Ch-1 is mixed-in-slurry by chitosan 1 % ; M-Ch-2 is mixed-in-slurry by chitosan 2 %; S-Ch-2 is spray-coated by chitosan 2 %; S-Ce-2 is spray-coated by nanocellulose 2 %; S-D-0.5 is spray-coated by DTPA 0.5 %; and S-Mix is spray-coated by the mixed solution (0.5 % DTPA+ 2% chitosan+2% nanocellulose)

The test procedures for determining the water absorption (T 441 om-04), burst strength (T 403 om-02), tear strength (T 414 om-98), and tensile strength (T 494 om-96) properties were conducted. These procedures were determined using the TAPPI standard protocols (TAPPI 2009). The air permeability was also measured by Air resistance of paper (Gurley method) (T 460 om-02) using a Lorentzen and Wettre (L&W) Air Permeance Tester.

The optical characterization of the samples focused on obtaining spectral data (Soltani *et al*. 2016). For the optical properties, the CIELab (L^*, a^*, and b^* values) color parameters were measured on handsheets using a Technibrite Micro TB-1C spectrophotometer (Elrepho Co., Stockholm Sweden) using TAPPI T1215 sp-03 (2007). In addition, the optical properties (brightness, opacity, yellowness, and greenness) of the hand-sheets were measured according to ASTM and TAPPI standard methods (according to TAPPI T452 om-98 (1996), T425 om-96 (1996), ASTM E313 (2015), and TAPPI T527 om-02 (2007), respectively.

For the scanning electronic microscopy (SEM) analysis, the handsheets were cut to small samples, mounted on a stub with adhesive, and then were placed under vacuum evacuated, and sputter-coated with gold. After preparation of the samples, the samples were investigated *via* SEM with a ZEISS DSM 960A (Oberkochen, Germany) microscope.

The statistical analyses for the mean differences in all treatments were tested using the Statistical Package for Social Science (SPSS Statistics, version 22, IBM, Armonk, NY) for Windows. The data were subjected to an analysis of variance procedure to examine the variability in the various properties. The Duncan multiple range test was used to separate the means of the various parameters at a 5% probability.

RESULTS AND DISCUSSION

Water Absorption (Cobb 60)

The water absorption (Cobb 60) results for the specimens at different treatment intensities are shown in Fig. 4. It was clear that the water absorption decreased when the sample was subjected to the chitosan treatment *via* the mix-in-slurry process. Under the experimental conditions, a chitosan dosage of 2% induced a decrease in the water adsorption of approximately 10%.

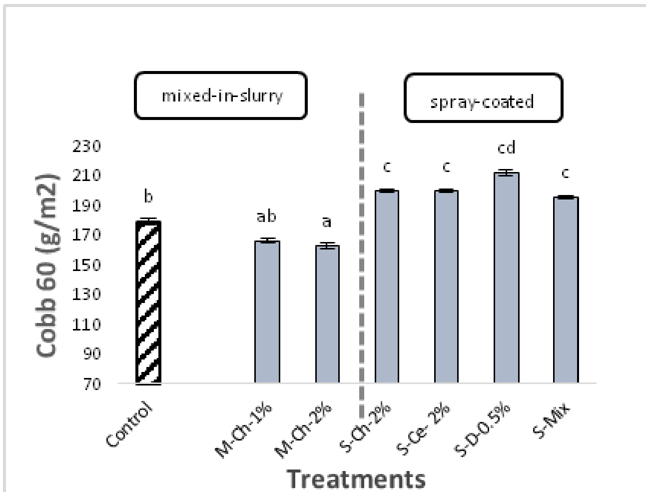

Fig. 4. Effects of the additives on the water absorption of the treated papers *via* the mixed-in-slurry and spray processes

It seems that the ability to establish hydrogen bonds between the amino groups of the chitosan and the hydroxyl groups of the fibers makes it possible to form electrostatic bonds between the anions of the fiber surface, especially the carboxyl groups and the cationic amine groups. In addition, the ability to form covalent bonds through the reaction of the chitosan groups with the aldehyde groups of fibers reduced some of the water-absorbing groups in the paper (Nikolaeva 2010; Vikele *et al*. 2017).

However, the water absorption values were greater after the samples underwent the spray-coating process. In addition, spraying the DTPA considerably increased the water adsorption, by approximately 20%. The role of air permeance on the Cobb index is well known, and the high amount of water absorption by the spray-coated paper sheets might have been a result of the high air permeability of the samples (Fig. 6) (Kjellgren *et al*. 2006).

Air Permeability (Gurley)

Another important property of paper sheets is air permeability (Gurley) . The results of the air permeability of the papers showed that there were obvious differences between the mixed-in-slurry and spray-coated samples (Fig. 5). The chitosan decreased the air permeability in the mix-in-slurry process samples by increasing the time in the Gurley test, especially for the 2% addition level samples. Chitosan can accumulate onto the paper surface during sheet formation, and it may modify the smoothness and porosity of the surface.

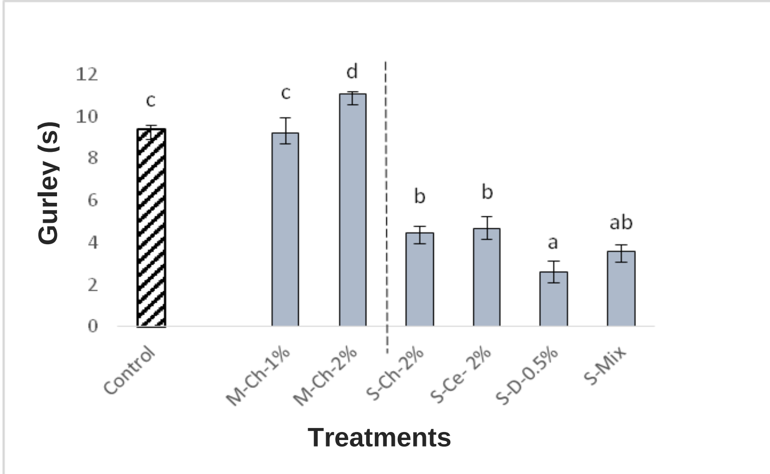

Fig. 5. Effects of the additives on the air permeability (Gurley) of the treated papers *via* the mixed-in-slurry and spray processes

Other investigators have also found that air permeability decreases by using molecular chitosan in coatings (Kjellgren *et al*. 2006; Vikele *et al*. 2017). They reported that the pores in the base paper were sealed, and a continuous chitosan film begin to develop by using the molecular chitosan. This phenomenon can be also observed through the SEM microphotography, when the chitosan was internally mixed in the pulp slurry (Fig. 6a).

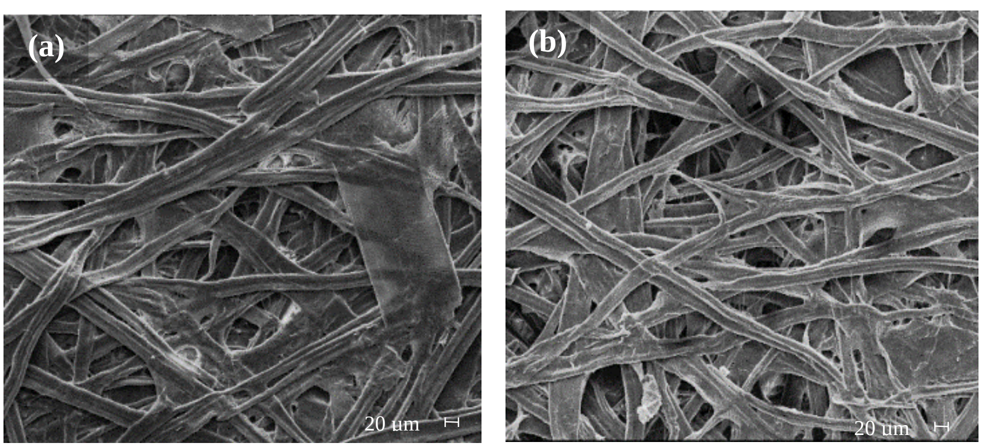

Fig. 6. The SEM microphotography of the a) 2% chitosan (mixed-in slurry) sample; and b) 0.5% DTPA (spray-coated) sample

Unlike the results from the mix-in-slurry process, the spray-coated papers showed a considerable reduction in the time of Gurley test in comparison to the control. In the spray process samples, there was no considerable difference in the air permeability of the paper sheets made with the 2% chitosan, 2% nanocellulose, or mixed-additives treatments, However, DTPA considerably increased the air permeability. DTPA as a chelating agent has shown a greater effect on metal ions and some coloring agents in mechanical and chemi-mechanical pulps, and may result in more significant on optical properties such as brightness. So, DTPA compared to others in the spray-coating process, cannot fill the voids or block the air passage, which resulted in higher permeability.

The high permeability of spray-coated samples may result from the dimensional changing of the micro-pores (which were made from the fiber cross entanglements) during the wetting-drying cycle when the paper sheets were sprayed with the treatment solutions. When water hits the dry paper, cellulose absorbs water and expands; however, the expansion is greater in the longitudinal fibre direction than in the diametrical direction. When the fiber is dried, it shrinks and crinkles as it loses water, which may cause the micro-pores to become bigger. Finally, it seems that the nano-sized additives cannot fill the submicroscopic voids of the paper sheets, which resulted in higher air permeability.

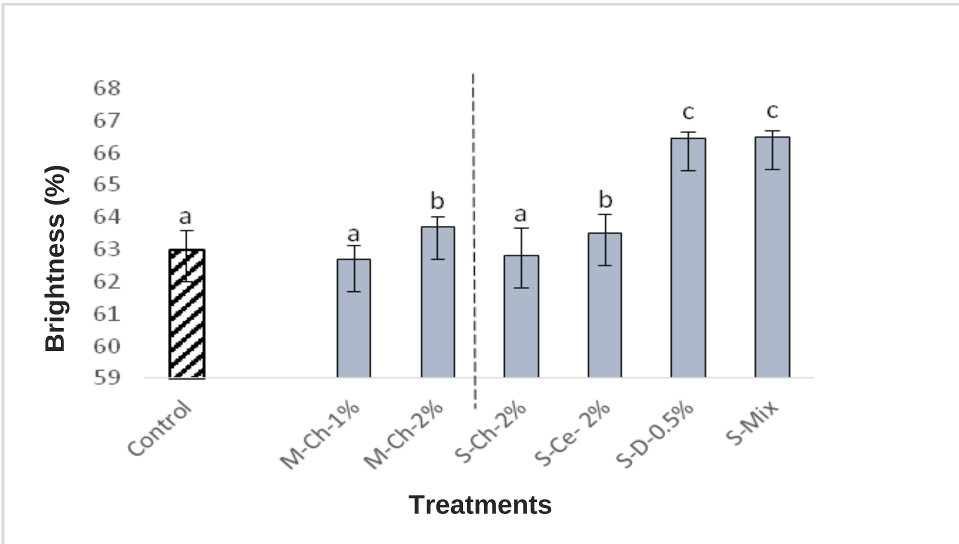

Fig. 7. Effects of the additives on the brightness of the treated papers *via* the mixed-in-slurry and spray processes

Brightness

The effects of the treatment processes on the brightness of the papers showed an increasing trend in the spray-coated paper, especially when the papers were treated with DTPA or the mixed-solution (Fig. 7). This implies that the DTPA and mixed-solution treatments had increasing effects of approximately 3.5% compared to the control. Similar results obtained by others suggest that less light breakdown light scattering resulted in better brightness when the paper was treated *via* a spraying process (Glittenberg 1993; Nogi *et al.* 2009; Yousefi *et al.* 2011).

Results also indicated a considerable increase in the brightness of the chitosan treated paper (2% in the mixed-in-slurry process) and the nanocellulose treated paper in the spray-coated process (Fig. 7).

Opacity

Opacity is the ability of paper to hide or mask a color or object in the back of the sheet. Good opacity is important in printing papers in order to prevent printed images or text from being seen from the reverse side of the sheet (Kasmani and Samariha 2019). The results from the opacity test showed a higher level of opacity when the spray-coating process was used as the treatment method (Fig. 8). The opacity was slightly increased in the 1% chitosan mixed-in-slurry treatment, but the highest opacity was observed in the 2% chitosan spray-coated treatment. In addition, the nanocellulose spray-coated paper had a high opacity in comparison to the control.

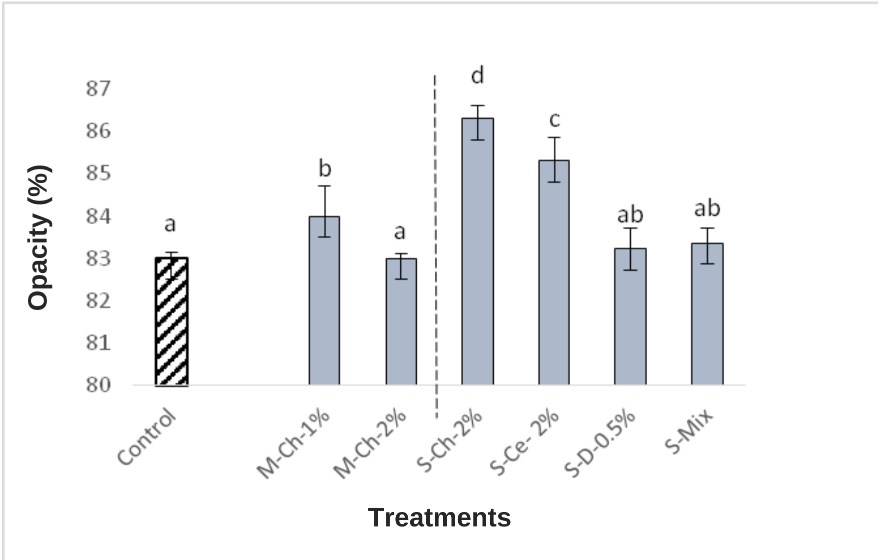

Fig. 8. Effects of Effects of the treatment variables on the opacity of the treated papers *via* the mixed-in-slurry and spray processes

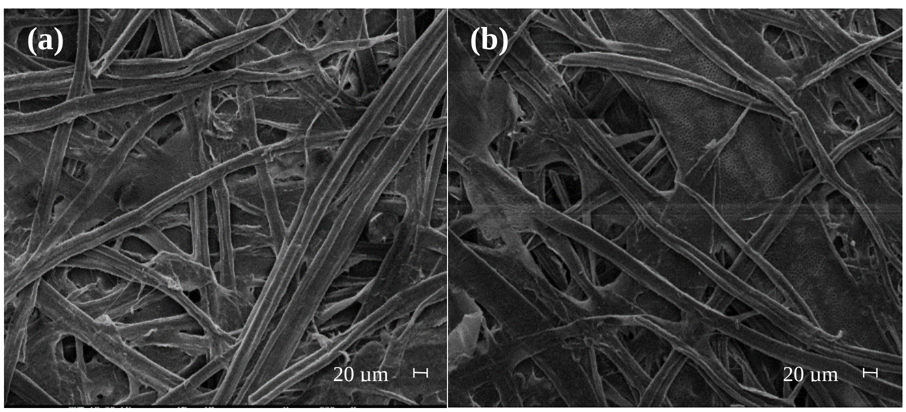

Fig. 9. The SEM microphotography of the a) 2% chitosan (spray-coated) sample; and b) 2% nanocellulose (spray-coated) sample

The use of chitosan and cellulose nanofibers in the spray-coated process may increase the density and retention, as well as increase the bonding between the fibers, the relative surface area, and homogenize the fiber surface in the paper, thus reducing light transmission through the paper and improving the opacity (Nogi *et al.* 2009; Vaysi and Kord 2013). These effects can also be observed through the SEM microphotography shown in Fig. 9.

*a** Factor

One of the other most important optical properties of writing and printing paper sheet is the greenness, which is represented by the *a** factor. Results from CIELab test indicated considerable changes in the *a** factor after the treatments (as shown in Fig. 10).

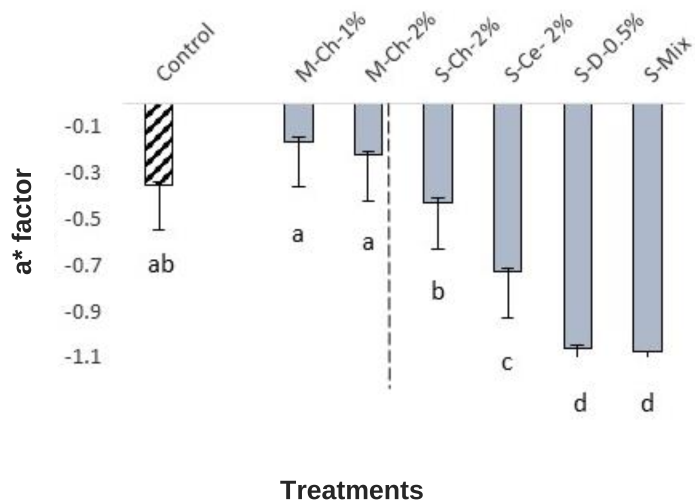

Fig. 10. Effects of the treatment variables on the *a** factor of the treated papers *via* the mixed-in-slurry and spray processes

The results showed that the *a** factor was increased in both the 1% and 2% chitosan mix-in-slurry treatments. However, the *a** factor was decreased in spray-coated papers. In addition, a decreasing *a** factor was as observed in the DTPA and mixed-solution treatments. The lowest and highest greenness levels resulted from the mixed-in-slurry chitosan treatment, and the spray-coating DTPA/mixed-solution treatments, respectively.

Mechanical Properties

The mechanical properties related to the tear, tensile, and burst resistances, were considerably affected by the treatments (as shown in Figs. 11, 12, and 13). The effects of the treatments on the tear index of the handsheets showed how the tear indices depended on the dosage and type of treatment. The application of the chitosan mixed-in-slurry, resulted in considerable increases in the tear index values (Fig. 11).

Similarly, at both chitosan dosages of 1% and 2% for the mixed-in-slurry treatments, the tensile index and burst index of the paper were considerably increased compared to the control (as shown in Figs. 12 and 13).

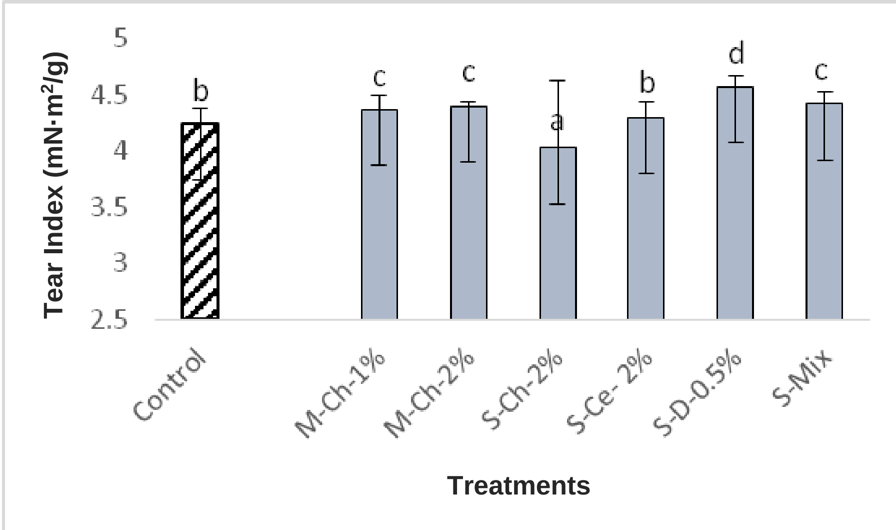

Fig. 11. Effects of the treatment variables on the Tear index of the treated papers *via* the mixed-in-slurry and spray processes

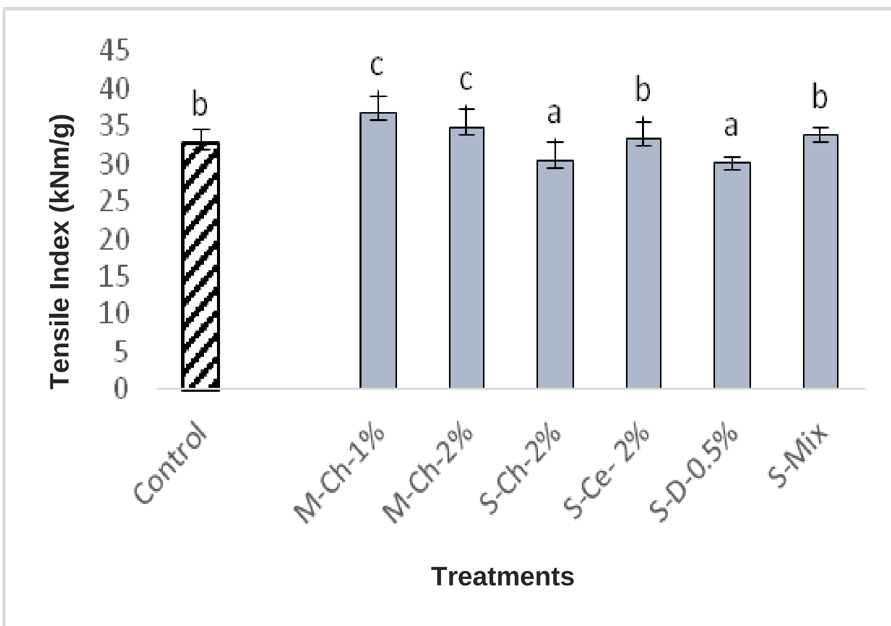

Fig. 12. Effects of the treatment variables on the Tensile index of the treated papers *via* the mixed-in-slurry and spray processes

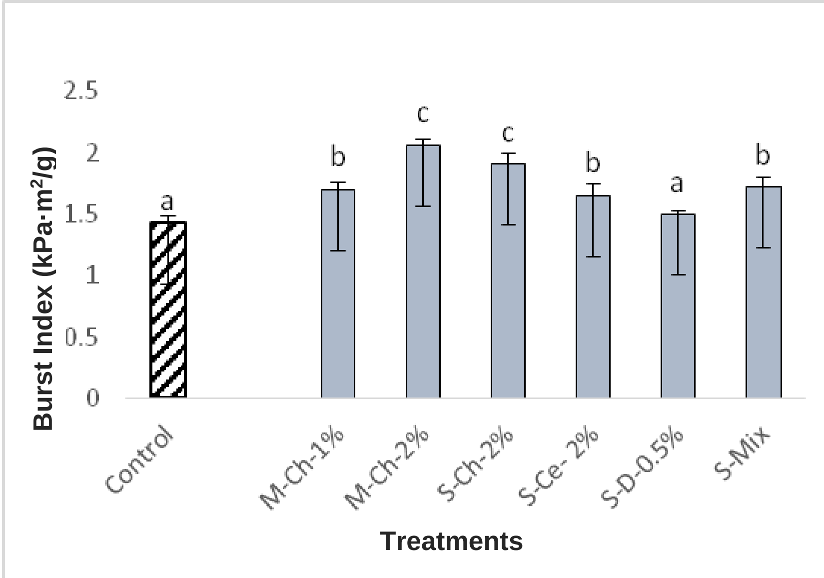

Fig. 13. Effects of the treatment variables on the burst index of the treated papers *via* the mixed-in-slurry and spray processes

The presence of chitosan in the slurry enhanced the interaction of the cellulose fibers by filling the empty spaces between the fibers during the paper sheet formation, helping to create a better bonding area (Fig. 6a). This can be explained by the fact that the positively charged amino-groups of the added chitosan may form ionic bonds and polyelectrolyte complexes with the pulp components, *e.g.*, hemicelluloses, which contain negatively charged carboxyl groups. In addition, the nanoparticles may fill the submicroscopic voids of the porous paper structure during the sheet forming stage and may then create additional bonds during the drying stage.

In the spray-coated process, the chitosan treatment severely decreased the tear index at dosage of 2% (Fig. 11). Results from the tensile testing also showed similar behavior, in which the chitosan treatment considerably decreased the amount of tensile index (Fig. 12). However, the burst index of the spray-coated paper was enhanced by the 2% chitosan spraying treatment (Fig. 13). The results from the spray-coating processes also indicated that there were no considerable differences in the tear and burst indexes between the nanocellulose treatment and control. However, the tear index values were considerably increased by the DTPA treatment, but considerable changes in the tensile and the burst indexes were not observed.

Spraying the mix-solution treatment considerably enhanced the mechanical properties, particularly the tear and burst indexes, in comparison with the control. In the mixed-solution, the addition of chitosan will cause the surface of the fibers to become charged (cation charge), which in the next step will be absorbed by the addition of cellulose nanofibers (with an anion charge). In fact, successive use of positive and negative polyelectrolytes stabilizes more of them on the fibers and results in greater dry strength (Wagberg *et al*. 2002; Hadilam *et al*. 2013). However, more physical fiber-entanglement can be observed in the mixed-solution treatment through SEM microphotography (Fig. 14b), which could be effective in enhancing the mechanical properties.

Compared to the control, however, the results showed significant increases in mechanical properties, but it seems that the results from the spray coated samples were less than what was expected. The reason could be due to wet-dry phenomena occurring during the spray-coating process. Paper is essentially an amorphous polymer. The cycle of wetting and drying the paper sheet during the spray-coating process heavily opens the polymer structure by allowing water to penetrate the matrix of hydrogen-bonded fibers and separate them. This leads to a bunch of related phenomena, leading to decreased strength and a conformational change that comes from the impingement of water. As the water leaves, this conformational change becomes locked in and usually results in wrinkling because that's a lower energy state than a completely flat sheet of paper (Rasi 2013).

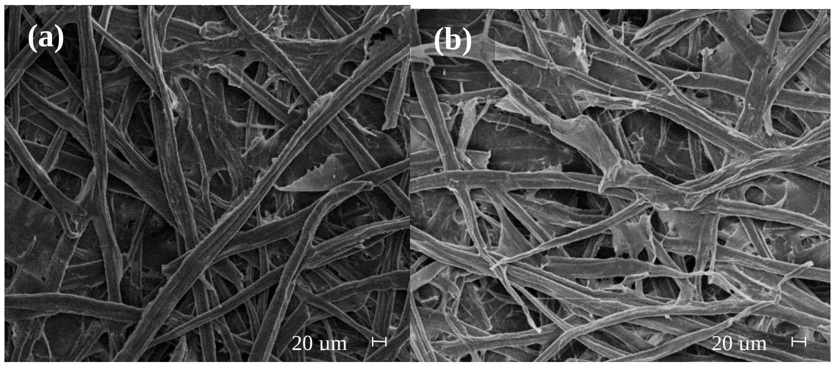

Fig. 14. SEM microphotography of the a) control sample; and b) mixed-solution (spray-coated) sample

CONCLUSIONS

1. The aim of this study was to investigate the effect of adding (mixed-in-slurry) and spraying (spray-coated) chitosan, nanocellulose, and a chelating agent (DTPA) on the properties of chemimechanical pulp (CMP) paper. The results showed that with increasing chitosan percentage, the tear, tensile, bursting, air permeability, opacity and brightness of the paper increased, but the water absorption and greenness in the paper decreased.
2. The results showed that by spraying nanocellulose on the test samples, the mechanical properties, air permeability, greenness, opacity, brightness, and water absorption increased. In addition, spraying DTPA resulted in an improvement in the tear resistance and brightness of treated samples, but the water absorption and greenness increased.
3. For the spray-coating treatments, all possible ionic bonds are probably already formed, and spraying implies that the treating material can only be linked with the cellulose on the surface by hydrogen bonds or van der Waals interactions; thus, it may not be enough to improve its strength. Therefore, it seems that in this case, the spray-coating treatment cannot be considered a mechanical enhancer, except in the case of the mixed-solution (which included 2% chitosan, 0.5% DTPA, and 2% nanocellulose) treatment.
4. In this case, the most suitable properties were observed in the paper resulting from the addition of 2% chitosan to CMP pulp *via* the mixed-in-slurry process.

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