



# Article Effect of Irradiation Process on Physical and Chemical Properties and Mildew Resistance of Bamboo

Shengfeng Mao <sup>1,2,†</sup>, Zhuchao Xu <sup>2,†</sup>, Qiuyi Wang <sup>2</sup>, Xin Han <sup>2</sup>, Xinzhou Wang <sup>2</sup>, Meiling Chen <sup>2,\*</sup> and Yanjun Li <sup>1,2,\*</sup>

- <sup>1</sup> School of Forestry and Biotechnology, Bamboo Industry Institute, Zhejiang A&F University, Hangzhou 311300, China; maosf@126.com
- <sup>2</sup> Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources,
- College of Materials Science and Engineering, Nanjing Forestry University, Nanjing 210037, China Correspondence: meiling\_chen@njfu.edu.cn (M.C.); lalyj@njfu.edu.cn (Y.L.)
- + These authors contributed equally to this work.

**Abstract:** With the scarcity of wood resources and calls for "substituting bamboo for wood" and "substituting bamboo for plastic", bamboo has gained greater popularity for its abundant reserves and outstanding mechanical properties. However, Mildew is a common problem for bamboo, which can significantly reduce the quality and service lives of bamboo products. In this work, a safe, eco-friendly, controllable and efficient method of gamma-ray irradiation was used to modify bamboo. The irradiation dose, moisture content (MC), and irradiation dose rate were adopted as factors of an orthogonal experiment. The results showed that the bamboo strips reached their best mechanical properties under the condition of irradiation at 150 KGy doses, moisture content of 40%, and irradiation dose rate of 44 KGy/H. In addition, the change in the chemical composition of bamboo and mildew resistance was also explored in this paper. The major chemical components (cellulose, hemicellulose and lignin), as well as starch, were degraded, and the bamboo strips exhibited excellent mildew resistance after gamma-ray irradiation.

**Keywords:** gamma ray irradiation; bamboo; physical properties; chemical composition; mildew resistance

# 1. Introduction

Due to the constant growth of the world's economy and population, the demand for wood and wood-based composites is rapidly increasing [1]. However, the supply of wood is diminishing as a result of the global need for biomass to generate green energy [2,3]. Bamboo is a taxonomic group of tall grasses with woody jointed stems [4]. Generally, bamboo can reach 3–30 m in 4 to 6 months and mature in 3 to 6 years [5,6]. It can be found extensively in the tropics and subtropics of Asia., especially in China, where the bamboo forest area has reached 6.41 million hectares, ranking among the top in the world [7,8]. Most importantly, bamboo is lightweight, high-strength, tough, and cost-effective, and its products have low carbon emissions throughout their entire lifecycle [9–11]. Therefore, bamboo and its products and pipelines [12–14]. However, bamboo contains a lot of nutrients such as starch, protein, and polysaccharide, making it susceptible to fungus during processing, transportation and use [15,16]. Therefore, the modification of bamboo is particularly crucial for its efficient utilization.

At present, chemical and physical modifications are constantly reported to improve the performance of bamboo [17–20]. By coating, impregnating, pressing, heating and other measures, chemical modifiers can be added to the bamboo and react with its major content, thus improving its service life and properties effectively [21–25]. However, chemical modifiers often contain toxic agents or heavy metal ions, which have poor leaching resistance and can



Citation: Mao, S.; Xu, Z.; Wang, Q.; Han, X.; Wang, X.; Chen, M.; Li, Y. Effect of Irradiation Process on Physical and Chemical Properties and Mildew Resistance of Bamboo. *Forests* **2023**, *14*, 1055. https:// doi.org/10.3390/f14051055

Academic Editor: Zeki Candan

Received: 20 April 2023 Revised: 7 May 2023 Accepted: 18 May 2023 Published: 20 May 2023



**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). cause certain harm to the environment and human health during their application [26–28]. Therefore, a series of improvements have been made to promote their performance, but their cost is too high to industrialize [29,30]. As one of the most widely used physical modifications in current industrial production, heat treatment is a process that bamboo undergoes when heated to a specific temperature for a certain amount of time [31–33]. It has been proved that the mechanical properties of bamboo can be enhanced under a certain temperature and heat treatment duration [34–36]. However, excessive temperature and heat treatment duration greatly reduce the strength of bamboo [37,38]. In addition, heat treatment is prone to generate a large amount of waste during processing [23,39]. Therefore, it is urgent to develop a safe, eco-friendly and industrialized method for promoting the mechanical properties and mildew resistance of bamboo.

The gamma-ray irradiation technique uses radioactive elements, such as <sup>60</sup>Co, to produce gamma rays to provide sterilization, inhibition or the promotion of growth, and modification of material properties [40–42]. As early as the 1970s, it was found that gamma rays from <sup>60</sup>Co could activate and excite molecules, ultimately leading to chain breakage and depolymerization or chain cross-linking reactions, which were beneficial for cross-linking with monomers and wood [43]. In recent years, it has been found that gamma-ray irradiation can produce some active particles in the main components of wood's cell walls, causing a series of changes in wood properties such as molecular structure and hygroscopicity, mechanical strength, and dimensional stability [44–47]. At the same time, researchers have also reported that gamma-ray irradiation can reduce the fiber structure of bamboo [48,49]. However, a systematic study of the physicochemical properties and mildew resistance of bamboo under gamma-ray irradiation has not yet been reported.

Here, we hypothesize that gamma rays could improve the mechanical properties as well as mildew resistance of bamboo. Therefore, an orthogonal experiment  $(L_9(3^3))$  was used to examine the effects of the irradiation dose, MC, and irradiation dose rate on the physical and chemical properties and the mildew resistance of bamboo strips. Environmental scanning electron microscopy (ESEM) was used to study changes in the microstructure of bamboo, while methods such as the National Renewable Energy Laboratory (NREL) method, X-ray diffractometer (XRD), and Fourier transform infrared spectroscopy (FT-IR) were used to study changes in its chemical composition. This study has a certain guiding significance for the industrial gamma irradiation treatment of bamboo.

## 2. Materials and Methods

# 2.1. Material

Six-year-old Moso bamboo culms (*Phyllostachys pubescens*) were purchased from Jiangxi Zhuangchi Home Technology Co. (Fuzhou, China). The bamboo culms were cut at a height of 1.5–2.0 m above the ground. Then, the bamboo culms were cut into an average dimension of 1100 mm  $\times$  20 mm  $\times$  5 mm (L  $\times$  T  $\times$  R) cm<sup>3</sup>. After removing the bamboo outer and inner layers, ten groups of bamboo strips were prepared. The orthogonal experiments were conducted with nine groups, and the remaining group was the control group.

#### 2.2. Method

#### 2.2.1. Gamma-Ray Irradiation

Gamma-ray irradiation treatment was carried out at Anhui Union Radiation Chemical., Ltd. (Hefei, China). The radiation source is  $^{60}$ Co-gamma radiation source with 0.7 million curies. The schematic diagram of gamma-ray irradiation treatment is illustrated in Figure 1, where Irradiation dose (KGy), MC (%), and irradiation dose rate (KGy/h) were selected as the factors of the L<sub>9</sub>(3<sup>3</sup>) orthogonal experiment. Each factor included three levels, as shown in Table 1. The orthogonal experiment results were analyzed by the analysis of variance (ANOVA). Six bamboo strips were treated for each group. The results were averaged.



Figure 1. The schematic diagram of Moso bamboo under gamma ray irradiation treatment.

**Table 1.** Scheme of orthogonal experiment  $L_9$  (3<sup>3</sup>).

Level	A Irradiation Dose (KGy)	В МС (%)	C Dose Rate (KGy/h)
1	50	0	0.88
2	150	60	22
3	250	80	44

2.2.2. Mechanical Properties of Bamboo Strips

The untreated and gamma-ray irradiation-treated bamboo strips were processed into a dimension of  $160 \times 10 \times 5$  mm (L  $\times$  T  $\times$  R). The testing procedures for the modulus of elasticity (MOE), modulus of rupture (MOR) and tensile strength (TS) were performed according to the GB/T 15780-1995. These experiments were carried out on an electronic universal testing machine (UTM5105SLXY, Shenzhen Suns Co., Ltd., Shenzhen, China). All samples were kept under a  $65 \pm 3\%$  R.H.,  $25 \pm 3$  °C condition for 2 weeks before the test. Each experiment was repeated 15 times, and variance analysis was performed for significance.

## 2.2.3. FT-IR of Bamboo Strips

The variation in functional groups of bamboo was determined by the VERTEX-80 V (Bruker, Bremen, Germany) infrared spectrometer. It scanned 32 times from 500 to  $4000 \text{ cm}^{-1}$  with a resolution of 4 cm<sup>-1</sup>.

#### 2.2.4. XRD of Bamboo Strips

The crystallinity of bamboo was determined by diffractometer T-6000 (Malvern Panalytical, Malvern, UK). It scanned from  $5^{\circ}$  to  $50^{\circ}$  at a speed of  $2^{\circ}$ /min. The crystallinity (*Crl*) and lattice spacing of cellulose were calculated by Equations (1) and (2).

$$Crl = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$
(1)

$$n\lambda = 2d\sin\theta \tag{2}$$

where *Crl* is the relative crystallinity; *d* is the lattice spacing;  $I_{002}$  is the diffraction intensity of the crystal (002) plane;  $I_{am}$  is the diffraction intensity of amorphous; *n* is the diffraction series, which is one;  $\lambda$  is the wavelength, which is 0.15406 Å;  $\theta$  is the peak position.

## 2.2.5. Major Chemical Composition Determination

The untreated and gamma-ray irradiation-treated bamboo strips were ground into 40~60 mesh powder for the determination. The relative content of major chemical compositions was measured according to the NREL method. The starch content was determined according to TAPPI's T419 Starch in the paper.

## 2.2.6. Surface Morphologies Characterization

The untreated and gamma-ray irradiation-treated bamboo strips were cut into  $10 \times 5 \times 5$  mm (L  $\times$  T  $\times$  R) for ESEM (Quanta 200, FEI, Eindhoven, Holland) for observation. The morphologies of the samples were observed with magnification from  $800 \times$  to  $1600 \times$ .

## 2.2.7. Mass Loss

The bamboo strips used to measure the mass loss were treated in an oven dry. The mass loss after gamma-ray irradiation could be calculated by Equation (3):

$$W = \frac{w_1 - w_2}{w_1} \times 100\%$$
(3)

where *W* is the mass loss ratio;  $w_1$  represents the mass of the untreated bamboo strip, and  $w_2$  represents the mass of the gamma-ray irradiation-treated bamboo strip. Each experiment was repeated 5 times.

## 2.2.8. Water Absorption Thickness Expansion Rate

The water absorption thickness expansion rate after 24 h was tested according to GB/T 17657-2013. The water absorption thickness expansion rate could be calculated according to Equation (4):

$$T = \frac{t_2 - t_1}{t_1} \times 100\% \tag{4}$$

where *T* is the water absorption thickness expansion ratio,  $t_1$  is the thickness of the bamboo strips before being immersed in water, and  $t_2$  is the thickness of the bamboo strips after being immersed in water for 3 days.

## 2.2.9. Mildew Resistance

The mildew resistance test was tested according to GB/T 18261-2013. The area of mildew infection was measured by Image Pro Plus (Media Cybernetics Inc., Sliver Spring, MD, USA). The infection value was calculated and evaluated according to Equation (5) and Table 2, respectively:

$$E = \left(1 - \frac{D_1}{D_0}\right) \times 100\% \tag{5}$$

where *E* is the control efficacy, %;  $D_1$  is the average infection value of the gamma-ray irradiation bamboo strips, and  $D_0$  is the average infection value of untreated bamboo strips.

Table 2. Rating	for the	infection	value	of mold	growth on	bamboo.
					()	

Rate	Area Infected with Bamboo Strips
0	No visible growth
1	Mold covering up to $1/4$ of the surface
2	Mold covering between $1/4$ and $1/2$ of the surface
3	Mold covering between $1/2$ and $3/4$ of the surface
4	Mold on greater than $3/4$ of the surface

## 3. Result and Discussion

3.1. Effect of Gamma-Ray Irradiation Treatment on Physical and Mechanical Properties of Bamboo

The results of the orthogonal experiment for mechanical properties are presented in Table 3. As shown in Table 3, when R1, R2, and R3 were the evaluation indices, the three factors, A, B, and C, had different impacts, with A being the most influential, followed by C and then B. The optimal combination of process parameters for bamboo was  $A_2C_2B_3$  (150 KGy-0%-44 KGy/h), the irradiation dose was 150 KGy, the moisture content was 40%, and the irradiation dose rate was 44 KGy/H. The range analysis of MOR, MOE, and TS is presented in Tables 4–6, respectively. It can be seen from Tables 4–6 that at the 5% significance level, the irradiation dose had a significant effect on the MOR, MOE, and TS of bamboo strips and was the main influencing factor.

#### Table 3. Results of orthogonal experiments and results.

		Factors				
Experimental Number	A (Irradiation Dose KGy)	B (Moisture Content %)	C (Irradiation Rate KGy/h)	R1 (MPa)	R2 (MPa)	R3 (MPa)
1	1	1	1	105.33	8.36	108.11
2	1	2	2	106.63	8.63	110.00
3	1	3	3	108.94	8.88	114.25
4	2	1	2	114.65	9.02	110.14
5	2	2	3	122.14	9.29	116.67
6	2	3	1	110.93	8.86	113.12
7	3	1	3	80.23	7.91	70.67
8	3	2	1	79.55	8.09	72.05
9	3	3	2	70.06	7.91	64.05
X <sub>1</sub> (R <sub>1</sub> )	106.97	99.74	98.60			
$X_2(R_1)$	115.91	102.78	97.11			
$X_{3}(R_{1})$	76.28	96.64	103.44			
R (R <sub>1</sub> )	39.63	6.13	6.33			
X <sub>1</sub> (R <sub>2</sub> )	8.62	8.39	8.42			
$X_2$ (R <sub>2</sub> )	9.02	8.65	8.48			
X <sub>3</sub> (R <sub>2</sub> )	7.95	8.55	8.69			
R (R <sub>2</sub> )	1.07	0.26	0.28			
X <sub>1</sub> (R <sub>3</sub> )	110.79	96.31	97.76			
$X_2 (R_3)$	113.31	99.57	94.73			
X <sub>3</sub> (R <sub>3</sub> )	68.92	97.14	100.53			
R (R <sub>3</sub> )	44.39	3.27	5.80			

Sources of Variance	Sum of Squares for Deviations	Degrees of Freedom	Mean Square	F-Value	Significance
А	2591.77	2	1295.89	323.01	* 1
В	56.44	2	28.22	7.04	
С	65.60	2	32.80	8.18	
Error Sum	8.02 2721.83	2	4.01		

Table 4. Analysis of variance for MOR.

<sup>1</sup> "\*" Indicates significant difference.

Table 5. Analysis of variance for MOE.

Sources of Variance	Sum of Squares for Deviations	Degrees of Freedom	Mean Square	<b>F-Value</b>	Significance
А	1.76	2	0.88	53.39	* 1
В	0.10	2	0.05	3.03	
С	0.12	2	0.06	3.79	
Error	0.03	2	0.01		
Sum	2.01				

<sup>1</sup> "\*" Indicates significant difference.

Table 6. Analysis of variance for TS.

Sources of Variance	Sum of Squares for Deviations	Degrees of Freedom	Mean Square	F-Value	Significance
Α	3729.03	2	1864.51	374.87	* 1
В	17.31	2	8.66	1.74	
С	50.43	2	25.22	5.07	
Error Sum	9.95 3806.72	2	4.97		

<sup>1</sup> "\*" Indicates significant difference.

With the increasing irradiation dose, the MOR and MOE of the bamboo increased initially and then decreased. Under the condition of irradiation dose at 150 KGy, the MOR of the bamboo reached a maximum value of 122.1 MPa, which was 17.29% higher than that of the untreated bamboo. This may be due to the fact that hemicellulose partially degraded and produced a small amount of acetic acid at lower irradiation doses [50,51]. Under acidic conditions, lignin and cellulose underwent cross-linking reactions, which enhanced the intermolecular forces between those components [48]. This increased the strength of the cell wall and restricted its movement perpendicular to the grain. With the increase in the irradiation dose, the MOR reached its minimum value of 70.06 MPa, which was decreased by 13.45% from that of the untreated bamboo. Lignin degraded, and the benzene ring structure was destroyed under high irradiation doses [43]. Thus, cellulose lost its support from lignin. Hemicellulose was degraded and produced a large amount of acetic acid. Cellulose degradation was accelerated under strongly acidic conditions [52]. In addition, the degradation of hemicellulose also weakened its binding strength with cellulose and lignin, which led to a decrease in MOR [53]. Compared with the effect of irradiation treatment on MOR, the change in MOE was relatively small. MOE increased at lowdose irradiation treatment due to amorphous cellulose crystallization [54]. Therefore, the stiffness of the bamboo increased, which resulted in an increase in MOE [55,56]. With further increases in the irradiation dose, the chemical composition of the bamboo decomposed significantly, resulting in a drastic decline in the MOE of the bamboo [54].

The TS of bamboo showed an increasing tendency and was followed by a decrease as the radiation dose increased. The tensile strength of bamboo reached a maximum value of 116.67 MPa at a radiation dose of 150 KGy, which was 12.75% higher than that of untreated bamboo. This could be due to the esterification reaction of lignin, which enhanced the weak

interfacial properties of bamboo and thus improved its mechanical strength [57]. As the radiation dose increased, the lignin degradation rate exceeded its cross-linking rate due to the side chain cleavage of benzene rings.

# 3.2. Effect of Gamma-Ray Irradiation Treatment on the Chemical Composition of Bamboo

Figure 2A presents the FT-IR curves of untreated and gamma-ray irradiation-treated bamboo strips. The peak at 3400 cm<sup>-1</sup> and 2900 cm<sup>-1</sup> was assigned to the OH stretching vibration and C-H stretching vibration groups, respectively. With the increase in the irradiation dose, the peak intensity of functional groups at 3400 cm<sup>-1</sup> and 2900 cm<sup>-1</sup> decreased. This might have resulted from cellulose degradation and the free hydroxyl (–OH) polymerizes, which formed aldehyde, ketone or carboxyl groups [18]. The peak at 1240 cm<sup>-1</sup> and 1740 cm<sup>-1</sup> was assigned to the C–O strength vibration peak and the C=O stretching vibrations of hemicelluloses, respectively. The intensity of these peaks at 1240 cm<sup>-1</sup> and 1740 cm<sup>-1</sup> decreased significantly due to the degradation of hemicellulose by deacetylation reaction [32]. The peaks at 1513 cm<sup>-1</sup>, 1600 cm<sup>-1</sup>, and 1423 cm<sup>-1</sup> were the skeletal vibrations of the benzene ring [58]. With the increase in the irradiation dose, the peak at 1513 cm<sup>-1</sup>, 1601 cm<sup>-1</sup>, and 1423 cm<sup>-1</sup> decreased, which indicates the degradation of lignin.



**Figure 2.** Chemical composition variation in bamboo before and after irradiation treatment. (**A**). FT-IR curves of untreated and gamma ray irradiation-treated bamboo; (**B**). XRD curves of untreated and gamma ray irradiation-treated bamboo.

The XRD curves of untreated and gamma ray irradiation-treated bamboo were demonstrated in Figure 2B. The (002) plane of cellulose crystal was responsible for the diffraction peak at  $22.00^{\circ}$ , while the (101) and (101) planes of cellulose corresponded to the peak at  $15.60^{\circ}$ .

Table 7 shows the variation in the cellulose crystal of untreated and gamma-ray irradiation-treated bamboo strips. The difference between the diffraction angles of gamma-ray irradiation-treated and untreated samples is negligible, indicating that gamma-ray irradiation did not alter the crystalline structure of the bamboo fibers. The relative crystallinity of cellulose reached a maximum value of 46.31% at 150 KGy, which increased by 5.72% compared with the untreated bamboo strips. This could have been due to the dehydration condensation of the hydroxyl groups; thus, the amorphous region of cellulose was turned into a crystalline region [59–61]. When the irradiation dose increased to 250 KGy, the relative crystallinity of cellulose reached a minimum value of 43.05. With the increase in the irradiation dose, acetyl groups of hemicellulose were hydrolyzed to form acetic acid [50]. The crystalline region of cellulose degraded under acidic conditions [52].

<b>2θ/</b> °	<b>Relative Crystallinity/%</b>	Lattice Spacing/nm
21.82	43.82	4.07
21.96	43.61	4.04
21.88	45.72	4.06
21.90	44.00	4.06
21.73	44.43	4.09
21.84	46.31	4.07
21.80	46.10	4.07
21.52	43.46	4.13
21.45	43.73	4.14
21.07	43.05	4.21
	<b>2θ/°</b> 21.82 21.96 21.88 21.90 21.73 21.84 21.80 21.52 21.45 21.07	20/° Relative Crystallinity/%   21.82 43.82   21.96 43.61   21.88 45.72   21.90 44.00   21.73 44.43   21.84 46.31   21.80 46.10   21.52 43.46   21.45 43.73   21.07 43.05

Table 7. The variation in the cellulose crystal of untreated and gamma ray irradiation treated bamboo strips.

The normalized relative content of the major chemical components of the untreated and treated bamboo strips are presented in Figure 3. The results show that with the increase in the irradiation dose, the relative content of hemicellulose decreased significantly. When the irradiation dose reached 250 KGy, the relative content of hemicellulose decreased by 40.03%. This indicates that gamma-ray irradiation could enhance the degradation of hemicellulose. The degradation of hemicellulose might improve the dimensional stability, as well as the antifungal and anti-mildew properties of bamboo products [62]. Although the FT-IR results showed that cellulose and lignin degraded, the relative content of lignin and cellulose increased with the increase in the irradiation dose. This increase in the relative content of lignin and cellulose may have resulted from the fact that the degradation of hemicellulose was much larger than that of cellulose and lignin. As the major chemical component of bamboo, cellulose plays a supporting role, and lignin provides bamboo hardness and rigidity [36]. At lower irradiation doses, gamma rays could not damage the structure of cellulose. Meanwhile, cross-linking reactions between cellulose and lignin improved the mechanical properties of bamboo [48]. With the increase in the irradiation dose, cellulose was degraded significantly, which resulted in a deterioration in the mechanical properties of bamboo [63].



**Figure 3.** The relative content of the major chemical components of the untreated and gamma ray irradiation-treated bamboo strips.

# 3.3. Effect of Gamma-Ray Irradiation Treatment on the Morphology of Bamboo

The morphology of untreated bamboo in the radial section is shown in Figure 4. The parenchyma cell wall of the untreated bamboo was rough with a large number of starch granules, as shown in Figure 4A. Figure 4B presents the morphology of bamboo after gamma-ray irradiation treatment. The cell wall of bamboo became smooth and had no



starch granules in the parenchyma cells' lumen. This is attributed to the polysaccharide chain break caused by a high dose irradiation [64].

**Figure 4.** The morphological characteristics of the bamboo strips. SEM images for the untreated bamboo at  $800 \times$  (**A1**) and  $1600 \times$  (**A2**); SEM images for the gamma ray irradiation-treated bamboo at  $800 \times$  (**B1**) and  $1600 \times$  (**B2**); (**C**). Starch content for untreated and gamma ray irradiation-treated bamboo; (**D**). Weight loss ratio for untreated and gamma ray irradiation-treated bamboo.

The reduction in starch was also consistent with the results of the starch content in Figure 4C. After gamma-ray irradiation treatment, the starch content of bamboo was significantly decreased by 77.17%. This was due to the drastic vibration of the starch molecular chain caused by gamma rays and the relaxation of hydrogen bonds, which unwound the double helix structure and broke the starch polysaccharide chain, thereby reducing the starch content [65]. The degradation of starch may also improve the antifungal, antimildew and antibacterial properties.

Figure 4D displays the mass loss of the bamboo strips. The mass loss rate of the bamboo strips increased as the irradiation dose increased. When the irradiation dose reached 250 KGy, the mass loss rate of the bamboo strips reached 16.65%. During gamma irradiation treatment, the degradation of the chemical composition of bamboo was inevitable. This mainly resulted from the degradation of starch and hemicellulose under gamma-ray irradiation [54].

The results of the water absorption thickness expansion rate for both untreated and gamma-ray irradiation-treated bamboo strips are shown in Figure 5. It is obvious that the water absorption thickness expansion rate declined after gamma-ray irradiation. As the radiation dose increased, the water absorption thickness expansion rate decreased. This could be attributed to the degradation of cellulose and hemicellulose after gamma-ray irradiation which decreased the number of free hydroxyl groups [66]. The decrease in the free hydroxyl group led to a decrease in bamboo hygroscopicity. With the radiation of doses increasing, the number of free hydroxyl groups was reduced, as shown in the result of FT-IR (Figure 2A). The decrease in bamboo hygroscopicity was beneficial to the dimensional stability and mildew resistance of bamboo.



**Figure 5.** Water absorption thickness expansion rate for untreated and gamma ray irradiation-treated bamboo strips.

## 3.4. Effect of Gamma-Ray Irradiation Treatment on Mildew Resistance of Bamboo

*Aspergillus niger*, a normal fungus easily infected by bamboo, was used to investigate mildew resistance. Figure 6 shows the mildew resistance of the untreated and gamma-ray irradiation bamboo strips. It can be seen that untreated bamboo strips were prone to mildew infection. The mycelium of *Aspergillus niger* was observed on the sample on the second day. It only took eight days for *Aspergillus niger* mycelium to cover the entire surface of the untreated bamboo. However, the infection rate of mildew and the final infection rate of the bamboo strips were alleviated after gamma-ray irradiation treatment. With the increase in the irradiation dose, the control efficacy of bamboo strips increased significantly. When the radiation dose was 250 KGy, the control efficacy reached a maximum value of 75.4%. On the one hand, the degradation of starch and other nutrients by irradiation reduced the nutrient source required for fungus growth. On the other hand, the cross-linking reaction and hemicellulose degradation resulted in a significant reduction in the free hydroxyl group, which reduced the hygroscopicity of bamboo. In addition, gamma rays could pass through the bamboo strips easily and kill the hidden eggs and dormant spores of insects and fungi, destroying fungi growth and their reproduction [46].



Figure 6. Fungi infection of untreated and gamma ray irradiation-treated bamboo.

#### 3.5. Limitations and Economic Analysis

The durability of bamboo increased after gamma ray treatment which contributed to the long service life of bamboo products and could be used in furniture, construction and other applications. However, the characteristics of the bamboo surface influence the manufacturing process of bamboo products and product properties, including the bonding strength. In addition, radiation source has a limited-service life. It is also necessary to balance the treatment fee and product income. Above all, the effect of gamma-ray irradiation on manufacturing bamboo products and its economic feasibility needs to be further studied in the future.

### 4. Conclusions

In this study, gamma-irradiation was used to modify bamboo. The orthogonal experiment was used to systematically analyze the effects of the radiation dose (50 KGy-250 KGy), moisture content (0%-80%) and radiation dose rate (0.88 KGy/h-44 KGy/h) on the mechanical bamboo. The orthogonal experiment results indicated that the optimal process parameters for gamma-ray irradiation treatment were  $A_2C_2B_3$  (250 KGy-80%-44 KGy/h), while the worst processing parameters were A<sub>3</sub>C<sub>3</sub>B<sub>3</sub> (150 KGy-60%-44 KGy/h). In addition, the most significant factor in the MOR, MOE and TS of bamboo was the irradiation dose. The chemical property results revealed that the cellulose, hemicellulose and lignin were degraded, especially hemicellulose. The degradation of hemicellulose increased the relative content of cellulose and lignin. The XRD results showed that gamma-ray irradiation treatment could not change the crystal type of cellulose, and the relative crystallinity of cellulose increased first and then decreased. The mildew resistance of irradiation-treated bamboo was improved effectively. This was mainly due to the degradation of starch and the decrease in hygroscopicity, which destroyed mold growth and reproduction. In addition, future studies should concentrate on whether and how gamma-ray irradiation affects bamboo product performance, such as the effect of gamma-ray irradiation on the surface and gluing property of bamboo.

**Author Contributions:** S.M.: Methodology, Investigation, Formal analysis, Visualization, Writing—original draft; Z.X.: Writing—original draft, review and editing; Q.W.: Formal analysis, Visualization; X.H.: Investigation, Methodology; X.W.: Methodology; M.C.: Conceptualization, Supervision, Investigation, Writing—review and editing; Y.L.: Conceptualization, Supervision, Project administration, Funding acquisition, Writing—review and editing. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the project of the "14th Five-Year" National Key R&D Plan (2022YFD2200902), the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (22KJA220001), metasequoia teacher research of Nanjing Forestry University, the Nanjing Science and Technology Innovation Project for Overseas Students, and the Zhejiang A&F University Research and Development Fund Talent Launch Project.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

#### References

- Chaowana, P. Bamboo: An Alternative Raw Material for Wood and Wood-Based Composites. J. Mater. Sci. Res. 2013, 2, 90. [CrossRef]
- Fei, B.; Su, Q.; Liu, H.; Fang, C.; Ma, X.; Zhang, X.; Sun, F. Research Progress of Bamboo Winding Technology. J. For. Eng. 2022, 7, 25–33.
- Chen, M.; Ye, L.; Semple, K.; Ma, J.; Zhang, J.; Weng, Y.; Yan, H.; Fei, B.; Dai, C. A New Protocol for Rapid Assessment of Bond Durability of Bio-Based Pipes: Bamboo Winding Composite Pipe as a Case Study. *Eur. J. Wood Wood Prod.* 2022, 80, 947–959. [CrossRef]
- 4. Liese, W.; Köhl, M. Bamboo-The Plant and Its Uses; Springer: Berlin/Heidelberg, Germany, 2015; Volume 10, ISBN 978-3-319-14133-6.
- 5. Liese, W.; Weiner, G. Ageing of Bamboo Culms. A Review; Springer: Berlin/Heidelberg, Germany, 1996; Volume 30.
- 6. Yanjun, L.; Zhichao, L. Progress of Bamboo Flatten Technology Research. J. For. Eng. 2021, 6, 14–23.
- 7. Li, Y.; Feng, P. Bamboo Resources in China Based on the Ninth National Forest Inventory Data. World Bamboo Ratt. 2019, 17, 45–48.

- Zhu, W.; Han, M.; Kim, D.; Park, J.; Choi, H.; Kwon, G.; You, J.; Li, S.; Park, T.; Kim, J. Highly Catalytic and Durable Nanocellulose Fibers-Based Nanoporous Membrane Film for Efficient Organic Pollutant Degradation. J. Water Process Eng. 2023, 53, 103620. [CrossRef]
- Li, H.; Chen, M.L.; Hu, L.X.; Wang, X.; Gu, Z.C.; Li, J.Z.; Yang, Z. Bin Optimization Design of Bamboo Filament Decorated Board Process Based on Response Surface. *Bioresources* 2023, 18, 73–86. [CrossRef]
- Gan, J.; Chen, M.; Semple, K.; Liu, X.; Dai, C.; Tu, Q. Life Cycle Assessment of Bamboo Products: Review and Harmonization. *Sci. Total Environ.* 2022, 849, 157937. [CrossRef] [PubMed]
- 11. Chen, M.; Ye, L.; Li, H.; Wang, G.; Chen, Q.; Fang, C.; Dai, C.; Fei, B. Flexural Strength and Ductility of Moso Bamboo. *Constr. Build. Mater.* **2020**, *246*, 118418. [CrossRef]
- 12. Chen, M.; Troughton, G.; Dai, C. Optimum Veneer Peeling Temperatures for Selected Softwood Species Using Big Roller Bars. *Eur. J. Wood Wood Prod.* **2021**, *79*, 151–159. [CrossRef]
- Chen, M.; Weng, Y.; Semple, K.; Zhang, S.; Hu, Y.; Jiang, X.; Ma, J.; Fei, B.; Dai, C. Sustainability and Innovation of Bamboo Winding Composite Pipe Products. *Renew. Sustain. Energy Rev.* 2021, 144, 110976. [CrossRef]
- Lou, Z.; Yuan, C.; Li, Y.; Shen, D.; Yang, L.; Liu, J.; Zhang, A. Effect of Saturated Steam Treatment on the Chemical Composition and Crystallinity Properties of Bamboo Bundles. J. For. Eng. 2020, 5, 29–35.
- Li, X.; Peng, H.; Niu, S.; Liu, X.; Li, Y. Effect of High-Temperature Hydrothermal Treatment on Chemical, Mechanical, Physical, and Surface Properties of Moso Bamboo. *Forests* 2022, *13*, 712. [CrossRef]
- 16. Chen, F.; He, Y.; Wei, X.; Han, S.; Ji, J.; Wang, G. Advance in Strength and Toughness of Hierarchical Bamboo under Humidity and Heat. *J. For. Eng.* **2022**. [CrossRef]
- 17. Li, H.; Zhang, Q.; Wu, G.; Xiong, X.; Li, Y. A Review on Development of Laminated Bamboo Lumber. J. For. Eng. 2016, 1, 10–16.
- 18. Hao, X.; Wang, Q.; Wang, Y.; Han, X.; Yuan, C.; Cao, Y.; Lou, Z.; Li, Y. The Effect of Oil Heat Treatment on Biological, Mechanical and Physical Properties of Bamboo. *J. Wood Sci.* **2021**, *67*, 26. [CrossRef]
- 19. Chen, M.; Ye, L.; Wang, G.; Ma, X.; Chen, Q.; Fang, C.; Fei, B.; Dai, C. In-Situ Investigation of Deformation Behaviors of Moso Bamboo Cells Pertaining to Flexural Ductility. *Cellulose* **2020**, *27*, 9623–9635. [CrossRef]
- 20. Lou, Z.; Wang, Q.; Sun, W.; Liu, J.; Yan, H.; Han, H.; Bian, H.; Li, Y. Regulating Lignin Content to Obtain Excellent Bamboo-Derived Electromagnetic Wave Absorber with Thermal Stability. *Chem. Eng. J.* **2022**, *430*, 133178. [CrossRef]
- 21. Wang, K.; Peng, H.; Gu, Q.; Zhang, X.; Liu, X.; Dong, Y.; Cai, Y.; Li, Y.; Li, J. Scalable, Large-Size, and Flexible Transparent Bamboo. *Chem. Eng. J.* 2023, 451, 138349. [CrossRef]
- Chen, M.; Liu, R.; Wang, G.; Fang, C.; Ma, X.; Zhang, S.; Fei, B. Parenchyma Cell Morphological Changes of Bamboo under Bending. Sci. Silvae Sin. 2020, 56, 142–147.
- 23. Gao, J.; Qu, L.; Qian, J.; Wang, Z.; Li, Y.; Yi, S.; He, Z. Effects of Combined Acid-Alkali and Heat Treatment on the Physiochemical Structure of Moso Bamboo. *Sci. Rep.* **2020**, *10*, 6760. [CrossRef] [PubMed]
- Sharma, B.; Gatóo, A.; Ramage, M.H. Effect of Processing Methods on the Mechanical Properties of Engineered Bamboo. Constr. Build. Mater. 2015, 83, 95–101. [CrossRef]
- Wu, L.; Zhu, W.; Li, Z.; Li, H.; Xu, J.; Li, S.; Chen, M. Urushiol Modified Epoxy Acrylate as UV Spray Painting Oriental Lacquer Ink. RSC Adv. 2023, 13, 1106–1114. [CrossRef]
- 26. Wu, Z.; Huang, D.; Wei, W.; Wang, W.; Wang, X.; Wei, Q.; Niu, M.; Lin, M.; Rao, J.; Xie, Y. Mesoporous Aluminosilicate Improves Mildew Resistance of Bamboo Scrimber with CuBP Anti-Mildew Agents. *J. Clean. Prod.* **2019**, 209, 273–282. [CrossRef]
- Wu, L.; Chen, M.; Xu, J.; Fang, F.; Li, S.; Zhu, W. Nano-SiO<sub>2</sub>-Modified Waterborne Acrylic Acid Resin Coating for Wood Wallboard. *Coatings* 2022, 12, 1453. [CrossRef]
- Zhu, Y.; Zhu, W.; Li, Z.; Feng, Y.; Qi, W.; Li, S.; Wang, X.; Chen, M. Enhancement of Wood Coating Properties by Adding Silica Sol to UV-Curable Waterborne Acrylics. *Forests* 2023, 14, 335. [CrossRef]
- Liu, G.; Lu, Z.; Zhu, X.; Du, X.; Hu, J.; Chang, S.; Li, X.; Liu, Y. Facile In-Situ Growth of Ag/TiO<sub>2</sub> Nanoparticles on Polydopamine Modified Bamboo with Excellent Mildew-Proofing. *Sci. Rep.* 2019, *9*, 16496. [CrossRef]
- Zhu, W.; Kim, D.; Han, M.; Jang, J.; Choi, H.; Kwon, G.; Jeon, Y.; Yeol Ryu, D.; Lim, S.H.; You, J.; et al. Fibrous Cellulose Nanoarchitectonics on N-Doped Carbon-Based Metal-Free Catalytic Nanofilter for Highly Efficient Advanced Oxidation Process. *Chem. Eng. J.* 2023, 460, 141593. [CrossRef]
- Weng, B.; Wang, Z.; Wang, F.; Xu, R.; Cheng, D.; Zhang, K.; Hong, L.; Guo, Y.; Chen, Y. Synergistic Effect of Luffa Seed Oil and Microwave Treatment on the Physicochemical Properties of Bamboo Slices. *Ind. Crops Prod.* 2023, 192, 116033. [CrossRef]
- 32. Yuan, T.; Yin, X.; Huang, Y.; Li, X.; Wang, X.; Chen, L.; Li, Y. Hydrothermal Treatment of Bamboo and Its Effect on Nano-Mechanic and Anti-Mildew Property. J. Clean. Prod. 2022, 380, 135189. [CrossRef]
- 33. Li, Z.Z.; Luan, Y.; Hu, J.B.; Fang, C.H.; Liu, L.T.; Ma, Y.F.; Liu, Y.; Fei, B.H. Bamboo Heat Treatments and Their Effects on Bamboo Properties. *Constr. Build. Mater.* 2022, 331, 127320. [CrossRef]
- Yang, T.H.; Lee, C.H.; Lee, C.J.; Cheng, Y.W. Effects of Different Thermal Modification Media on Physical and Mechanical Properties of Moso Bamboo. *Constr. Build. Mater.* 2016, 119, 251–259. [CrossRef]
- 35. Tang, T.; Zhang, B.; Liu, X.; Wang, W.; Chen, X.; Fei, B. Synergistic Effects of Tung Oil and Heat Treatment on Physicochemical Properties of Bamboo Materials. *Sci. Rep.* **2019**, *9*, 12824. [CrossRef]
- Wang, Q.; Wu, X.; Yuan, C.; Lou, Z.; Li, Y. Effect of Saturated Steam Heat Treatment on Physical and Chemical Properties of Bamboo. *Molecules* 2020, 25, 1999. [CrossRef] [PubMed]

- Brito, F.M.S.; Paes, J.B.; da Silva Oliveira, J.T.; Arantes, M.D.C.; Vidaurre, G.B.; Brocco, V.F. Physico-Mechanical Characterization of Heat-Treated Glued Laminated Bamboo. *Constr. Build. Mater.* 2018, 190, 719–727. [CrossRef]
- Cheng, D.; Li, T.; Smith, G.D.; Xu, B.; Li, Y. The Properties of Moso Bamboo Heat-Treated with Silicon Oil. *Eur. J. Wood Wood Prod.* 2018, 76, 1273–1278. [CrossRef]
- Zhuang, X.; Zhou, W.; Hong, Y.; Li, W.; Pan, X.; Chen, S. Experiment on Pretreatment of Waste Water from Bamboo Heat Treatment by Combination of Iron-Carbon Micro-Electrolysis and Fenton Method. Nord. Pulp Pap. Res. J. 2019, 34, 354–361. [CrossRef]
- 40. Xu, Z.; Chen, L.; Zhou, B.; Li, Y.; Li, B.; Niu, J.; Shan, M.; Guo, Q.; Wang, Z.; Qian, X. Nano-Structure and Property Transformations of Carbon Systems under γ-Ray Irradiation: A Review. *RSC Adv.* **2013**, *3*, 10579–10597. [CrossRef]
- 41. Kawai, T.; Inoshita, T. Effects of Gamma Ray Irradiation on Growing Rice Plants—I: Irradiations at Four Main Developmental Stages. *Radiat. Bot.* **1965**, *5*, 233-IN11. [CrossRef]
- 42. Kim, S.; Jeong, J.O.; Lee, S.; Park, J.S.; Gwon, H.J.; Jeong, S.I.; Hardy, J.G.; Lim, Y.M.; Lee, J.Y. Effective Gamma-Ray Sterilization and Characterization of Conductive Polypyrrole Biomaterials. *Sci. Rep.* **2018**, *8*, 3721. [CrossRef]
- Zhang, C.Y.; Su, X.J.; Xiong, X.Y.; Hu, Q.L.; Amartey, S.; Tan, X.H.; Qin, W. 60Co-γ Radiation-Induced Changes in the Physical and Chemical Properties of Rapeseed Straw. *Biomass Bioenergy* 2016, *85*, 207–214. [CrossRef]
- Şolpan, D.; Güven, O. Preservation of Beech and Spruce Wood by Allyl Alcohol-Based Copolymers. *Radiat. Phys. Chem.* 1999, 54, 583–591. [CrossRef]
- Severiano, L.C.; Lahr, F.A.R.; Bardi, M.A.G.; Santos, A.C.; MacHado, L.D.B. Influence of Gamma Radiation on Properties of Common Brazilian Wood Species Used in Artwork. *Prog. Nucl. Energy* 2010, 52, 730–734. [CrossRef]
- 46. Kalawate, A.; Mehetre, S. Isolation and Characterization of Mold Fungi and Insects Infecting Sawmill Wood, and Their Inhibition by Gamma Radiation. *Radiat. Phys. Chem.* 2015, 117, 191–197. [CrossRef]
- Gérardin, P. New Alternatives for Wood Preservation Based on Thermal and Chemical Modification of Wood—A Review. *Ann. Sci.* 2016, 73, 559–570. [CrossRef]
- Chen, Z.; Yang, Y.; Li, Q.; Peng, Y.; Geng, D.; Huang, W. Effect of <sup>60</sup>Co-γ Ray on Structure and Absorption Performance of Bamboo Fiber. *Hubei For. Sci. Technol.* 2020, 49, 18–22.
- 49. Zhou, Y.; Fan, M.; Chen, L. Interface and Bonding Mechanisms of Plant Fibre Composites: An Overview. *Compos. B Eng.* **2016**, 101, 31–45. [CrossRef]
- Chen, J.; Wang, L.; Su, X.; Wang, K.; Wu, X.; Chen, L.; Xiong, X.; Zhou, H.; Liu, Y. Structure, Morphology, Thermostability and Irradiation-Mediated Degradation Fractions of Hemicellulose Treated with Γ-Irradiation. *Waste Biomass Valorization* 2016, 7, 1415–1425. [CrossRef]
- 51. Driscoll, M.S.; Stipanovic, A.J.; Cheng, K.; Barber, V.A.; Manning, M.; Smith, J.L.; Sundar, S. Ionizing Radiation and a Wood-Based Biorefinery. *Radiat. Phys. Chem.* **2014**, *94*, 217–220. [CrossRef]
- Ravinder, T.; Swamy, M.V.; Seenayya, G.; Reddy, G. Clostridium Lentocellum SG6—A Potential Organism for Fermentation of Cellulose to Acetic Acid. *Bioresour. Technol.* 2001, *80*, 171–177. [CrossRef]
- Zhang, X.; Yang, W.; Blasiak, W. Modeling Study of Woody Biomass: Interactions of Cellulose, Hemicellulose, and Lignin. *Energy Fuels* 2011, 25, 4786–4795. [CrossRef]
- 54. Sun, F.; Jiang, Z.; Sun, Q.; Lu, F. Changes in Chemical Composition and Microstructure of Bamboo after Gamma Ray Irradiation. *Bioresources* **2014**, *9*, 5794–5800. [CrossRef]
- Windeisen, E.; Strobel, C.; Wegener, G. Chemical Changes during the Production of Thermo-Treated Beech Wood. *Wood Sci.* Technol. 2007, 41, 523–536. [CrossRef]
- 56. Okano, T.; Ohta, M. Bending Strength and Toughness of Heat-Treated Wood. J. Wood Sci. 2000, 46, 8–15.
- 57. Chen, M.; Dai, C.; Liu, R.; Lian, C.; Yuan, J.; Fang, C.; Fei, B. Influence of Cell Wall Structure on the Fracture Behavior of Bamboo (*Phyllostachys Edulis*) Fibers. *Ind. Crops Prod.* **2020**, *155*, 112787. [CrossRef]
- 58. Wu, X.; Chen, L.; Chen, J.; Su, X.; Liu, Y.; Wang, K.; Qin, W.; Qi, H.; Deng, M. The Effect of <sup>60</sup>Co γ-Irradiation on the Structure and Thermostability of Alkaline Lignin and Its Irradiation Derived Degradation Products. *Waste Biomass Valorization* 2019, 10, 3025–3035. [CrossRef]
- 59. Cave, I.D. Theory of X-Ray Measurement of Microfibril Angle in Wood Part 1. The Condition for Reflection X-ray Diffraction by Materials with Fibre Type Symmetry; Springer: Berlin/Heidelberg, Germany, 1997; Volume 31.
- Yang, G.; Zhang, Y.; Wei, M.; Shao, H.; Hu, X. Influence of γ-Ray Radiation on the Structure and Properties of Paper Grade Bamboo Pulp. *Carbohydr. Polym.* 2010, *81*, 114–119. [CrossRef]
- Ma, X.; Zheng, X.; Zhang, M.; Yang, X.; Chen, L.; Huang, L.; Cao, S. Electron Beam Irradiation of Bamboo Chips: Degradation of Cellulose and Hemicelluloses. *Cellulose* 2014, 21, 3865–3870. [CrossRef]
- 62. Wang, Q.; Han, H.; Lou, Z.; Han, X.; Wang, X.; Li, Y. Surface Property Enhancement of Bamboo by Inorganic Materials Coating with Extended Functional Applications. *Compos. Part A Appl. Sci. Manuf.* **2022**, *155*, 106848. [CrossRef]
- 63. Liu, Z.; Sun, F.; Zhu, L. Radiation Techniques and Its Application to Wood Science. World For. Res. 2014, 27, 48–53.
- 64. Sun, F.; Jiang, Z.; Fei, B.; Yu, Z.; Wang, H. Effect of γ-Ray Application on Bamboo Mold Resistance. *China Wood Ind.* **2011**, *25*, 23–25.

- 65. Ghobashy, M.M.; Abd El-Wahab, H.; Ismail, M.A.; Naser, A.M.; Abdelhai, F.; El-Damhougy, B.K.; Nady, N.; Meganid, A.S.; Alkhursani, S.A. Characterization of Starch-Based Three Components of Gamma-Ray Cross-Linked Hydrogels to Be Used as a Soil Conditioner. *Mater. Sci. Eng. B* 2020, 260, 114645. [CrossRef]
- Yuan, T.; Wang, X.; Liu, X.; Li, Y. Dynamic Response of Arc-Shaped Bamboo Sheets during Flattening Process. Ind. Crops Prod. 2023, 192, 116073. [CrossRef]

**Disclaimer/Publisher's Note:** The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.