Characteristics of TEMPO-Oxidized Cellulose Nanofibers from Oil Palm Empty Fruit Bunches Produced by Different Amounts of Oxidant

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Abstract. The use of oil palm waste as a source of raw materials for nanocellulose production is a promising approach for turning agricultural waste into valuable products. This study aimed to characterize cellulose nanofibers (CNFs) derived from oil palm empty fruit bunches (OPEFB) produced by 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)/NaBr/NaClO. TEMPO-mediated oxidation was carried out at pH 10 by applying different amounts of oxidant: 10, 15 and 20 mmol/g-cellulose at room temperature for 2 h, where the resultant CNFs were denoted as T-10, T-15 and T-20, respectively. Characterization results revealed that the carbon content of each CNF decreased as compared to the starting pulp, from 40% to ca. 37%. Microscopic analysis showed that the aspect ratios of obtained CNFs remained almost unchanged by increasing the amounts of oxidant, which were ca. 40. The crystallinity indices (CrIs) ranged from 34 to 55%. The carboxy contents of CNFs increased by adding higher amounts of oxidant, but the thermal resistance properties were slightly decreased. High-performance nanomaterials such as TEMPO-oxidized CNFs were successfully prepared to show good characteristics, from low-quality biomass waste such as OPEFB.

1. Introduction
Indonesia is acknowledged as the largest producer of palm oil in the world. Oil palm plantation expanded 100-fold in the last half-century, most of them locating on Sumatra, Kalimantan and Sulawesi island [1,2]. After isolation of crude palm oil and palm kernel oil, a large amount of residual oil palm empty fruit bunches (OPEFB) are left as the main waste in the plantation site without further processing [3]. Recently, OPEFBs have attracted much attention as cellulose resource because they contain about 50-60% of cellulose by weight [4,5]. Utilization of OPEFB, hugely abundant agricultural waste in Indonesia, as cellulose source hopefully addresses the environmental issue by turning it into valuable products.

Among cellulose-derived materials, nanocellulose has attracted great interest in recent years because of its promising properties such as mechanical strength and thermal stability. Applications of nanocellulose are now in intensive study in academia and industry, including...
nanocomposites, gas-barrier films, and electronic devices [6]. Nanocellulose has been determined as cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) based on their morphological characteristics. Furthermore, CNCs are produced by chemical treatments, followed by mechanical disintegration, and CNFs are obtained by either mechanical or chemical treatments. CNCs are highly crystalline with a length less than 500 nm and CNFs are consist of mixture amorphous and crystalline with length of up to several micrometers [7]. One of the obvious methods to produce CNFs is done by 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-mediated oxidation. TEMPO has been widely studied for catalytic and selective oxidation of primary hydroxy groups under aqueous condition. In case of CNFs production by applying TEMPO/NaBr/NaClO system at pH 10, C6 primary hydroxy groups of cellulose effectively converted to sodium carboxylate groups, while maintaining fibrous morphologies such as their crystallinity [8].

In this study, we produce cellulose nanofibers from oil palm empty fruit bunches (OPEFB) by 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO)-mediated oxidation. This process was effective to produce cellulose nanofibers with the surface-modified nanocellulose with various functional groups, long and individualized cellulose fibrils dispersed in water [8,9]. This method also effectively catalyzed the regioselective conversion on primary hydroxy groups of C6 of pulp fibers [10]. Different amounts of oxidant, sodium hypochlorite (NaClO), were applied in the oxidation process. The obtained characteristics of TOCNs from OPEFB are potential to be applied in producing nanocellulose-based biomaterials.

2. Materials and method

2.1. Materials
Bleached kraft pulp of oil palm empty fruit bunches (OPEFB) was kindly supplied from Biomaterial Research Institute, Indonesian Institute of Sciences (Bogor, Indonesia). 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO), sodium bromide, sodium hypochlorite, and sodium borohydride were purchased from Sigma-Aldrich (Tokyo, Japan) and used without further purification. The water used in this study was purified with an Arium Ultrapure Water System (Sartorius Co., Ltd., Tokyo, Japan).

2.2. Preparation of TOCNs
The bleached kraft pulp of OPEFB was soaked in a 0.01 M HCl solution for 30 min for demineralization. TOCN was prepared by TEMPO/NaBr/NaClO system at pH 10 according to the literature [8,9]. In brief, a 2.5-g of dry weight of demineralized OPEFB pulp (about 85% of cellulose content) was suspended in water (250 mL) containing TEMPO (16 mg/g-cellulose) and NaBr (100 mg/g-cellulose). The oxidation reaction was initiated by adding 2 M NaClO aq as oxidant (10, 15, 20 mmol/g-cellulose). The pH of suspension was maintained at 10 by adding 0.5 M aqueous NaOH with a pH titrator (Mitsubishi Chemical Analytech, Yamato, Japan) during the reaction. After 2 h, the reaction was quenched by adding ethanol (2 mL), followed by addition of NaBH₄ (100 mg/g-cellulose), and the resultant mixture was further stirred for 1 h. The obtained suspension was thoroughly washed using deionized water by centrifugation and then sonicated by an ultrasonic homogenizer for 5 min (US-300E, Nihonseiki Ltd., Tokyo, Japan). Residual unfibrillated fibers were removed by further centrifugation at 12000 g for 10
min. Obtained TOCNs, denoted as T-10, T-15, and T-20 corresponding to the amount of NaClO used in the oxidation, were kept at 4°C until further use.

2.3. Characterization of TOCNs
Elemental analysis was performed with an Organic Micro Analyzer CHN CORDER MT-6 (Yanaco Ltd., Tokyo, Japan). The surface morphology of original OPEFB pulp was observed using a scanning electron microscope (SEM SU-3500, Hitachi Ltd., Tokyo, Japan) at the Center of Advanced Instrumental Analysis, Kyushu University. Samples were mounted on carbon tape without any coating, and the machine was operated at an acceleration voltage of 15 kV and pressure of 30 Pa. The length and width of TOCNs were measured by a transmission electron microscopy (TEM) (JEM 2100-HC, JEOL Ltd., Tokyo, Japan) operated at an acceleration voltage of 120 kV at the Ultramicroscopy Research Center, Kyushu University. The size was measured using Image-J version 1.51s. Structural analysis was observed by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) and thermogravimetric analysis (TGA) of TOCNs were conducted as described in our previous work [11]. The carboxylate contents were measured by conductometric titration [8].

3. Results and discussion
3.1. Elemental Analysis and Carboxylate Content
Elemental analysis revealed that the carbon content (C%) of obtained TOCNs decreased as compared to the starting pulp (Table 1). Higher amounts of oxidant applied in this study revealed that the C% almost unchanged by increasing the oxidant, indicating that TEMPO-mediated oxidation selectively occurred on the primary hydroxy groups of cellulose and did not affect cellulose polymorph. The increase of carboxylate content by increasing the amount of primary oxidant (NaClO) indicated that the carboxylate and aldehyde groups were formed more in the water-insoluble fractions by the oxidation. However, at certain amount of NaClO addition, the carboxylate content will not exceed a certain level even by the excess of NaClO addition [8].

| Sample | Carbon content (C%) | Carboxylate content (mmol/g) |
|--------|---------------------|-----------------------------|
| Raw pulp | 40.13 | n.d. |
| T-10 | 38.32 | 1.08 |
| T-15 | 38.67 | 1.34 |
| T-20 | 37.77 | 1.50 |

Remarks: n.d. = not determined; T-10 produced by 10 mmol/g-cellulose of NaClO; T-15 produced by 15 mmol/g-cellulose of NaClO; T-20 produced by 20 mmol/g-cellulose of NaClO

3.2. Morphology and size of TOCNs
Morphology of raw pulp and obtained TOCNs was shown in Figure 1. Microscopy analysis of original pulp showed that TEMPO-mediated oxidation, followed by ultrasonication successfully afforded nanofibrillated fibers from OPEFB pulp. The length of resultant TOCNs was 100–291 nm, and the width was 3–9 nm. The aspect ratios were 40 ± 22 for T-10, 41 ± 19 for T-15, and 41 ± 14 for T-20 (Fig. 1). Notably, the aspect ratios of resultant TOCNs were almost unchanged by increasing the amount of oxidant. These results were in good accordance that the carboxylate groups are not formed inside the cellulose crystallite during TEMPO-mediated oxidation [8]. The oxidation occurred only on C6 primary hydroxy groups on the surfaces of fibrils in cellulose fibers, therefore no significant changes in the fibrous morphology [9]. The aspect ratios of obtained TOCNs were much higher than those reported in the previous study, in which TOCNs were produced from microcrystalline cellulose (MCC) of OPEFB [12]. The results showed that TEMPO-oxidized cellulose nanofibrils (TOCNs) were successfully obtained from low quality biomass waste with a relatively high content of carboxy groups and aspect ratios.

![Figure 1. SEM image of raw OPEFB pulp (A) and TEM images of the resultant TOCN T-10 (B), T-15 (C), and T-20 (D)](image)

3.3. Structural Analysis

The FTIR and XRD analyses of the starting pulp and resultant TOCNs are shown in Figure 2. In FTIR spectra, the peaks at 1618 cm⁻¹ of resultant TOCNs are attributed to carboxylate groups, and small absorption bands at 1720 cm⁻¹ are C=O groups in the protonated carboxyl groups [13]. This absorption band was not found on the starting pulp spectra. The FTIR spectra justified that during the oxidation process, a significant amount of carboxylate groups were introduced into nanocellulose surface [9].
XRD profiles showed that crystallinity indices (Cr.I) of resultant TOCNs decreased after the oxidation process (Fig. 2). It might be caused by the regio-selective conversion of primary hydroxy groups at the C6 position of raw pulp (cellulose) to carboxylate ones by having sodium glucuronosyl units and made the structure of raw cellulose turn to disordered structure [9,14]. The 200 and 110 diffraction peak positions of TOCNs slightly changed after oxidation, it may indicate the introduction of carboxylate and aldehyde groups on the surface of cellulose I [8]. The Cr.I of raw pulp was 61% and for T-10, T-15 and T-20 were: 34%, 46%, and 55%, respectively. The higher amount of oxidant added in the oxidation slightly changed the Cr.I. It was assumed that the crystalline region slightly changed with the addition of oxidant. Presumably, the carboxylate groups were mostly present on the crystal surface and in disordered region [8,10]. The Cr.I values of resultant TOCNs were lower than the previous study conducted by Rohaizu and co-author (60.5%). This lowering is affected by the difference of starting cellulose source, whereas microcrystalline cellulose of OPEFB was used in the previous study which was relatively highly crystalline [12].

Thermal analysis was performed by thermogravimetry (TG) and differential thermogravimetry (DTG); the onset temperature ($T_{on}$) and the maximum degradation temperature ($T_{max}$) as shown in Figure 3. Thermal stability of resultant TOCNs was sharply decreased compared to the starting pulp, because carboxylate groups trigger rapid decomposition of polysaccharides at a lower temperature [16]. The amount of oxidant in the preparation of TOCN did not affect the thermal properties of resultant TOCNs. On the other hand, the char residue remaining after 500°C of resultant TOCNs was much higher compared to that with the starting pulp. It indicates that carboxylate groups on TOCNs have a flame retardant effect [12]. These thermal properties parameters were close to TOCNs made of MCC OPEFB but lower than TOCNs made from corn husk pulp [12,15].
Figure 3. TG curves (A); DTG curves (B); and thermal properties of raw pulp and resultant TOCNs (C)

4. Conclusion

TEMPO-oxidized cellulose nanofibers (TOCNs) were successfully produced from low quality of agricultural residue, oil palm empty fruit bunches (OPEFB). The differences in applying the amount of primary oxidant, NaClO, were not affected by the TOCNs morphologies which were observed by microscopy and XRD analysis. Higher amount of oxidant slightly increased the carboxylate content and induced lower thermal stability of TOCNs OPEFB than raw pulp. High aspect ratios and the presence of carboxylate groups of TOCNs are promising properties for further application such as reinforcing agents in plastics and nanoparticle anchor in catalytic reactions.

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