

Impact of Electrolytes on the Rheology of TEMPO-oxidized Cellulose Nanofibril

Rahmini¹, Soyoung Juhn², Kyung-Haeng Lee^{3†}, Soo-Jeong Shin^{4‡}

Received May 11, 2020; Received in revised from September 22, 2020; Accepted September 24, 2020

ABSTRACT

Cellulose nanofibril (CNF) gels are interesting natural materials that have various potential applications, but some applications require specific gel properties: producing stiffer/strong gels. In this study, CNFs were prepared by TEMPO-mediated oxidation pre-treatment under three conditions (CNF-1, CNF-2, CNF-3). Gelation of CNFs was initiated by the addition of various concentrations of monovalent (Na^+) and divalent (Ca^{2+}) ions (500, 1,000, 5000, 10,000 ppm) in order to improve the mechanical strength of the gels. CNF gels were analyzed and characterized in terms of shear viscosity, storage moduli, and loss moduli using a rheometer at the temperature of 25°C. The results showed that the amount of carboxyl content on the surface charge of CNF strongly affected the rheological properties of CNF gels. Increasing the carboxyl content contributes to enhancing the mechanical strength of CNF gel. Similar effect to the addition of cations in which the viscosity and storage moduli of CNF gels significantly increased as the concentration of added cation increased from 500 to 10,000 ppm. However, CNF gels with calcium showed higher strength than those with sodium, this may due to the different charge and ionic radii of both sodium and calcium. Ionic radii, a charge of cation, and concentration of cation used, carboxyl group contents as well, played an important role in influencing the mechanical properties of CNF gels. However, further analysis is required related to a concentration of cation used to form a maximum strength of CNF gel.

Keywords: Cellulose nanofibril, rheology, sodium, calcium

1. Department of Wood & Paper Science, Chungbuk National University, Chungbuk, 28644, Republic of Korea, MS student.

2. NatureCostech Inc., Chungbuk, 28444, Republic of Korea, Director for R & D.

3. Department of Food and Nutrition, Korea National University of Transportation, Chungbuk, 27909, Republic of Korea, Professor.

4. Department of Wood & Paper Science, Chungbuk National University, Chungbuk, 28644, Republic of Korea, Professor.

† Co-Corresponding Author: E-mail: leekh@ut.ac.kr

‡ Corresponding Author: E-mail: soojshin@cbnu.ac.kr

1. Introduction

Nanocellulose is a new form of cellulose material that has been gained large interest in a huge number of applications especially in biomedical, tissue engineering, drug delivery, composite due to its high specific surface area, crystallinity, renewable, biocompatible, biodegradable, lack of toxicity, low-density properties, etc.¹⁻⁶⁾ Nanocellulose is classified into three main types: cellulose nanofibril, cellulose nanocrystal, and bacterial cellulose.⁷⁾ In general, CNFs and cellulose nanocrystals are produced from wood pulp by breaking down the cellulose fibers into nanosize particles (1–100 nm width).⁸⁾ CNFs can be produced through mechanical disintegration include grinding, refining, high-pressure homogenization, microfluidization, etc.⁹⁻¹⁰⁾ However, introducing the enzymatic and chemical pre-treatment such as enzyme hydrolysis, carboxymethylation, TEMPO-mediated oxidation into the fibrillation process is needed to be effective and energy-efficient instead of mechanical treatment only.¹¹⁻¹⁴⁾ Nevertheless, enzymatic and chemical pre-treatment have different properties. For example, pre-treatment using carboxymethylated and TEMPO-based present highly charges systems and exhibit 3–4 nm widths compared to enzymatic pre-treatment (width 20–30 nm).¹¹⁻¹²⁾ Furthermore, the applied mechanical shearing combined with carboxymethylation and/or TEMPO-mediated oxidation in the production process significantly influences the rheological properties of CNFs by the presence of strong anionic charge on the surface (lots of negative charges) which causes electrostatic repulsion between fibrils.¹⁵⁻¹⁸⁾

Interest in CNF-based hydrogels is growing rapidly marked by numerous studies related and promising a wide variety of potential applications.¹⁹⁻²⁴⁾ However, CNF hydrogels displayed relatively weak mechanical properties. Therefore, understanding and controlling the mechanical

properties of CNF suspension is important especially for improving the gel strength. Several works of literature related to enhancing the mechanical strength of CNF hydrogels through rheology test have been published.²⁵⁻³¹⁾ It was discovered that the presence of metal cation significantly increases the rheological properties of CNF suspension. For example, Sim et al.³⁰⁾ induce stiffer gels by utilizing monovalent (Na^+) and divalent (Ca^{2+}) cation to bind with negatively charged carboxylated groups on the surface of CNF suspensions. The impact of mono, di-, and trivalent cations in increasing the storage moduli (G') and loss moduli (G'') value of CNF gels has also been reported.³¹⁾ It is noticeable that the higher G' value results in the stiffer gels. Furthermore, increasing the concentration of metal cations leads to an increase in gel strength.²⁷⁾ However, the opposite result was found where the G' value decreases monotonically as the concentration of cation gradually increases.¹⁴⁾

There are several studies on the rheological properties CNF gels. To the best of our knowledge, reports of TEMPO-mediated oxidation CNF gel using metal cation particularly at high concentration (up to 10,000 ppm) is very limited. Therefore, in this study, we focused on the rheological properties of CNF gel produced by TEMPO-mediated oxidation under various conditions. We also examined the impact of monovalent and divalent cations at the concentration of 500, 1,000, 5,000, and 10,000 ppm.

2. Materials and methods

2.1 Materials

Dried hardwood kraft pulp supplied by M. Company was used as material to produce CNFs. Chemicals used in (TEMPO-mediated oxidation) pretreatment and hydrogel making process were presented in Table 1. Distilled water used through-

out this study was gained from the Department of Wood and Paper Science at Chungbuk National University.

2.2 Preparation of TEMPO-mediated oxidation CNF

TEMPO-mediated oxidation CNF was prepared according to the previous method described by Saito et al.¹²⁾ with slight modification. Briefly, Kraft pulp (300 g) was disintegrated in distilled water containing 0.5 g TEMPO and 2.5 g NaBr and stirred for 10 min. Then, NaClO solution was added into the suspension and kept under stirring to start the oxidation process. The pH was maintained at 10 by adding 1 M KOH until the pH stayed constant. The oxidation process occurred at room temperature for 2 h. The oxidized fibers were then rinsed and filtered with distilled water until neutral to stop the reaction. Afterward, the treated fibers were suspended in distilled water to obtain 3 wt% consistency. The fibrillation process was performed by two steps. First, 3 wt% fiber suspension was

passed two times through the supermasscolloider (MKZA10-15IV; Masuko Sangyo, Japan). Then, the fiber suspensions were homogenized two passes using high-pressure homogenizer processor (Panda Plus, GEA, Italy) at the pressure of 600–800 bar. Detailed treatment conditions is presented in Table 2.

2.3 Zeta potential

Zeta potential of CNF samples was performed at 25°C by a Zetasizer Nano ZS. The samples were prepared by diluting CNF with distilled water at a concentration of 0.02%. The zeta potential data is calculated based on the average of three repetitions of each sample.

2.4 CNF gels preparation

CNF gels with different concentrations of cation were prepared by first diluting NaCl and CaCl₂ in distilled water to create 500, 1,000, 5,000, and 10,000 ppm of Na⁺ and Ca²⁺. Thereafter, the cation solution was added to the 3% CNF suspension to obtain 2% CNF gels. CNF with added cation was

Table 1. Information of chemicals used in this study

Chemical name	Company	Origin country
2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)	Sigma-Aldrich	Germany
Sodium bromide (NaBr)	Samchun Pure Chemical Co., Ltd.	Korea
Sodium hypochlorite (NaClO)	Sungju Industrial	Korea
Potassium hydroxide (KOH)	Showa Chemical Co., Ltd.	Japan
Sodium chloride (NaCl)	Junsei Chemical Co., Ltd.	Japan
Calcium chloride (CaCl ₂)	Junsei Chemical Co., Ltd.	Japan

Table 2. Conditions of the TEMPO-oxidized CNF production

Conditions	Samples		
	CNF-1	CNF-2	CNF-3
a)TEMPO/NaBr/NaClO (mM/g cellulose)	0.03/0.24/0.7	0.03/0.24/1	0.03/0.24/3
b)Grinding	Yes	Yes	Yes
c)Homogenization	Yes	Yes	Yes

a) TEMPO/NaBr/NaClO concentration in millimol per gram of cellulose, b) Disintegration using a supermass-colloider (MKZA10-15IV; Masuko Sangyo, Japan,) for 2 passes, c) passing through a GEA Homogenizer processor (Panda Plus, GEA, Italy) for 2 times at the pressure of 600–800 bar.

finally homogenized by a hand, shaking for 2 min at an average speed of 5 times/s,

2.5 Rheological properties

Mechanical properties of CNF gels were characterized by rheology tests using a rheometer (MCR 102, Anton Paar, Austria). In this study, we measured the shear viscosity and strain sweep of TEMPO-oxidized CNF with cation using a 25 mm diameter parallel plate and a 1 mm gap setting between both plates. The sample measurements were performed three times under the control temperature at 25°C. The viscosity was applied to understand the flow behavior of the samples at the constant shear rate of 1 s^{-1} to 100 s^{-1} . Strain sweep was measured to determine the linear viscoelastic (LVE) region over the strain ranging from 0.01 to 100% at the frequency of 10 rad/s.

3. Results and discussion

Gelation of CNFs was induced by introducing monovalent and divalent cations to form a binding affinity with carboxylate groups on the TEMPO-oxidized CNF surfaces. To determine the effect of cation on the rheology of CNF gels, vari-

ous concentrations of cation were used (500, 1,000, 5,000, and 10,000 ppm). All samples show increasing on the viscosity and storage moduli as the concentration of cation increased, indicating the strongest gels occurs at the higher concentration. However, the addition of an excessive amount of cation results in coagulation of CNF which causes the gel to lose its strength.²⁹⁾

Fig. 1 shows the viscosity as a function of shear rate of CNF-1 with different cation concentrations. Fig. 1a shows the addition of Na^+ gradually increased the viscosity of CNF-1 from 20,38 Pa·s at 500 ppm to 46,58 Pa·s at 10,000 ppm. Similar effect to Ca^{2+} addition in CNF-1 (Fig. 1b), with increasing the cation concentration, the viscosity increased from 32,80 Pa·s at low concentration to 113,78 Pa·s at high concentration. It is interesting that a higher concentration of cation proposed a strong screening effect on the CNF gel. Some studies related to increasing the amount of cation strongly affect the viscosity of CNF gel were reported.^{16,27,30-35)}

However, another CNF system shows the opposite effect to the salt addition where the viscosity diminishes as the concentration of NaCl increases from 0.1 mM to 10 mM. Increasing electrolyte concentration contributes to reducing electrostatic

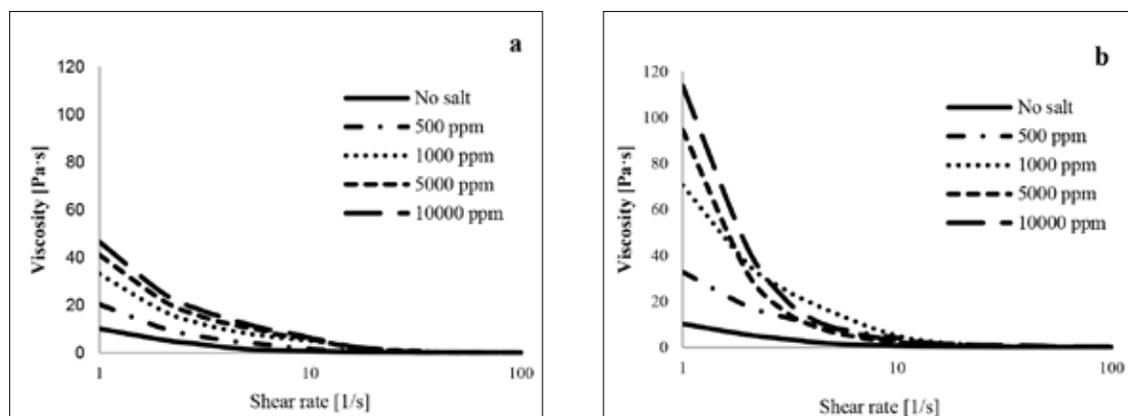


Fig. 1. The viscosity as a function of shear rate of 2% TEMPO-oxidized CNF-1 with various cation concentrations: (a) Na^+ , (b) Ca^{2+} .

repulsion forces between fibrils, causing CNF to flocculate and water released from the network to form a stronger network. However, fluid-like behavior may also occur result in a reduction in rheology response.¹⁴⁾

As can be seen the viscosity values of CNF-1 with sodium ion were lower than those CNF-1 with calcium ion at the same concentration. For example, the CNF-1 required 1,000 ppm of Na⁺ to reach 33.12 Pa·s whereas Ca²⁺ attained 32.80 Pa·s at 500 ppm concentration only. Noteworthy, there is a difference by about 50% in viscosity value when using the same concentration of monovalent (Na⁺) and divalent (Ca²⁺) cation. It was reported that the impact of divalent ion (Ba²⁺, Mg²⁺, and Ca²⁺) on the viscosity of carboxymethylated CNFs were higher than those with monovalent ion (Na⁺, K⁺, and Li⁺).²⁸⁻²⁹⁾ This is probably due to the difference in ionic radii and the charged number of the cation used.

The effect of various cation concentrations on the viscosity of CNF-2 is presented in Fig. 2. The viscosity of CNF-2 increased with increasing the concentration of sodium and calcium ion. This obviously pointed out that the amount of cation added into CNF suspension influenced the gel strength which caused increasing the viscosity.

Similar phenomena are shown in Fig. 3 where added sodium and calcium ion increased the viscosity of CNF-3. Adding sodium and/or calcium ion in CNF reduces repulsion forces between fibrils and forms a strong network.³⁰⁾ All samples displayed shear-thinning behavior, it can be explained by the viscosity decreased as the shear rate increased.^{11,14,36,37)} Increasing the shear rate is attributed to the entanglement breakage between particles of cellulose and their alignment.³⁸⁾

Figs. 1-3 show the effect of various carboxyl contents on the viscosity of CNF gels. The results indicated that the viscosity increased with increasing the carboxyl content during pre-treatment. Zeta potential can be used to determine the carboxyl content in each CNFs. As can be seen in Fig. 4, CNF-3 had a lower zeta potential of -51.9 mV and thus result in higher carboxyl content than those from CNF-2 (-38.8 mV) and CNF-1 (-26.8 mV). In this context, CNF-3 contained lots of carboxyl groups that can be bonding with Na⁺ and/or Ca²⁺ ion and thus resulted in the strongest gel compared to those from CNF-1 and CNF-2.

Furthermore, CNFs obtained in this experiment showed higher gel strength than those carboxymethylated CNFs from our previous work at the same added cation concentration.^{28,29)} This may

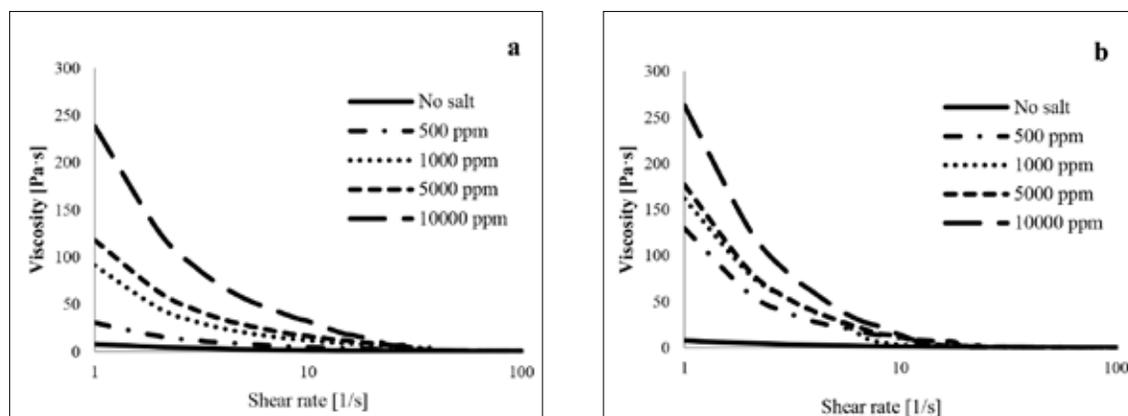


Fig. 2. The viscosity as a function of shear rate of 2% TEMPO-oxidized CNF-2 with various cation concentrations: (a) Na⁺, (b) Ca²⁺.

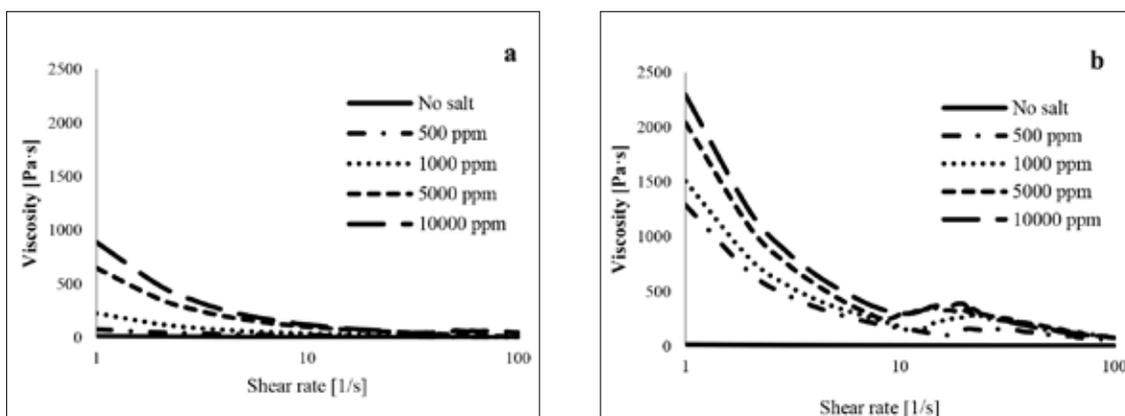


Fig. 3. The viscosity as a function of shear rate of 2 % TEMPO-oxidized CNF-3 with various cation concentrations: (a) Na^+ , (b) Ca^{2+} .

be caused by different pretreatment, in which CNF used in this study was treated by TEMPO-mediated oxidation whereas the previous study used carboxymethylation pretreatment. It was reported that TEMPO-oxidized CNF has a higher total surface charge than that of carboxymethylated CNF ($550 \mu\text{mol/g}$ for carboxymethylated CNF and $1063 \mu\text{mol/g}$ for TEMPO-CNF).¹⁷⁾ In addition, different amounts of chemical, pH, temperature, and reaction time also affected.^{15,34,41)}

Further analysis of the storage modulus of TEMPO-oxidized CNFs as a function of cation concentration are presented in Figs. 5–6. Fig. 5 shows a variation of storage modulus for CNF gels with Na^+ . The storage moduli of CNF-1 increased from 624 Pa at 500 ppm to 2,814 Pa at 10,000 ppm. Similar effect to CNF-2 and CNF-3, storage moduli increased by increasing sodium concentration from 500 to 10,000 ppm. This behavior implied the higher stiffness occurred at high cation added and showed lower stiffness at low cation added. It is obvious that increasing the concentration of Na^+ from 500 to 10,000 ppm lead to enhancing the gel strength. Sim et al.³⁾ reported the effect of increasing NaCl concentration from 0 to 3 M lead to an increase in the storage moduli of CNF. However, Naderi et al.¹⁴⁾ showed the opposite result:

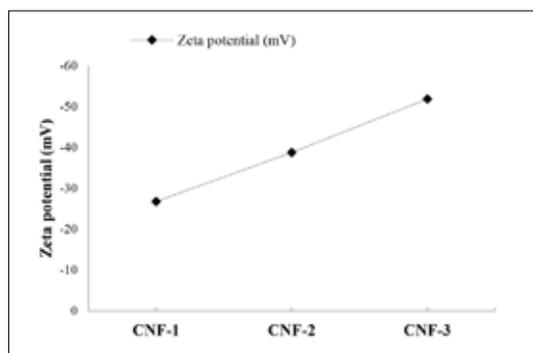


Fig. 4. Zeta potential of TEMPO-oxidized CNFs.

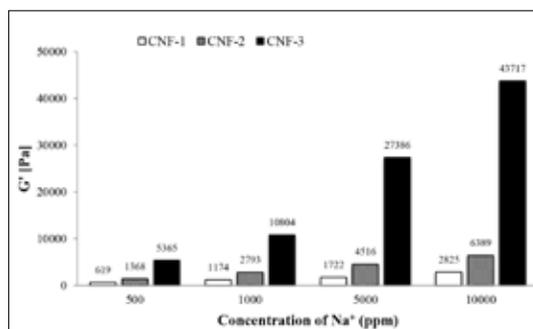


Fig. 5. Storage modulus [G'] of TEMPO-oxidized CNF with various concentration of Na^+ at a frequency of 10 rad/s and strain of 0.1%.

the storage moduli of carboxymethylated CNF decreases as NaCl concentration increases. It was observed that CNF used in the system has a low

swelling ability which complicates the delamination process result in decreases the electroviscous effect when the concentration of the electrolyte is increased.¹⁴⁾

A similar effect is also shown in Fig. 6 where the storage modulus increased as the concentration of Ca^{2+} increased from 500 to 10,000 ppm. As evidence, storage moduli of CNF-3 increased from 17,454 Pa (500 ppm) to 122,500 Pa (10,000 ppm). This behavior has also been reported for the increase in storage and loss modulus for added NaCl and CaCl_2 in carboxymethylated CNF.²⁸⁻³⁰⁾ However, CNF being treated with TEMPO-mediated oxidation had a higher total surface charge, a smaller reduction in the crystallinity index, lower in fibril width, and thus resulted in higher storage moduli than that of carboxymethylated CNF.¹⁷⁾ Therefore, CNF in this study proposed the higher gel strength than that from our previous study.²⁸⁻²⁹⁾ An increase of the storage and loss modulus of CNFs strongly related to the presence of electrostatic repulsive forces on the surface of the fibrils, physical entanglement, and van der Waals forces.^{36,40)}

Furthermore, it is noticeable that CNFs treated by calcium had a tighter gel structure than those for sodium. By comparison, CNF-3 with sodium had a storage modulus value of 5,492 Pa at the

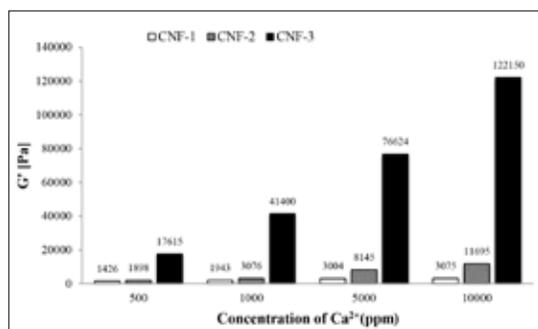


Fig. 6. Storage modulus [G'] of TEMPO-oxidized CNF with various concentration of Ca^{2+} at a frequency of 10 rad/s and strain of 0.1%.

concentration of 500 ppm, whereas calcium exhibited 17,454 Pa at the same concentration, indicating that added calcium in improving the gel strength is preferable. This may be caused by the different ionic radii and the charge number of cation used, where calcium has a higher charge number and smaller ionic radii that contribute to forming stronger gel than sodium ion.²⁸⁻²⁹⁾

The graph in Figs. 5-6 also display the impact of different pretreatment conditions using TEMPO-mediated oxidation on the storage moduli of each CNF gels, which is noteworthy that CNF-3 exhibits the strongest gel, followed by CNF-2, and CNF-1 the weakest (CNF-1 < CNF-2 < CNF-3). For example, CNF-3 attained the highest stiffness (26,753 Pa), followed by CNF-2 (4,436 Pa), and the lowest CNF-1 (1,723 Pa) at 500 ppm of sodium ion. This can be explained considering the difference carboxyl content of each CNFs that can be seen in Fig. 4. Serra et al.³⁸⁾ reports that the more NaClO addition during TEMPO-mediated oxidation CNF, the higher the carboxyl content, which contributed to increase the CNF strength.

4. Conclusions

This study investigated the rheological properties of CNF prepared by TEMPO-mediated oxidation at different degrees of oxidation. The rheology of the CNF gels was examined in terms of the viscosity and viscoelastic properties by the addition of monovalent and divalent cation. We found that the more NaClO addition during TEMPO-mediated oxidation, the higher carboxyl content on the surface charge of CNF and thus contributed to enhancing the mechanical strength (CNF-1 < CNF-2 < CNF-3). The results also implied that the added monovalent (Na^+) and divalent (Ca^{2+}) cation strongly influenced the viscosity and storage moduli of CNF gel specifically by increasing the concentration from 500

ppm to 10,000 ppm. However, CNF gels prepared by calcium exhibited the strongest gel compare to that from sodium ion. The difference in ionic radii between Na^+ and Ca^{2+} cations significantly affects the strength of the gels. Further evaluation is needed to determine the maximum strength of TEMPO-mediated oxidation CNF with added cation.

Acknowledgment

This research was supported by the National Research Foundation of Korea government (NRF) funded by Ministry of Education (NRF-2019R1I1A3A01058481).

Literature Cited

1. Klouda, L. and Mikos, A. G., Thermoresponsive hydrogels in biomedical applications, *Eur. J. Pharm. Biopharm.* 68(1):34–45 (2008).
2. Habibi, Y. and Dufresne, A., Highly filled bionanocomposites from functionalized polysaccharide nanocrystals, *Biomacromolecules* 9(7):1974–1980 (2008).
3. Hassan, M. L., Hassan, E. A., and Oksman, K. N., Effect of pretreatment of bagasse fibers on the properties of chitosan/microfibrillated cellulose nanocomposites, *J. Mater. Sci.* 46(6):1732–1740 (2011).
4. Lin, N. and Dufresne, A., Nanocellulose in biomedicine: Current status and future prospect, *Eur. Polym. J.* 59:302–325 (2014).
5. Jorfi, M. and Foster, E. J., Recent advances in nanocellulose for biomedical applications, *J. Appl. Polym. Sci.* 132(14):1–19 (2015).
6. Sharma, A., Thakur, M., Bhattacharya, M., Mandal, T., and Goswami, S., Commercial application of cellulose nano-composites - A review, *Biotechnol.* 21 (2019).
7. Prakash, M. M., Selvakumar, R., Kumar, P. S., and Ramakrishna, S., Extraction and modification of cellulose nanofibers derived from biomass for environmental application, *RSC Adv.* 7(68):42750–42773 (2017).
8. Shak, K. P. Y., Pang, Y. L., and Mah, S. K., Nanocellulose: Recent advances and its prospects in environmental remediation, *Beilstein J. Nanotechnol.* 9(1):2479–2498 (2018).
9. Chaker, A., Mutje, P., Vilaseca, F., and Boufi, S., Reinforcing potential of nanofibrillated cellulose from nonwoody plants, *Polym. Compos.* 34(12):1999–2007 (2013).
10. Khalil, A. H. P. S., Davoudpour Y., Islam, M., Mustapha, A., Sudesh, K., Dungani, R., and Jawaid, M., Production and modification of nanofibrillated cellulose using various mechanical processes: A review, *Carbohydr. Polym.* 99:649–665 (2014).
11. Pääkko, M., Ankerfors, M., Kosonen, H., Nykänen, A., Ahola, S., Osterberg, M., Ruokolainen, J., Laine, J., Larsson, P. T., Ikkala, O., and Lindström, T., Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gel, *Biomacromolecules* 8(6):1934–1941 (2007).
12. Saito, T., Kimura, S., Nishiyama, Y., and Isogai, A., Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose, *Biomacromolecules* 8(8):2485–2491 (2007).
13. Isogai, A., Saito, T., and Fukuzumi, H., TEMPO-oxidized cellulose nanofibers, *Nanoscale* 3(1):71–85 (2011).
14. Naderi, A., Lindström, T., and Sundström, J., Carboxymethylated nanofibrillated cellulose: Rheological studies, *Cellulose* 21(3):1561–1571 (2014).
15. Naderi, A. and Lindström, T., A comparative study of the rheological properties of three

- different nanofibrillated cellulose systems, *Nord, Pulp Pap. Res. J.* 31(3): 354–363 (2016).
16. Moberg, T., Sahlin, K., Yao, K., Geng, S., Westman, G., Zhou, Q., Oksman, K., and Rigdahl, M., Rheological properties of nanocellulose suspensions: effects of fibril/particle dimensions and surface characteristics, *Cellulose* 24(6):2499–2510 (2017).
 17. Onyianta, A. J., Dorris, M., and Williams, R. L., Aqueous morpholine pre-treatment in cellulose nanofibril (CNF) production: comparison with carboxymethylation and TEMPO oxidation pre-treatment methods, *Cellulose* 25(2):1047–1064 (2018).
 18. Šebenik, U., Krajnc, M., Alič, B., and Lapasin, R., Ageing of aqueous TEMPO-oxidized nanofibrillated cellulose dispersions: a rheological study, *Cellulose* 26:917–931 (2019).
 19. Chai, Q., Jiao, Y., and Yu, X., Hydrogels for biomedical applications: Their characteristics and the mechanisms behind them, *Gels* 3(1):649–665 (2017).
 20. Nascimento, D. M., Nunes, Y. L., Figueirêdo, M. C. B., Azeredo, H. M. C., Aouada, F. A., Feitosa, J. P. A., Rosa, M. F., and Dufresne, A., Nanocellulose nanocomposite hydrogels: Technological and environmental issues, *Green Chem.* 20(11):2428–2448 (2018).
 21. Kabir, S. M. F., Sikdar, P. P., Haque, B., Bhuiyan, M. A. R., Ali, A., and Islam, M. N., Cellulose-based hydrogel materials: chemistry, properties and their prospective applications, *Prog. Biomater.* 7(3):153–174 (2018).
 22. Fu, L. H., Qi, C., Ma, M. G., and Wan, P., Multifunctional cellulose-based hydrogels for biomedical applications, *J. Mater. Chem. B* 7(10):1541–1562 (2019).
 23. Du, H., Liu, W., Zhang, M., Si, C., Zhang, X., and Li, B., Cellulose nanocrystals and cellulose nanofibrils based hydrogels for biomedical applications, *Carbohydr. Polym.* 209(1):130–144 (2019).
 24. Liu, X., Qu, J., Wang, A., Wang, C., Chen, B., Wang, Z., Wu, B., Wei, B., Wen, Y., and Yuan, Z., Hydrogels prepared from cellulose nanofibrils via ferric ion-mediated crosslinking reaction for protecting drilling fluid, *Carbohydr. Polym.* 212:67–74 (2019).
 25. Zander, N. E., Dong, H., Steele, J., and Grant, J. T., Metal cation cross-linked nanocellulose hydrogels as tissue engineering substrates, *ACS Appl. Mater. Interfaces* 6(21):18502–18510 (2014).
 26. Syverud, K., Pettersen, S. R., Draget, K., and Chinga-Carrasco, G., Controlling the elastic modulus of cellulose nanofibril hydrogels—scaffolds with potential in tissue engineering, *Cellulose* 22(1):473–481 (2015).
 27. Cuomo, F., Cofelice, M., and Lopez, F., Rheological characterization of hydrogels from alginate-based nanodispersion, *Polymers* 11(2):1–11 (2019).
 28. Rahmini, Juhn, S., Seong, H. A., and Shin, S. J., Impact of monovalent cations on the rheology of cellulose nanofibrils, *J. of Korea TAPPI* 52(2):12–22 (2020).
 29. Rahmini, Juhn, S., Seong, H. A., and Shin, S. J., Impact of divalent cations on the rheology of cellulose nanofibrils, *J. of Korea TAPPI* 52(2):78–87 (2020).
 30. Sim, K., Lee, J., Lee, H., and Youn, H. J., Flocculation behavior of cellulose nanofibrils under different salt conditions and its impact on network strength and dewatering ability, *Cellulose* 22:3689–3700 (2015).
 31. Dong, H., Snyder, J. F., Williams, K. S., and Andzelm, J. W., Cation-induced hydrogels of cellulose nanofibrils with tunable moduli, *Bio-macromolecules* 14(9):3338–3345 (2013).
 32. Masruchin, N., Park, B. D., Causin, V., and Um, I. C., Characteristics of TEMPO-oxidized cellulose fibril-based hydrogels induced by

- cationic ions and their properties, *Cellulose* 22(3):1993–2010 (2015).
33. Moberg, T., Rigdahl, M., Stading, M., and Bragd, E. L., Extensional viscosity of microfibrillated cellulose suspensions, *Carbohydr. Polym.* 102: 409–412 (2014).
 34. Jowkarderis, L., Theo, G. M. and Ven, D. V., Intrinsic viscosity of aqueous suspensions of cellulose nanofibrils, *Cellulose* 21:2511–2517 (2014).
 35. Chau, M., Sriskandha, S. E., Pichugin, D., Thérien-Aubin, H., Nykypanchuk, D., Chauve, G., Méthot, M., Bouchard, J., Gang, O., and Kumacheva, E., Ion-mediated gelation of aqueous suspensions of cellulose nanocrystals, *Biomacromolecules* 16(8): 2455–2462 (2015).
 36. Lasseguette, E., Roux, D., and Nishiyama, Y., Rheological properties of microfibrillar suspension of TEMPO-oxidized pulp, *Cellulose* 15(3):425–433 (2008).
 37. Iotti, M., Gregersen, Ø. W., Moe, S., and Lenes, M., Rheological Studies of Microfibrillar Cellulose Water Dispersions, *J. Polym. Environ.* 19(1):137–145 (2011).
 38. Butchosa, N. and Zhou, Q., Water redispersible cellulose nanofibrils adsorbed with carboxymethyl cellulose, *Cellulose* 21(6):4349–4358 (2014).
 39. Serra, A., González, I., Oliver-Ortega, H., Tarrès, Q., Delgado-Aguilar, M., and Mutjè, P., Reducing the amount of catalyst in TEMPO-oxidized cellulose nanofibers: Effect on properties and cost, *Polymers* 9(11):557 (2017).
 40. Lindström, T., Aspects on nanofibrillated cellulose (NFC) processing, rheology and NFC-film properties, *Curr. Opin. Colloid Interface Sci.* 29:68–75 (2017).
 41. Benini, K. C. C., Pereira, P. H. F., Cioffi, M. O. H. and Voorwald, J. C., Effect of acid hydrolysis conditions on the degradation properties of cellulose from *Imperata brasiliensis* fibers, *Procedia Eng.* 200: 244–252 (2017).