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Influence of γ -ray radiation on the structure and properties of paper grade bamboo pulp

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ABSTRACT

Paper grade bamboo pulp with high molecular weight was irradiated in air by 60 Co γ -ray to improve its dissolving property in N-methylmorpholine-N-oxide monohydrate (NMMO·H₂O). The effects of γ -ray radiation on the structure and properties of the bamboo cellulose were investigated. The results showed that the bamboo cellulose with a G(s) value of 0.94 μ mol J⁻¹ was easily degraded by the 60 Co γ -ray radiation. When the radiation dose increased, the average degree of polymerization ($\overline{\rm DP}$) of bamboo cellulose was decreased and its molecular weight distribution (MWD) became narrow, while its crystalline structure did not change obviously. Consequently, a spinning dope with high cellulose concentration and good spinnability was obtained in the range of absorbed dose from 5 to 10 kGy. This work presented an economic method to prepare regenerated bamboo cellulose fiber from paper grade bamboo pulp.

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1. Introduction

Bamboo cellulose fiber is a novel kind of fiber developed in recent years. Compared to the fibers from cotton and wood, the bamboo cellulose fiber has significantly different properties, such as good abrasion resistance, good drapability, good dyeing property, soft, cool, comfortable feelings, and lustrous looking (Shen, Liu, Gao, & Chen, 2004). Moreover, it has a delicate bamboo smell, negative ion effect, and anti-bacteria property (Yang, Zhang, Shao, & Hu, 2009). At present, the production of regenerated bamboo cellulose fiber has already been industrialized in China by using traditional viscose process. However, the viscose process has serious pollution problem and requires paper grade bamboo pulp to be denaturalized to obtain a low degree of polymerization (DP) and high content of α -cellulose for easy dissolving and spinning (Kim, Kim, Kwak, Ko, & Kwon, 2006). Hence, it is neither economical nor environmentally friendly for producing regenerated bamboo cellulose fiber.

Lyocell process is a simple and environmentally friendly process for the production of regenerated cellulose fiber. It adopts *N*-meth-ylmorpholine-*N*-oxide monohydrate (NMMO·H₂O), a non-toxic solvent, to directly dissolve cellulose and then uses a dry-jet wet spinning method to spin Lyocell fiber (Chanzy, Paillet, & Hagège, 1990; Fink, Weigel, Purz, & Ganster, 2001; Loubinoux & Chaunis, 1987; Thomas, Antje, Herbert, & Paul, 2001). Furthermore, it does

not require high α -cellulose content pulp as viscose process does. In contrast, an appropriate amount of hemicellulose in the pulp can improve the spinnability, the dyeing property and the antifibrillation property of resultant fiber (Duchesne et al., 2001). Therefore, we only need to decrease the DP of the paper grade bamboo pulp by a pre-degradation process before spinning regenerated bamboo cellulose fiber by using Lyocell process. Normal degradation methods for cellulose are acid hydrolysis degradation (Håkansson, Germgård, & Sens, 2005), oxidative degradation (Dollimore & Hoath, 1987), alkaline degradation (Berggren, Molin, Berthold, Lennholm, & Lindström, 2003), enzymatic degradation (Eriksson, Malmsten, & Tiberg, 2005; Ishigakia, Suganob, & Ikec, 2002), etc. All these methods require complicated process control and discharge lots of waste water. Compared to these regular methods, high energy radiation technique is simpler, cheaper and has no discharge of waste water (Andrzej, Mohammad, & Shamshad, 2005; Kawano & Amadeu, 1995). It is also effective for reducing molecular weight of different polymers including natural polymer such as cellulose and chitosan (Stepanik, Ewing, & Whitehouse, 2000; Stepanik, Rajagopal, Ewing, & Whitehouse, 1998; Ulanski & Rosiak, 1992). In order to obtain the bamboo pulp with good spinnability for Lyocell process, it is important to choose proper irradiation conditions. In this paper, paper grade bamboo pulp with high DP was irradiated by 60 Co γ -ray. Then viscosimetry and gel permeation chromatography (GPC) were used respectively to characterize the molecular weight (MW) and the molecular weight distribution (MWD) of the bamboo cellulose before and after irradiation. The crystalline structure was studied by Fourier

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transform infrared spectroscopy (FTIR) and wide-angle X-ray diffraction (WAXD). Moreover, the influences of γ -ray radiation on the dissolving property and the spinnability were evaluated.

2. Experimental

2.1. Materials

Paper grade bamboo pulp (sulfate pulp) was provided by Sichuan Yaan Zhongzhu Paper Group (Sichuan, China). N,N-Dimethylacetamide (DMAc) was obtained from Fluka (HPLC Grade; Buchs, Switzerland). Lithium chloride (LiCl; analytical reagent grade), methanol (HPLC grade) and polystyrene standards with MWs of 1.3×10^4 , 6.55×10^4 , 1.85×10^5 , 6.68×10^5 , 1.01×10^6 and 2.54×10^6 were purchased from Waters (Milford, MA, USA), and N-methylmorpholine-N-oxide (NMMO) aqueous solution (50 wt%) was obtained from BASF (Germany).

2.2. Radiation treatment of paper grade bamboo pulp

Samples of bamboo pulp with 10 wt% of water were irradiated in air by γ -ray from cobalt-60 source with a dose rate of 1.3 kGy/ h in Shanghai Institute of Applied Physics, Chinese Academy of Sciences. The doses were 0, 5, 10, 30, 60 kGy, respectively, and the treated samples were coded as 0#, 1#, 2#, 3#, 4#, accordingly.

2.3. MW and MWD analysis

2.3.1. Viscosimetry method

Bamboo cellulose pulp was dissolved in cuprammonium hydroxide solution. The viscosity of the solution was measured by an Ubbelohde viscometer with an inner diameter of 0.6 mm capillary in 25 °C. The specific viscosity (η_{sp}) and the viscosityaverage degree of polymerization $(\overline{DP_v})$ were calculated according to Eqs. (1) and (2), respectively:

$$\eta_{\rm sp} = (t_i - t_0)/t_0,\tag{1}$$

$$\overline{\mathrm{DP_{v}}} = \frac{2000\eta_{\mathrm{sp}}}{C \times \left(1 + 0.29\eta_{\mathrm{sp}}\right)},\tag{2}$$

where t_0 is the efflux time of the original cuprammonium hydroxide solution, t_i is the efflux time of the bamboo cellulose cuprammonium hydroxide solution and C is the weight percent of the bamboo cellulose in cuprammonium hydroxide solution.

2.3.2. GPC

2.3.2.1. Bamboo cellulose dissolution. Ten milligrams of the bamboo cellulose sample and 5 ml of distilled water were mixed in a 10 ml centrifugal tube and were left overnight to allow the sample to be swollen thoroughly. The sample was centrifuged at 4000 rpm for 15 min, then the supernatant was decanted and 5 ml of methanol (MA) was added into the tube. After 15 min of stirring and 30 min of placement, the centrifugation and decantation were repeated. The above procedure of methanol exchange was then repeated two more times, and followed by a similar procedure of DMAc exchange for three times. Finally, 1.25 ml of 8% (wt/vol) LiCl/DMAc was added into the tube to dissolve the cellulose completely by 60 s of stirring and 48 h of placement. The solution was then diluted to 0.5 mg/ml with DMAc and was filtered through a 0.45 µm Acrodisc membrane filter (Gelman Sciences Ltd., Ann Arbor, MI, USA) (Jerosch, Lavedrine, & Cherton, 2001; Silva, Arene, & Laver, Murry, 1997).

2.3.2.2. GPC analysis. The MWDs for the bamboo pulps were determined by GPC in a liquid chromatography (1525, Waters, Milford, MA, USA) with a refractive index detector (2410, Waters, Milford, MA, USA). The mobile phase of 0.5% (wt/vol) LiCl/DMAc was pumped into the system at a flow rate of 1 ml/min. Columns were Ultrastyragel 10³, 10⁴ and 10⁵ (Waters, Milford, MA, USA) preceded by a guard column. The system was operated at 50 °C controlled by a Waters column temperature system. The injection volume was 200 µl and the run time was 45 min. A linear calibration curve was constructed with polystyrene standards (MW = 2.54 M - 13 K) dissolved directly in 0.5% (wt/vol) LiCl/DMAc. Data acquisition and MWD calculations were performed using Breeze software (Ver. 3.2, Waters, Milford, MA, USA).

2.4. α-Cellulose content analysis

Bamboo pulp was firstly dried to a constant weight at 60 °C under vacuum. Two grams of the bamboo pulp (w_0) was then treated in 30 ml of NaOH aqueous solution with a concentration of 17.5 wt% at 20 °C for 45 min. Afterwards, the mixture was diluted by adding 30 ml distilled water with following stirring for 1–2 min. The liquid of the mixture was then removed by filtration. The remainder filtered was neutralized via additional washing with water. Finally, the remainder was dried to a constant weight (w_1) in a drying cabinet. The α -cellulose contents in bamboo pulps were calculated according to Eq. (3)

$$\alpha$$
-cellulose (%) = $\frac{w_0 - w_1}{w_0} \times 100$. (3)

2.5. Crystal structure analysis

2.5.1. Wide-angle X-ray diffraction (WAXD)

WAXD measurements were performed on a D/Max-2550PC diffractometer (Rigaku Corporation, Tokyo, Japan) under the following experimental conditions: Cu $K\alpha$ wavelength = 0.154 nm, 40 kV voltage, 300 mA current, 10°/min scanning speed, and 5- 50° scanning scale (2 θ). The obtained data were analyzed using a Peakfit software (Ver. 4.12, Seasolve Software Inc., Framingham, MA, USA) to calculate the crystallinity (α) and crystalline index (CrI) according to Eqs. (4) and (5), respectively:

$$\alpha \ (\%) = \frac{S_c}{S_c + S_a} \times 100\%, \tag{4}$$

$$CrI = \frac{I_{002} - I_{am}}{I_{002}}, \tag{5}$$

$$CrI = \frac{I_{002} - I_{am}}{I_{occ}},\tag{5}$$

where S_c and S_a are the crystalline area and the amorphous area, respectively. I_{002} is the maximum intensity (in arbitrary units) of the 002 lattice diffraction and $I_{\rm am}$ is the intensity of amorphous diffraction at about 18° of 2θ .

2.5.2. FTIR analysis

Infrared spectra were taken on a NEXUS-670 FTIR spectrophotometer (Nicolet Instrument Corp., Madison, WI, USA) in the range of the wavelength from 4000 to 400 cm⁻¹. Samples were prepared as a thin film with potassium bromide. The obtained spectra were the result of 24 scans at the resolution of 4 cm^{-1} .

2.6. Spinning process of the regenerated bamboo fiber

A NMMO aqueous solution of 50 wt% was concentrated to 74 wt% by vacuum distillation. The distilled solution and bamboo pulp were mixed and stirred in a dissolving tank at 100 °C. At the same time, a vacuum distillation was performed again until the molar ratio of NMMO to water reached 1:1, then a brown-yellow cellulose solution was prepared. The obtained cellulose solution with different cellulose content (from 6% to 14%) as a spinning dope, of which the viscosity was determined with a NDJ-7 rotary viscosimeter (Shanghai Tianping Instrument Corp., China) at 90 °C, was extruded through a spinneret with 100 orifices (each orifice was 80 μ m in diameter) at 100 °C by a metering pump. The extrudates were drawn in an air gap of 50 mm in length and in a coagulation bath (5 wt% NMMO aqueous solution, 20 °C), which flowed in a funnel-shaped device with a velocity of about 90 m/min below the air gap. Afterward, the as-spun fibers were immersed in a second coagulation bath with the same composition and temperature as the first bath. The precipitated filaments were then washed with water of about 40 °C, and taken up at 100 m/min prior to air drying.

2.7. Mechanical properties measurements of fibers

The mechanical properties of the fibers were measured with an XQ-1 tensile tester (China Textile University, Shanghai, China). The gauge length was 20 mm, and the extension rate was set at 5 mm/min. The statistical results came from more than 20 measurements for each specimen at 20 $^{\circ}\text{C}$ and 65% relative humidity.

3. Results and discussions

3.1. Effect of γ -radiation on the average degree of polymerization for bamboo cellulose

The viscosity-average degree of polymerization for bamboo pulp irradiated with different doses was determined by cuprammonium hydroxide solution method, the results are shown in Fig. 1. It can be seen that the $\overline{\rm DP_v}$ was decreased continuously with increasing absorbed dose. This implies that the bamboo cellulose was degraded with the degree of irradiation. The degradation was more significant at low radiation doses (less than 15 kGy). Furthermore, Fig. 1 shows a good linear relationship between $\frac{1}{{\rm DP_v}}$ and the absorbed doses (D), which corresponds well with Eq. (6)

$$\frac{1}{\overline{DP}_v} = 9.38 \times 10^{-4} + 7.87 \times 10^{-4} D. \tag{6} \label{eq:6}$$

It was known that the relationship between $\frac{1}{DP_y}$ and D was linear only when the MWD was close to random for typical radiation degradation of polymer (Dole, 1972). Therefore, it could be thought that the original bamboo cellulose has a random MWD.

Since the molecular weight of the repeat unit of cellulose is 162, Eq. (6) can be transformed to Eq. (7) accordingly:

$$\frac{10^5}{\overline{M}_{v}} = 0.58 + 0.49D,\tag{7}$$

where *D* is the absorbed dose with a unit of 10 kGy, $\overline{M_v}$ is viscosity-average molecular weight.

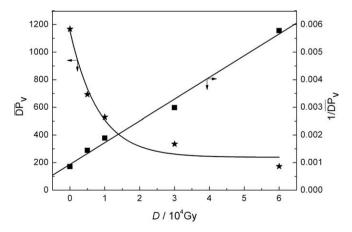


Fig. 1. Dependence of average degree of polymerization $(\overline{DP_v})$ and $1/\overline{DP_v}$ on the absorbed dose (D).

Eqs. (6) and (7) indicate that the $\overline{DP_v}$ or the $\overline{M_v}$ of irradiated bamboo cellulose related with the absorbed dose. Consequently, we can obtain the bamboo cellulose samples with expected \overline{DP} or MW by controlling the absorbed dose during irradiation.

3.2. Radiation chemical yield of chain scission for bamboo cellulose

Radiation chemical yield, G(s), represents the number of radiolysis events caused by the absorption of 100 eV of radiation. It expresses the degradation susceptibility of the polymer during radiation and can be calculated by the following equation (Nagasawa, Mitomo, Yoshii, & Kume, 2000):

$$N_{\rm A}/\overline{M_{\rm n}} = N_{\rm A}/\overline{M_{\rm n}^0} + G(s)D \times 6.25 \times 10^{17},$$
 (8)

where $M_{\rm n}^0$, $\overline{M_{\rm n}}$ are number average molecular weights of the polymer before and after degradation, respectively. $N_{\rm A}$ is Avogadro constant, D is the absorbed dose with a unit of 10 kGy. When the MWD of the polymer is a random distribution, the relation between $\overline{M_{\rm n}}$ and $\overline{M_{\rm v}}$ can be expressed with a gamma function $\Gamma(\alpha+1)$ (Flory, 1953), namely,

$$\overline{M_{\rm v}}/\overline{M_{\rm n}} = [(\alpha + 1)\Gamma(\alpha + 1)]^{1/\alpha},\tag{9}$$

where α is the exponential constant in Mark–Houwink equation, which is 0.81 in our case (Liu, 1985). Since MWD of bamboo cellulose was near random distribution as discussed in Section 3.1, thus, $\overline{M_{\nu}}/\overline{M_{n}}$ of 1.91 was obtained and Eq. (8) was re-expressed as:

$$\frac{10^5}{\overline{M_v}} = \frac{10^5}{\overline{M_v^0}} + 0.054G(s)D. \tag{10}$$

By comparison of Eq. (10) and Eq. (7), it can be obtained that G(s) of the bamboo cellulose was 0.94 μ mol J⁻¹, which indicates that the bamboo cellulose was easily degraded by ⁶⁰Co γ -ray radiation. Therefore, it is possible and economical to degrade the bamboo cellulose by irradiation method.

3.3. Effect of $\gamma\text{-radiation}$ on the MW and the MWD of the bamboo cellulose

The MW and the MWD changes of the bamboo cellulose during irradiation process were also investigated by GPC method. The results are shown in Table 1 and Fig. 2. The data obtained from the cuprammonium hydroxide solution method were also listed in Table 1 and were compared with the data obtained from GPC method. It can be seen that the relative molecular weights of bamboo celluloses determined by the two methods were different, but the tendency was accordant. Namely, the relative average molecular weight decreased with the increasing of the absorbed dose. Hence, although the data obtained from GPC are relative values due to using polystyrene standards in this study, the GPC method is still effective to investigate the influence of γ -ray radiation on the molecular weight and its distribution of bamboo cellulose.

Fig. 2 shows the differential MWDs for bamboo cellulose samples irradiated with different absorbed doses. It can be seen that the MWD of all bamboo cellulose samples were asymmetrical and a blended peak composed of peaks corresponding low, moderate and high MW components was found. Moreover, the MWD shifted to the low MW region and became narrow with the increasing of radiation dose. One of the possible reasons is that the degradation of the bamboo cellulose was random and high energy ray penetrated both amorphous and crystal regions of bamboo cellulose. As a result, the cellulose molecules in different regions had same probabilities to react with the high energy ray. For the high MW components, their degradation probabilities during the irradiation process were higher than these of the low and moderate components due to their long chain.

Table 1The comparison of the results obtained from GPC and cuprammonium hydroxide solution method.

Sample No.	Absorbed dose (kGy)	GPC method				Cuprammonium hydroxide solution method	
		$\overline{M}_n~(\times 10^4)$	$\overline{M}_{\rm W}~(\times 10^4)$	$M_{\rm p}~(\times 10^4)$	$D = \overline{M}_{\sf w}/\overline{M}_{\sf n}$	\overline{DP}_{v}	$\overline{M}_{\rm v}^{\rm a} (\times 10^4)$
0#	0	25.20	152.5	278.5	6.05	1168	18.92
1#	5	20.97	112.0	180.0	5.34	693	11.23
2#	10	18.78	86.5	71.6	4.61	529	8.57
3#	30	16.19	51.1	47.8	3.16	335	5.43
4#	60	11.64	26.9	27.5	2.31	173	2.80

 $^{^{}m a}$ $\overline{M}_{
m v}$ is the viscosity-average molecular weight determined by the cuprammonium hydroxide solution method.

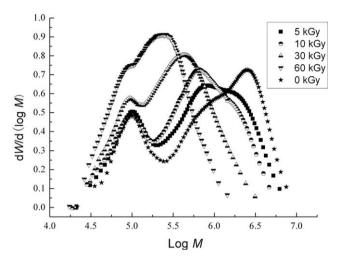


Fig. 2. The differential MWDs for paper grade bamboo pulp irradiated with different doses.

3.4. Effect of γ -radiation on the α -cellulose content in bamboo cellulose pulp

Fig. 3 shows the relationship between α -cellulose content and irradiation dose. It can be seen that the influence of irradiation on α -cellulose content is small when the irradiation dose is less than 15 kGy, but the α -cellulose content decreases obviously with increasing irradiation dose above 15 kGy. As mentioned before, the bamboo pulp used in our study consists of low, moderate and high MW components. The radiation degradation probabilities for high MW components are higher than those of the low and moderate MW components due to their long chain. Therefore, the high MW

components were firstly degraded to low, moderate MW components in the early stages of the irradiation process. As a result, no obvious change of $\alpha\text{-cellulose}$ content was observed when the irradiation dose is less than 15 kGy. However, when the dose is above 15 kGy, the degradation reaction might occur mainly in the low and moderate MW components. The resultant smaller cellulose molecules and complex plycan increase the hemicellulose content and decrease the $\alpha\text{-cellulose}$ content in the pulp.

3.5. Effect of γ -radiation on the supermolecular structure of the bamboo cellulose

3.5.1. X-ray diffraction analysis

3.5.1.1. Crystalline forms analysis. It is well known that all crystalline forms of cellulose belong to monoclinic crystal system, therefore the locations of characterization peaks for cellulose I can be calculated by Bragg equation from known lattice parameters of cellulose I. 2θ values of 101, $10\overline{1}$ and 002 lattices are 14.8°, 16.6° and 22.7°, respectively (Liu, Hu, & Zhang, 1998).

Fig. 4 shows the X-ray diffraction spectra of bamboo cellulose samples irradiated with different absorbed doses. The locations of the characterization peaks of the bamboo cellulose were obtained by deconvoluting the spectra with Peakfit software. The results were listed in Table 2. It can be noticed that the crystalline forms of the bamboo cellulose irradiated by $^{60}\text{Co}~\gamma\text{-ray}$ did not change and still belonged to cellulose I.

3.5.1.2. Crystallinity analysis. The crystallinity and crystalline index were calculated by foregoing Eqs. (4) and (5) after the WAXD spectra were deconvoluted. From the results listed in Table 2, it can be seen that the crystallinity and crystalline index of the bamboo cellulose had no obvious change before and after radiation. This indicates that the crystalline structures of the bamboo cellulose were

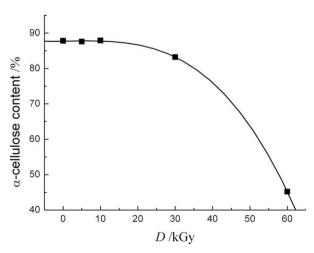


Fig. 3. Relationship between α -cellulose content and irradiation dose (*D*).

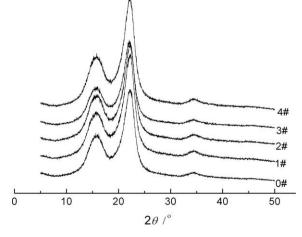


Fig. 4. X-ray diffraction spectra of paper grade bamboo pulp irradiated with different doses: 0 kGy (0#), 5 kGy (1#), 10 kGy (2#), 30 kGy (3#), and 60 kGy (4#).

Table 2Characterization peaks and crystalline parameters of paper grade bamboo pulp irradiated with different doses obtained from WAXD and FTIR experiments.

Sample No.	Location of cha	Location of characterization peak, 2θ (°)			Crystalline index (%)	K_1
0#	14.79	16.20	22.25	75.16	82.12	1.1883
1#	14.90	16.31	22.28	75.57	83.30	1.1305
2#	15.00	16.19	22.16	75.48	82.73	1.2618
3#	15.37	16.45	22.23	75.59	82.22	1.1739
4#	15.05	16.28	22.27	75.19	83.13	1.2208

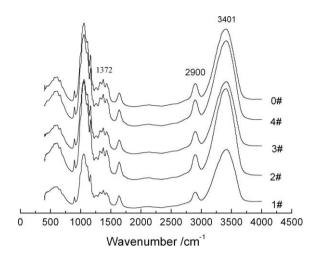


Fig. 5. IR spectra of paper grade bamboo pulp irradiated with different doses: 0 kGy (0#), 5 kGy (1#), 10 kGy (2#), 30 kGy (3#), and 60 kGy (4#).

not destroyed evidently, though the DP greatly decreased during irradiation in the range of our experiment conditions. Moreover, this further proved that the degradation of bamboo cellulose was random and high energy ray could penetrate both crystal and amorphous regions of the bamboo cellulose.

3.5.2. FTIR analysis

Fig. 5 shows the IR spectra of the bamboo cellulose irradiated with different absorbed doses. The relative crystallinity of cellulose was usually characterized using crystalline index (K_1) which could be calculated by the following equation provided by Nelson and O'Connor for cellulose I and cellulose II (Nelson & O'conner, 1964):

$$K_1 = a_{1372}/a_{2900}, (11)$$

where a_{1372} is the absorbance intensity at $1372~{\rm cm}^{-1}$ band associated with symmetric C–H bending from methoxyl group, a_{2900} is the absorbance intensity at $2900~{\rm cm}^{-1}$ associated with the C–H stretching vibration. The calculated K_1 of the bamboo cellulose are listed in Table 2. The results show that the relative crystallinity did not change obviously, and that is consistent with the above results from WAXD.

3.6. Effect of γ -radiation on the dissolving property and the spinnability of the bamboo cellulose

The dissolving property and the spinnability of the bamboo pulp irradiated with different doses were investigated. The results are presented in Table 3. The data indicate that a spinning dope with higher cellulose content and improved spinnability could be prepared via proper irradiation. It is also deduced from the viscosity shown in Table 3 that degraded pulp allows a higher cellulose content in solution. However, too large dose of irradiation resulted in excessive degradation of the cellulose and high hemicellulose content in the bamboo pulp. Consequently, for the pulp irradiated by 30 kGy, the spinnability became deteriorative and the fiber could not be obtained due to the too low viscosity causing overflow of the dope on the spinneret, when the cellulose content was 11%. Although the viscosity of the dope was enhanced by increasing the cellulose content from 11% to 14%, the filaments were drawn to break easily at the high flow velocity of the coagulation bath (ca. 90 m/min) in the bunching device. This might be due to the less effective chain entanglements resulted from the lower DP. Thus no fibers were also obtained even the cellulose content was 14%. The optimum dose for fiber spinning might ranges from 5 to 10 kGy in our experiment. Furthermore, the fibers made from the bamboo pulp irradiated by 5 kGy showed a tensile strength, a modulus and a elongation at break of 3.4 cN/dtex, 55.0 cN/dtex and 6.1%, respectively. These values are higher than those of the fibers made from the bamboo pulp irradiated by 10 kGy (a tensile strength of 3.2 cN/dtex, a modulus of 42.6 cN/dtex and a elongation at break of 6.0%). The data indicate that the fibers could be applied in many fields, including apparel industry.

4. Conclusions

The results presented in this paper show that the bamboo cellulose with a G(s) value of 0.94 μ mol J⁻¹ was easily degraded by ⁶⁰Co γ -ray radiation. Since the average DP or the relative MW of the bamboo cellulose was the function of the absorbed dose, we could easily obtain the bamboo cellulose with expectant DP by controlling the absorbed dose of radiation. With increasing absorbed dose, the average DP decreased and the MWD became narrow. The results from WAXD and FTIR show that the crystalline structures of the bamboo cellulose were not destroyed when the absorbed dose of irradiation ranging from 0 to 60 kGy. Since the average DP of the bamboo cellulose decreased greatly after irradiation, it was easier

Table 3The dissolving property and the spinnability of the bamboo cellulose by irradiation treatment.

Sample No.	Cellulose content (wt%)	Viscosity (Pas)	Dissolution time (h)	Appearance of spinning dope	Spinnability
0#	6	>1000	7.5	Brown-yellow, translucent	Poor spinnability, a small quantity of fibers obtained at low take-up velocity
1#	11	720	4.5	Brown-yellow, transparent	Good spinnability, fiber obtained continuously at a take-up velocity of 100 m/min
2#		650	4.5		
3#		230	4.5		Could not obtain fiber
3#	14	620	4.5		

for the irradiated bamboo cellulose pulp to be dissolved in NMMO·H $_2$ O. Consequently, a spinning dope with higher concentration and good spinnability could be obtained to prepare a bamboo cellulose fiber by Lyocell process in the range of absorbed dose from 5 to 10 kGy.

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References

- Andrzej, G. C., Mohammad, H.-S., & Shamshad, A. (2005). Progress in radiation processing of polymers. Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms. 236(1-4), 44-54.
- Berggren, R., Molin, U., Berthold, F., Lennholm, H., & Lindström, M. (2003). Alkaline degradation of birch and spruce: Influence of degradation conditions on molecular mass distributions and fibre strength. Carbohydrate Polymers, 51(3), 255–264.
- Chanzy, H., Paillet, M., & Hagège, R. (1990). Spinning of cellulose from *N*-methylmorpholine *N*-oxide in the presence of additives. *Polymer*, 31(3), 400–405
- Dole, M. (1972). The radiation chemistry of macromolecules. New York: Academic Press.
- Dollimore, D., & Hoath, M. J. (1987). The kinetics of the oxidative degradation of cellulose and cellulose doped with chlorides. *Thermochimica Acta*, 121, 273–282.
- Duchesne, I., Hult, E., Molin, U., Daniel, G., Iversen, T., & Lennholm, H. (2001). The influence of hemicellulose on fibril aggregation of kraft pulp fibres as revealed by FE-SEM and CP/MAS 13C-NMR. Cellulose, 8(2), 103–111.
- Eriksson, J., Malmsten, M., & Tiberg, F. (2005). Enzymatic degradation of model cellulose films. *Journal of Colloid and Interface Science*, 284(1), 99–106.
- Fink, H. P., Weigel, P., Purz, H. J., & Ganster, J. (2001). Structure formation of regenerated cellulose materials from NMMO-solutions. *Progress in Polymer Science*, 26(9), 1474–1476.
- Flory, P. J. (1953). *Principles of polymer chemistry*. Ithaca, New York: Cornell University Press.

- Håkansson, H., Germgård, U., & Sens, D. (2005). Influence of xylan on the degradability of laboratory kraft pulps from hardwood and reed canary grass in acid hydrolysis. *Cellulose*, 12(6), 621–628.
- Ishigakia, T., Suganob, W., & Ikec, M. (2002). Effect of UV irradiation on enzymatic degradation of cellulose acetate. *Polymer Degradation and Stability*, 78(3), 505-510.
- Jerosch, H., Lavedrine, B., & Cherton, J. C. (2001). Study of the stability of celluloseholocellulose solutions in *N,N*-dimethylacetamide–lithium chloride by size exclusion chromatography. *Journal of Chromatography A*, 927(1–2), 31–38.
- Kawano, Y., & Amadeu, J. M. Logarei (1995). X-ray induced degradation of regenerated cellulose membrane films. *Polymer Degradation and Stability*, 50(1), 125–130.
- Kim, I. S., Kim, J. P., Kwak, S. Y., Ko, Y. S., & Kwon, Y. K. (2006). Novel regenerated cellulosic material prepared by an environmentally-friendly process. *Polymer*, 47(4), 1333–1339.
- Liu, R. Q. (1985). The basic chemistry of cellulose. Beijing: Science Press.
- Liu, R. G., Hu, X. C., & Zhang, T. L. (1998). Transformation of crystalline structure of linter pulp during dissolving in NMMO·H₂O. Journal of China Textile University, 24(4), 7–10.
- Loubinoux, D., & Chaunis, S. (1987). An experimental approach to spinning new cellulose fibers with N-methylmorpholine-oxide as a solvent. *Textile Research Journal*, 57, 61–65.
- Nagasawa, N., Mitomo, H., Yoshii, F., & Kume, T. (2000). Radiation-induced degradation of sodium alginate. *Polymer Degradation and Stability*, 69(3), 279–285.
- Nelson, M. L., & O'conner, R. T. (1964). Relation of certain infrared bands to cellulose crystal lattice type. *Journal of Applied Polymer Science*, 8(3), 1130–1135.
- Shen, Q., Liu, D. S., Gao, Y., & Chen, Y. (2004). Surface properties of bamboo fiber and a comparison with cotton linter fibers. *Colloids and Surfaces B: Biointerfaces*, 35(3-4), 193-195.
- Silva Arene, A., & Laver Murry, L. (1997). Molecular weight characterization of wood pulp cellulose: Dissolution and size exclusion chromatographic analysis. *Tappi Journal*, 80(6), 173–180.
- Stepanik, T. M., Ewing, D. E., & Whitehouse, R. (2000). Electron treatment of wood pulp for the viscose process. Radiation Physics and Chemistry, 57(3-6), 377-379.
- Stepanik, T. M., Rajagopal, S., Ewing, D. E., & Whitehouse, R. (1998). Electronprocessing technology: A promising application for the viscose industry. *Radiation Physics and Chemistry*, 52(1–6), 505–509.
- Thomas, R., Antje, P., Herbert, S., & Paul, K. (2001). The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process). *Progress in Polymer Science*, 26(9), 1765–1774.
- Ulanski, P., & Rosiak, J. M. (1992). Preliminary studies on radiation induced changes in chitosan. *Radiation Physics and Chemistry*, 39(1), 53–57.
- Yang, G. S., Zhang, Y. P., Shao, H. L., & Hu, X. C. (2009). A comparative study of bamboo Lyocell fiber and the other regenerated cellulose fibers. *Holzforschung*, 63, 18–22.