EFFECT OF GAMMA IRRADIATION ON PHYSICOCHEMICAL PROPERTIES OF SOLID-STATE CELLULOSE NANOFIBER UNDER ATMOSPHERIC CONDITIONS

TARO KINUMOTO, MANAMI NODA, MIKI MATSUOKA, KANAKO KAI, RYOTARO TAKAYAMA and MASAYA MORIYAMA

Department of Integrate Science and Technology, Faculty of Science and Technology, Oita University, 700 Dannoharu, Oita, 870 1192, Japan

✉ *Corresponding author: T. Kinumoto, kinumoto@oita-u.ac.jp*

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The effect of gamma irradiation on a solid-state cellulose nanofiber (SS-CNF) sheet was investigated. Changes in the physicochemical properties, such as the chemical structure, morphology, thermal stability and maximum stress, measured by tensile tests, were demonstrated after gamma irradiation under atmospheric conditions. The chemical structure investigated by using Fourier transform infrared spectroscopy and X-ray diffraction was unchanged after irradiation at 60 kGy; on the other hand, a dramatical change with yellowing was found after irradiation at 300 kGy, especially, a decrease in the thermal stability as well as the maximum stress of the CNF sheet was obvious. The physicochemical properties of CNF could be kept up to at least 60 kGy, with minor changes in the chemical structure, but were affected by further increases in the total dose of gamma irradiation.

Keywords: solid-state cellulose nanofiber, gamma irradiation, atmospheric condition

INTRODUCTION

Aiming at the achievement of "sustainable development goals (SDGs)", the biorefinery technology is required as an alternative to the petroleum-based industry, which produces many chemicals and materials. Plant sources, such as softwood, hardwood, annual plants and/or agricultural waste, are focused on to produce nanocellulose materials, including cellulose and lignocellulose nanofibers (CNF and LCNF) and short-length nanocrystals (CNC). Such plant-based nano-materials have environment-friendly features, because they are produced from raw materials that consume carbon dioxide from the atmosphere and are biodegradable. They could be used not only for reinforcement, as a filler, but also for replacement of some plastic materials, owing to the high mechanical strength.[1,2]

The interest in nanocellulose research for CNF and CNC has increased significantly in recent years, with a focus on production processes, physicochemical properties and potential applications. Then, numerous types of CNF and CNC have been being developed, and their properties have been found to be typically dependent on the plant source and the production process.[2]

Catalytic oxidation of softwood bleached kraft pulp with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) is a typical method to isolate cellulose.[1-3] The product, "TEMPO-CNF (TOC)", having surely narrow diameter, of 3-4 nm, is often employed in the research field of CNF.[1-3] However, TOC should be unfortunately categorized as an oxidized cellulose because the hydroxy group at C6 position of the glucose unit is oxidized to the carboxy group. The conversion to the carboxy group leads to lower thermal stability. In fact, the thermal decomposition point (TDP) has been reported as 222 °C, which is quite lower than that of the original cellulose (275 °C).[4] We believe that we should use CNF, which has as high TDP as possible to investigate the physicochemical properties of "CNF".

Bamboo derived cellulose nanofiber, CELEENA®, is one of the desirable "CNFs"

regarding its high cellulose content, without any chemical modification (revealed from FT-IR – Fourier transform infrared spectroscopy). The TDP of CELEENA® is higher than 260 °C (as shown further below) and therefore, we determined that CELEENA® is suitable for being used to study the physicochemical properties of CNF.

There are numerous applications expected for CNFs; in particular, a possible application is in biomedical materials, using neat CNFs and/or combined with other polymers, such as poly(lactic acid) (PLA).[5,6] Aouat *et al*. reported that the composite of CNF and PLA is expected to be used in medical materials involving sutures, as support for tissue engineering and 3D scaffolds, owing to the biocompatibility, biosafety and high mechanical strength of CNF.[6]

The gamma irradiation technique is one of the most practical methods for sterilization of biomedical products. Criado *et al.* investigated the gamma irradiation of aqueous CNC suspension and reported that the content of carboxy groups increased due to the reaction with the radical species (•OH, •H, *etc*.), which were produced by water radiolysis.[7] Although their research is interesting, the effect of gamma irradiation on cellulose and CNF should be studied in the presence of water molecules, at the level of humidity in operating conditions for the applications mentioned above and for essential research on CNF. Unfortunately, there are no reports about the effects of gamma irradiation on the physicochemical properties of CNF under such conditions.

Thus, we prepared a solid-state CNF (SS-CNF) sheet specimen using CELEENA® and investigated the effect of gamma irradiation at 60 kGy as a sufficient total dose on both morphology and physicochemical properties. We also observed the changes occurring in the CNF with further irradiation up to 300 kGy.

EXPERIMENTAL

CNF

In the present study, the CNF was prepared by delignification and defibrillation of *Phyllostachys bambusoides* (giant timber bamboo), naturally grown in Oita prefecture, Japan. This type of CNF is also commercially available from Oita CELEENA Co., Ltd.[8] An aqueous suspension with 1 wt% CNF was used in this study. The cellulose component of CNF was estimated to be over 95% by the detergent analysis performed at Tokai Techno Co., Ltd,[9] and no chemical transformation occurred on the molecular structure of cellulose, as shown later in the FT-IR analysis. The average diameter was about 15 nm, with a standard deviation of about 4 nm.

Preparation of SS-CNF

A SS-CNF sheet was prepared without any binders by means of pressure filtration as described below. A determined volume of the aqueous suspension was poured into a filtration apparatus (UHP-76K, Advantec Toyo), equipped with a membrane filter (pore diameter = 1.0 μm, filter diameter = 90 mm, H100A090C, Advantec Toyo). After that, the wet sheet was dried and pressed by a hot press machine (AH-2003, AS ONE Corporation) to obtain a dry SS-CNF sheet with normalized thickness of *ca*. 50 μm. The typical appearance of the SS-CNF sheet prepared is shown in Figure 1 (a) and it was used in this study, unless otherwise specified.

Gamma irradiation and characterization of SS-CNF

Gamma irradiation was carried out at Chiyoda Technol ^{60}Co irradiation facility, Laboratory for Zero-Carbon Energy, Institute of Innovative Research, Tokyo Institute of Technology. The irradiation was performed under atmospheric conditions. The total dose of irradiation was first determined as 60 kGy according to the literature published by Sugimatsu *et al*.[10] They reported that the tensile strength of unbleached kraft pulp was significantly decreased after gamma irradiation of 60 kGy.[10] Thus, this total dose value was considered reasonable to investigate the changes occurring in the physicochemical properties of CNF.[6,7]

The chemical structure changes caused by gamma irradiation were the most probable; thus, FT-IR (Nicolet iS5 FT-IR, Thermo Scientific) and XRD (MiniFlex-600, Rigaku) measurements were performed before and after the gamma irradiation.[7] The FT-IR spectra were obtained by the Attenuated Total Reflection (ATR) method. The microscopic morphology of CNF (not SS-CNF, as mentioned in the next section) was investigated using field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL) after drying the aliquot CNF suspension following platinum deposition.

Thermogravimetric analysis (TG) was performed on a TG-DTA8122 (Rigaku) under atmospheric air using an alumina crucible. The TG curve was taken after keeping the sample at 100 °C for 1 h to avoid the influence of adsorbed water molecules.

A mechanical testing system, digital force gauge ZTA-50N and test stand MX2-500N (IMADA), was used for the tensile tests of SS-CNF. We prepared several SS-CNF rectangle sheets, which were 40 mm long and 10 mm wide. The average thickness was *ca*. 50 μm and the average weight was *ca*. 20 mg. The tensile test was conducted at room temperature, around 22-23 °C, and at ambient humidity at 25-40% RH.

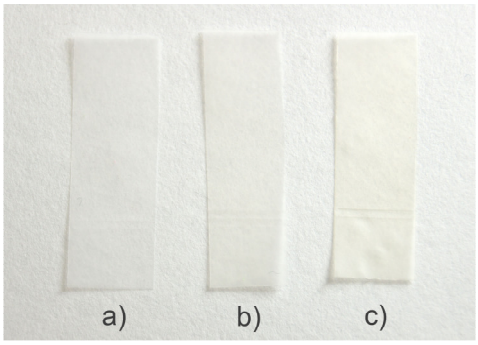

Figure 1: Photographs of SS-CNF (a) before and after gamma irradiation at (b) 60 kGy and (c) 300 kGy

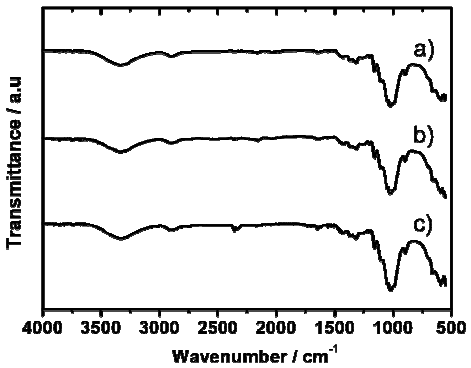

Figure 2: FT-IR spectra of SS-CNF (a) before and after gamma irradiation at (b) 60 kGy and (c) 300 kGy

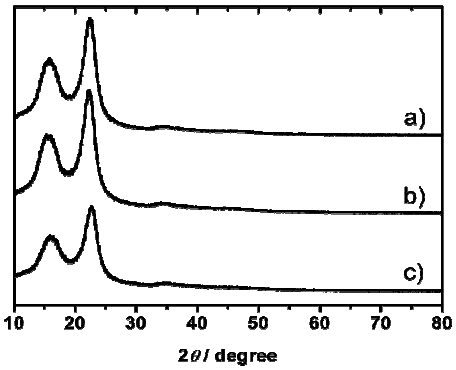

Figure 3: XRD patterns of SS-CNF (a) before and after gamma irradiation at (b) 60 kGy and (c) 300 kGy

The SS-CNF sheet was mounted on the chuck of the tester (10 mm at both sides of the sheets was gripped, tensile part is 20 mm long) and extended at 10 mm min^{-1}. The average values and standard deviation of tensile strength and tensile modulus were evaluated from the load and displacement values.

RESULTS AND DISCUSSION

Figure 2 (a) shows the FT-IR spectrum of virgin SS-CNF. There are only typical absorption peaks ascribed to cellulose, for example, the peaks appearing at 3300, 2900 and 1100 cm^{-1} are attributed to the stretching vibrations of O-H, C-H and C-C-O bonds, respectively. Thus, it was confirmed that the CELEENA® CNF used in this study was composed of cellulose, without any chemical modification. The spectrum obtained after 60 kGy is shown in Figure 2 (b). There is no significant change as compared to Figure 2 (a), suggesting that the chemical structure of CNF did not obviously change during the irradiation at 60 kGy. We can, therefore, consider that there are only minor changes in the chemical structure of cellulose in CNF at ambient humidity, compared to those in an aqueous suspension, as found in the research of Criado *et al*.[7]

This result is also in agreement with the results of XRD measurements. As shown in Figure 3 ((a) and (b)), there are no significant changes after the irradiation and both patterns (before and after irradiation) are classified into cellulose I type. Cellulose is a polysaccharide consisting of a linear chain of β(1→4) linked D-glucose units, and also, its crystal structure is known to be cellulose I type, unless any modifications interfere. Thus, we can calculate the crystallinity of cellulose units following the report of Isogai and Ueda.[11] The crystallinity index was estimated at 82%, despite the gamma irradiation. We assumed that no major chemical structure changes occured in CNF during the gamma irradiation up to 60 kGy under atmospheric conditions.

The effect of gamma irradiation on the microscopic morphology of CNF was also interesting. Unfortunately, it is very difficult to observe the microscopic morphology of CNF in the test specimen because of the relatively low

electric conduction. In this case, we had no choice but to use an aqueous CNF suspension (1 wt%) for this objective. Typical FE-SEM images before and after the irradiation at 60 kGy are shown in Figure 4. Although the cellulose fibers of uniform diameter can be clearly recognized before the irradiation, several short length fibers, which could be formed by blanching the original CNF, are observed, as indicated by arrows after the irradiation. The average diameter of CNF increased to 22 nm upon the irradiation. The changes in morphology and diameter could be caused by the reaction of cellulose and the radicals produced by water radiolysis, in accordance with the report of Criado *et al*.[7] The radicals attacked the cellulose molecules, and then cross-linking reactions might have occurred, leading to an increase in the diameter of CNF.

Figure 5 shows the typical TG curves of CNF, at a heating rate of 10 °C min^{-1}. The large weight loss, which corresponds to the thermal decomposition of cellulose, was observed when the temperature was over 260 °C (=TDP). On the other hand, TDP was more than 15 °C lower after gamma irradiation at 60 kGy, which may be related not only to microscopic morphology changes, as shown in Figure 4 (b), but also to minor changes occurring in the chemical structure, which possibly we could not determine.

CNF is expected to be used as a filler in composite reinforcement applications, and thus any changes in the physical properties of CNF upon gamma irradiation are of high concern, as they may affect the properties of the composite. The maximum stress of SS-CNF before and after gamma irradiation is summarized in Table 1. It was clarified that the tensile maximum stress and modulus recorded after 60 kGy gamma irradiation were almost similar to those of the non-irradiated sample, which suggests that the mechanical strength of the CNF sheet is retained even after gamma irradiation at 60 kGy. However, a drastic decrease to nearly half was observed when the total dose of irradiation was increased from 60 kGy to 300 kGy.

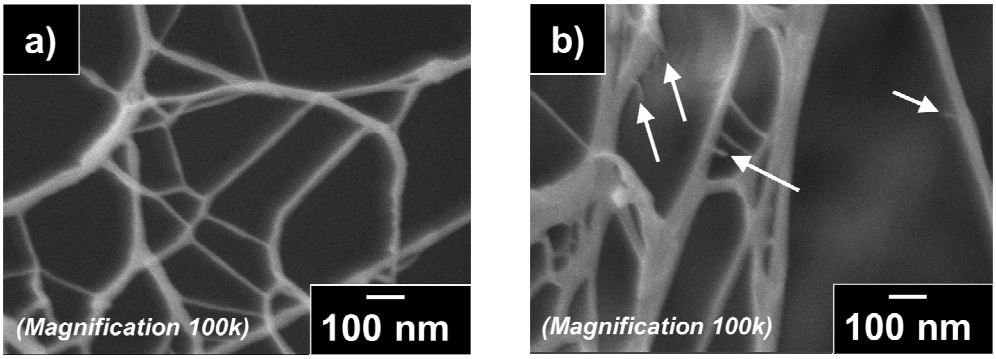

Figure 4: Typical FE-SEM images of CNF (a) before and (b) after gamma irradiation at 60 kGy

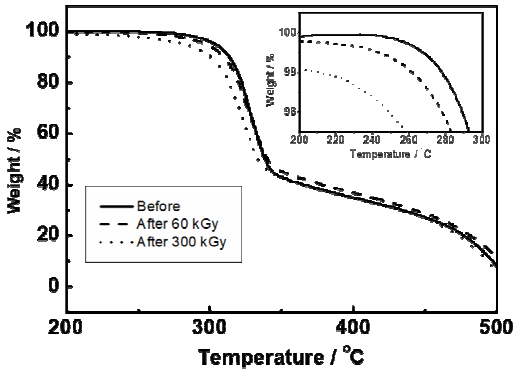

Figure 5: Typical TG curves of SS-CNF (the solid, dashed and dotted lines correspond to the sample before and after gamma irradiation at 60 kGy and 300 kGy, respectively; inset figure shows a close-up for the range from 200 to 300 °C

Table 1
Maximum stress and modulus of SS-CNF before and after gamma irradiation at 60 and 300 kGy

Sample	Maximum stress, MPa		Modulus, GPa	
	Average	Standard deviation	Average	Standard deviation
Initial	71.0	11.9	1.54	0.23
Irradiated at 60 kGy	66.2	8.3	1.59	0.27
Irradiated at 300 kGy	30.2	6.1	0.90	0.19

Figure 1 (b) and (c) shows the appearance of the SS-CNF sheet after the irradiation at 60 kGy and at 300 kGy, respectively. The color of the sheet turned to yellow with the increase in the total dose of irradiation. The reason for cellulose yellowing may be related to the chemical structure changes, which caused discoloration upon heat degradation of cellulose.[12] In accordance with the report of Si *et al*., we speculated that unsaturated structures formed by the elimination of small molecules from SS-CNF induced absorption of visible light, resulting in discoloration of the gamma irradiated SS-CNF.

However, no major differences could be found in the FT-IR spectra and XRD patterns when comparing the virgin (Fig. 2 (a) and Fig. 3 (a)), the 60 kGy irradiated (Fig. 2 (b) and Fig. 3 (b)), and the 300 kGy irradiated (Fig. 2 (c) and Fig. 3 (c)). Thus, structural changes that occurred during gamma irradiation were quite minor, compared to what was expected, and therefore, they were not detected by the available FT-IR and XRD measurements.

CONCLUSION

In the present study, we investigated the effect of the gamma irradiation on the physicochemical properties of SS-CNF under atmospheric conditions. No significant changes in the chemical structure of the sample were observed after irradiation at 60 kGy, with the exception of the fact that the thermal stability of CNF slightly decreased under the effect of gamma irradiation. It should be mentioned, however, that if the total dose is increased to 300 kGy, the physicochemical properties of CNF deteriorate in terms of both mechanical strength and thermal stability.

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