Effect of Chitosan Molecular Weight on the Performance of Chitosan-silica Nanoparticle System in Recycled Pulp

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The application of chitosan biopolymer with and without nanoparticles in the papermaking process was investigated. The effect of the chitosan's molecular weight on its interaction with silica nanoparticles in recycled old corrugated container pulp was studied. Initially, the nanosilica particles were analyzed *via* atomic force microscopy and scanning electron microscopy, which confirmed the spherical shape of the silica nanoparticles with diameter less than 5 nm. Dynamic light scattering method was used to determine the zeta potential and the hydrodynamic radius of the chitosan with different molecular weights. Infrared spectroscopy was used to show the possibility of hydrogen bonding between the chitosan and the nanosilica. The results showed that the chitosan with low and medium molecular weights in alkaline and in some neutral suspensions had better process performances. Increasing the molecular weights of the chitosan improved the mechanical properties. The influence of chitosan on the process parameters was dependent on different factors such as its configuration in the aqueous media before and after adsorption, its ability to penetrate the fiber pores, and its charge density. In contrast, the effect of chitosan on the strength of paper was influenced by its performance following adsorption and retention within the fibrous mat.

Keywords: Chitosan; Molecular weight; Nanosilica; Papermaking wet end; Recycled old corrugated container; Cellulosic fiber

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INTRODUCTION

Chitosan (Ch) biopolymer is the product of the chitin de-acetylation process. This valuable biopolymer is a linear polysaccharide which has α (1→4)-linked 2-amino-2-deoxy-ß-D-glucose bonds and is able to be dissolved in acidic aqueous solutions to produce a cationic polyelectrolyte. As a nontoxic, biocompatible, antifungal, and antibacterial biopolymer, Ch possess a considerable number of amino groups in its structure (Deng *et al.* 2011, 2012; Kim *et al.* 2017). The similar molecular structures of Ch and cellulose have created strong compatibility between the two valuable biopolymers (Nicu *et al.* 2011; Rohi *et al.* 2016).

As a cationic polyelectrolyte, Ch has various applications in the papermaking industry (Huang *et al.* 2007; Ashori *et al.* 2013; Rahmaninia *et al.* 2018). Chitosan can be particularly useful in recycled cellulosic pulps with critical conditions (higher conductivity, existence of more undesirable substances, higher fiber fines content, and weaker fibers in comparison with virgin pulp) (Rahmaninia *et al.* 2008; Rahmaninia and Khosravani 2015). Old corrugated container (OCC) is one of the most abundant waste paper grades. Therefore,

much attention has been given to improving the process and product properties of OCC (Hamzeh *et al.* 2013; Rahmaninia *et al.* 2016).

Currently, the application of nanoparticles with polyelectrolytes (as nanoparticle systems) is common for improving the drainage and fines retention of papermaking systems (Carr and Tokarz, 2006; Cho *et al.* 2006; Khosravani and Rahmaninia 2013). In this regard, colloidal nanosilica is one of the most popular and important nanoparticles used in papermaking, due to its tiny dimensions and high specific surface area. These spherical nanoparticles may have a specific surface area in the range of 500 to 1200 m^2/g and high anionic charge, which allows them to interact with cationic long chain polyelectrolytes (Hubbe 2005).

Polyelectrolytes are an important complement in the nanoparticle system. It is expected that Ch biopolymer with special characteristics, such as abundant amino groups and a linear structure, can be a prospective alternative as a cationic polyelectrolyte in this system (Alince *et al.* 1996; Jahan *et al.* 2009; Sabazoodkhiz *et al.* 2017).

The molecular weight (MW) and de-acetylation degree (DD) of Ch varies according to its synthesis methods and production conditions. Therefore, the MW of Ch ranges from 100 to 1100 kilodaltons, and its DD ranges from 67% to 95% (Hwang *et al.* 2002). The variability of the MW and DD affects the characteristics and applications of Ch (Li *et al.* 2004; Myllytie *et al.* 2009).

Previous studies have investigated the MW of chitosan and its effect on the flocculation in pulp suspensions and process properties in single Ch and Ch-bentonite systems (Agusnar *et al.* 2013; Nicu *et al.* 2013; Habibie *et al.* 2016; Miranda *et al.* 2016; Vikele *et al.* 2017). Considering the drainage performance, low molecular weight (LMW) of Ch showed the best results (Agusnar *et al.* 2013; Miranda *et al.* 2016).

Previous studies also indicated that the single application of MMW Ch was more effective in improving the mechanical properties of paper compared to LMW Ch (Agusnar *et al*. 2013; Vikele *et al*. 2017). However, Habibie *et al.* (2016) reported that the single application of LMW Ch was more successful in improving the mechanical properties of paper rather than MMW Ch.

Vikele *et al.* (2017) reported that micro-Ch could easily fill the submicroscopic pores and voids in the porous structure of paper and had a greater impact on the dry strength. Alince *et al.* (1996) indicated that LMW polyethylenimine, in a similar manner, easily penetrated the pores and spaces between the components of the pulp suspension compared to the high MW (HMW) polyethylenimine. Moreover, as a nanoparticle system, LMW Ch has been successfully applied with silica nanoparticle for improving drainage and retention (Sabazoodkhiz *et al.* 2017).

Considering previous studies, there is an inconsistency about the effect of Ch MW (low, medium, and high) on its performance in various systems applied in pulp suspensions.

The authors' previous work on the Ch-nanosilica system has shown a proper performance in recycled suspension (Sabazoodkhiz *et al.* 2017). Considering the idea that the MW of Ch can influence its configuration in the pulp suspension, which then affects its penetration of fiber pores and the spaces between the components of the pulp suspension, the influence of Ch MW in the mentioned nanoparticle system needs to be investigated.

Therefore, this study considers the effect of Ch MW on the performance of Ch-nanosilica system in the recycled pulp.

EXPERIMENTAL

Materials

The OCC was collected from Noor city, Mazandaran providence, Iran. Chitosan with low, medium, and high MWs were purchased from Sigma-Aldrich (Steinheim, Germany). Table 1 shows the characteristics of the Ch types according to the supplier's data sheet. Aqueous Ch solution at a concentration of 0.5% (w/w) was prepared by dissolving the Ch in 1% (w/w) acetic acid at room temperature for 2 h.

Table 1. Chitosan Characteristics

Chitosan Type	Degree of Deacetylation (%)	Viscosity at 24 °C (cp)	MW (kDa)
LMW	75 to 85	20 to 300	100 to 120
MMW	75 to 85	200 to 800	400 to 600
HMW	75 to 85	800 to 2000	800 to 1100

Colorless anionic nanosilica (Sol-type) colloid with 8.5% solids content, 15 cp viscosity (at 24 °C), and a specific surface area of 850 m^2/g was purchased from EKA Paper Chemicals (Marietta, GA, USA) under the commercial name NP320. The Ch and nanosilica dosages were 1% and 0.1% (w/w) (based on oven-dry (OD) weight of the pulp), respectively, according to optimum dosages of previous works (Sabazoodkhiz *et al.* 2017). The control sample did not contain any additive.

Methods

Characterization of nanosilica

An atomic force microscope (AFM) (Easyscan 2 Flex; Nanosurf, Liestal, Switzerland) was used for the size distribution measurements. One drop of diluted nanoparticle (0.05 mg/mL) was poured onto a clean glass surface and dried at room temperature to prepare for microscopic imaging. The size dimensions and size distribution of the nanoparticle were observed and recorded with the analytical digital software in the apparatus (Nanosurf easyScan 2 Control Software, version 1.3., Switzerland).

For a more accurate analysis of the dimensions and the shape of the nanoparticles, field emission scanning electron microscope (FESEM) images were taken at various magnifications using a Mira3 XMU FESEM apparatus (TESCAN, Brno, Czech Republic), at an accelerating voltage of 10 kV.

Determination of zeta potential and the hydrodynamic radius (HR) of Ch

The dynamic light scattering method (DLS) was applied to determine the zeta potential and the HR of Ch with different MWs dissolved in 1% acetic acid. For this purpose, a Nano Zetasizer (Malvern Panalytical, Malvern, UK) was used.

Chitosan and nanosilica probable interaction in suspension

Fourier-transform infrared (FTIR) spectroscopy was applied to identify the possible interaction between Ch and nanosilica in alkaline conditions. For this purpose, the 0.5 g Ch solution prepared in 1% acid acetic (with 0.5% concentration) was mixed with 0.5 g nanosilica colloid (with 0.5% concentration). The mixture was in alkaline conditions. A Shimadzu FTIR 8400s (Shimadzu, Kyoto, Japan) was used for the FTIR analysis. A range of 4000 to 400 cm^{-1} was examined at a resolution of 4 cm^{-1} for 32 scans.

Preparation of the pulp suspension

For the pulp preparation, 360 g (OD weight) of OCC was soaked in deionized water with 20 µs/cm conductivity for 24 h. The fiber was disintegrated and refined up to 300 ± 20 mL. CSF (Canadian Standard Freeness) with a laboratory Valley beater (Siami Co., Karaj, Iran) based on the TAPPI T200 sp-01 (2001) standard. After preparation, the pulp was stored in a refrigerator until its use.

Application of the nanoparticle system

The chemicals were added in the pulp suspension with 0.5% consistency. The Ch was mixed with the pulp at 1000 rpm for 45 s. Then, nanosilica was added and mixed for 15 s at 800 rpm. The conductivity of the pulp before chemical addition was approximately 200 µs/cm at ambient temperature (25 °C).

Handsheet preparation

The paper handsheets were prepared based on the TAPPI T205 sp-02 (2002) standard. To prepare the 130 g/m^2 paper, 2.6 g of refined pulp (OD weight) was diluted to 0.5% consistency with deionized water. Following the chemical addition to the suspension, the handsheets were prepared in a mold handsheet maker. At least 10 sheets were produced for each treatment. Finally, the handsheets were dried using a cylindrical drier at 60 °C for 2.5 h.

Pulp drainage

The pulp drainage was measured based on the TAPPI T227 om-04 (2004) standard, with the CSF tester. The pulp pH was considered as a variable (5.5, 7, and 8.5) before application of the system and following each treatment, 3 g of furnish (OD weight) was poured into a graduated cylinder. Deionized water was added to the cylinder to reach a total volume of 1000 mL. Then, the homogenized suspension was transferred to the freeness tester.

Fines content

The fines content was defined as the amount of solids in the furnish that passed through a 200-mesh screen. The fines content of the recycled furnish was measured based on the TAPPI T261 cm-00 (2000) standard using a Britt Dynamic Drainage Jar (BDDJ) (Paper Research Materials, Seattle, USA). The fines content of the suspension was calculated according to Eq. 1,

$$F = \frac{A}{B \times C} \times 100 \quad (1)$$

where F is the fines content by weight (%), B is the weight of original sample (g), C is the consistency (g/g), and A is the weight of the fines collected on the filter paper (g). The experiment was replicated three times and the average fines content (%) of the pulp was measured as 48.22%.

Fines retention

The first pass retention of the fines was calculated according to TAPPI T261 cm-00 (2000) standard using a BDDJ. For this purpose, 500 mL of pulp suspension at a consistency of 0.5% was transferred to the BDDJ. After the pH adjustment (in 3 levels:

5.5, 7, and 8.5) and the addition of chemicals, the filtrate was collected while being agitated at 750 rpm for 30 s. The fines retention was calculated according to Eq. 2,

$$R = 1 - \frac{A \times W}{U \times T} \quad (2)$$

where T is the total fines in the sample (g), R is the fines retention (%), U is the weight of the filtrate (g), W is the weight of the solids (fines) in the filtrate (g), and A is the weight of the original sample (g).

Mechanical properties

The tensile index according to TAPPI T494 om-01(2001), the tear index according to TAPPI T414 om-04 (2004), the burst index according to TAPPI T403 om-02 (2002), and the internal bonding strength according to TAPPI T569 pm-00 (2000) were evaluated (Sabazoodkhiz *et al.* 2017).

Statistical analysis

Each treatment was tested at least three times. The results were statistically analyzed using a completely randomized design (CRD), and the standard deviations were calculated. Duncan's multiple range test (DMRT) was applied to categorize the averages. The Duncan grouping results were categorized alphabetically. The data groups that did not share the same letter were found to be significantly different from each other (99% confidence level). The statistical analysis was conducted using SPSS software (IBM, version 16.0, Armonk, NY, USA).

RESULTS AND DISCUSSION

Characterization of Silica Nanoparticles

AFM analysis

The topography and dimensions of the silica nanoparticles were studied using AFM (Fig. 1). According to Fig. 1, the size of the silica nanoparticles ranged from 1 nm to 5 nm.

FESEM analysis

The nanosilica dimensions were investigated further with FESEM images. Figure 2 demonstrates the nanosize of the silica particles, which confirmed the results of the AFM technique. The large particles were agglomerated nanosilica particles due to the preparation steps of the FESEM images.

Zeta potential and the HR of chitosan

Table 2 shows the zeta potential and the HR of the low and high MW Ch determined by the DLS method.

Table 2. Zeta Potential and the HR of Low and High MW Ch

Molecular Weight	Zeta Potential (mV)	HR (nm)*
Low	+ 86	115
High	+ 90	112

* Hydrodynamic Radius (HR)

The zeta potential was positive in both the low and high MW Ch, which was a result of the increased number of protonated amine groups dissolved in 1% acetic acid. The HR values in both MWs were in the same range.

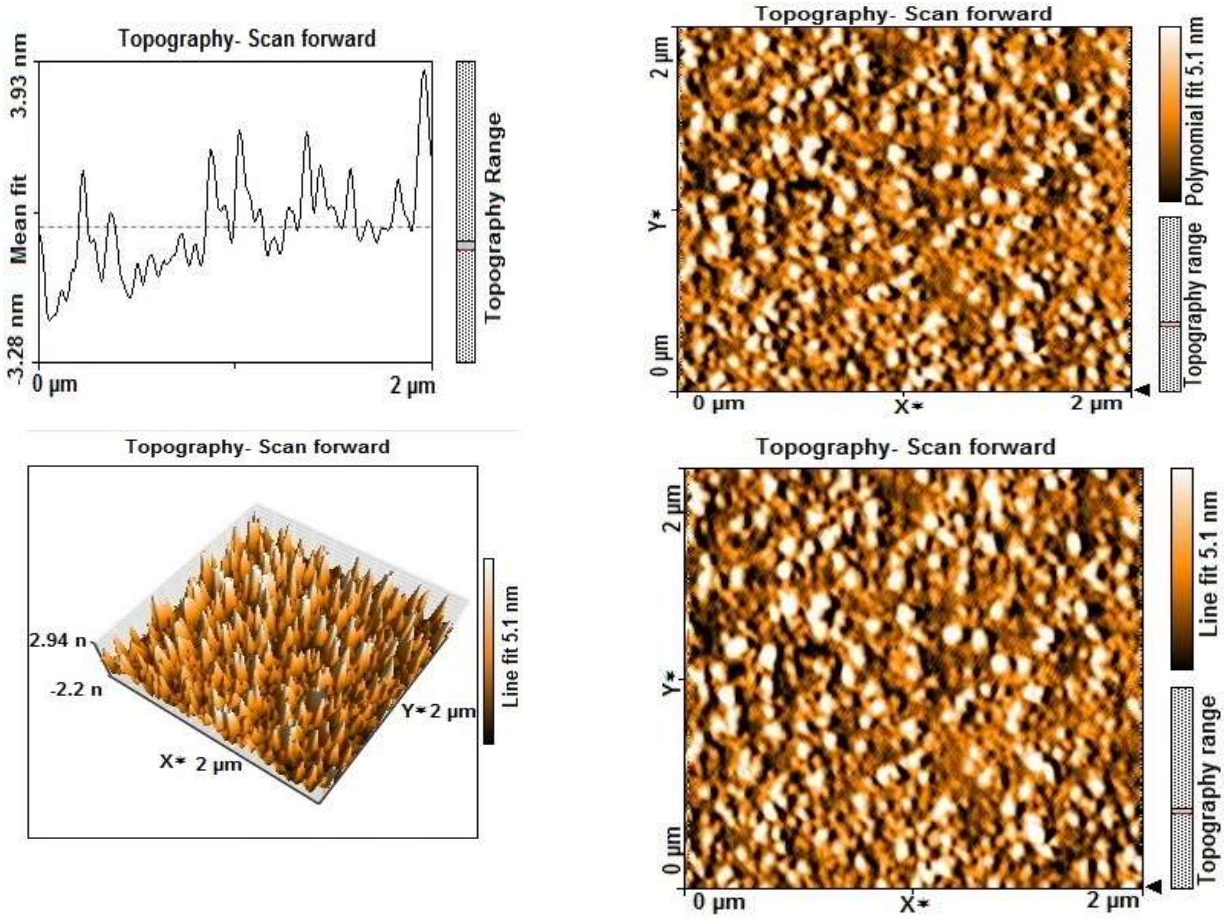

Fig. 1. Silica nanoparticles topography and diameter size estimation with the AFM images

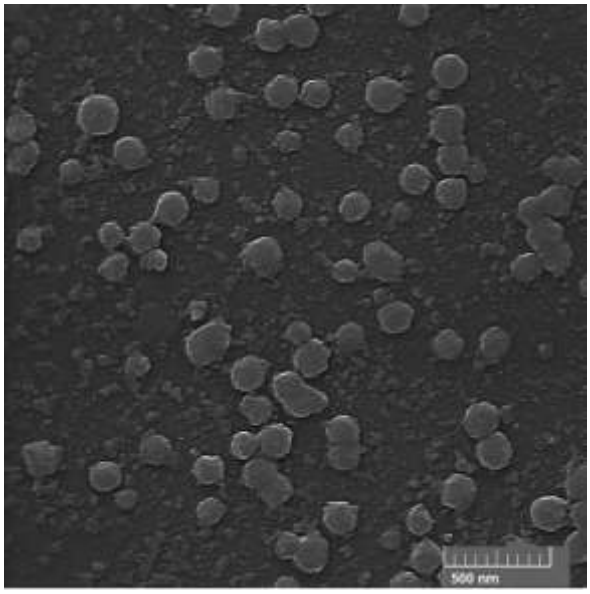

Fig. 2. The FESEM image of the spherical nanosilica (magnitude: 75 kx)

FTIR spectroscopy of nanosilica, Ch, and Ch-nanosilica

The probable interaction between the nanosilica and the Ch was evaluated using FTIR spectroscopy. The FTIR spectroscopic data from the nanosilica can be seen in Fig. 3.

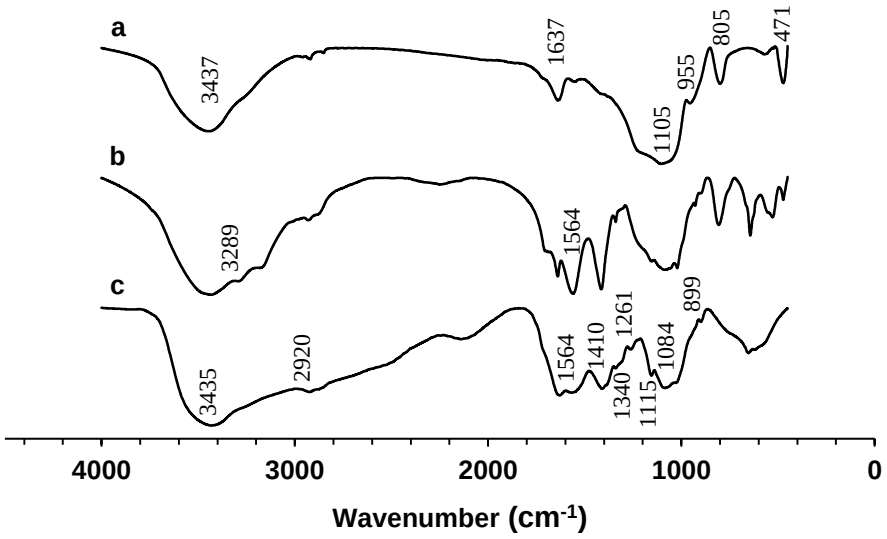

Fig. 3. The FTIR spectroscopy of (a) nanosilica, (b) Ch-nanosilica, and (c) Ch

The FTIR spectra of Ch and nanosilica have been investigated in a previous study (Sabazoodkhiz *et al.* 2017). The FTIR spectra of the Ch-nanosilica interaction in alkaline pH showed that the peak at 3435 cm^{-1} in Ch, which corresponds to the stretching vibration of the O-H groups, overlapped with the stretching vibration of N-H. This indicated a double peak in the Ch-nanosilica mixture in alkaline condition. The peak at 3289 cm^{-1} is possibly related to shifting due to the hydrogen bonding between the OH of silanol groups on the nanosilica surface and the OH or NH_2 Ch (Budnyak *et al.* 2015).

The Effect of Chitosan MW on the Nanoparticle System Performance

Drainage and fines retention parameters

During the production of paperboard, dewatering from the wet web is critical due to the high basis weight of the web. Improving the drainage has many advantages for the paper industry. Some advantages include increasing the machine speed and productivity, reducing energy consumption, and finally lower production costs (Scott 1996). Paper machine drainage is largely affected by the retention system and the structure of the flocs. Fiber-fiber, fiber-fine, and fine-fine relations are all important to be considered (Khosravani *et al.* 2010). When fines (total particles below 76 μm) is a large portion of furnish, their retention in the final sheet is more important. In this study, fines content was about 48.2% of furnish, and thus retention was a critical factor.

The performance of Ch as a polyelectrolyte in combination with nanosilica (nanoparticle system) on the drainage and retention is observable in Table 3. The probable mechanism of chitosan-nanosilica interaction in pulp suspension has been explained elsewhere (Sabazoodkhiz *et al.* 2017). The cited article emphasized the forming of proper flocs in the pulp slurry based on a semi-reversible bridging mechanism.

Because the pH of the fibrous suspension may highly affect the performance of the Ch as a polyelectrolyte, the data was analyzed under different pH conditions.

Table 3. The Effect of pH on Ch-nanosilica Performance in Process Properties

	LMW Ch			MMW Ch			HMW Ch		
pH	5.5	7	8.5	5.5	7	8.5	5.5	7	8.5
Drainage (mL CSF)	233 (e) *	303 (bc)	383 (a)	291 (c)	389 (a)	373 (a)	252 (d)	321 (b)	317 (b)
Standard Deviation	6.39	8.76	8.60	8.94	17.89	10.44	8.94	14.45	2.51
Retention (%)	-	69.7 (d)	79.03 (a)	72.91 (cd)	77.99 (ab)	75.08 (bc)	61.2 8(f)	65.64 (e)	66.0 (e)
Standard Deviation	-	1.85	0.32	1.18	1.65	1.65	1.30	1.56	1.07
*The data that do not share the same letter in parentheses were found significantly different from each other (99% confidence level)									

The results in Table 3 indicated that better drainage and retention was obtained in alkaline and neutral conditions. Some studies investigated Ch alone or Ch-micro/nanoparticles in acidic conditions (Ashouri *et al.* 2006; Sabazoodkhiz *et al.* 2017; Rahmaninia *et al.* 2018). But this research showed that Ch performed better in alkaline and neutral conditions in combination with nanosilica. It seems that the presence of too much active amine groups in chitosan structure results in its very high positive charge in acidic condition (Rohi *et al.* 2016), so increasing the pH can reduce the charge density of the Ch to an optimum level. In this manner the Ch configuration tends to be in a loop and tail shape rather than flat one. This provides a greater chance for this bio-polyelectrolyte to bridge between the fines and fibers (Fig. 4) (Saarinen 2008).

Moreover, increasing the pH, induces more negative charge to the fibers surface due to the de-protonation of the carboxyl groups. Thus, more cationic polyelectrolyte is able to adsorb onto the fibers (Scott 1996).

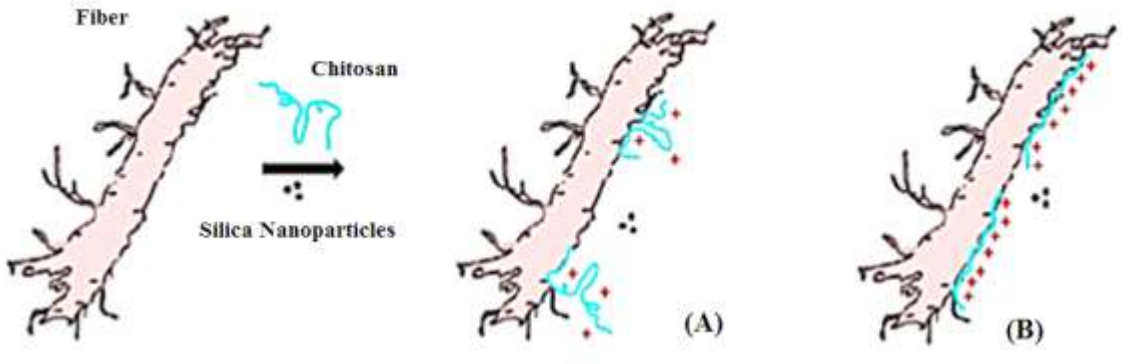

Fig. 4. Possible configuration states of Ch in (a) alkaline pH and (b) acidic pH

Considering the effect of MW on drainage and retention, the best results were obtained from LMW Ch and MMW Ch. Agusnar *et al.* (2013) and Miranda *et al.* (2016) support this observation, which showed that LMW Ch and MMW Ch had the best and second-best drainage gains, respectively. In a dual system, Miranda *et al.* (2016) reported that the best drainage results were obtained by LMW Ch.

It was expected that HMW Ch would yield better drainage and fines retention due to its longer chain and better bridging ability. However, the HMW Ch was unable to penetrate the fiber pores and the spaces between the components of the pulp suspension (Alince *et al.* 1996; Vikele *et al.* 2017). This electrostatically enabled the maximum soluble polymers to adsorb on top of the fiber pores, causing the zeta potential of the suspension to be positive. A positive zeta potential can deteriorate the performance of the nanoparticle system and the formation of fiber flocs.

As optimum drainage and retention was obtained in alkaline conditions for Ch of various MWs and also paper machines are generally run in alkaline conditions, so the mechanical properties were evaluated for this pH.

Mechanical Properties of Paper Sheets

Apparent density

The effects of Ch MW on the apparent density of the recycled paper treated with the nanoparticle system are shown in Fig. 5. The MW had little effect on the density of the samples. This was attributed to the grammage to thickness ratio. The use of retention aids increased the grammage through better fines retention, while the formation of flocs increased the thickness (Hubbe 2006). Therefore, the apparent density (grammage to thickness ratio) did not change. However, it should be mentioned that according to the previous studies, the nano/microparticle systems will deteriorate the formation and uniformity of paper less than other common retention aids such as cationic polyacrylamide single polymer system (Sabazoodkhiz *et al.* 2017; Yousefhashemi *et al.* 2019).

Tear index

The tear index has a significant role in the ability of paper to pass through the papermaking machine and go through the converting process. The fundamental factors affecting the tear index are the fiber length, the inherent fiber strength, the bonding ability of the fibers, and the fiber orientation in sheet (Kermanian *et al.* 2013). Generally, in pulps with low bonding ability, such as mechanical pulps, tear strength can be improved by increasing the surface bonding. However, in pulps with high internal bonding, the limiting factors are the fiber length and the strength of the individual fibers.

The nanoparticle system had no effect on the fiber length and the strength of individual fibers. Therefore, the nanoparticle system may only increase the tear strength by increasing the bonding area in the paper sheet.

As shown in Fig. 5, the different treatments had little effect on the tear strength. At first glance, it was concluded that the Ch-nanosilica did not affect the tear strength. However, it is important to consider that by applying this system, more fines and fillers will be retained in the handsheets. The increased fine and filler content can decrease the tear strength considerably. Therefore, the lack of change in the tear index was attributed to both increasing in bonding area and increasing in retention of fines and fillers.

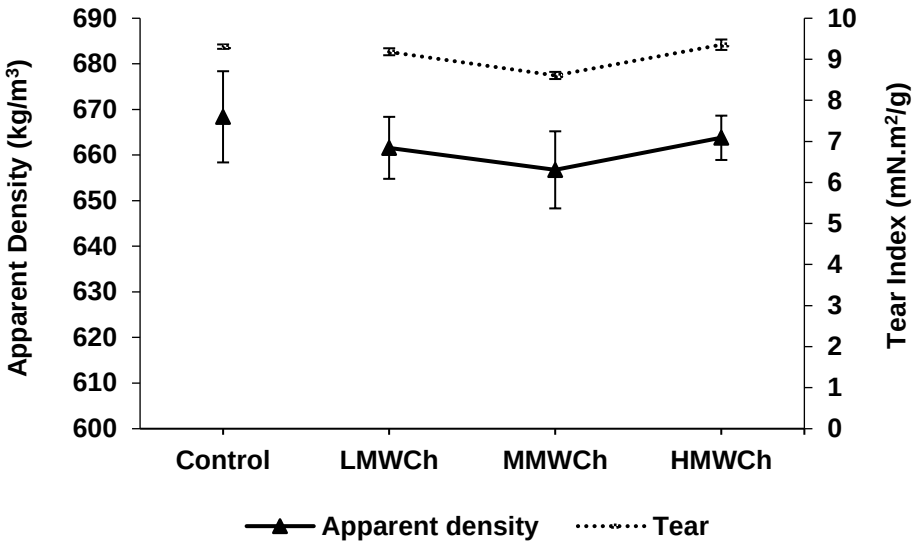

Fig. 5. The effects of Ch MW on the tear index and the apparent density

Tensile and burst indices

Figure 6 shows the tensile and burst indices of the samples treated with nanoparticle system containing different MW Ch. These samples were compared to the control treatment. The tensile and burst indices are critical properties that can be affected by the inherent fiber strength, the bonding strength of the fibers, the bonding area, the fiber distribution, and the sheet formation quality. The individual fiber strength is affected by the wood species, the pulping process, the bleaching process, and the amount of times the fibers have been recycled. Therefore, wet end additives in the papermaking process have little effect on the individual fiber strength. However, chemical treatments, such as wet end additives, can influence the distribution of fibers and the bonding capabilities (Kermanian *et al.* 2013). As demonstrated in Fig. 6, both the tensile and burst indices increased in all of the treated samples compared to the control treatment.

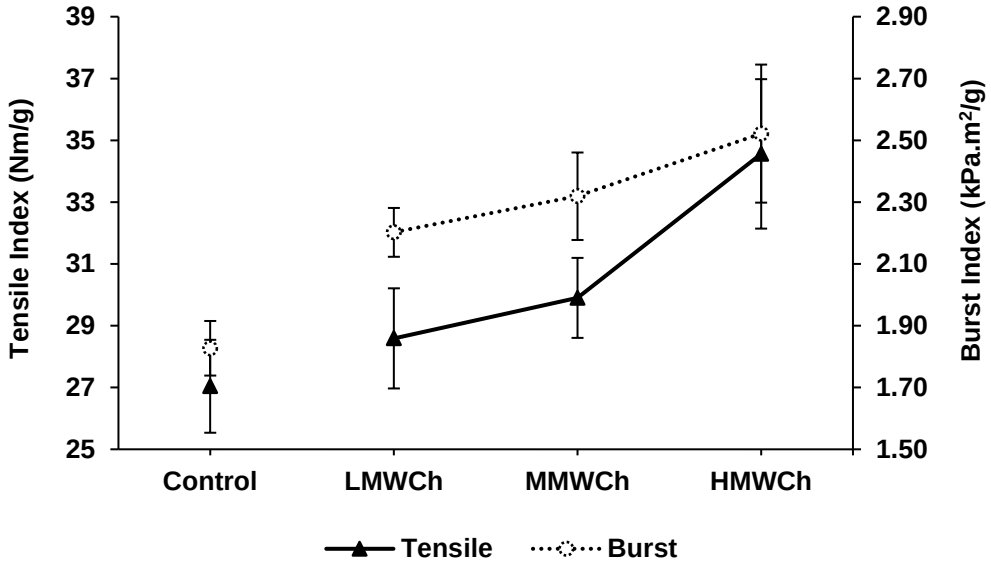

Fig. 6. The effects of Ch MW on the tensile index and the burst index

The increase in strength was attributed to the performance of the nanosilica system. Previous research indicated that using additives, especially polyelectrolytes, in pulp suspensions can deteriorate the paper formation due to the formation of fiber flocs (Hubbe 2006). However, the positive performance of the Ch-nanoparticle in treated samples was due to the unique characteristics of Ch. Chitosan has a similar structure to cellulose, along with active hydroxyl and amino groups. This allows for more bonding among the fibers and fines, which improves the bonding area in the paper sheet.

As the MW of the Ch samples increased, the tensile and burst indices increased as well. This was explained by the longer chain of high MW Ch, which provided more bonding sites for fibers and fines. Agusnar *et al.* (2013) and Vikele *et al.* (2017) indicated that the single application of MMW Ch had better results compared to the LMW Ch. However, Habibie *et al.* (2016) reported that the single application of LMW Ch was more successful than MMW Ch in improving the mechanical properties of paper.

Internal bond index

The results for the internal bond index (Scott bond) are shown in Fig. 7. According to these results, the internal bond strength increased using the Ch-nanosilica in all the MW levels of Ch. As a polyelectrolyte with active functional groups, such as hydroxyl and amino groups, Ch can improve the internal bonding through means of hydrogen bonding, while also acting as an effective dry strength additive. Moreover, nanosilica may help to improve the internal bond strength due to the formation of smaller and denser flocs (Khosravani and Rahmaninia 2013).

Furthermore, increasing the MW of chitosan greatly improved the internal bond index. High MW chitosan has longer chains, which probably improve the chitosan ability to make more bridges among the solid components.

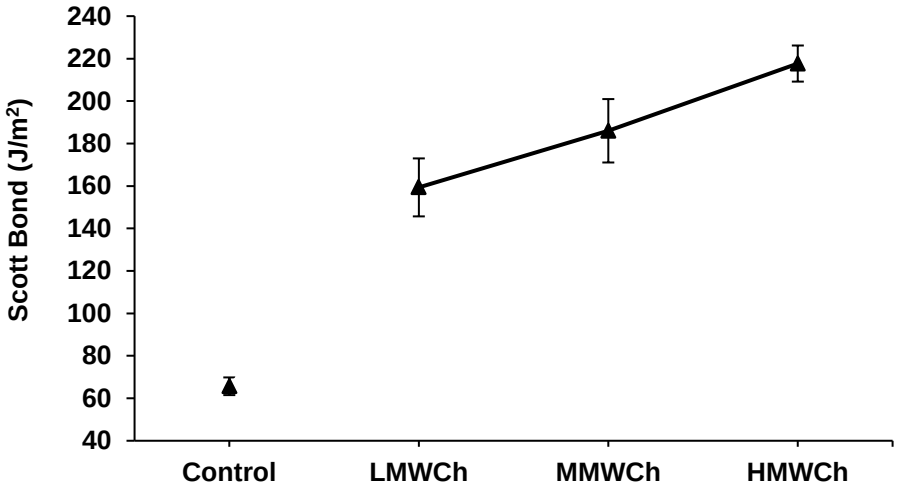

Fig. 7. The effects of Ch MW on the internal bond of paper

CONCLUSIONS

1. The chitosan-nanosilica system improved the production process through increasing the fiber mat drainage and higher first pass retention. The optimum drainage and retention values were observed for the Ch of low and medium MWs. The interaction of this cationic polyelectrolyte with other components of the recycled pulp suspension was affected by its configuration in the aqueous media before and after adsorption, its ability to penetrate fiber pores, its charge density, and also the charge density of fibers. The interaction between the MW of Ch and the pH of the pulp suspension was also an important factor.
2. The best mechanical properties were obtained from the Ch of high MWs. The improved strength properties were likely attributable to Ch's performance following adsorption and retention within the fibrous mat, rather than the colloidal effects.
3. Previous studies have suggested that Ch usually works better in acidic conditions. However, this research showed that Ch-nanosilica performed better in alkaline conditions and to some extent in neutral conditions.

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