

# Critical Concentration for Clogging of TEMPO-oxidized Bamboo Pulp Suspensions in a High-Pressure Homogenizer

Haowei Hu,<sup>a</sup> Hao Ji,<sup>b</sup> Jiali Pu,<sup>a</sup> Qi Zhang,<sup>b</sup> Huifang Zhao,<sup>a</sup> Lizheng Sha,<sup>a</sup> Yinchao Xu,<sup>a</sup> Faith Ngaatendwe Katsande,<sup>a</sup> and Xuejin Zhang<sup>a,b,\*</sup>

Clogging is a critical problem that restricts the delamination of fibers in a high-pressure homogenizer (HPH). In this work, bleached bamboo pulp fibers were pretreated in TEMPO/NaBr/NaClO system prior to high-pressure homogenization to study the clogging condition in a high-pressure homogenizer. Effects of the additional amount of NaClO on the functional groups and morphologies of the bamboo pulp fiber were evaluated by conductometric titration, Fourier transform infrared spectroscopy (FTIR), fiber morphology analysis, and scanning electron microscopy (SEM). The fiber morphology analyzer revealed that the addition of NaClO facilitated to reduce the length of the fiber. The SEM images showed that TEMPO-mediated oxidation had a destructive effect on the fiber surface. The carboxylate contents of bamboo pulp fibers increased with the addition of NaClO, which were beneficial for increasing the critical concentrations of suspensions in the HPH. Nanocelluloses were successfully isolated from the TEMPO-oxidized bamboo pulp with different clogging critical concentrations, as were revealed by atomic force microscopy (AFM).

*Keywords:* Clogging concentration; High-pressure homogenizer; TEMPO; Carboxylate group

*Contact information:* a: College of Environment and Resources, Zhejiang University of Science & Technology, Hangzhou, 310023, China; b: Zhejiang Kaifeng Special Paper Co. Ltd., Quzhou, 324000, China; \*Corresponding author: xuejinzhang@126.com

## INTRODUCTION

Nanocellulose has aroused considerable academic and industrial interest as one of the most promising nanomaterials derived from renewable natural resources (Zhang *et al.* 2013; Kargarzadeh *et al.* 2017). Nanocellulose has great potential in a wide range of applications in innovative nanostructured materials due to the nanoscale dimensions, biodegradable character, high potential bonding, high aspect ratio, light weight, and sustainability (Abdul Khalil *et al.* 2014; Kalia *et al.* 2014). These advantages have made nanocellulose suitable as a substitute for fossil materials, and they have been widely used for packaging, medicines, cosmetics, and tissue engineering (Wang *et al.* 2015).

Wood cellulose is composed of elementary fibrils aggregated into larger microfibrils and several microns in length, sticking together in a spiral manner within a multiple-layer-composite to form the cellulose fibers (Chaker and Boufi 2015). The hierarchical structure of wood fibers makes it possible to isolate nanocellulose by mechanical fibrillation. Nanocellulose can be isolated by a large number of different mechanical disintegration processes. High-pressure homogenizers delaminate fibers by intensive mechanical shearing action to delaminate the cell wall and break down the hydrogen-bonding network, resulting in conventional mechanical production of

nanocellulose. Unfortunately, the preparation of nanocellulose by mechanical methods has many problems such as the high-energy consumption, the low consistency of the nanocellulose, and frequent clogging during the disintegration process (Baati *et al.* 2017). Many studies have attempted to reduce the high-energy consumption in the mechanical preparation process and to produce high solid content nanocellulose (Khalil *et al.* 2014; Baati *et al.* 2017; Rol *et al.* 2017; Zhuo *et al.* 2017; Ang *et al.* 2019). Another limiting factor is the clogging of cellulose fibers in HPH, which hinders the mechanical production of nanocellulose (Nechyporchuk *et al.* 2016). However, there are numerous factors affecting the clogging of cellulose fibers in an HPH. Seydibeyoğlu and Oksman (2008) tested different hard wood cellulose fibers concentrations for the homogenization process and found that the slurry concentrations over 0.025% could clog the homogenizer. Some researchers pretreated the pulp fibers by passing them through a refiner and then treating them in an HPH to reduce the risk of clogging (Spence *et al.* 2010, 2011). Li *et al.* (2012) found that the bagasse fiber slurry could pass through HPH without any clogging after pretreatment with ionic liquid prior to homogenization. TEMPO oxidization pretreatment before HPH processes is favorable for the preparation of nanocellulose (Gamelas *et al.* 2015; Lu *et al.* 2017; Wu *et al.* 2017; Feng *et al.* 2018). Pretreatment is an important factor affecting the preparation of nanocellulose by an HPH, and hence it is closely related to HPH clogging. Clogging is related to the aggregation of fibers (Lindström 2017). Electrostatically induced swelling of the fibers reduces the hydrogen bonding and effects the flocculation of fibers (Chaker and Boufi 2015; Lindström 2017). The charge on the fiber surface is highly efficient in avoiding the clogging phenomenon in an HPH. However, the details of clogging in a HPH is not clear. It is necessary to study the relationship between fiber concentration of clogging in a homogenizer and fiber properties after treatment.

In the present study, bamboo pulp fibers were first treated by TEMPO-mediated oxidation (TEMPO/NaBr/NaClO system). Fibers with different degrees of oxidation were obtained by addition of various amounts of NaClO. The oxidized pulp fibers were fibrillated in an HPH, and the critical concentrations of clogging were recorded. Finally, the oxidized pulp fibers were further analyzed by conductometric titration, Fourier transform infrared spectroscopy (FTIR), fiber morphology analysis, and scanning electron microscopy (SEM) in order to elucidate the possible reasons for clogging. This study will facilitate large-scale production of cellulose nanofibers by high-pressure homogenization.

## EXPERIMENTAL

### Materials

The bamboo bleached kraft pulp used as the raw material was provided by Fuyang Huabaozhai Co., Ltd. (Hangzhou, China). 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO), sodium bromide (NaBr), and sodium hypochlorite (NaClO) solution with active chlorine content of 14 wt.%, were purchased from Aladdin Industrial Inc. (Shanghai, China). All other chemicals were of analytical grade and used without further purification.

### Pretreatment by TEMPO-Mediated Oxidation

The bamboo bleached kraft pulp was oxidized using the method of Saito *et al.* (2006) with minor modifications. The water-washed pulp (5 g, based on o.d pulp) was suspended in distilled water (375 mL) containing TEMPO (0.0625 g) and sodium bromide

(0.625 g). To obtain the bamboo pulp fibers with different degrees of oxidation, various amounts of NaClO solution were added to the pulp fiber suspensions under continuous stirring to the target the reaction time. The target reaction time was achieved until the pH no longer decreased. During the reaction process, the pH was maintained between 10 and 10.5 by adding 0.5 M NaOH. The TEMPO-oxidized fibers were repeatedly washed by centrifugation with deionized water until the filtrate became neutral. Finally, the TEMPO-oxidized pulp fibers were stored at 4 °C before further treatment or analysis.

### Fibrillation Process in HPH

The oxidized pretreated pulp fibers with different degrees of oxidation fibers were dispersed in water at a concentration between 0% and 1%. The oxidized pulp fibers were fibrillated with a laboratory scale AH-BASIC homogenizer (Antos Nanotechnology Co., Ltd., Suzhou, China). Fifteen passes were applied at a pressure of 800 bars, and the temperature was kept at 0 °C by ice-water cycle. Different oxidized pulp fibers were diluted to different concentrations and then poured into the feed outlet of the HPH. Finally, critical concentrations of clogging were observed and recorded during the operation of the HPH.

### Fourier Transform Infrared (FTIR) Spectra

After oven drying, raw pulp fibers and oxidized pulp fibers were finely ground and mixed with potassium bromide, then pressed into ultra-thin pellets. The spectra of raw pulp fibers and oxidized pulp fibers were recorded on an attenuated total reflection FTIR spectrometer (IR Prestige-21, Shimadzu, Kyoto, Japan) in the range of 400 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ .

### Conductometric Titration

The carboxylate contents of oxidized pulp fibers were determined by the calcium-acetate method (Praskalo *et al.* 2009; Wu *et al.* 2017). Briefly, the bamboo pulp fibers were treated with 0.01 M HCl under continuous shaking. After 1 h, the treated pulp fibers were washed with distilled water, and then 50 mL of distilled water and 30 mL 0.25 M of calcium-acetate solution were added. The resulting pulp fiber suspensions were ready after 2 h with frequent shaking. Most of the supernatant was collected by centrifugation, and 30 mL of filtrate was collected as titration solution. The final titration was carried out with 0.01 M sodium hydroxide, using phenolphthalein as indicator. The carboxylate contents were calculated according to Eq. 1,

$$\text{COOH} = \frac{80}{30} \times M \times V \left( \frac{\text{mmol}}{\text{g}} \right) \quad (1)$$

where  $M$  is concentration of NaOH,  $V$  is volume (mL) of NaOH solution consumed in titration, and  $m$  is weight of treated wet pulp fibers after washed with distilled water (g).

### Fiber Morphology Analysis

The oxidized pulp suspensions were dispersed using a disintegrating machine to obtain well-distributed cellulose suspensions. The pulp fiber morphology was measured using a MORFI device (Techpap SAS, Grenoble, France) at 0.003% concentration. The lengths and widths of the oxidized pulp fibers were evaluated by statistics software.

## SEM

Surface microstructures of oxidized pulp fibers were observed using a Phenom<sup>TM</sup> SEM device (Fei Na, Netherlands). A sputtering procedure was used to coat the surfaces with gold to dissipate electrical charge.

## AFM

The prepared samples were diluted into suspensions with 0.01% concentration and dispersed by ultrasound for 30 min. A diluted droplet of the MFC/NFC suspension was dried at ambient temperature on freshly cleaved mica and characterized by Atomic Force Microscopy (XE-100E, Korea).

## RESULTS AND DISCUSSION

### Carboxylate Contents of Oxidized Pulp

TEMPO/NaClO/NaBr oxidation system selectively oxidizes cellulose and other polysaccharides, converting the C6 primary hydroxyl group of the polysaccharide into aldehyde and carboxyl groups (Yin *et al.* 2010; Song and Hubbe 2014). The FTIR spectra of raw pulp fibers and TEMPO-oxidized pulp fibers in the presence of 10.5 mmol NaClO/g pulp are shown in Fig. 1. The most important change was the appearance of a C=O stretching band at 1610  $\text{cm}^{-1}$  (carboxylate) due to excessive NaOH in the reaction system, which indicated that the carboxyl group was converted from a hydroxyl group. The lack of an absorption band in the range of 1740 to 1745  $\text{cm}^{-1}$  for all materials suggested the absence of carbonyl groups (C=O) (Wong *et al.* 2009). The presence of the carboxyl group was illustrated by infrared spectra.

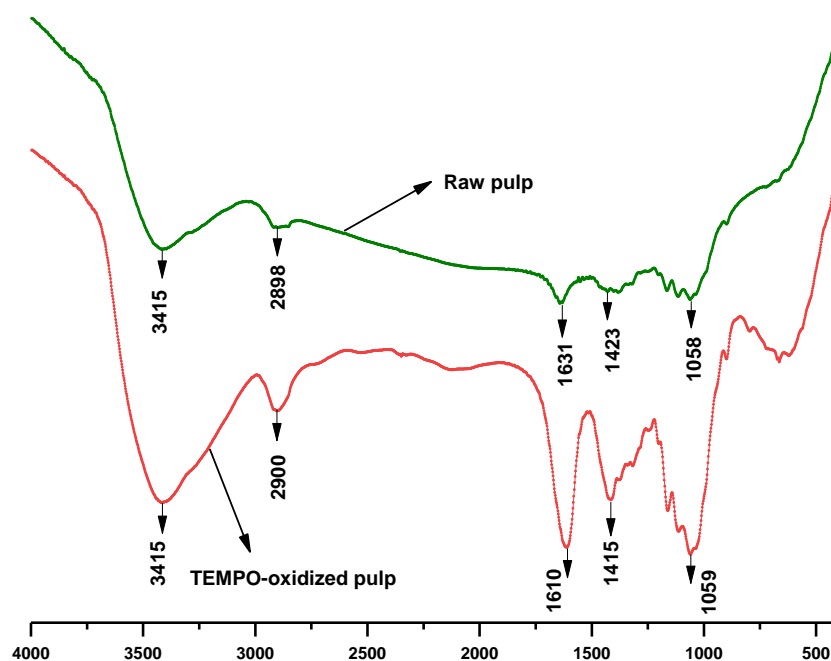


Fig. 1. FT-IR spectra of raw pulp and TEMPO-oxidized pulp with 10.5 mmol NaClO/g pulp

The carboxylate contents of oxidized pulp fibers were determined by the calcium-acetate method. The effect of NaClO addition on carboxylate contents in the water-insoluble fractions of TEMPO-oxidized bamboo pulp fibers is shown in Fig. 2. In the experimental range of the amount of added NaClO, the carboxylate contents of different oxidized pulp fibers were in the range of 0.053 to 1.30 mmol/g pulp. The carboxylate contents of raw bamboo pulp fibers were 0.053 mmol/g pulp. During the TEMPO-mediated oxidation of bamboo pulp fibers, the carboxylate contents increased with the addition of oxidation agent (NaClO). The introduction of carboxyl group led to an increase in the amount of charges, which induced swelling of fibers and hence had a significant effect on the mitigation of clogging of homogenizers (Lindström 2017).

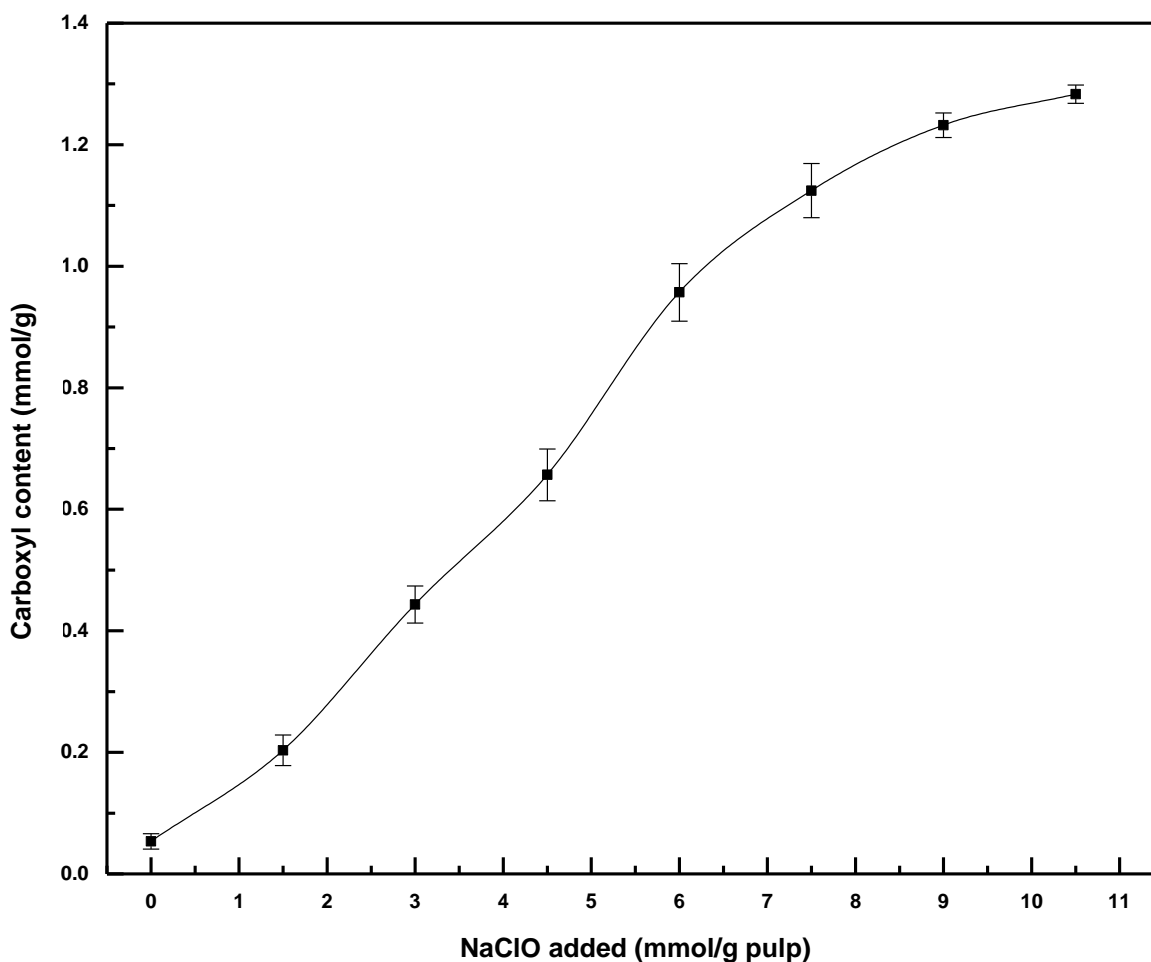
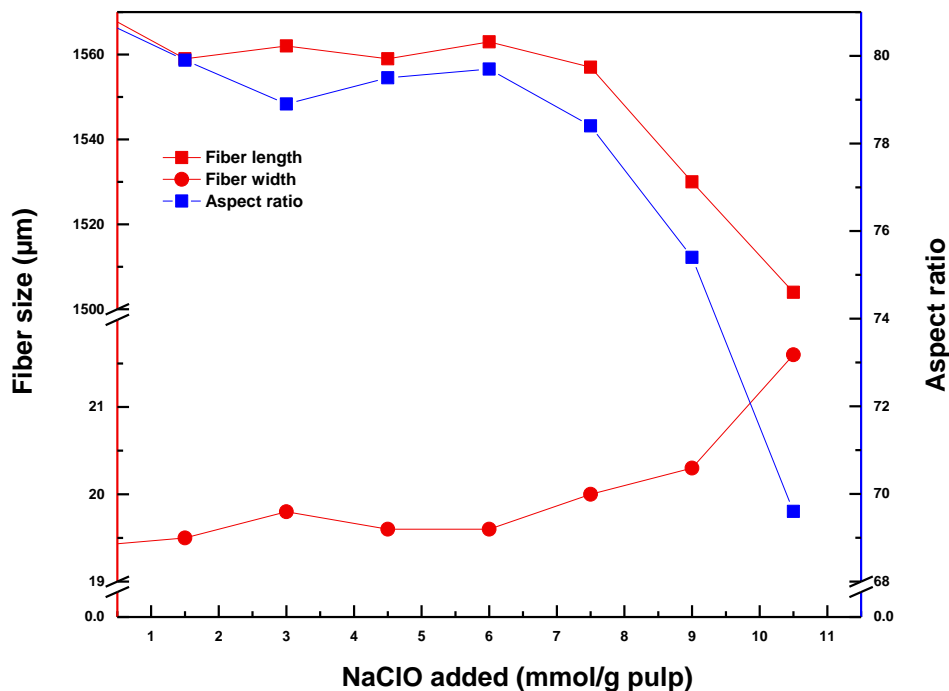


Fig. 2. Effect of NaClO addition on carboxylate contents of the oxidized pulp

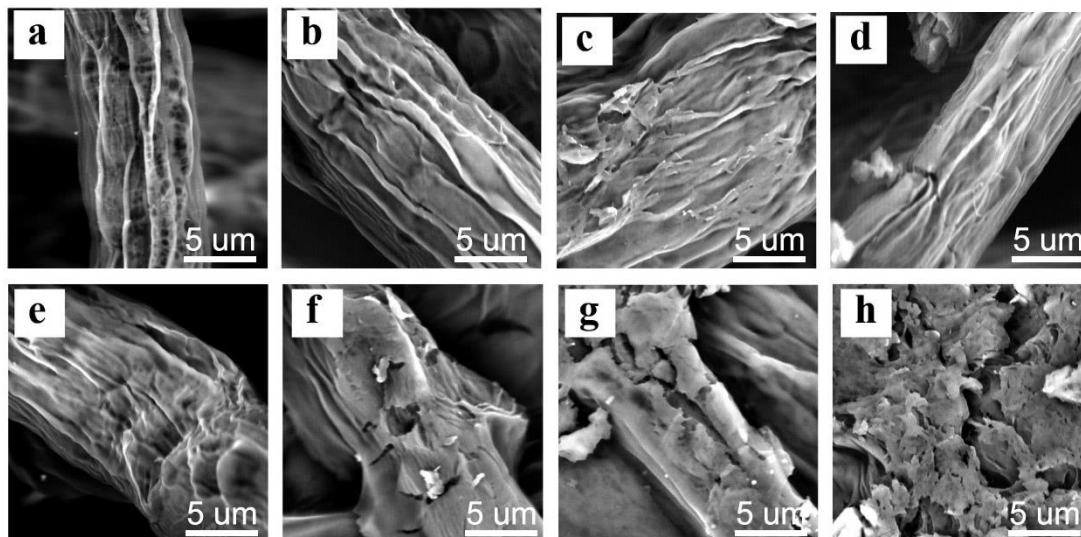
### Morphology of Oxidized Pulp

The morphology of pulp fibers had a certain impact on defibrillation in HPH. The effect of NaClO addition on morphology of pulp fibers is shown in Fig. 3.



**Fig. 3.** Effect of NaClO addition on morphology of the oxidized pulp

In differently oxidized pulp fibers, some changes in fibrous morphology were observed. The length of the oxidized fibers decreased with the addition of NaClO, while the width of the fibers increases. The length of oxidized fibers was remained 1504  $\mu\text{m}$  even at excessive dosage (10.5 mmol/g pulp), which slightly decreased by 4.3% compared with pulp fibers without oxidation. In contrast, the widths of oxidized fibers lightly increased by 8%, which indicated pulp fibers were swollen. The aspect ratio was changed by 14.1%. Montanari *et al.* (2008) reported an experiment for preparing nanofibers by excessive TEMPO oxidized cellulose, which caused formation of short cellulose microfibrils or cellulose micro-crystallites by cleavages of the microfibrils. It could be inferred that TEMPO-mediated oxidation contributed to splitting and size reduction of pulp fibers, which led to the softening of pulp fibers and disintegration.

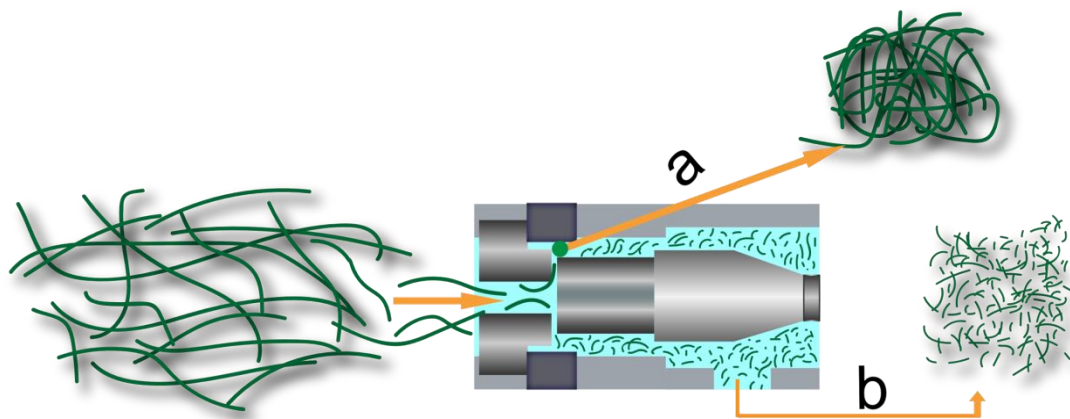


**Fig. 4.** SEM images of pulp fibers with various NaClO addition. The amounts of NaClO in the TEMPO/NaBr/NaClO oxidation of pulp fibers were (a) 0, (b) 1.5, (c) 3.0, (d) 4.5, (e) 6.0, (f) 7.5, (g) 9.0 and (h) 10.5 mmol/g of the bamboo pulp.

The surface of the fibers had significant changes after TEMPO oxidation (Fig. 4). The pulp fibers without oxidation were complete and unbroken. However, the cracks on the surface of fiber increased gradually and disintegrated with the increase of NaClO. Upon addition of 10.5 mmol NaClO/g pulp, the fibers collapsed into mud, and complete fibers could not be seen. Thus, TEMPO oxidation had a great influence on the micro-surface of the pulp fibers. The oxidized pulp fibers were washed by high-speed centrifugation before SEM to observe the microscopic surface. The high-speed centrifugal force destroyed the oxidized pulp fibers. The mechanical force of high-speed centrifugation led to the breakage of oxidized fibers. These results confirmed that TEMPO oxidation increased cracks and the accessible surface area of pulp fibers, which facilitated the homogenization process.

### Clogging Critical Concentration in Fibrillation Process

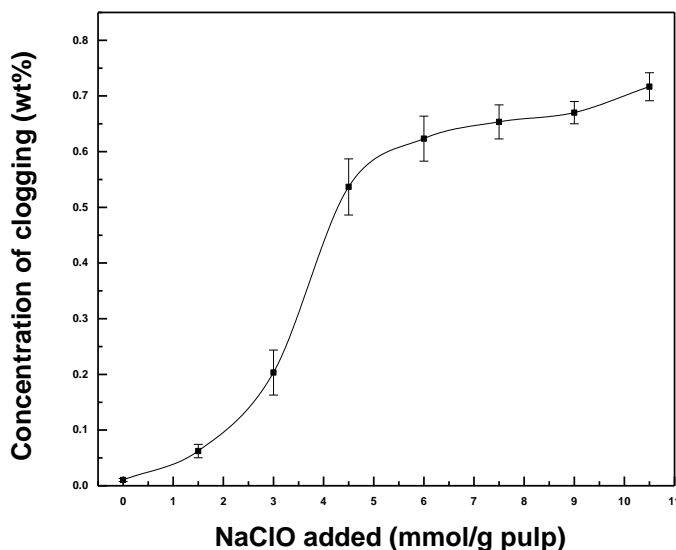
Successful operation of HPH was related to the continuous industrial production of nanocellulose. However, a higher fiber concentration increased clogging in the HPH (Seydibeyoğlu and Oksman 2008). The nozzle of HPH was blocked if the concentration of pulp fibers was too high or if there was poor pretreatment. The passing process of pulp fibers in the HPH is shown in Fig. 5. As shown in Fig. 5(a), the clogged pulp fibers agglomerate into fiber clusters, which resulted in the HPH being unable to squeeze the fibers through the nozzle during fibrillation. In Fig. 5(b), the fine fibers were transformed into cellulose microfibrils in the HPH after several homogenizations.



**Fig. 5.** The passing process of pulp fibers in HPH by (a) clogging or (b) passing

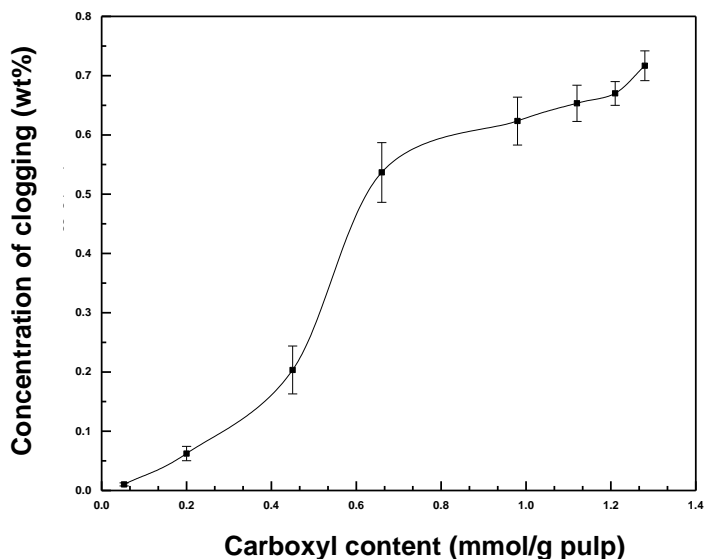
In this experiment, the bamboo pulp fiber suspensions pretreated by TEMPO-mediated oxidation were uniformly stirred and poured into feed port of HPH. If the suspensions couldn't pass through the homogenizer more than three times during the homogenization process, the suspensions were further diluted until they could be circulated in the homogenizer. The concentration at that time was called the clogging critical concentration.

TEMPO oxidization pretreatment is favorable for defibrillation of fibers in homogenization processes (Wu *et al.* 2017). The oxidized pulp fibers with different degrees of oxidation due to different dosages of NaClO were homogenized in the HPH. The greater the amount of NaClO added, the higher the clogging critical concentration of bamboo pulp fiber suspension, as shown in Fig. 6.



**Fig. 6.** The relationship between the clogging critical concentrations and NaClO addition.



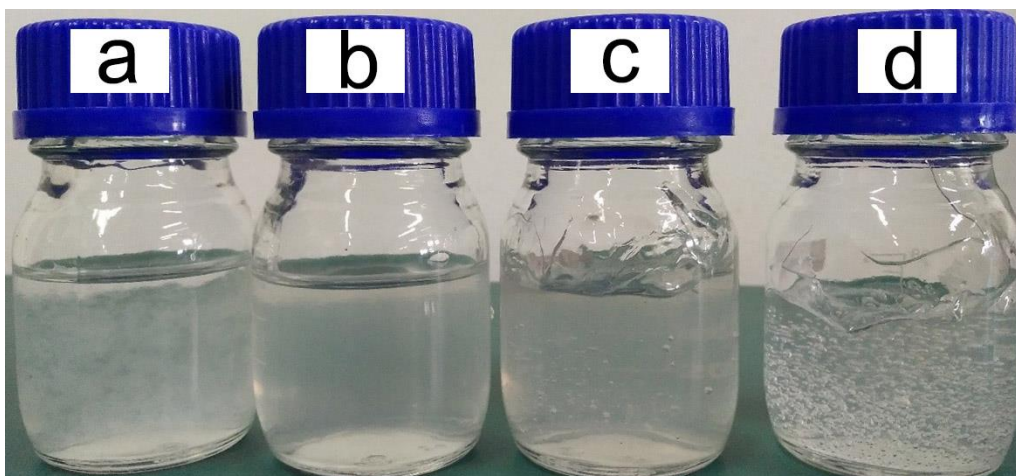


**Fig. 7.** The relationship between the clogging critical concentrations and the carboxyl content.

The clogging critical concentrations of pulp fiber suspensions remarkably increased from 0.21% to 0.54% when the amount of NaClO added was increased from 3.0 mmol/g to 4.5 mmol/g. With further addition of NaClO, the homogeneous concentration increased slowly. However, Fig. 7 showed the same trend as Fig. 6, which indicated that the intrinsic factor affecting the clogging critical concentration of bamboo pulp fiber suspensions in the homogenizer was closely related to the carboxyl contents of bamboo pulp fibers. The appropriate dosage was 4.5 mmol/g pulp, which was favorable to get as high concentration of the product as possible with as little chemicals as possible. The clogging critical concentration in the HPH would increase gently when the addition of NaClO was over 4.5 mmol/g pulp. Further increase in the concentration of the bamboo pulp microfiber suspension led to deterioration of fluidity, and it was not possible to significantly increase the homogenization concentration even when large amount of carboxyl groups were obtained due to TEMPO-mediated oxidation. Interestingly, raw bamboo pulp fibers without any treatment were homogenized successfully with a concentration of 0.01%. However, the sharp increase in energy consumption makes it expensive.

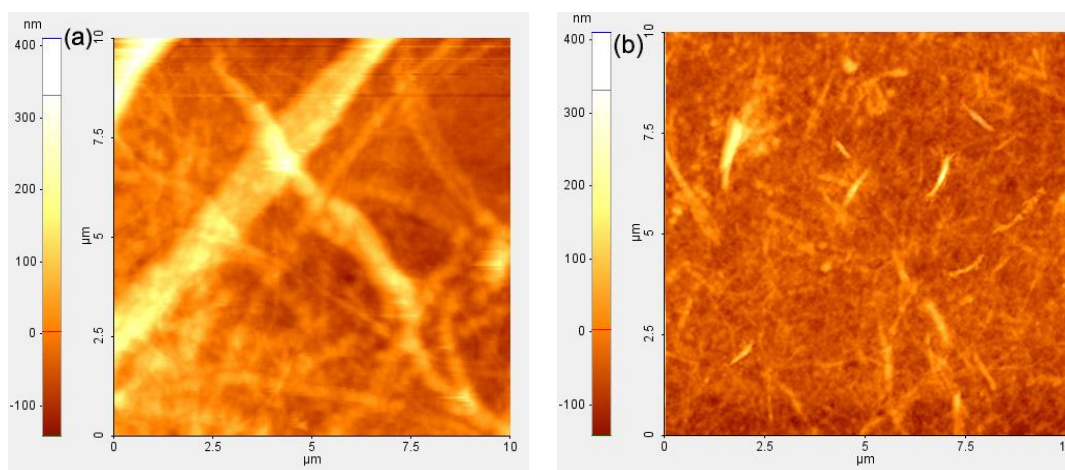
### Morphological Analysis of the Homogeneous Fibers

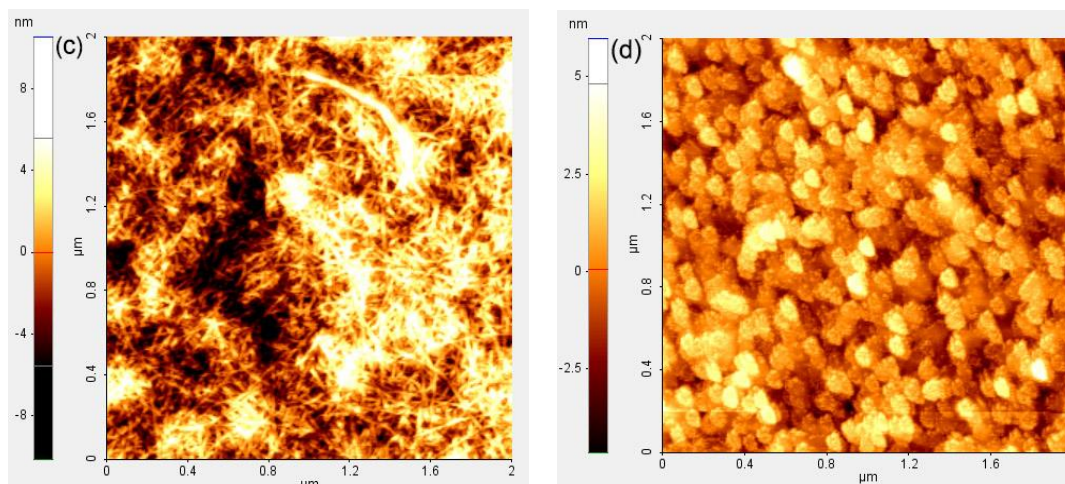
The homogenized bamboo microfilaments were characterized by selecting the minimum, maximum and two clogging critical concentrations with remarkably rise in concentration. The bamboo pulp microfiber suspensions obtained by homogenization under the conditions of four different clogging critical concentrations is shown in the Fig. 8. After bamboo pulp fiber was homogenized at the lowest clogging critical concentration, some macroscopic microfibrils in the suspension could be observed with the naked eye. The homogeneous pulp fiber suspensions became thick with increasing homogenization concentration, which hindered the homogenization process. When the clogging critical concentration was 0.54 %, the fluidity of the suspension deteriorated and the slurries had reached a gel state. The suspension prepared at the highest homogeneous concentration in this experience had the best viscosity and exhibited transparent colloidal suspension.



**Fig. 8.** Photograph of bamboo pulp microfiber suspensions prepared by homogenization of four different clogging critical concentrations: (a) 0.01 % (b) 0.21 %, (c) 0.54 %, (d) 0.72 %.

The morphology and size of the bamboo pulp microfibers homogenized in the HPH were characterized by AFM (Fig. 9.). Different clogging critical concentrations had a large impact on the morphology and size of the bamboo pulp microfibers. Bamboo pulp, without TEMPO-mediated oxidation pretreatment, retained a large size after homogenization and maintained the morphology of plant fibers (large aspect ratio). Due to the absence of TEMPO-mediated oxidation, the amorphous and crystallized regions of the bamboo pulp fibers were not chemically destroyed. Therefore, the fibers maintained a large strength and were difficult to be fibrillated. In addition, the concentration of the sample suspension during the homogenization process was very low, so the probability of the fibers contacting each other was low and the fibers suffered less mechanical damage. The bamboo pulp fibers homogenized in the concentration of 0.21% had a significantly smaller size after homogenization, and most of the bamboo pulp fiber's morphology was converted into short rods, and the width of the fiber was approximately in the range of 100 to 400 nm. Since the surface of the pulp fiber was partially oxidized, the destruction of the amorphous region resulted in a decrease in fiber strength, which caused the fiber to be continuously peeled off during the homogenization.





**Fig. 9.** AFM images of bamboo pulp microfibers prepared by homogenization of four different clogging critical concentrations: (a) 0.01 % (b) 0.21 %, (c) 0.54 %, (d) 0.72 %

With the addition amount of 4.5 mM NaClO/g pulp, further oxidation caused more damage on the fiber. The nanocellulose, with a width of 15 ~ 26 nm and a uniform size, was successfully isolated though HPH. The homogenized bamboo pulp fibers were granulated when the homogeneous concentration was 0.72 %. This may be due to the violent oxidation of the bamboo pulp fibers by the excessive NaClO, which caused the fibers to undergo unprecedented damage and become muddy, as shown in Fig. 4(h). Not only the amorphous regions were destroyed, but also the crystallized regions suffered a certain degree of damage. The excessive pretreatment could ensure that the bamboo pulp fiber didn't clog through the homogenizer at a higher concentration. However, the finally prepared nanocellulose was in the form of particles and tended to accumulate agglomerates.

## CONCLUSIONS

1. The presence of carboxyl group was revealed by infrared spectra, and carboxylate contents increased with the addition of oxidation agent. Increasing the carboxylate contents led to reduction of clogging. This could be explained that higher charges induced swelling of fibers and hence had a significant effect on the mitigation of clogging of homogenizers.
2. Micro-surface and morphology of the pulp fibers suffered from some changes after the TEMPO-mediated oxidation, which facilitated the homogenization process and increased clogging critical concentration.
3. The fiber suspensions with high concentration were more likely to cause clogging in the HPH. TEMPO-mediated oxidation pretreatment prior to homogenization process thickened the concentration of pulp fibers suspension and reduced the risk of clogging in the HPH. The clogging critical concentration of pulp fibers remarkably increased from 0.21% to 0.54% when NaClO was added from 3.0 mmol/g to 4.5 mmol/g.
4. Nanocellulose suspensions were successfully isolated from the TEMPO-oxidized bamboo pulp with different clogging critical concentration. Nanocellulose prepared by the HPH with different carboxyl content of bamboo pulp fiber under different clogging critical concentrations, the morphology and size of which were significantly different.

## ACKNOWLEDGMENTS

This work was supported by Key Project of Science and Technology Plan of Zhejiang Province (Grant No. 2017C03061 and Grant No. 2019C03136).

## REFERENCES CITED

- Abdul Khalil, H. P. S., Davoudpour, Y., Islam, M. N., Mustapha, A., Sudesh, K., Dungani, R., and Jawaid, M. (2014). "Production and modification of nanofibrillated cellulose using various mechanical processes: A review," *Carbohydrate Polymers* 99(1), 649-665. DOI: 10.1016/j.carbpol.2013.08.069
- Ang, S., Haritos, V., and Batchelor, W. (2019). "Effect of refining and homogenization on nanocellulose fiber development, sheet strength and energy consumption," *Cellulose* 26(8), 4767-4786. DOI: 10.1007/s10570-019-02400-5
- Baati, R., Magnin, A., and Boufi, S. (2017). "High solid content production of nanofibrillar cellulose via continuous extrusion," *ACS Sustainable Chemistry & Engineering* 5(3), 2350-2359. DOI: 10.1021/acssuschemeng.6b02673
- Chaker, A., and Boufi, S. (2015). "Cationic nanofibrillar cellulose with high antibacterial properties," *Carbohydrate Polymers* 131, 224-232. DOI: 10.1016/j.carbpol.2015.06.003
- Feng, Y., Li, J., Wang, B., Tian, X., Chen, K., Zeng, J., Xu, J., and Gao, W. (2018). "Novel nanofibrillated cellulose/chitin whisker hybrid nanocomposites and their use for mechanical performance enhancements," *BioResources* 13(2), 3030-3044. DOI: 10.15376/biores.13.2.3030-3044
- Gamelas, J., Pedrosa, J., Lourenço, A., Mutjé, P., González, I., Chinga Carrasco, G., Singh, G., and Ferreira, P. (2015). "On the morphology of cellulose nanofibrils obtained by TEMPO-mediated oxidation and mechanical treatment," *Micron* 72, 28-33. DOI: 10.1016/j.micron.2015.02.003
- Kalia, S., Boufi, S., Celli, A., and Kango, S. (2014). "Nanofibrillated cellulose: Surface modification and potential applications," *Colloid and Polymer Science* 292(1), 5-31. DOI: 10.1007/s00396-013-3112-9
- Kargarzadeh, H., Mariano, M., Huang, J., Lin, N., Ahmad, I., Dufresne, A., and Thomas, S. (2017). "Recent developments on nanocellulose reinforced polymer nanocomposites: A review," *Polymer* 132, 368-393. DOI: 10.1016/j.polymer.2017.09.043
- Li, J., Wei, X., Wang, Q., Chen, J., Chang, G., Kong, L., Su, J., and Liu, Y. (2012). "Homogeneous isolation of nanocellulose from sugarcane bagasse by high pressure homogenization," *Carbohydrate Polymers* 90(4), 1609-1613. DOI: 10.1016/j.carbpol.2012.07.038
- Lindström, T. (2017). "Aspects on nanofibrillated cellulose (NFC) processing, rheology and NFC-film properties," *Current Opinion in Colloid & Interface Science* 29, 68-75. DOI: 10.1016/j.cocis.2017.02.005
- Lu, H., Guccini, V., Kim, H., Salarzar Alvarez, G., Lindbergh, G., and Cornell, A. (2017). "Effects of different manufacturing processes on TEMPO-oxidized CNF performance as binder for flexible lithium-ion batteries," *ACS Applied Materials & Interfaces* 9(43), 37712-37720. DOI: 10.1021/acsmi.7b10307
- Montanari, S., Roumani, M., Heux, L., and Vignon, M. R. (2008). "Topochemistry of

- carboxylated cellulose nanocrystals resulting from TEMPO-mediated oxidation," *Macromolecules* 38(5), 1665-1671. DOI: 10.1021/ma048396c
- Nechyporchuk, O., Belgacem, M. N., and Bras, J. (2016). "Production of cellulose nanofibrils: A review of recent advances," *Industrial Crops and Products* 93, 2-25. DOI: 10.1016/j.indcrop.2016.02.016
- Praskalo, J., Kostic, M., Potthast, A., Popov, G., Pejic, B., and Skundric, P. (2009). "Sorption properties of TEMPO-oxidized natural and man-made cellulose fibers," *Carbohydrate Polymers* 77(4), 791-798. DOI: 10.1016/j.carbpol.2009.02.028
- Rol, F., Karakashov, B., Nechyporchuk, O., Terrien, M., Meyer, V., Dufresne, A., Belgacem, N., and Bras, J. (2017). "Pilot-scale twin screw extrusion and chemical pretreatment as an energy-efficient method for the production of nanofibrillated cellulose at high solid content," *ACS Sustainable Chemistry & Engineering* 5(8), 6524-6531. DOI: 10.1021/acssuschemeng.7b00630
- Saito, T., Nishiyama, Y., Putaux, J. L., Vignon, M., and Akira, I. (2006). "Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose," *Biomacromolecules* 7(6), 1687-1691. DOI: 10.1021/bm060154s
- Seydibeyoğlu, M. Ö., and Oksman, K. (2008). "Novel nanocomposites based on polyurethane and micro fibrillated cellulose," *Composites Science & Technology* 68(3), 908-914. DOI: 10.1016/j.compscitech.2007.08.008
- Song, X., and Hubbe, M. A. (2014). "TEMPO-mediated oxidation of oat  $\beta$ -d-glucan and its influences on paper properties," *Carbohydrate Polymers* 99, 617-623. DOI: 10.1016/j.carbpol.2013.08.070
- Spence, K., Venditti, R., Rojas, O., Habibi, Y., and Pawlak, J. (2011). "A comparative study of energy consumption and physical properties of microfibrillated cellulose produced by different processing methods," *Cellulose* 18(4), 1097-1111. DOI: 10.1007/s10570-011-9533-z
- Spence, K. L., Venditti, R. A., Habibi, Y., Rojas, O. J., and Pawlak, J. J. (2010). "The effect of chemical composition on microfibrillar cellulose films from wood pulps: Mechanical processing and physical properties," *Bioresource Technology* 101(15), 5961-5968. DOI: 10.1016/j.biortech.2010.02.104
- Wang, Y., Wei, X., Li, J., Wang, F., Wang, Q., Chen, J., and Kong, L. (2015). "Study on nanocellulose by high pressure homogenization in homogeneous isolation," *Fibers and Polymers* 16(3), 572-578. DOI: 10.1007/s12221-015-0572-1
- Wu, B., Geng, B., Chen, Y., Liu, H., Li, G., and Wu, Q. (2017). "Preparation and characteristics of TEMPO-oxidized cellulose nanofibrils from bamboo pulp and their oxygen-barrier application in PLA films," *Frontiers of Chemical Science and Engineering* 11(4), 554-563. DOI: 10.1007/s11705-017-1673-8
- Yin, W., Chu, C., Lu, Q., Tao, J., and Liu, R. (2010). "Iron chloride/4-acetamido-TEMPO/sodium nitrite-catalyzed aerobic oxidation of primary alcohols to the aldehydes," *Advanced Synthesis & Catalysis* 352(1), 113-118. DOI: 10.1002/adsc.200900662
- Zhuo, X., Liu, C., Pan, R., Dong, X., and Li, Y. (2017). "Nanocellulose mechanically isolated from *Amorpha fruticosa* Linn," *ACS Sustainable Chemistry & Engineering* 5(5), 4414-4420. DOI: 10.1021/acssuschemeng.7b00478

Article submitted: June 19, 2019; Peer review completed: November 1, 2019; Revised version received and accepted: November 23, 2019; Published: November 26, 2019.  
DOI: 10.15376/biores.15.1.444-456