A FACILE ISOLATION METHOD OF CELLULOSE NANOCRYSTALS FROM MICROCRYSTALLINE CELLULOSE

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In this study, we investigated an effective isolation method of cellulose nanocrystals (CNCs) from commercial microcrystalline cellulose (MCC) using electron beam irradiation (EBI). The EBI of the MCC was performed at various doses ranging from 50 to 200 kGy, and then MCC was hydrolyzed with 65% sulfuric acid at 45 ℃ in a pre-heated oven for 30, 60, 90, and 120 min. The hydrolysate of MCC was characterized using gel permeation chromatography (GPC), a particle size analyzer, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). CNCs of virgin MCC were obtained with a 44% yield, 319 nm average particle size, and 78.2% crystallinity index after 120 min of acid-hydrolysis. However, CNCs isolated from 50 kGy irradiated MCC were obtained with 51% yield, 330 nm average particle size, and 80.2% crystallinity after 30 min of acid-hydrolysis. In addition, TEM morphology analysis clearly showed the isolation of rod-like shaped CNCs.

Keywords: electron beam, microcrystalline cellulose, nanocellulose, cellulose nanocrystal, acid hydrolysis

INTRODUCTION

Cellulose is the most abundant, renewable, biocompatible, and biodegradable organic biopolymer that can be isolated into whisker-like nano- and micro-fibrils.[1] Cellulose is a linear homopolymer of a β-1,4 glycosidic bond linked glucopyranose units (or monosaccharides).[2] Microcrystalline cellulose (MCC) is a purified residue with high crystallinity and partially depolymerized powder, which can be obtained through mineral acid hydrolysis from wood pulp and cotton.[3] Cellulose nanocrystals (CNCs) are a crystalline region (highly ordered) in virgin cellulose. CNCs are rod-shaped and they are typically reported to have diameters of 5-20 nm and a length distribution of 100-600 nm.

Acid hydrolysis has been commonly used for CNC isolation from virgin cellulose, because its amorphous region can be easily hydrolyzed.[4] CNCs can be isolated from a great variety of natural sources, such as MCC,[5] cotton linter,[6] maize straw,[7] corn stover,[8] and jute.[9] CNCs have attracted the attention of scientists to be utilized as a potential candidate in applications of green polymer composites, pharmaceuticals, scaffolds for tissue engineering, coating, and films, due to their low density, excellent mechanical properties, nanoscale reinforcement, biocompatibility, and biodegradability.[10-12] However, many limitations of the CNC isolation process still need to be overcome, such as the long duration of the process and the low yield with longer hydrolysis time.

The use of EBI has been well known to decrease the degree of polymerization and the crystallinity of cellulose.[13] In this study, the effects of EBI on the key factors (time consumption and yield) determining the efficiency of the hydrolysis process were characterized.

EXPERIMENTAL

Materials and methods

Avicel PH-101 (MCC) and a dialysis tubing cellulose membrane (MWCO: 14,000) were purchased from Sigma-Aldrich. Sulfuric acid (98%) was purchased from Daejung Chemicals and Metals Co., LTD.

MCC was irradiated by a 2.5 MeV ELV-8-type electron accelerator (EB Tech Co., Korea). The total absorbed doses used were of 50, 100, 150, and 200 kGy, respectively. Virgin and irradiated MCC were hydrolyzed by 65% (w/w) sulfuric acid at 45 °C for 30, 60, 90, and 120 min. The suspension was centrifuged with DI water to stop the reaction, and then centrifuged for 15 min at 10,000 rpm. After the removal of the supernatant liquid, dialysis was conducted using a dialysis tubing cellulose membrane in DI water until neutrality was attained, followed by freeze-drying. The resulting sample powders are denoted as d-CNCs-t (d: the EBI dose, t: the hydrolysis time).

Characterization

The EBI effects on the molecular weight of MCC were investigated using GPC (EcoSEC HLC-8320, Tosoh) with a column (Guard SuperMP (HZ)-M+2 x TSKgel supermultipore HZ-M (4.6 x 150 mm)) and refractive index (RI) detector. The particle size of CNC dispersion in DI water was measured by a particle size analyzer (DelsaNano C, Beckman Coulter Inc.). X-ray diffraction (XRD) analysis was employed to study the physical properties using an XRD diffractometer (D8 DISCOVER, Bruker AXS). CNCs were measured over the range of 2θ = 5 - 70° with a scan step size of 0.03°. The crystallinity index (CI) was calculated using Segal's method[14] and Eq. (1):

The crystallinity index

$$CI, \% = (1 - (I_{am} / I_{002})) * 100 \quad (1)$$

where I_{002}: the maximum intensity of the (002) plane diffraction, I_{am}: the intensity of the amorphous portion at 2θ = 18°.

The thermal properties of the CNCs were characterized by thermogravimetric analysis (TGA). The TGA was conducted from 25 °C to 800 °C under N_2 gas atmosphere at a heating rate of 10 °C/min, using a thermogravimetric analyzer (TGA/DSC 1, Mettler-Toledo Inc.). The morphology of the CNCs was observed by TEM (Tecnai G2 F20 460L, FEI). A droplet of a dilute suspension of CNCs was deposited on a grid and dried.

RESULTS AND DISCUSSION

Table 1 shows that as the EBI dose on MCC is increased, the CI and molecular weight are decreased. The Mw of the non-irradiated MCC (0 kGy) is 134,000 Da, but is remarkably reduced to 43,600 Da for the 200 kGy irradiated MCC. Moreover, the CI of MCC decreases slightly from 80.4% to 75.8%, when irradiated at doses of 0-200 kGy. These results (lower CI and reduced Mw) show that the irradiated MCC was much more quickly hydrolyzed than the non-irradiated MCC because the EBI makes it easily accessible to chemicals. Figure 1a shows that the average particle sizes of the 0-CNCs-30, 0-CNCs-60, and 0-CNCs-90 were excluded in the range of the nanometer-scale. As a result, 0-CNCs-120 was obtained with an average particle size of 318.9 nm in the range of nanometer-scale. However, CNCs from the irradiated MCC were obtained with average particle sizes of 330.0 nm (50 kGy), 295.3 nm (100 kGy), 166.8 nm (150 kGy), and 152.0 nm (200 kGy) after 30 min of acid hydrolysis. The yields of CNCs after acid hydrolysis under various experimental conditions (EBI dose and hydrolysis time) are shown in Figure 1b. The yield of 50-CNCs-30 was higher than that of 0-CNCs-120. However, the high dose (150-200 kGy) irradiated MCC was the most degraded at the same hydrolysis time. These results indicate that sulfuric acid can easily penetrate into the EBI-induced disordered structure of MCC, which facilitates the hydrolytic cleavage of the glycosidic bonds.[15]

XRD results of 0-CNCs-120 and 50-CNCs-30 are shown in Figure 2. 50-CNCs-30 possesses a higher value of CI (80.2%) compared to 0-CNCs-120 (78.2%). A lower CI of 0-CNCs-120 is related to the duration of acid hydrolysis. The TGA and its derivatives (DTG) for MCC and CNCs are shown in Figure 3.

Table 1
Effect of EBI on MCC

Dose (kGy)	CI (%)	Mw (Da)	Mn (Da)	PDI
0	80.4	134,000	29,200	4.58
50	78.4	88,200	20,700	4.26
100	77.6	74,900	19,900	3.76
150	76.7	58,600	17,200	3.40
200	75.8	43,600	13,700	3.18

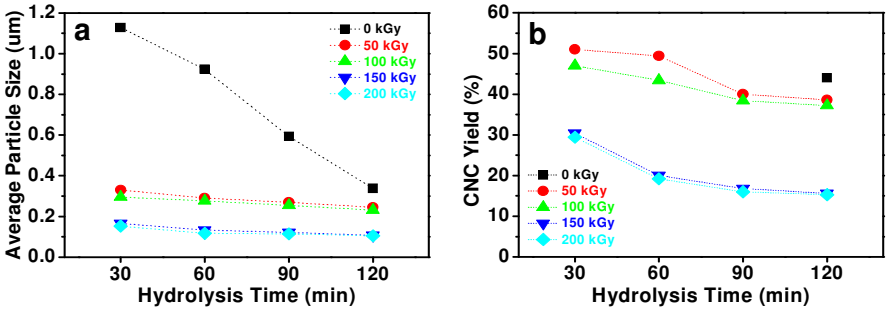

Figure 1: Average particle size and yield of CNCs

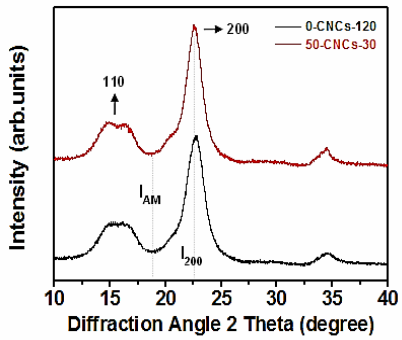

Figure 2: XRD diffractogram of 0-CNCs-120 and 50-CNCs-30

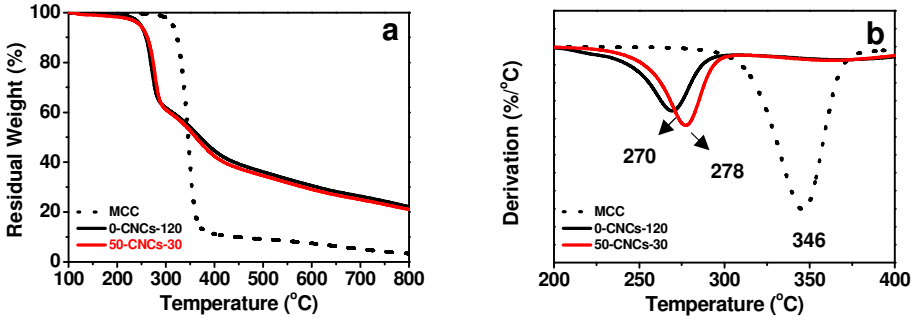

Figure 3: Thermogram and DTG curves of MCC and its CNCs

The thermal stability of 0-CNCs-120 and 50-CNCs-30 was lower than that of the MCC (Fig. 3a). This shows that the sulfate groups introduced onto the surface of MCC during the acid hydrolysis decreased the thermal stability of the CNCs as a result of the dehydration reaction.[16] The char fraction of 0-CNCs-120 was higher than that of 50-CNCs-30. This result can be explained by the increased amount of sulfated groups (as flame retardants) with an increase in the hydrolysis time.[17] In addition, based on the DTG curves in Fig. 3b, the peaks of the maximum thermal decomposition appeared at 346, 270, and 278 °C for MCC, 0-CNCs-120, and 50-CNCs-30, respectively. The thermal stability of the CNCs was lower than that of MCC. It is widely thought that the sulfate groups (negative charged) introduced into the surface of the CNCs result in a decrease in the thermal stability.[17] The TEM morphology analysis clearly showed the isolation of rod-like shaped CNCs, as indicated in Figure 4. This result is consistent with that of the particle size analysis.

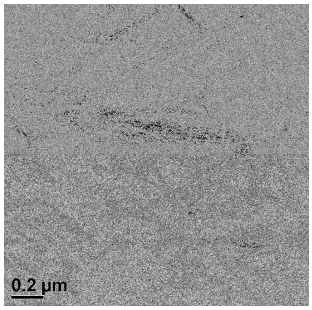

Figure 4: Morphological observation of 50-CNCs-30

CONCLUSION

In this study, an effective method employed for the isolation of CNCs from MCC was demonstrated to be successful. Morphologically, the CNCs of MCC were rod-like in shape with a size of 330 nm, obtained with a yield of 51%, and CI of 80.2%. EBI decreased the degree of polymerization and crystallinity of the MCC, and the CNCs were then isolated for around 30 min. EBI is a facile and environmentally treatment for determining the efficiency of the hydrolysis process (consuming less time and producing a better yield).

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