



# Influence of sonication treatment on supramolecular cellulose microfibril-based hydrogels induced by ionic interaction



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## ABSTRACT

This study investigated effects of sonication treatment on characteristics and drug release behavior of hydrogels prepared by supramolecular cellulose microfibrils (CMFs) isolated by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation which made carboxylate negative charge available on the CMFs' surface. The hydrogels were fabricated by inducing ionic interactions between negatively charged CMFs and a positive metal ion ( $Al^{3+}$ ). The sonication time showed no influence on the carboxylate content of CMFs, but it greatly influenced characteristics and drug release behavior of the hydrogels. These results indicate that the sonication time has an impact on hydrogels' characteristics and drug release behavior.

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## Introduction

Hydrogels are three dimensional network structure materials that are highly hydrophilic and are able to absorb a large amount of water. Hydrogels are widely used as absorbents, in water purification, in sensors, contact lenses, tissue engineering, and drug delivery systems [1]. Hydrogels can be fabricated from synthetic polymers or natural polymers, where a micro-porous structure is formed by either physical or chemical cross-linking interactions. Cellulose-based hydrogels, generated using a natural polymer, are particularly attractive due to the abundance, renewability, biodegradability, and non-toxicity of cellulose [2]. Although bacterial cellulose (BC)-based hydrogels are commonly utilized in numerous biomedical applications and has been well reviewed for drug delivery systems application [3], such BC-hydrogels are produced by an expensive and inefficient process [4]. On the other hand, nanocellulose material could be isolated effectively from wood and other lignocellulosic materials on mass production [5–8]. The utilization of nanocellulose material is a burgeoning field in which systems such as cellulose nanofibrils (CNFs) and cellulose nanowhiskers (CNWs) have been used for

hydrogels. These nanocelluloses are one of the most promising materials for advanced futuristic applications [9–11].

The rationale reason for introducing nanocellulose as drug carrier are the high surface area-to-volume [8] and negative charge of nanocellulose which suggest large amounts of drugs might be bound to the surface of this material with the potential for high payloads and optimal control of dosing [12]. The release of the drug from the hydrogel is linearly correlated to the internal structure of hydrogel and degree of crosslinking [13]. However, studies on pure cellulose hydrogel with regard to drug release are rarely being reported [14].

Recently, cellulose hydrogels have been made by cross-linking cellulose molecules dissolved in various organic solvents. However, the use of these organic solvents limits the applications of cellulose hydrogels because of the undesirable effects of the toxic solvents. Abe and Yano [15] reported the formation of a hydrogel from highly crystalline CNFs by alkaline treatment (9–15 wt% NaOH). The gelation network was formed by entanglement and coalescence of the CNFs; these effects possibly originate from the effect of mercerization on longitudinal shrinkage of the cellulose nanofibers in aqueous alkaline solutions [16]. Syverud et al. [17] evaluated the formation of hydrogels from CNFs isolated by TEMPO-mediated oxidation of cellulose combined with poly-ethyleneimine and poly-N-isopropylacrylamide-co-allylamine-co-methylenebisacrylamide. The aldehyde groups were recognized as suitable reaction sites for cross-linking. Dong et al. [18]

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successfully synthesized CNFs by TEMPO-oxidation and applied them to the fabrication of a tunable hydrogel with the addition of various cations (mono-, di-, and tri-valent). The anionic carboxylate groups (from oxidation process) and cationic metal salts formed ionic cross-links, resulting in firm hydrogels. Saito et al. [14] investigated the surface carboxylate groups of CNFs that self-aligned into a stiff hydrogel in water by adjusting the pH below the pKa. This hydrogel was reported as having outstanding properties, and aerogels generated from the hydrogel had a large surface area and ultralow density.

Compared to CNF-based hydrogels, herein, we propose a quite simple and effective method for producing hydrogels by introducing surface charge on hardwood bleached kraft pulp (HW-BKP) using TEMPO-oxidation followed by different levels of sonication treatment. The suspension was termed cellulose microfibrils (CMFs). The diameters of the CMFs are estimated to be in the range of nano to micron size ( $7.07 \pm 0.99$  nm to  $10 \mu\text{m}$ ) [19]. The sonication technique is an emerging method for preparing cellulose fibrils with nano size [20]. However, because of the complicated hierarchical structure of the plant cell wall and the interfibrillar hydrogen bonds, the fibers obtained by TEMPO-oxidation are aggregated nanofibers with a wide distribution in width. Therefore, by applying sonication treatments subsequent to TEMPO-oxidation, aggregation of the nanofibrils could be prevented owing to the effect of electrostatic repulsion of the negatively charged cellulose surface [21]. Herein, effect of sonication time on the properties of the oxidized-cellulose suspension is studied in terms of the carboxylate group content, viscosity, transparency, and morphology. Cellulose microfibrils (CMFs) hydrogels were formed by addition of trivalent cations, and the resulting assemblies were characterized in terms of their mechanical properties and chemical and internal structure. Finally, a drug was loaded into the hydrogels to study the behavior of the hydrogels in controlling release drug. The present approach is proposed as a very simple and energy-efficient means of producing cellulose fibril-based hydrogels.

## Experimental

### Materials

Dried hardwood bleached kraft pulp (HW-BKP) was obtained from Moorim Paper Co., Ltd., and stored in a constant humidity chamber at  $25^\circ\text{C}$  before use. TEMPO, sodium bromide (NaBr), and sodium hypochlorite (NaClO) solutions were purchased and used as received from Sigma-Aldrich. Aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was purchased from Duksan Pure Chemicals Co. Ltd., and was used as received as a cross-linker for surface-charged cellulose. Water (conductivity:  $6 \mu\text{S}/\text{cm}$ ) from a reverse osmosis system was obtained by purification using a Upure system (ROtech, Daegu, Korea). As a model for drug release evaluation, anhydrous theophylline (MW = 180.16; purity  $\geq 99\%$ ) was purchased from Sigma-Aldrich and used as received.

### Methods

#### TEMPO-mediated oxidation and sonication

Carboxylated cellulose fibrils were obtained by TEMPO/NaBr/NaClO oxidation in water at pH 10.5 [22]. Cellulose pulps (2 g) were dispersed in 150 mL of water containing diluted TEMPO (0.025 g) and NaBr (0.25 g). NaClO solution (12.5%, 8 mL, 7.85 mmol/g) was added dropwise to the solution to initiate the oxidation. The pH of the mixture was controlled at 10.5 by dropwise addition of 0.5 M NaOH. The reaction was conducted at room temperature ( $23^\circ\text{C}$ ) for a course of about 75 min until no further change in pH was observed, indicating the end of the reaction. The mixture was neutralized by adding HCl (0.5 M). In

order to obtain a dilute soluble fraction, the oxidized pulps were filtered and washed with reverse osmosis water several times. Water (200 mL) was added to obtain a 2% (w/w) suspension of the water-insoluble TEMPO-oxidized cellulose fibril suspension. The suspension was subjected to ultrasonic treatment for different times (i.e., 20, 40, and 60 min) using a Sonomasher (power 30%, frequency 20,320 Hz) with a probe diameter of 1 cm. In order to prevent overheating, the sonication process was performed in intervals of 10 min.

#### Carboxyl content measurement

The carboxylate group content of the CMFs was measured via conductometric titration according to procedures reported by Saito et al. [22]. In brief, the cellulose suspension with 0.05% solid content was agitated with addition of 80 mL deionized water and 5 mL 0.01 M NaCl to the CMF suspension. The pH of the suspension was adjusted to 2.5–3 by addition of 0.1 M HCl, after which 0.01 M NaOH was added at a rate of 0.1 mL/min up to pH 11. A typical graph for the conductometric titration is shown in Fig. 1. The conductivity decreased until the acid was neutralized by the addition of NaOH. At the end of neutralization ( $V_1$ ), the conductivity remained unchanged to the end of step ( $V_2$ ). Further addition of NaOH increased the conductivity. Conductivity changes were recorded using a conductometer (SevenGo, METTLER TOLEDO, China). As a comparison, CNFs were also isolated from the CMF suspension by centrifugation at 12,300g for 40 min (Labogene 1580 centrifuge, Gyrozen Co., Ltd., Daejeon, Korea) and the carboxylate group content was also measured. The carboxylate group content was determined by means of Eq. (1), presented below:

$$\text{Carboxyl content} \left( \frac{\text{mmol}}{\text{g}} \right) = \frac{(V_2 - V_1) \times M \text{ NaOH}}{\text{weight of cellulose}} \quad (1)$$

#### Viscosity and transparency

The viscosity of the sonicated suspensions was measured with a Brookfield Viscometer (model DV-II + Pro). Spindle number 2 with 5 cm diameter was used to achieve accurate viscosity measurements. The measurements were conducted with 250 mL of sample at a temperature  $22^\circ\text{C}$ , using a speed of 60 RPM and torque of 1–15%. Three replicate measurements were performed for each parameter.

The light transmittance of the sonicated suspensions was measured using a UV-VIS spectrophotometer (Optizen 3220UV, Mecasys Co., Ltd., Daejeon, Korea). The concentration of the cellulose suspension was controlled at 0.3% (w/v). Data were collected in the wavelength range of 200 to 1000 nm.

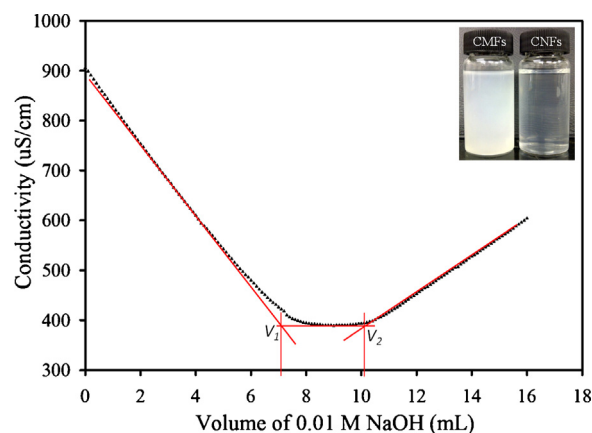


Fig. 1. Typical conductometric titration curve and equation for calculating carboxyl content. Inset shows images of the CMF and CNF suspensions.

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