Effects of ultrasonic wave pretreatment on the fibrillation of cellulose fiber

YONGJIAN XU, YING YAN, XIAOPENG YUE, ZHENFENG ZHU, DINGJUN ZHANG, AND GUANGQIANG HOU

ABSTRACT: *Pinus massoniana* Lamb. was used as the raw cellulose fiber material to investigate effects of ultrasonic wave pretreatment and PFI pretreatment on fiber bonding and absorbability. Influences of ultrasonic wave pretreatment on fiber crystalline structure and hydrogen bonds were also analyzed by wide-angle X-ray diffraction and Fourier transform infrared (FTIR) spectroscopy. The absorption and internal bond strength of fiber pretreated by ultrasonic waves increased by 23.49% and 4.07%, respectively, in comparison with those of virgin fiber, which would result in the improvement of weak bonding and absorbability. Instead, when fiber was pretreated by PFI, absorption decreased in comparison with virgin fiber and internal bond strength increased as much as 1.33 times than that of virgin fiber. The analysis of wide-angle X-ray diffraction curves and FTIR spectroscopy curves revealed that the crystallinity of fiber decreased by 20.59% in comparison with that of virgin fiber when treated by ultrasonic waves. Moreover, the effect of ultrasonic wave pretreatment on intramolecular hydrogen bonds was rather stronger than that of intermolecular hydrogen bonds. Therefore, the optimal swelling ability of fiber would be obtained.

Application: Cellulose fiber for making absorbent material, such as fluff pulp, can be pretreated with ultrasonic waves to increase strength properties.

Cellulose, the most abundant renewable resource, is produced by nature at an annual rate of 10^{11}–10^{12} tons. It has been widely used for centuries in all kinds of practical applications, including paper, regenerated fiber, and cellulosic functional materials [1,2]. An important utilization of cellulose fiber is to make super-absorption materials, such as fluff pulp used in hygienic products. Generally, the process of making and using fluff pulp is quite complex. For example, if we choose bleached pulp as the raw material, it will be pretreated by certain equipment or additives according to the established technology. After that, the fluff pulp is delivered to the papermaking stage and made into fluff pulpboard so that it can be easily transported and stored. When the fluff pulpboard is used, it must be defibered in a dry condition [3]. Therefore, relatively weak bonding strength and appropriate absorbability of fluff pulp fibers are required [4,5]. In traditional processes, this was achieved by the addition of weak-bonding additives, such as debonder. However, weak bonding additives exhibit detrimental effects on the absorbability of the pulp [6–9]. The contradiction between weak bonding and fiber absorbability has been a critical problem for many years in the field of fluff pulp.

From the view of fiber bonding, cellulose fibers are connected by hydrogen bonds (2-OH…O-6, 3-OH…O-5, 6-O…HO-3') to obtain superior strength properties. When the hydrogen bonds were ruptured or generated, the released energy resulted in variations of cellulose fiber properties [10]. Normally, certain pretreatment methods, such as beating, were employed to change the connection status of hydrogen bonds so that we could obtain the cellulose materials that could achieve the production requirement. There are two fibrillation effects of cellulose fiber during the beating process: (1) the external fibrillation effect on the fiber surface and (2) the inner fibrillation effect. The effects of inner fibrillation on cellulose fiber can exhibit as more free hydroxyl groups, weakened rigidity, increased plasticity, and improved absorbability [11,12]. Consequently, an optimal pretreatment method, which would acquire sufficient inner fibrillation as much as possible with limited external fibrillation, can be used to improve the fluff pulp quality.

As an important pretreatment method, ultrasonic waves are widely used in many fields, such as organic synthesis [13], biochemistry [14], and petrochemical engineering [15]. It has been reported that ultrasonic wave treatment could change the structure of lignin macromolecules and accelerate the speed of hypochlorite bleaching reaction [16]. In addition, ultrasonic waves can transfer energy to pulp stock, thus inducing mechanical beating effects on pulp. According to the study by Huang [11], effects of ultrasonic wave treatment on cellulose fiber are similar to those of mechanical beating or refining. Displacement and deformation effects (i.e., inner

fibrillation of fiber cell walls), may occur during the ultrasonic wave treatment process. Simultaneously, the P and S1 layers of fiber cell walls can be reserved [12]. Li researched the ultrasonic effects on internal and external fibrillation and found that fibers became swollen and flexible when they were treated by ultrasonic waves [17]. Therefore, we can use ultrasonic wave treatment to balance inner and external fibrillation of the fiber. Furthermore, the contradiction between bonding and absorbability of fiber can be expected to be solved to a certain extent.

In this paper, the effects of ultrasonic wave pretreatment on the strengths and absorbability of cellulose fiber were investigated. In order to provide basic data to further investigation, the crystalline structure and hydrogen bonds of cellulose fiber were also analyzed by wide-angle X-ray diffraction and Fourier transform infrared (FTIR) spectroscopy.

EXPERIMENTAL

Raw material

Bleached kraft pulp, supplied by Feng Huang Co. Ltd. (Nanning, Guangxi, China), was chosen as the raw material.

Ultrasonic wave pretreatment and PFI pretreatment

Cellulose fiber was dispersed in water with a concentration of 2.0%. An ultrasonic transducer probe was dipped into the suspension slurry and ultrasonic waves were emitted into the suspension, producing beating action. A BILON-1200Y ultrasound generator (Xi'an Bi Lang Biotechnology Co. Ltd.; Xi'an, Shaanxi, China) was employed in the experiment. The ultrasonic wave pretreatment was performed by treating for 0.9 s at 2-s intervals for different times. Working power and frequency of the apparatus was 200W, 20±1KHz, respectively. Type of the ultrasonic transducer probe was ϕ20. After treatment, the suspension was washed with water and then concentrated using a vacuum pump (SHB-3, Zhengzhou Du Fu Apparatus Co. Ltd.; Zhengzhou, Henan, China).

A PFI beating apparatus (DCS-041PT, Kumagat Riki Kogyo Co. Ltd.; Tokyo, Japan) was used to pretreat the cellulose fiber with a concentration of 10.0%. Samples were obtained according to the beating degree of the pulp.

Water retention value and hornification determination

A centrifuge apparatus (LD4-2A, Beijing Medical Centrifugal Apparatus Factory; Beijing, China) was used to determine the water retention value (WRV) of cellulose fiber according to TAPPI Useful Method 256 "Water retention value (WRV)" and the method described in [18] at a centrifugal force of 2800 g (4000 rev/min) for 15 min.

X-ray diffraction analysis

A D/Max 2200PC (Rigaku Corp.; Tokyo, Japan) X-ray diffraction was used to analyze the crystalline degree of cellulose fiber samples with 5°/min scan speed. Nickel-filtered copper Kα radiation (k=0.154 nm) generated at a voltage of 40 kV was utilized [19].

The crystallinity (X_C) was analyzed by multipeaks-fitting method. The crystallite sizes were determined from the 101, $10\bar{1}$, 002 lattice planes of cellulose fiber samples, and then calculated using the Scherrer equation [20,21] (Eq. [1]):

$$D=\frac{k\lambda}{\beta\cos\theta} \quad (1)$$

where D is the crystal size, β is the breadth of the peak of a specific phase, k is a constant that varies from 0.89 to 1, λ is the wavelength of incident X rays, and 2θ is the corresponding Bragg angle [18,19].

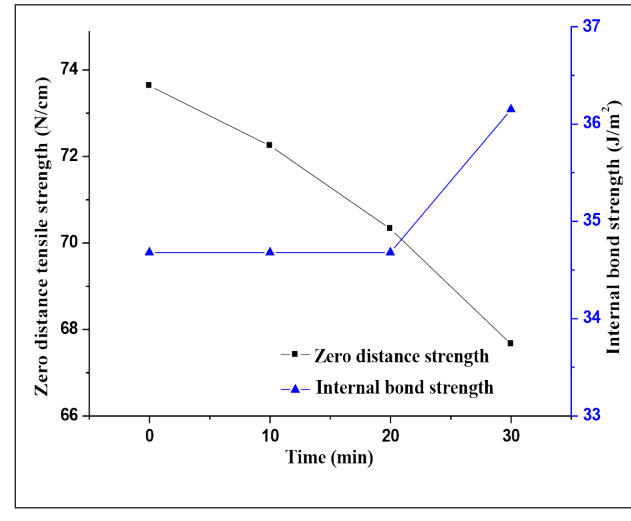
FTIR analysis

FTIR spectra were recorded using a VECTRO-22 (Bruker; Karlsruhe, Germany) FTIR spectrometer. The infrared crystallization index (N-O'KI)[22] was calculated using Eq. (2):

$$N-O'KI=\frac{a_{1372}}{a_{2900}} \quad (2)$$

where a_{1372} and a_{2900} are band intensity; 1372 cm^{-1} is C–H bending vibration, 2900 cm^{-1} is C–H, and CH_2 is stretching vibration.

The overlapped hydrogen peak in the 3700 cm^{-1}–3000 cm^{-1} wave number range was dealt with by applying the Gaussian multipeaks-fitting method to distribute it into three or four bands in Origin software (OriginLab; Northampton, MA, USA). Furthermore, the absorbance bands of intermolecular or intramolecular hydrogen bonds were confirmed by Fengel [23–25].



1. Effect of the ultrasonic wave pretreatment time on zero distance strength and internal bond strength.

RESULTS AND DISCUSSION

Effect of ultrasonic wave pretreatment on fiber strengths and absorbability

Zero distance strength, internal bond strength, absorption, and WRV of pulp fiber were detected in order to investigate changes of fiber strengths and absorbability. The results are shown in **Figs. 1** and **2**.

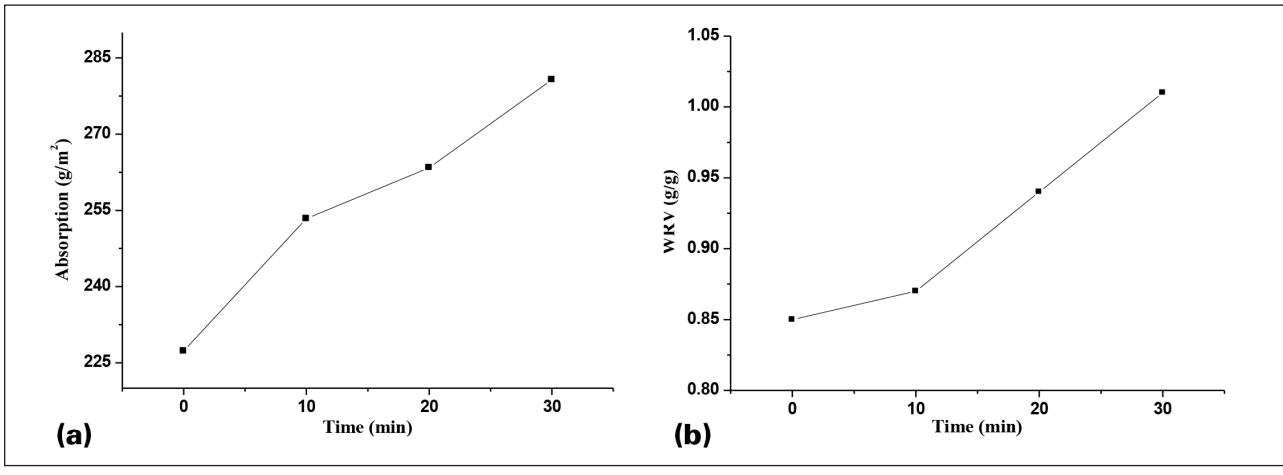
We can see in Fig. 1 that zero distance tensile strength of the fiber decreased with the increasing pretreatment time. The maximum value decreased 8.11% when fiber was treated for 30 min compared with that of virgin fiber. Internal bond strength was maintained to a certain level in the initial pretreatment stage; however, when the pretreatment time exceeded 20 min, internal bond strength exhibited a significant increase.

We can find in Fig. 2 that the absorption and WRV of the fiber increased with increasing pretreatment time. In comparison with that of virgin fiber, the maximum value of the absorption and WRV increased by 23.49% and 16.47%, respectively, when fiber was treated for 30 min. According to the study of Jayme and Rosenfeld [26], fiber would swell in water more easily when it was treated by ultrasonic waves. It is well known that WRV is a good indicator of fiber swelling and fibrillation [27]. The varied performance of fiber was mainly attributed to cavitation of ultrasonic waves. A proper fiber-water system was very important for cavitation to produce a strong beating action effect on fibers. Also, it had been researched that the stock consistency of 2.0% was probably suitable to ultrasonic frequency; intensive convective flows were being observed at this consistency [17]. The intensive convective flows generated by ultrasonic waves changes the properties of the interface diffusion layer in cellulose-water binary system, which can accelerate penetration speed of water into fiber [28]. As a result of ultrasonic wave pretreatment, concentric layers among fiber secondary cell walls slid, cohesion decreased, and absorbability increased significantly [11].

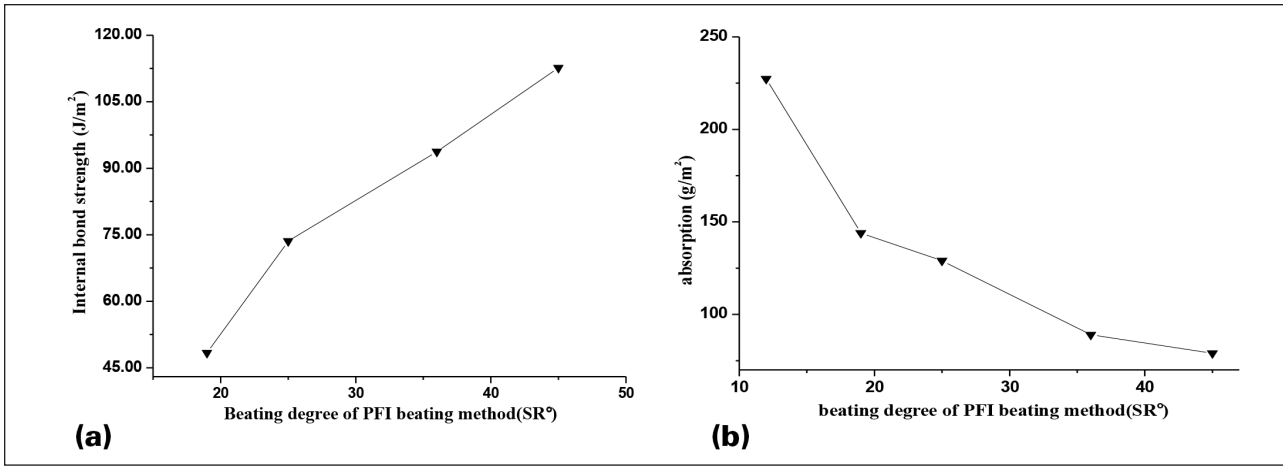
Analysis of superiority by ultrasonic wave pretreatment

We also investigated effects of PFI pretreatment on fiber bonding and absorbability. The properties of fiber at varied beating degrees were measured and the results are shown in **Fig. 3**.

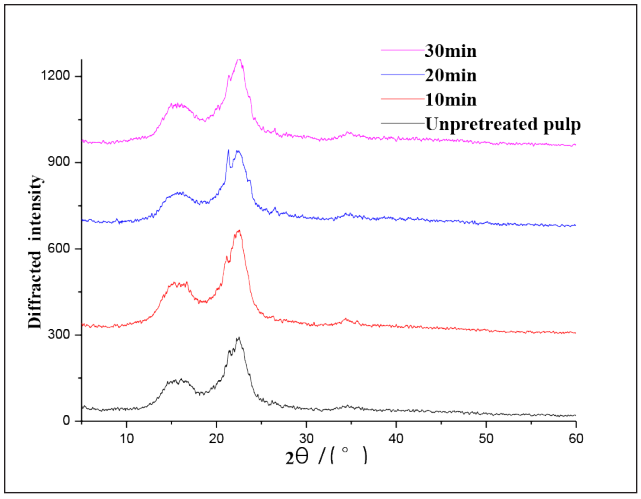
Figure 3(a) shows that internal bond strength of the fiber increased dramatically when fiber was treated by PFI. In compar-



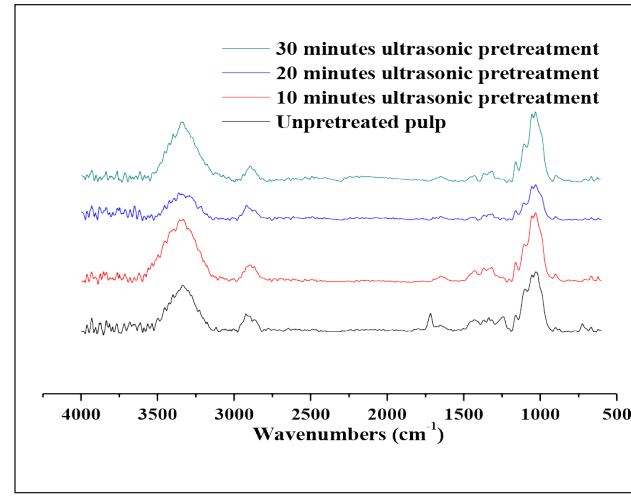
2. Effect of ultrasonic wave pretreatment time on (a) absorption and (b) water retention value.



3. Effect of PFI pretreatment on (a) internal bond strength and (b) absorption.



4. Wide-angle X-ray diffraction curves of the fiber after ultrasonic wave pretreatment.



5. Fourier transform infrared (FTIR) spectroscopy curves of the fiber after ultrasonic wave pretreatment.

ison with that of virgin fiber, the maximum value increased by 1.33 times, which was mainly due to the hydrogen bonds formed by exposed hydroxyl groups during PFI treatment. However, the value increased by just 4.07% when fiber was treated by ultrasonic waves for 30 min, as shown in Fig. 1. We can find in Fig. 3(b) that the absorption of fiber decreased when fiber was treated by PFI and achieved stronger fiber bonding strength and closer fiber connection. Instead, as shown in Fig. 2(a), absorption was 23.49% more than that of virgin fiber when treated by ultrasonic waves for 30 min. The internal bond strength and absorption of fiber pretreated by PFI were unexpected in fluff pulp preparation; consequently, little external fibrillation occurred during ultrasonic wave pretreatment, which was shown to be superior to PFI pretreatment.

Effect of ultrasonic wave pretreatment on crystalline structure and hydrogen bonds of fiber

In order to provide basic data for further research, crystalline structure and hydrogen bonds of cellulose fiber were also analyzed by wide-angle X-ray diffraction and FTIR spectroscopy.

Ultrasonic Wave Pretreatment Time (min)	Crystallinity (%)	D_{002} (nm)	D_{001} (nm)
0	52.94	6.7	1.7
10	57.68	9.5	2.0
20	43.46	5.9	1.8
30	40.98	3.7	1.9

I. Effect of ultrasonic wave pretreatment time on fiber crystallinity.

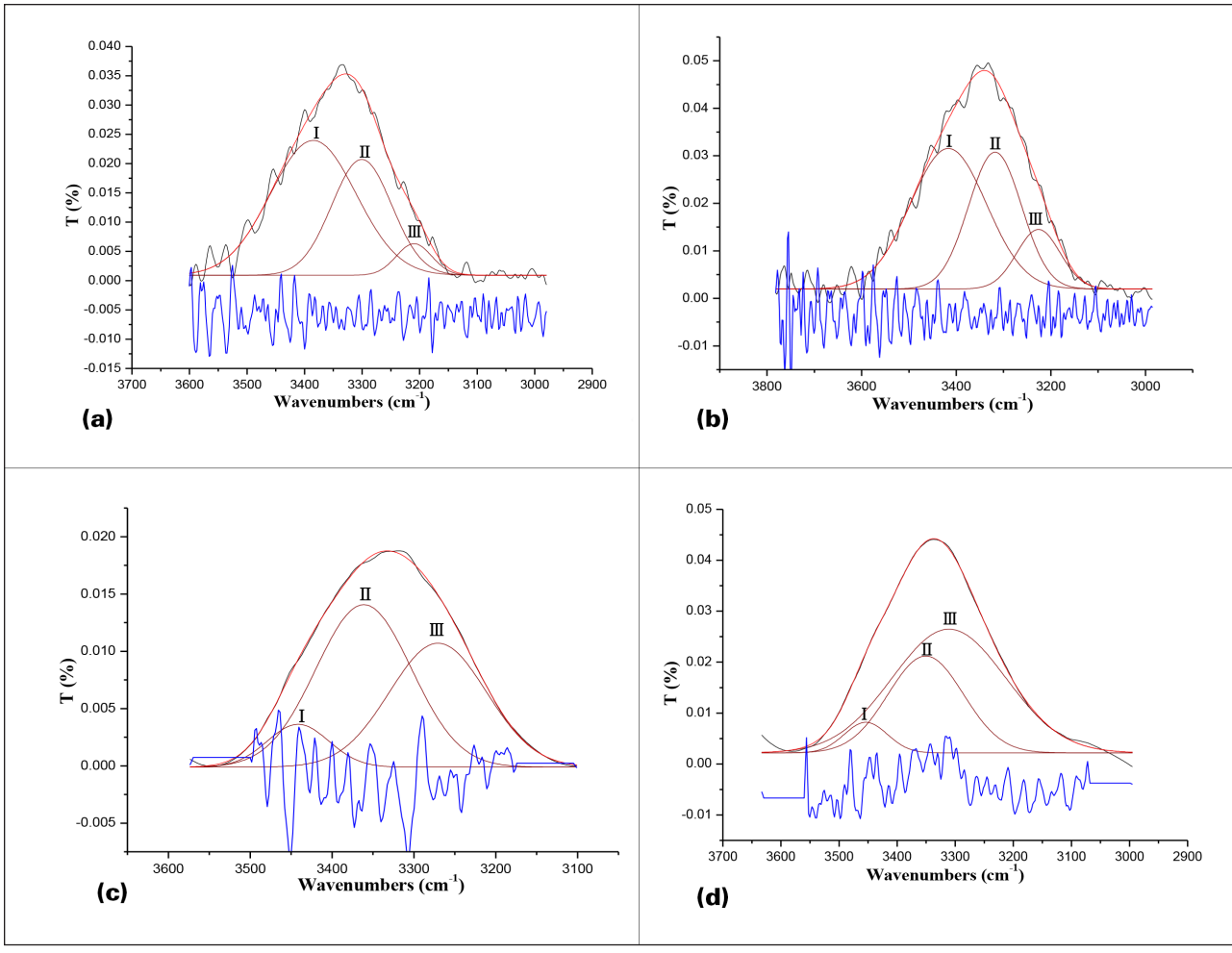
Fiber crystallinity

Wide-angle X-ray diffraction curves of cellulose fiber are shown in **Fig. 4**. The crystalline type of cellulose was not varied, and the type was still typical cellulose I structure. The crystalline and amorphous region both existed. Similar conclusion was also drawn by Scott [29]. Crystallinity and crystallites size of 101, 002 lattice planes were calculated using the Scherrer equation, as shown in shown in **Table I**.

We can see that the crystallinity of fiber increased slightly in the initial 10 min and then decreased with the increasing pretreatment time. Crystallinity decreased by 20.59% when fiber was treated for 30 min in comparison with that of virgin pulp. A similar trend was also found in the results for crystallite sizes. The influences mentioned previously were mainly attributed to ultrasonic cavitation and certain sonochemical effects in the cellulose-water binary system. The sonochemical effect was made by ultrasonic microjet at the speed of 100 $m \cdot s^{-1}$ when the cavitation bubble collapsed. With this effect, some pitting on the surface of fibers appeared and some crystal defects on the intact surface of the crystalline region were corroded as impulse force generated by ultrasonic waves increased, which led to the decrease of fiber crystallinity [30]. As a result, crystallinity of fiber would decrease dramatically with increasing pretreatment time to a certain extent. Simultaneously, destruction of the crystalline structure amplified with the sharply increasing impulse force and a more amorphous region was obtained, which resulted in the improvement of fiber absorption. Changes of crystallite size in the 002 lattice plane indicated the changes of the hydrogen bond proportion of the cellulose chain in FTIR [31].

Hydrogen bonds of fiber

FTIR spectra of cellulose fiber are shown in **Fig. 5**. We can find that no new absorption peak appeared with the increasing pretreatment time in comparison with that of virgin fiber.



6. Resolution of hydrogen-bonded O–H stretching for (a) unpretreated pulp, (b) 10-min ultrasonic wave pretreated pulp, (c) 20-min ultrasonic wave pretreated pulp, and (d) 30-min ultrasonic wave pretreated pulp. Note that I = intramolecular hydrogen bond O(2)H···O(6), II = intramolecular hydrogen bond O(3)H···O(5), and III = intermolecular hydrogen bond O(6)H···O(3').

It indicated that no new functional group was generated in the process of ultrasonic wave pretreatment.

Analysis of hydrogen bonds in FTIR curves by multipeak fitting

The hydroxyl groups (OH) in crystalline regions of the cellulose were connected through intermolecular and intramolecular hydrogen bonds. The absorption wave numbers of these bonds were different in FTIR spectra. According to the reports of Fengel, FTIR spectra of hydrogen-bonded O–H stretching vibrations at around 3352 cm^{-1} were resolved into three bands for cellulose I, assuming that all the vibration modes follow Gaussian distribution. The bands of 1 (3518 cm^{-1}), 2 (3349 cm^{-1}), and 3 (3195 cm^{-1}) were related to the intramolecular hydrogen bond of 2-OH…O-6, the intramolecular hydrogen bond of 3-OH…O-5, and the intermolecular hydrogen bond of 6-O…HO-3', respectively [24,26]. In addition, the crystalline type of ultrasonic wave pretreatment sample was still the typical cellulose I structure, as shown in Fig. 4. The results of resolving cellulose I hydrogen-bonded O–H stretching are shown in Fig. 5. The data analyzed by Gaussian method and absorbent intensity of these three resolved bands are shown in **Table II**.

We can see in **Fig. 6** that hydrogen-bonded O–H stretching was resolved into three bands expressed by I, II, and III, respectively. On the basis of the data in Table II, the following conclusions could be obtained. The proportion of intramolecular hydrogen bond intensity (2-OH…O-6 and 3-OH…O-5) to total hydrogen bond deceased with the increasing ultrasonic wave pretreatment time and that of intermolecular hydrogen bond (6-O…HO-3') increased. The infrared crystallization index (N-O'KI) increased initially but then decreased after a certain pretreatment time, which was similar to the result of X-rays. The variation of fiber mentioned above was due to the stronger ultrasonic wave effect on intramolecular hydrogen bonds than that of intermolecular hydrogen bonds. As a result, it was expected that after the rupture of intramolecular hydrogen bonds, more free hydroxyl groups would be exposed and the cohesion of fiber would decrease, which would improve the absorbability of fiber.

Ultrasonic Wave Pretreatment Time (min)	Infrared Crystallization Index (N-O'KI)	Three Distributed Bands	Wave Numbers (cm^{-1})	Area of Distributed Bands	Absorbent Intensity (%)
0	0.5097	I	3384.81	4.8	58.81
		I I	3300.56	2.58	35.50
		I I I	3209.76	0.41	0.69
10	0.5298	I	3416.54	5.96	52.03
		I I	3317.86	4.05	35.39
		I I I	3226.05	1.44	12.58
20	0.5170	I	3441.45	0.35	8.77
		I I	3361.22	2.07	51.38
		I I I	3270.52	1.60	39.85
30	0.4967	I	0053.83	0.556	5.82
		I I	3350.01	3.09	32.18
		I I I	3310.73	5.96	62.00

II. Basic data of resolving hydrogen-bonded O–H stretching in FTIR spectroscopy.

CONCLUSIONS

The absorption of fiber pretreated by ultrasonic waves was 23.49% more than that of virgin pulp. However, the absorption of fiber pretreated with PFI method decreased. In comparison with that of virgin fiber, internal bond strength of fiber increased by just 4.07% when fiber was treated by ultrasonic waves for 30 min. However, the maximum value increased by 1.33 times as a result of PFI pretreatment.

The effect of ultrasonic wave pretreatment on intramolecular hydrogen bonds was rather stronger than that of intermolecular hydrogen bonds. Therefore, the optimal swelling ability of fiber would be obtained. The effect indicated that ultrasonic wave pretreatment was superior to PFI pretreatment in fiber weak bonding and absorbability improvement, which was expected in fluff pulp making. **TJ**

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ABOUT THE AUTHORS

We have done research in absorbent materials for several years. The cavitation mechanism of ultrasonic waves gave us some inspiration. In the initial stage, we analyzed changes of cellulose fiber morphology when it was treated by ultrasonic waves. It showed that concentric layers of fiber cell wall slid and cohesion decreased, which was conducive to fiber absorbability. As a result, we begin to treat cellulose fiber, which is the raw material of fluff pulp, by ultrasonic waves. This work differs from the existing research because there is no use of debonder and other weak-bonding additives. We treat the cellulose fiber with mechanical methods.

The most difficult aspect of this research was the accurate indication of fiber inner fibrillation. We used WRV and absorption of fiber, which are also significant property parameters of fluff pulp, to characterize it. The internal bond strength of cellulose fiber was analyzed and was used to explain fiber bonding.

This research indicated that absorption of fiber pretreated by ultrasonic waves increased and highlighted the superiority of the method to PFI pretreatment in fluff pulp making. Some basic data about crystalline structure and hydrogen bonds of cellulose fiber was obtained and revealed that the effect of ultrasonic wave pretreatment on intramolecular hydrogen bonds was rather stronger than that of intermolecular hydrogen bonds.

As far as we know research in fluff pulp is not mature, and quality improvement of fluff pulp is still a significant topic for investigation. In the next stage, we will put this technology into the process of fluff pulp making. The cellulose fiber will be pretreated by ultrasonic waves and then be used to make fluff pulp board.

This study will add to the body of research in absorbent materials such as fluff pulp.

Xu and Zhu are professors, Yan and Hou are graduate students, and Yue is a lecturer at Shaanxi University of Science and Technology, Xi'an, Shaanxi, China. Zhang is an engineer in Guizhou Chitianhua Paper Industry Co., Ltd., Guizhou, China. Email Xu at xuyongjian@sust.edu.cn.


Xu


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