TEMPO-mediated oxidation cellulose pulp modified with Monosodium Glutamate (MSG)

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Abstract. Monosodium glutamate (MSG) was conjugated onto cellulose microfibrils (CMF) by the reaction in acetone solvent at the presence of triethylamine and paratoluene sulfonyl chloride. Results showed that the thermal decomposition of CMF-MSG slightly decreased to lower temperature decomposition confirmed by thermogravimetry analysis (TGA) after MSG was present on CMF surfaces which was confirmed by the reduction of intensity in carboxyl groups bands under infra-red spectroscopy (FTIR) observation. After drying, CMF-MSG was agglomerated, and the color of CMF after modification turned from white into light-brown. This study provides another way to modify nanocellulose with cheap and edible chemical reagent using monosodium glutamate. The modified cellulose probably could be applied in copper (Cu) detection paper kit at mining extraction.

1. Introduction
Cellulose is the most abundant polymer on earth [1, 2]. It is renewable, low cost, good carbon storage and biodegradable. Therefore, many attempts have been done to utilize those green polymer into myriad applications from food, medicine to smart and advanced materials [3–6]. The drawbacks of using cellulose come from its difficulties of obtained pure cellulose structure because in nature, cellulose is composed of lignocelluloses structure. In addition to that, cellulose is low thermal stability, hydrophilic, nonresistant to weather, fungi, and termite attack [7]. Further, in order to expand the application of cellulose, some surface modification is applied, for example, to improve the hydrophobicity of cellulose. Our previous study [8, 9] converted the hydroxyl groups of cellulose, especially at C6 (the primary alcohol) into carboxyl groups by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) oxidation. Owing to negative surface charge from carboxylate groups, by small force, could mechanically disintegrate the cellulose pulp, resulted in small fibrils and more hydrophilic characteristics [10, 11]. Therefore, further modification is necessary to improve the hydrophobicity of oxidated cellulose.

Monosodium glutamate (MSG), a sodium salt of glutamic acid, is readily available as a flavor enhancer with a relatively high (> 99%) purity. To the best of author knowledge, MSG so far is only used for food application. Here is the other example of the application of MSG: Glutamate is a naturally occurring non-essential amino acid which reacts with copper (II) in aqueous solution to form a blue complex. This reaction could potentially be exploited in determining the copper content of an ore sample.
[12]. MSG also had been used to modify the cellulose acetate membrane [13]. Idris et al. [14] showed that MSG based membrane with the 6 wt% of MSG achieved the best urea clearance at 53.2%. MSG promoted macro voids formation and finally transits to the finger-like structure. Further, MSG can be used as nitrogen sources in the production of bacterial cellulose (nata-de-coco) [15], indicating that MSG is not harmful chemical reagents.

So, this study aimed to modify cellulose surface from TEMPO-mediated oxidation cellulose pulp with cheap and edible chemical reagent using monosodium glutamate. This reaction will promote a concept of eco-friendly technology since MSG is not corrosive to equipment, edible, soluble in water and environmentally friendly. The conjugation of MSG onto cellulose was conducted in the presence of para-toluene sulfonyl chloride, which is sensitive to water and triethyleneamine. The surface modification of cellulose was analyzed using infrared spectroscopy and thermogravimetry analysis. This result will promote the new application of MSG and cellulose as new green based materials.

2. Materials and methods

2.1. Materials

Cellulose microfibril (CMF) from dried hardwood bleached kraft pulp (HW-BKP) was obtained from Moorm Paper Co. Ltd., Korea in the form of a paper sheet. It was stored in a humidity chamber (JSR, LowTempIncubator, JSBL-250C, Korea) at 25 °C before being used. The materials used in this study were as follows: TEMPO (C₅H₆NO, 99%, Sigma-Aldrich), sodium bromide (NaBr, Sigma-Aldrich), sodium hypochlorite solution with chlorine content 12% (NaClO, Sigma-Aldrich), dimethylformamide (DMF, ACS reagent grade 99.8%, Sigma-Aldrich), MSG (monosodium glutamate) from local brand “Sasa” PT. Sasa Inti Indonesia, para-toluene sulfonyl chloride (p-TsCl), Sigma-Aldrich, triethyleneamine (ET₃N, Sigma-Aldrich). Purified water with conductivity around 6 μS/cm was obtained using Ultras-pure (ROtech, Korea).

2.2. TEMPO-oxidation of cellulose

Isolation of CMF was conducted following a previously published procedure [8]. In brief, 2 g of HWBKP was diluted in a water suspension containing 0.025 g TEMPO and 0.25 g NaBr. The mixture temperature was kept constantly at 23 °C using thermostat. The CMF oxidation reaction was started by adding NaClO as the oxidant reagent, 7.85 mmol/g. The pH rapidly increased as the NaClO was added, therefore in order to keep the pH below 10 during the addition, NaClO solution was added dropwise. The pH was adjusted by adding 0.5 N NaOH at 10.5, throughout the oxidation process. When the pH reached constantly at 10.5, it indicated that the reaction finished. The excess NaClO was quenched by adding ethanol (ca. 5 mL). Afterwards, the pH of the solution was neutralized by 0.5 N HCl. The TEMPO-oxidized pulp slurry was filtered and washed three times.

2.3. Modification with Monosodium Glutamate

Before modification, never dried CMF was solvent exchanged from water solvent into acetone solvent using multiple washing with ethanol and acetone. The methods were as follow: 1 gr dry weight basis CNF was diluted into Ethanol 92% (1:200 mL), stirred for 15 min and centrifuged (Labogene 1580, Centrifuge, Gyrozen Co., Ltd., Daejeon, Korea) for 10 min at 8,000 rpm, then decanted and replaced. These steps were repeated five times. The slurry was diluted into Acetone (1:200 mL), stirred for 15 min, centrifuged for 10 min at 8,000 rpm, and decanted. These steps were repeated five times. After the solvent was completely exchanged, the slurry directly was poured into round-bottomed flask and covered with a rubber stopper. Nitrogen gas was added simultaneously before the addition of ET₃N (1 g:150 mL Acetone) and p-TsCl. The mixture was continuously stirred for five h at 50 °C. Then, MSG was added and stirred for another five h in the same reaction condition. The sediment from the reaction was filtered and washed with distilled water to leach out the unreacted MSG.

2.4. Thermogravimetric analysis (TGA)

About 10 mg of dried powder samples were heated up at a heating rate of 10 °C/min. from 25 to 600 °C under nitrogen atmosphere. Weight loss changing due to the increasing temperature was measured using
thermogravimetry instrument (TGA Q500 V20.13, Korea). While the derivative weight loss to temperature (DTG) was calculated using OriginLab Pro 32bit software.

2.5. Attenuated infra red spectroscopy (ATR-FTIR)
Modified CMF were freeze-dried (Ilshin BioBase Co. Ltd, FDA8508, Korea). Then, it was ground and analyzed using ALPHA-P model attenuated total reflectance infrared (ATR-IR) equipment (Bruker Optics, Germany). Absorption in the range of 4000–400 cm\(^{-1}\) was measured as the average value of 25 scans at 4 cm\(^{-1}\) resolution. The measurement was conducted in two replications.

3. Results and discussions

3.1. ATR-FTIR spectroscopy
Figure 1 compares the spectra of oxidized cellulose and MSG modified cellulose. For the oxidized cellulose, the broad and sharp peaked at 3341 cm\(^{-1}\) and those at 1160 cm\(^{-1}\) were assigned to OH stretching and bending, respectively. CH\(_2\) stretching frequency appeared as a small band at 2891 cm\(^{-1}\). The band at 1038 cm\(^{-1}\) was resulted from CO stretching, while the peak of 902 cm\(^{-1}\) was attributed to the chemical bond of \(\beta\)-glycosidic linkage (–C–O–C). The intensity of the –COO– bands was located at 1608 and 1400 cm\(^{-1}\) (asymmetrical and symmetrical stretching vibrations, respectively). On the other hand, the MSG modified CMF showed some new peaks such as at 1347 cm\(^{-1}\) and the shift of COO- band at 1596 cm\(^{-1}\) indicated that the presence of MSG disrupted the carboxyl groups function. The very sharp peaks at 1347 cm\(^{-1}\) showed the strong symmetrical stretching of COO- which represents the conjugation of MSG onto cellulose surface. The strong peak at 812 cm\(^{-1}\) belonged to unreacted sulfonyl function groups from p-TsCl.

![Figure 1](image.png)

**Figure 1.** The ATR-FTIR spectra of TEMPO-oxidized and modified CMF with MSG.

The main drawback of surface modification of cellulose using negatively surface charge such as carboxyl groups (COO-) or sulfonate (-SO\(_3\)H) groups is the decreasing of thermal stability of cellulose. It will limit the application of cellulose when it requires higher thermal stability at accelerated temperature application.

3.2. Thermogravimetry analysis (TGA)
During this study, the authors used microfibril cellulose instead of cellulose nanofibrils due to the difficulties of handling nanocellulose during the filtration at the solvent exchange. However, we reported the different thermal stability of cellulose and oxidized cellulose pulp in the form of microsize and nanosized. The nanosized of cellulose was obtained by ultrasonication of the oxidated cellulose using Sonomasher, power 30%, frequency 20,320 Hz. The formation of micro-bubble and its cavitations caused mechanically disintegration of negatively surface charge TEMPO-oxidized cellulose. The
treatment was conducted for 40 min sonication. The nanosized was separated from its aggregated cellulose using centrifugation (12,000 g) (Labogene 1580, Centrifuge, Gyrozen Co., Ltd., Daejeon, Korea). The nanosized was obtained from the supernatant part. The thermogravimetry analysis of micro and nanosized oxidized cellulose is presented in figure 2.

![Figure 2](image1)

**Figure 2.** TGA and DTG diagram of raw material and nanocellulose.

As expected, the degradation peak of oxidized cellulose abruptly decreased from 360 °C to around 230 °C due to the presence of sodium carboxylate groups (-COO-Na+) [16] although the crystallinity of cellulose and oxidized cellulose was reportedly unchanged during the oxidation reaction [17, 18]. However, from figure 2, it shows that microfibril has slightly higher peak temperature degradation around 295 °C than that of the nanosized. It might be caused by the fact that the surface modification of oxidation only occurs at the C6-OH on the surface of the cellulose fibril aggregate [19]. In other words, the inside of cellulose aggregate is higher hydroxyl groups packing density which remain resistant to the accelerating temperature changes [20]. Interestingly, the char formation after the temperature reached 600 °C was quite high, around 29% compared to that of HWBKP. It indicated that during oxidation and filtration, the noncellulosic components of HWBKP were dissolved in water and leached out during washing and filtration. The thermogravimetry of microfibril modified MSG is reported in figure 3.

![Figure 3](image2)

**Figure 3.** TGA and DTG diagram of TEMPO-oxidized cellulose and CMF-MSG.

From figure 3, the onset degradation of MSG-modified CMF slightly decreased from 230 °C to 211.7 °C. However, the maximum temperature degradation increased from 288.9 °C to 317 °C. Both modified cellulose had water content evaporation peak around 48 °C. Further, the effect of the attached MSG on the cellulose surface decreased the char formation after the temperature reached 600 °C. Those results indicated that the presence of MSG initiated more complex pyrolysis of cellulose during accelerating temperature. It might be caused by the chemical structure of MSG which contains sodium carboxylate group and a carboxyl group.
The successfully modified oxidized cellulose with MSG was proven by ATR-FTIR and TGA. From figure 4, the color of MSG-modified cellulose turned from white to light-brown color. The morphology of cellulose changed from fluffy into powdered aggregated cellulose. It might be caused by the agglomeration of some nanosized cellulose during freeze-drying [21]. We tried to dissolve the MSG-modified cellulose into water solvent. It showed that they could disperse well in water, but when they immersed into the water due to the higher density of cellulose, 1.58 g/cm³ [22], they tended to sediment on the bottom of the flask. From this behavior, we think that the MSG-modified cellulose can be added as filler during the paper formation. Therefore, we can make a paper-based kit for sensing Cu (copper) in mining extraction site [12]. It will be our next research goals.

![Figure 4. Photo appearance of (1) CMF-TEMPO and (2) CMF-TEMPO after modification with MSG.](image)

4. Conclusions
To sum up, a simple modification of oxidized microcellulose with monosodium glutamate (MSG) was successfully conducted, although the conjugation of MSG did not hinder the decarboxylation of CMF at elevated temperature. This study provides another way to modify nanocellulose with cheap and edible chemical reagent using monosodium glutamate. The modified cellulose in the near future can be applied in copper (Cu) detection as a paper-based kit detector.

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