

論文の内容の要旨

生物材料科学専攻

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論文題目 Studies on preparation and characterization of TEMPO-oxidized cellulose nanofibrils from non-wood resources
(非木材資源からの TEMPO 酸化セルロースナノフィブリルの調製と特性解析に関する研究)

The quantitative and qualitative expansion of utilization of renewable natural resources in place of petroleum-based materials has been increasingly gaining attention in recent years for establishment of a sustainable society. Wood is still in great demand for diverse applications such as houses and buildings, furniture, pulp and paper and also raw materials for green energy generation. In addition, illegal harvesting of wood has caused worldwide depletion of forests, and also may have brought about global heating. Thus, not only wood resources but also non-wood plant resources should be used more efficiently with environmentally friendly process. Especially, in developing countries, non-wood and agricultural cellulose resources will be of significance as natural resources to revitalize regional economies.

The scientific community has paid considerable attention to renewable resources such as non-wood and annually agricultural crops, which can be used as raw materials for cellulose fibers production. Because agricultural crops are produced every year, fast growing, available in abundance, and inexpensive sources of cellulose fibers, they have been used as starting materials of many industrial products (paper, films, fibers, additives, etc.). Cellulose fibers have been isolated primarily from wood resources using pulping processes in large scale, in which wood chips are undergone with chemicals under high temperature and pressure conditions. The following bleaching process is often applied to unbleached wood pulps to increase brightness or cellulose purity, where multi-stage sequences are applied to unbleached wood pulps with bleaching chemicals under various pH and temperature conditions. Because non-wood plant resources have

generally lower lignin contents than for wood, environmental impact of pulping and bleaching processes of the former resources, due to energy consumption, usage of chemicals, and treatments of effluents, are more moderate. Utilization of agricultural crops and residues, such as flax, hemp, jute, kenaf, sisal, bamboo, oil palm, bagasse, etc., for industrial applications would be more valuable and additional sources for farmers particularly in developing countries in South East Asia. Cellulose originating from these agricultural crops and residues have been studied in the scientific and technological fields of, for instance, nanocelluloses and bionanocomposites.

Cellulose is one of the structural components of plant cell walls, and has become much more significant in bio-based nanotechnology. Cellulose is the most abundant and renewable polymer consisting of β -1,4-linked D-glucosyl units, and forms into highly crystalline cellulose microfibrils, each of which consists of 30-40 fully extended cellulose chains. Numerous hydrogen bonds and also hydrophobic interactions are present between cellulose molecules, forming such crystalline cellulose microfibrils.

Oxidation of native celluloses using a catalytic amount of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) is a powerful technique for preparation of highly crystalline and individualized wood cellulose nanofibers homogeneous ~3-4 nm and a few microns in width and length, respectively. Because TEMPO-oxidized wood cellulose nanofibers (TOCNs) have such high crystallinities and aspect ratios, TOCN self-standing and coated films have some unique and characteristic properties, which are promising as new bio-based nanomaterials. Regioselective oxidation of C6-OH groups exposed on crystalline wood cellulose microfibrils to C6-carboxylate groups can be achieved by TEMPO/NaBr/NaClO treatment in water at pH 10 and room temperature, and aqueous TOCN dispersions are obtained by gentle mechanical disintegration of the oxidized celluloses in water. Because only TEMPO-mediated oxidation used as a pretreatment allows wood celluloses to be converted to completely individualized TOCN/water dispersions with high aspect ratios almost quantitatively, this oxidation process has potential applications to other native celluloses such as non-wood fibers for preparation of new bio-based nanofibers at the industrial level.

In this thesis, therefore, TEMPO-mediated oxidation was applied to non-wood cellulose fibers to prepare TOCNs thereof. Relationships between oxidation conditions and properties of TEMPO-oxidized celluloses and TOCNs were studied in detail, and compared with those prepared from wood cellulose. Moreover, optical and mechanical properties of TOCN films prepared from non-wood fibers were estimated for further applications of agricultural cellulose fibers to high-tech materials.

TEMPO-mediated Oxidation of Hemp Bast Holocellulose to Prepare Cellulose Nanofibrils Dispersed in Water

First, the relationships between TEMPO-mediated oxidation conditions of hemp bast holocellulose (HBH) and properties of TOCNs prepared thereof were studied in detail, particularly focusing on the amount of NaClO added in the TEMPO/NaBr/NaClO oxidation system in water at pH 10. The used HBH had α -cellulose content of 79.4%. Figure 1 shows the relationships between the amount of NaClO added in the oxidation and either carboxylate/aldehyde content and viscosity-average degree of polymerization

(DP_v) of the oxidized HBHs. The carboxylate content of the TEMPO-oxidized HBHs increased from 0.22 to 1.73 mmol/g with increasing the NaClO addition level from 0 to 12.5 mmol/g-HBH. Small amounts of C6-aldehydes, which can be converted to C6-carboxylates by the post-NaClO₂ oxidation, were present in the TEMPO-oxidized HBHs. The HBH behaved like kraft pulp in the TEMPO-mediated oxidation. Because almost no lignin was present in the HBH, oxidation efficiency to form C6-carboxylate and C6-aldehyde groups in the TEMPO-oxidized HBHs was higher than that for lignin-containing hemp bast fibers before the holocellulose treatment at the same NaClO addition levels. The DP_v values clearly decreased from 1120 to 380 as the NaClO addition level in the TEMPO-mediated oxidation was increased; remarkable depolymerization of cellulose chains in the TEMPO-oxidized-HBHs (TO-HBHs) was inevitable during the TEMPO/NaBr/NaClO oxidation in water at pH 10. The β-elimination at the C6-aldehyde groups formed as intermediates under alkaline conditions and/or oxidative depolymerization by NaClO are likely to cause the depolymerization. The TEMPO-oxidized HBHs maintained the original cellulose I crystal structure, while crystallinity index and crystal width were slightly decreased by the oxidation.

When the NaClO addition levels were 7.5-12.5 mmol/g-HBH, the oxidized HBHs were able to be converted to transparent dispersions by mechanical disintegration in water to form almost completely individualized TEMPO-oxidized cellulose nanofibrils in the nanofibrillation yields of 98-100% (Figure 2). The carboxylate content of the TO-HBHs, which is controllable by the NaClO addition level in the TEMPO-mediated oxidation process, is

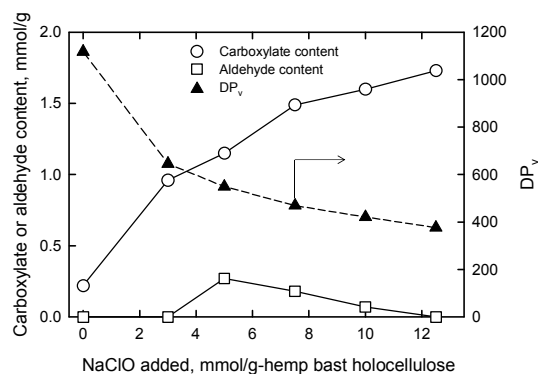


Figure 1. Carboxylate and aldehyde contents and viscosity-average degree of polymerization (DP_v) of TEMPO-oxidized hemp bast holocelluloses.

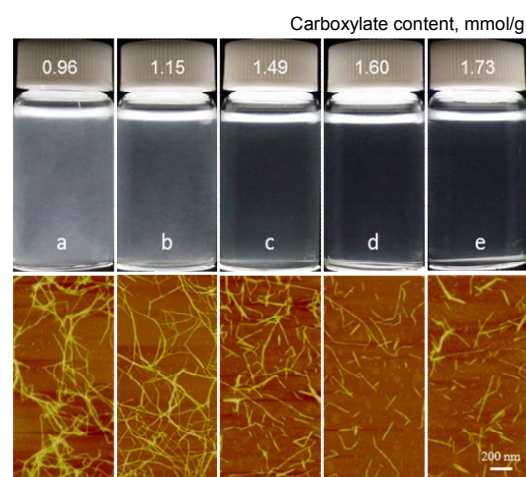


Figure 2. Photographs of 0.1% TEMPO-oxidized hemp holocellulose nanofibrils dispersed in water and AFM images.

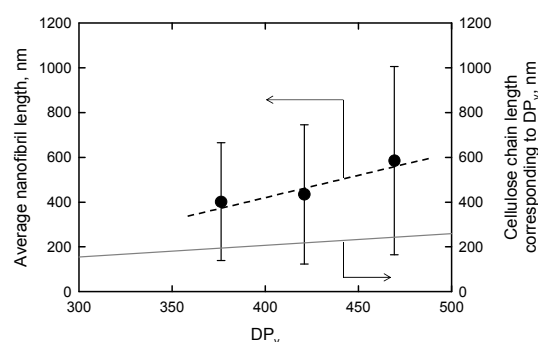


Figure 3. Relationship between DP_v of TEMPO-oxidized hemp bast holocelluloses and either average nanofibril length of TO-HBH nanofibrils obtained from AFM height images or cellulose chain length corresponding to each DP_v value.

the primary factor influencing the

nanofibrillation behavior of TO-HBHs. When a sufficient amount of C6-carboxylate groups is formed on crystalline cellulose microfibril surfaces in the HBH, electrostatic repulsion effectively works between anionically-charged TEMPO-oxidized cellulose nanofibrils in water, achieving the almost complete individualization of cellulose nanofibrils in the TO-HBHs.

The average cellulose nanofibril length was always greater than the cellulose chain length at the corresponding DP_v value; each nanofibril in TO-HBHs consists of cellulose chains shorter than the nanofibril length (Figure 3).

Comparative Characterization of Cellulose Nanofibril Films Prepared from Non-Wood Celluloses by TEMPO-Mediated Oxidation

In this part, TEMPO-oxidized cellulose nanofibrils were prepared from bagasse and bamboo pulps, and their nanofiber films were compare with TO-HBHs in terms of mechanical and optical properties. Here, the oxidized non-wood celluloses were prepared by the TEMPO/NaBr/NaClO system with 7.5 mmol g⁻¹ of cellulose in water at pH 10. The weight recovery ratios of the water-insoluble TEMPO-oxidized celluloses thus obtained were 70–80%, and their carboxylate contents reached 1.5–1.7 mmol g⁻¹. The DP_v values of the all non-wood TEMPO-oxidized celluloses remarkably decreased from 800–1100 to 200–480 by partial depolymerization occurring during the oxidation. The TOCNs prepared by mechanical disintegration of the TEMPO-oxidized celluloses in water consisted of mostly individual TOCN elements and their nanofibrillation yields were 82–98%. The average lengths and widths of the TOCNs were 500–650 nm and 2.4–2.9 nm, respectively, in all cases. The self-standing TOCN films prepared by casting and drying of the TOCN/water dispersions had high light-transparencies (>87% at 600 nm), high tensile strengths (140–230 MPa), high Young’s moduli (7–11 MPa), low coefficients of thermal expansion (4–6 ppm K⁻¹) in spite of low densities of 1.4–1.7 g cm⁻³. In particular, the TOCN films prepared from HBH had clearly high works of fracture (~30 MJ m⁻³), whereas those prepared from other two non-wood celluloses had 2–8 MJ m⁻³ as shown in Table 1. These results show that non-wood cellulose fibers can be used as resources to prepare TOCNs, and moreover, TO-HBHs had high potential application as new bio-based nanofibers.

Table 1. Fundamental and mechanical properties of TEMPO-oxidized cellulose nanofibril films prepared from hemp bast holocellulose, and bamboo and bagasse pulps

| | Hemp bast holocellulose | Bamboo pulp | Bagasse pulp |
|---|-------------------------|-------------|--------------|
| Density (g cm ⁻³) | 1.65 | 1.61 | 1.41 |
| Moisture content at 23°C and 50% R.H. (%) | 11.2 | 9.6 | 8.1 |
| Tensile strength (MPa) | 232 ± 7 | 170 ± 9 | 137 ± 14 |
| Elongation at break (%) | 11.2 ± 0.9 | 3.6 ± 0.6 | 1.4 ± 0.3 |
| Young’s modulus (GPa) | 6.8 ± 1.5 | 9.5 ± 1.8 | 10.9 ± 0.5 |
| Work of fracture (MJ m ⁻³) | 29.6 ± 1.5 | 7.8 ± 1.8 | 1.5 ± 0.3 |
| Coefficient of thermal expansion (ppm K ⁻¹) | 5.7 | 5.2 | 4.1 |