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Radiation Degradation of Microcrystalline Cellulose in Solid Status

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ABSTRACT: Pulverization and degradation are important pretreatment procedures in producing bio-ethanol from cellulose. In this study, microcrystalline cellulose (MCC), a pure α-cellulose, was degraded by γ-irradiation. The average degree of polymerization, content of reducing sugar, crystalline structure, and molecular structure were investigated to elucidate the radiation effect on the degradation of MCC. The results manifested that γ-ray destroyed part of the chemical bond and hydrogen bond, leading to the degradation of cellulose and increasing of the reducing sugar content. According to the Fourier transform infrared result, radiation degradation led to the formation of reductive carbonyl group. Meanwhile, radiation had slight influence on the crystalline structures of MCC. Therefore, the radiation degradation procedure is expected to benefit the further proceedings such as ultrafine treatment and enzyme hydrolysis of cellulose. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: microcrystalline cellulose; γ-irradiation; radiation degradation

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INTRODUCTION

Lignocellulosic materials, mainly composed of cellulose, hemicellulose and lignin, are the most abundant renewable resources all over the world. Cellulose is a polysaccharide consisted of anhydro D-glucose unit linked together by β-1,4 glucosidic bonds, which can be further converted to ethanol via hydrolysis and fermentation. However, because of its crystalline structure and inaccessible morphology, the application of cellulosic biomass should be processed after pretreatment.

A combination of acid and enzyme hydrolysis has been intensively investigated in bio-fuel field. To enhance the efficiency of enzyme hydrolysis and to lower the cost, a variety of pretreating methods to degrade cellulose, which include mechanical milling, steam explosion, chemical treatment, exposure to supercritical fluids, or radiation degradation, have been developed to improve the accessibility of cellulose.[1,2]

Aiming at enhancing the enzyme hydrolysis in bio-fuel process, radiation degradation of cellulose was investigated for decades. Radiation degradation of various lignocellulosic materials, such as bagasse, rice straw, wheat straw, and corn stalk, have been studied.[2] The cellulose containing biomass was subjected for radiation by electron beam or γ-ray with an absorbed dose of 10–1000 kGy. Ionizing radiation can penetrate the cellulosic biomass and disrupt the microcrystalline structure of lignocellulose, which lead to the degradation of cellulose.[1–4] The results of the literature showed that irradiation will increase the accessibility of cellulose, lead to higher glucose yield and finally benefit the bio-fuel processing as well as several other applications.[2,5–8]

Microcrystalline cellulose (MCC) is prepared by hydrolysis of naturally occurring cellulose, which are composed of nearly 100% cellulose with tight bundles of cellulose chains in a rigid linear arrangement.[9] Because of its unique gelling ability, MCC has been widely used as an additive for pharmaceuticals, foods, and cosmetics.[10] Ultrafine MCC powder can provide excellent stability without interfering the taste when using as additives for ice-cream, milky drinks, and so on. According to its purity on cellulose composition, the study on the radiation effect of MCC will bring new insights into the radiation degradation mechanism of cellulose. Furthermore, radiation degradation is expected to benefit for the ultrafine treatment of MCC.

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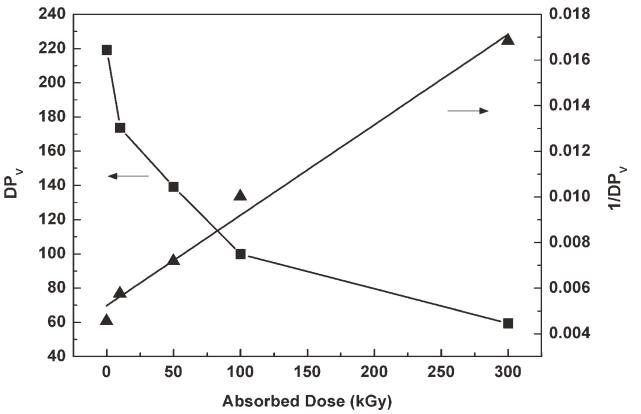

Figure 1. Dependence of the viscometric degree of polymerization (DP_v) and $1/DP_v$ on the absorbed dose.

In this work, radiation effect of MCC in solid status under γ-irradiation was investigated. The degree of polymerization (DP) was measured by viscosity method to evaluate the extent of degradation. Fourier transform infrared (FTIR), X-ray diffraction (XRD), thermogravimetry (TG), and scanning electron microscopy (SEM) were analyzed to understand the structural changes of MCC before and after irradiation. The reducing sugar content was analyzed to evaluate the accessibility of cellulose for bio-fuel processing. The particle size of MCC after irradiation and jet mill treatment was measured to broaden its application as food additive.

EXPERIMENTAL

Materials

MCC (pharmaceuticals grade) was purchased from Ruitai Cellulose Co., China. Other chemicals used were analytical reagents.

Irradiation of MCC

MCC powder was filled into glass tubes and subjected for γ-irradiation to desired absorbed dose at a dose rate of 50 Gy min^{-1} in a Cobalt-60 facility. After the irradiation, all the samples were stored in tubes at room temperature in the dark and the relative humidity was 60% ± 5%.

Measurement of DP

The average DP of MCC was determined by viscosity measurement. MCC was dissolved in saturated cupriethylenediamine solution. The viscosity of the solution was measured by an Ubbelohde viscometer with capillary (inner diameter 0.6 mm) at 25 ± 0.1°C. The intrinsic viscosity, [η], is determined according to the Martin Equation.[11] The viscometric degree of polymerization (DP_v) was calculated by Immergut formula, namely, Eq. (1)[12]:

$$DP_v^{0.905} = 0.805[\eta] \quad (1)$$

X-Ray Diffraction Analysis

XRD measurements were performed at a Philips X'Pert Pro diffractometer under the following experimental condition: Cu Kα wavelength = 0.154 nm, voltage 40 kV, current 40 mA, scanning speed 2°·min^{-1}, and scanning scale (2θ) 5–50°. The data were analyzed using Jade 5.0 software to calculate the crystalline index (CI) and crystallites sizes.

CI was calculated by Eq. (2) using the peak intensity method[13,14]:

$$CI = (I_{002} - I_{am})/I_{002} \times 100 \quad (2)$$

where I_{002} is the intensity of the peak at 2θ = 22.5°. I_{am} is the lowest intensity at around 2θ = 18.5°, which is correspond to the amorphous content of MCC.[13]

The dimensions of the crystal lattice of the lattice planes were calculated by the Scherrer formula [Eq. (3)]:

$$D(hkl) = \frac{k\lambda}{B(hkl)\cos\theta} \quad (3)$$

where $D(hkl)$ is the size of crystallite (nm), k is the Scherrer constant which is equal to 0.94, λ is X-ray wavelength which is equal to 0.154 nm, $B(hkl)$ is the full-width at half-maximum of the characteristic peak, and θ is the corresponding Bragg angle.

Fourier Transform Infrared Analysis

FTIR analysis was performed at a Nicolet Magna-IR 750, using Nicolet NicPlan IR microscope attachment (resolution 2 cm^{-1}, scan 64 times) and MCT/A detector, over a range of 500–4000 cm^{-1}.

Analysis of Reducing Sugar Content

The reducing sugar generated during radiation degradation was analyzed with the dinitrosalicylicacid (DNS) assay.[15] Briefly, the DNS reagent was prepared with 2 g 1,4-dinitrosalicylicacid, 0.4 g phenol, 0.1 g sodium sulfite, and 2 g sodium hydroxide in 200 mL deionized water. A total of 15 mL DNS reagent and 15 mL MCC dispersion was mixed in a test tube. Then, the mixture was heated at 90°C for 15 min. After that, 5 mL of 40% potassium sodium tartrate solution was added to the mixture to obtain a red-brown color solution. The absorbance was recorded with a UV–Vis Spectrophotometer (UV-3010, Hitachi,

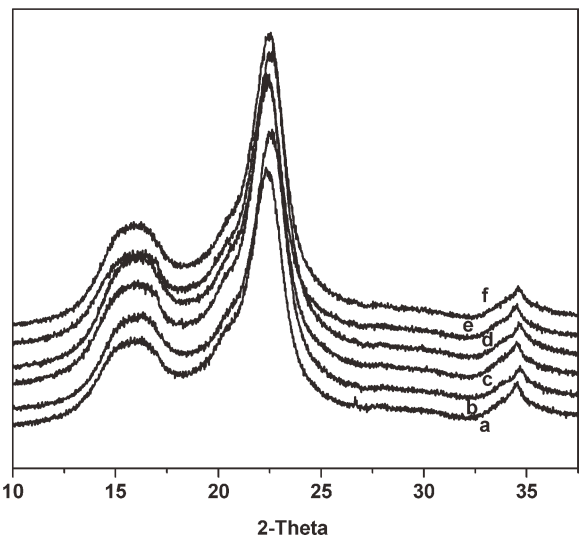

Figure 2. X-ray diffraction spectra of MCC irradiated with different absorbed doses: (a) 0 kGy, (b) 10 kGy, (c) 50 kGy, (d) 100 kGy, (e) 300 kGy, and (f) 500 kGy.

Table I. Characterization Peaks and Crystalline Parameters of MCC Irradiated with Different Absorbed Doses

Absorbed dose	Location of characterization peak			CI (%)	CI_{IR}	Dimensions of the 002 crystal lattice (nm)
	101	10$\bar{1}$	002			
0 kGy	14.80	16.34	22.74	68.2	1.82	4.2
10 kGy	14.85	16.41	22.69	70.2	1.55	4.3
20 kGy	14.94	16.32	22.73	69.4	1.63	4.5
30 kGy	14.79	16.42	22.69	68.9	1.69	4.2
50 kGy	14.96	16.36	22.78	67.7	1.77	4.0
100 kGy	14.86	16.34	22.72	68.7	1.63	4.2
300 kGy	14.85	16.60	22.71	65.2	1.64	4.2
500 kGy	14.87	16.40	22.62	61.1	1.47	4.1

Japan) at 575 nm after the solution cooling down to room temperature and being filtrated with a 0.45-μm syringe filter. The calibration curve was measured using pure glucose as control under the same experiment conditions.

Thermal Analysis

Thermal analysis was performed at a thermal analysis instrument (Q50TGA, Thermal Analysis, USA), which is a simultaneous measurement instrument combining TG with the highly flexible differential thermal analysis (DTA) feature. The measurements were carried out from room temperature to 500°C with a heating rate of 5°C min^{-1} and a nitrogen flow rate of 60.0 mL min^{-1}. TG and DTA were measured simultaneously to get comprehensive understanding on the composition and thermal decomposition behavior of the samples.

Scanning Electron Microscopy

MCC dispersion was treated by ultrasonic with a power of 150 W for 1 min to improve the distribution of MCC in deionized water. After that, a drop of MCC dispersion was applied to single monocrystal silicon sheet and dried in vacuum. The morphology of MCC was observed by a SEM (Hitachi S-4800) at an accelerating voltage of 1.0 kV.

Measurement of Average Particle Size

The particle-size and the specific surface area of the samples were measured with a laser diffraction instrument (Mastersize 2000, Malvern, UK). The samples were ultrasonic treated in deionized water with a power of 50 W for 3 min.

RESULTS AND DISCUSSIONS

DP Analysis

It is well-known that γ-irradiation will lead to the degradation of cellulose and reduce the molecular weight of cellulose. Figure 1 shows the effect of absorbed dose on the DP_v. The DP_v of MCC was reduced from 220 to 100 under the irradiation of 50 kGy. However, the decrease of DP_v with further increasing of the absorbed dose slowed down, and up to the irradiation of 300 kGy, DP_v of MCC was reduced to 59. The results were consistent with previous studies on cotton and other lignocelluloses, the DP_v decreased rapidly at first and then retarded as the absorbed dose increased. The decrement of DP can be ascribed to the splitting of glucosidic bond.[1,4,7]

To quantify the relationship between the DP_v and absorbed dose, Eq. (4)[16] was used to determine the radiation chemical yield of polymer degradation (G^0).

$$\frac{1}{DP_v} = \frac{1}{DP_0} + \frac{G^0 mD}{10^2 N_A k} \tag{4}$$

where D is the absorbed dose (eV), m is the unit molecular weight of cellulose which equals to 162, N_A is the Avogadro number, G^0 is the radiation chemical yield in degradation, and the k coefficient takes account of the actual ratio of viscosity-average and number-average degrees of polymerization which is set to 2 according to the Ref. 16.

The $1/DP_v$ had a good linearity with absorbed dose with a correlation coefficients (R^2) of 0.983 in the range of 0–300 kGy.

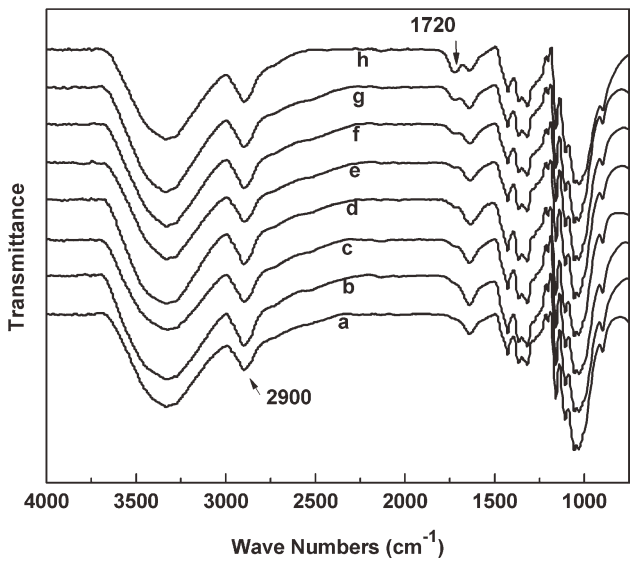

Figure 3. The FTIR spectra of MCC irradiated with different absorbed doses: (a) 0 kGy, (b) 10 kGy, (c) 20 kGy, (d) 30 kGy, (e) 50 kGy, (f) 100 kGy, (g) 300 kGy, and (h) 500 kGy.

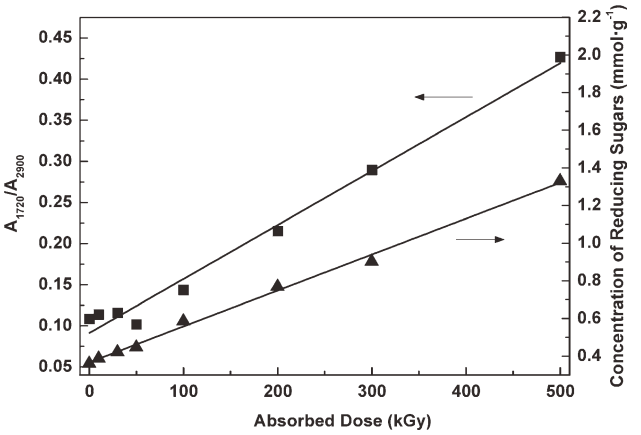

Figure 4. The influence of absorbed dose on the ratio of peak intensity at 1720 cm^{-1} to that at 2900 cm^{-1} and the concentration of reducing sugars.

The G^0 was calculated to be 4.8 (100 eV^{-1}) in the degradation process.

The results suggest that random scission in glucosidic bond predominates in the degradation procedure[8,17] and the number of scissions has a positive correlation with the absorbed dose. The decreasing of DP will make MCC more accessible for further usage.

XRD Analysis

Figure 2 shows the XRD spectra of MCC irradiated with different absorbed doses. The position of the characteristic peaks and the crystalline parameters of the MCC were obtained by deconvoluting the spectra with Jade 5.0 XRD software. The results were listed in Table I. According to the analysis, MCC was mainly composed of cellulose I. The 2θ values of the characteristic peaks for 101, 10ī, and 002 lattices of cellulose I are 14.8°, 16.6°, and 22.7°, respectively.[18,19] It was found that the crystalline structure of the irradiated MCC did not change remarkably. The CI of MCC had little change in low absorbed dose, and decreased gradually when the absorbed dose was higher than 100 kGy. The CI (%) decreased from 68% to 61% when the absorbed dose increased to 500 kGy. The dimensions of the crystal lattice did not change evidently during the radiation degradation in this study. The dimensions of the 002 crystal lattice maintained at about 4.2 nm. Comprehensively, although DP decreased significantly during the irradiation, MCC maintained its original crystalline structure.

FTIR Analysis

The FTIR spectra of the MCC irradiated with different absorbed doses are presented in Figure 3. It is known that irradiation of cellulose by high absorbed dose in the presence of oxygen will lead to the formation of carbonyl and carboxyl groups due to oxidative degradation.[2,5,6] In this study, the characteristic peak at around 1720 cm^{-1} ascribed to the carbonyl groups (C=O stretching vibration) became observable at 50 kGy and the intensity of this peak increased gradually with the increasing absorbed dose.

To further investigate the relationship between the concentration of carbonyl groups and absorbed dose, the ratio of peak intensity at 1720 cm^{-1} to that at 2900 cm^{-1} as a function of absorbed dose is shown in Figure 4. The absorbance at 2900 cm^{-1} used as a reference is ascribed to the C—H stretching vibration. The dependence of the carbonyl groups on the absorbed dose is linear. The results suggested that the process of MCC degradation is accompanied with the formation of carbonyl groups containing compounds.

Furthermore, the band at around 3300 cm^{-1} attributed to the vibration of hydrogen bonded OH-groups shifted to lower wavenumber at first and then to higher wavenumber when the absorbed dose exceeded 50 kGy. Such a shift indicates the interruption of γ-irradiation on the intramolecular hydrogen bonds and the intermolecular hydrogen bonds in cellulose.[14,20] At lower absorbed dose, γ-irradiation mainly destroyed the original intramolecular hydrogen bonds and the peak at around 3300 cm^{-1} shifted to lower wavenumber. The increasing content of carbonyl groups strengthen the hydrogen bond of C=O···H—O and induced the blue shift at higher absorbed dose.

The relative crystallinity of cellulose can be calculated by Eq. (5) using the data of infrared spectra.

$$CI_{IR} = A_{1430}/A_{897} \quad (5)$$

where CI_{IR} is the relative crystallinity of cellulose, A_{1430} is the peak intensity at 1430 cm^{-1} assigned as symmetric CH_2 bending, and A_{897} is the intensity at 897 cm^{-1} band ascribed to the C—O—C stretching at the β-(1–4)-glycosidic linkage.[21–23]

The calculated CI_{IR} of the MCC is listed in Table I. The results show that the relative crystallinity did not change obviously in low absorbed doses and decreased slightly at high absorbed doses (more than 100 kGy). It is consistent with the changes of CI determined by XRD.

Analysis of Reducing Sugar Content

The result of FTIR shows that the yields of carbonyl groups increased with increasing absorbed doses. The concentration of

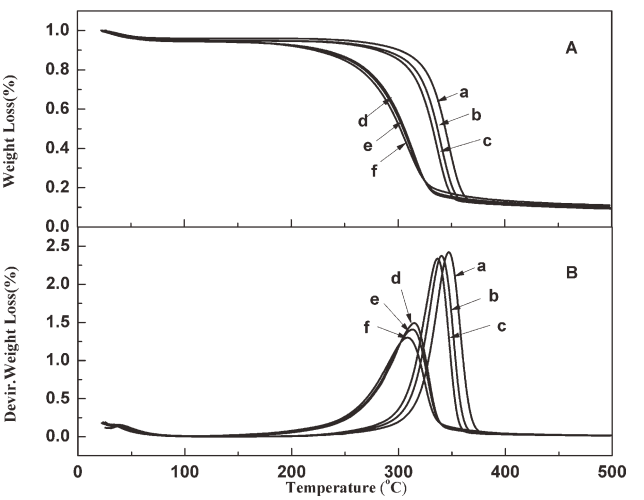

Figure 5. TGA (A) and DTG (B) curves of MCC irradiated with different absorbed doses: (a) 0 kGy, (b) 20 kGy, (c) 100 kGy, (d) 200 kGy, (e) 300 kGy, and (f) 500 kGy.

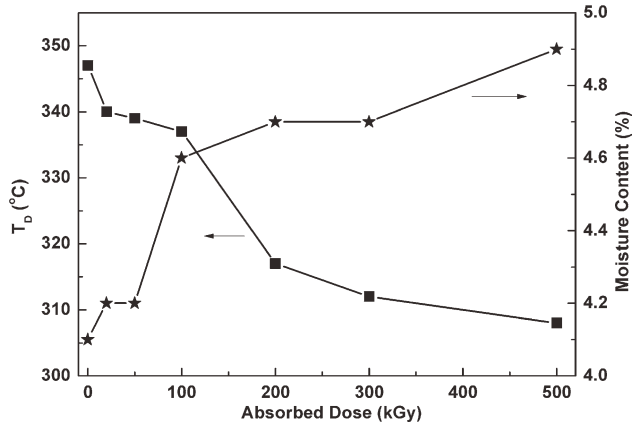

Figure 6. T_D and moisture content of MCC irradiated with different absorbed doses.

reducing sugars was measured as another evidence of the yielding of carbonyl group containing compounds.

The concentration of reducing sugars was expressed as the ratio of molar of glucose to the mass of sample. Yield of reducing sugars was calculated by Eq. (6):

$$c = c_0 + \frac{G(\mathrm{RS})D}{10^2 N_A} \tag{6}$$

where D is the absorbed dose (eV), c is the concentration of reducing sugars (mol g^{-1}), N_A is the Avogadro number, and G (RS) is the yield of reducing sugars.

The concentration of reducing sugars as a function of absorbed dose is shown in Figure 4. The results showed that the concentration of reducing sugars had a good linearity with the absorbed doses. The correlation between the concentration of reducing sugars and the absorbed dose was calculated to be $c = 3.6669\ \mathrm{E}\ -4 + 3.058\ \mathrm{E}\ -25 \times D$. The correlation coefficients (R^2) was 0.996 and G (RS) was determined as 19 (100 eV^{-1}).

G (RS) is higher than G^0, which can be explained as: irradiation of cellulose caused the scission of glucosidic bond and glucopyranose ring, resulting in polymeric compounds containing terminal carbonyl groups; meanwhile, it caused the formation of other small molecules containing carbonyl groups. DP of the original and irradiated MCC is low so that the proportion of small molecules cannot be ignored.

Thermal Analysis

TGA and DTG curves of MCC irradiated with different absorbed doses are shown in Figure 5. The weight loss due to the dehydration mainly happened in the region between 20°C and 120°C. As shown in Figure 6, moisture content (%) in MCC increased with the increasing absorbed dose. The increasing moisture content implies a higher hygroscopicity of irradiated MCC, which ascribed to the higher content of hydrophilic groups such as carbonyl group, carboxyl group, and free hydroxyl group. The major weight loss occurred between 250°C and 380°C. When the absorbed dose increased from 0 to 500 kGy, the onset temperature of the depolymerization and decomposition of MCC decreases from 310°C to 240°C and the terminative temperature reduced from 380°C to 340°C. At the same

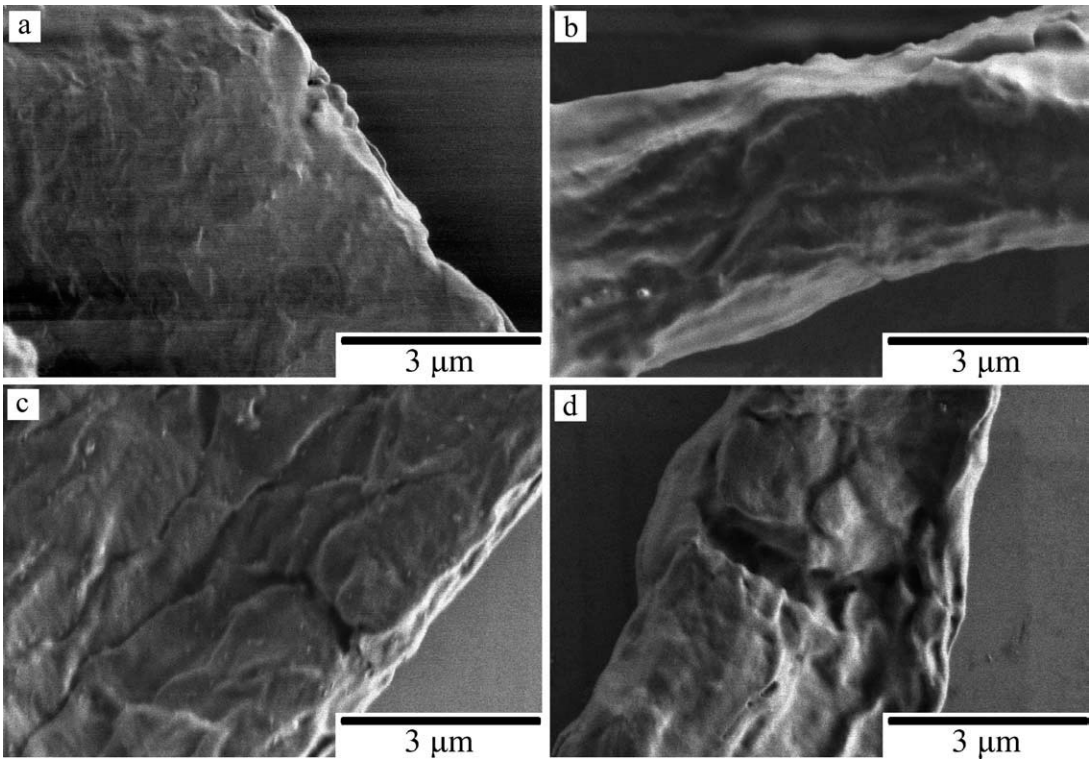

Figure 7. SEM images of MCC before irradiation (a,b) and after irradiation with 500 kGy (c,d).

Table II. Particle-Size and Specific Surface Area of Irradiated MCC Crushed by Jet Mill

Absorbed dose	0 kGy	50 kGy	100 kGy	150 kGy
Specific surface area (m^2/cm^3)	0.653	0.899	0.923	0.923
$d_{(0.5)}$ (μm)	16.008	12.186	11.637	11.589

time, the DTA peaks became wider and moved to the lower temperature region.

Figure 6 shows the dependence of absorbed dose on the peak temperature T_D at which the rate of degradation reaches the maximum value. It can be noticed that the T_D decreased with the increase of absorbed dose, which is coincident with the effect of absorbed dose on DP. The reduction of DP is the main reason for the degeneration of thermal stability of MCC.[24] The slight decreasing in crystallinity as observed in XRD also decreased the thermal stability of irradiated MCC. DTA peaks became wider because of the presence of a large number of low molecular weight fragments, random distributed cleavages, and breakdowns of anhydroglucose units in cellulose chains.[8,25,26] The radiation degradation not only decreased the DP of MCC but also lead to the wider distribution of molecular weight. This result also reflected the randomicity of the radiation degradation.

SEM Analysis

The surface morphology of MCC before and after irradiation was visualized by SEM and shown in Figure 7. Cracks and trenches can be clearly observed on the surface of the samples irradiated with 500 kGy, whereas the surface of original MCC was comparatively smooth. The cracks and trenches can be ascribed to the radiation degradation of MCC.[7]

To further study the effect of radiation on the structure of MCC, MCC samples irradiated with different absorbed doses were crushed by jet mill for once. The particle-sizes of the ultrafine samples were listed in Table II. The original particle size of MCC was 30 μm. When the absorbed dose increased from 0 to 50 kGy, the particle-sizes of the crushed ultrafine MCC decreased from 16 to 12 μm. The specific surface area increased concurrently. The results implied that radiation significantly influence the substantial structural and mechanical properties of MCC. However, the particle-sizes did not show a greater decline when the absorbed dose exceeding 100 kGy due to the ultimate ability of jet mill technology on ultrafine treatment.

CONCLUSIONS

γ-Irradiation caused the degradation of MCC, resulting in the reducing of DP and decrement of thermal stability. However, the crystalline structure of the MCC was not destroyed evidently. Radiation degradation led to the generation of carbonyl groups contained compound and increasing of reducing sugar content. Radiation influenced the structural and mechanical properties of MCC substantially, which favors for the ultrafine treatment. The radiation effects of cellulose such as decreasing of DP will benefit its further proceeding such as enzyme hydrolysis to yield bio-fuel.

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REFERENCES

1. Driscoll, M.; Stipanovic, A.; Winter, W.; Cheng, K.; Manning, M.; Spiese, J.; Galloway, R. A.; Cleland, M. R. *Radiat Phys Chem* **2009,** *78*, 539.
2. Yang, C. P.; Shen, Z. Q.; Yu, G. C.; Wang, J. L. *Bioresour Technol* **2008,** *99*, 6240.
3. Takacs, E.; Wojnarovits, L.; Foldvary, C.; Hargittai, P.; Borsa, J.; Sajo, I. *Radiat Phys Chem* **2000,** *57*, 399.
4. Xin, L. Z.; Kumakura, M. *Bioresour Technol* **1993,** *43*, 13.
5. Toth, T.; Borsa, J.; Takacs, E. *Radiat Phys Chem* **2003,** *67*, 513.
6. Foldvary, C. M.; Takacs, E.; Wojnarovits, L. *Radiat Phys Chem* **2003,** *67*, 505.
7. Takacs, E.; Wojnarovits, L.; Borsa, J.; Foldvary, C.; Hargittai, P.; Zold, O. *Radiat Phys Chem* **1999,** *55*, 663.
8. Khan, F.; Ahmad, S. R.; Kronfli, E. *Biomacromolecules* **2006,** *7*, 2303.
9. Hall, M.; Bansal, P.; Lee, J. H.; Realff, M. J.; Bommarius, A. S. *FEBS J* **2010,** *277*, 1571.
10. Phillips, G. O.; Williams, P. A., Eds. Handbook of Hydrocolloids; Woodhead Publishing Limited: Abington Cambridge, England, **2000.**
11. ISO5351/1. Cellulose in dilute solutions—Determination of limiting viscosity number. Part 1: Method in cupri-ethylene-diamine (CED) solution. **1981.**
12. Pala, H.; Mota, M.; Gama, F. M. *Carbohydr Polym* **2007,** *68*, 101.
13. Wang, D.; Shang, S. B.; Song, Z. Q.; Lee, M. K. *J Ind Eng Chem* **2010,** *16*, 152.
14. Oh, S. Y.; Yoo, D. I.; Shin, Y.; Kim, H. C.; Kim, H. Y.; Chung, Y. S.; Park, W. H.; Youk, J. H. *Carbohydr Res* **2005,** *340*, 2376.
15. Bommarius, A. S.; Katona, A.; Cheben, S. E.; Patel, A. S.; Ragauskas, A. J.; Knudson, K.; Pu, Y. *Metab Eng* **2008,** *10*, 370.
16. Ershov, B. G. *Usp Khim* **1998,** *67*, 353.
17. Takacs, E.; Wojnarovits, L.; Foldvary, C.; Borsa, J.; Sajo, I. *Res Chem Intermed* **2001,** *27*, 837.
18. Kumar, S.; Gupta, R.; Lee, Y. Y.; Gupta, R. B. *Bioresour Technol* **2010,** *101*, 1337.
19. Zhang, L. P.; Chen, G. W.; Tang, H. W.; Cheng, Q. Z.; Wang, S. Q. *J Appl Polym Sci* **2009,** *112*, 550.
20. Schwanninger, M.; Rodrigues, J. C.; Pereira, H.; Hinterstoisser, B. *Vib Spectrosc* **2004,** *36*, 23.

21. Yang, G. S.; Zhang, Y. P.; Wei, M. Y.; Shao, H. L.; Hu, X. C. *Carbohydr Polym* **2010,** *81*, 114.
22. Ek, R.; Wormald, P.; Ostelius, J.; Iversen, T.; Nystrom, C. *Int J Pharm* **1995,** *125*, 257.
23. Schultz, T. P.; McGinnis, G. D.; Bertran, M. S. J. *Wood Chem Technol* **1985,** *5*, 543.
24. Bouchard, J.; Abatzoglou, N.; Chornet, E.; Overend, R. P. *Wood Sci Technol* **1989,** *23*, 343.
25. Basak, R. K.; Saha, S. G.; Sarkar, A. K.; Saha, M.; Das, N. N.; Mukherjee, A. K. *Text Res J* **1993,** *63*, 658.
26. Qua, E. H.; Hornsby, P. R.; Sharma, H. S. S.; Lyons, G. *J Mater Sci* **2011,** *46*, 6029.