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Effects of Ultra-sonification Assisting Polyethylene Glycol Pre-treatment on the Crystallinity and Accessibility of Cellulose Fiber

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In order to prepare the advanced cellulosic super-absorbent polymer with high grafting level, we tried the novel ultrasound wave assisting polyethylene glycol (PEG) pre-treatment method to decrease the crystallinity and increase the accessibility of cellulose fiber. The effects of ultrasonification assisting PEG method on the crystallinity and swelling capacity of cellulose fiber were investigated. To optimize the experimental condition, the Taguchi method was employed in the treatment process. The influence factors such as ultrasonic wave power, ultrasonic wave time and PEG molecular weight relative to the crystallinity of cellulose fiber were studied systematically. The degree of crystallinity of cellulose fiber was measured by wide-angle X-ray diffraction (WAXD). The morphology of cellulose fiber was observed by environment scanning electron microscopy (ESEM). The effects of pre-treatment variables on the water absorbency and water retention values of cellulose fiber were also investigated. The research results revealed that, under the optimal experimental condition (ultrasonic powder, 500 W; ultrasonic time, 150 s; PEG molecular weight, 600 g/mol), the crystallinity of cellulose fiber decreased from 72.16 to 42.95%. Accordingly, the absorbency of cellulose fiber increased from 1.436 to 2.063 g/g, and the water retention value increased from 47.21 to 113.4%. However, the morphology of cellulose fiber did not change thoroughly compared with the original cellulose fiber. It can be hypothesized that the original inter- and intra-macromolecular hydrogen bonds in cellulose network were weakened, resulting from the high level dispersion of PEG within cellulose network without breaking the surface morphology of fiber.

Keywords: Cellulose fiber, cellulosic water absorbent, crystallinity, PEG, pre-treatment

1 Introduction

Cellulose is the most abundant renewable organic material on earth (1). Making use of cellulose to produce various products will not only protect our environment from pollution, but also save the limited oil resource, due to its biodegradability and potential to be substituted for some petrochemical (2). However, cellulose has not reached its potential in many areas of applications because of its infusibility and insolubility. Cellulose is a polymer consisting of unbranched $\beta(1\rightarrow4)$ D-glucopyranosyl units. There are large amounts of intra- and inter-molecular hydrogen bonds in cellulose, which interrupt the dissolution and accessibility of cellulose into chemical solution. Therefore, the pre-treatment process is necessary for cellulose fiber to increase the accessibility in the cellulose functionalization (3–5). Currently, there are several known effective pre-treatments methods for cellulose, among which ultrasonification method as a kind of physical treatment is attracting more and more attention (6, 7). The ultrasound treatment is a green chemistry process because no chemicals are used and no polluting effluents are produced. The ultrasound wave treatment technique may be an effective and prospective means for activation of cellulose and could replace chemical treatment used in cellulose functionalization.

Super water-absorbent polymers can absorb a large amount of water in a few minutes and retain water under pressure. They have received considerable attention and are now widely used in agriculture and horticulture, sealing composites, artificial snow, disposable diapers, drilling

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additives, medicine for drug delivery system (8, 9). Among them, the application of super absorbents in agriculture for improvement of water-holding capacity of soils is the most attractive. Cellulosic water absorbents are widely accepted around the world because of their economical advantages and environment conservation (10). Cellulosic water absorbents can be prepared by grafting acrylonitrile, acrylamide and acrylic acid onto cellulosic chains. It is important to note that the degree of grafting plays a major role in the water absorbency property of resulting super-absorbent polymer. In order to prepare the advanced cellulosic super-absorbent polymer with high grafting level, it is necessary to increase the accessibility of cellulose fiber.

We tried the novel ultrasound wave assisting polyethylene glycol (PEG) pre-treatment method to decrease the crystallinity and increase the accessibility of cellulose fiber. PEG is used as a swollen reagent in the present work, and can act as the pore-forming agent in the further grafting experiment. Therefore, the resulting very small quantity of PEG is useful to improve the water absorbency for the grafting cellulosic water absorbents. The aim of this work is to study the effects of ultrasonification assisting PEG method on the crystallinity and accessibility of cellulose fiber. The influence factors of the experimental condition such as PEG molecular weight, ultrasonic wave time, and ultrasonic wave power relative to the crystallinity of cellulose fiber were studied systematically. To optimize the experimental condition, the Taguchi method as a simple and effective experimental design, was employed in the treatment process. The degree of crystallinity of cellulose fiber was measured by wide-angle X-ray diffraction (WAXD). The morphology of cellulose fiber was observed by environment scanning electron microscopy (ESEM). The effects of pre-treatment variables affecting the water absorbency and water retention values of cellulose fiber were also investigated.

2 Experimental

2.1 Materials

Cotton linters were purchased from Hubei Chemical Fiber Group Ltd. (Hubei, China), and its viscosity-average molecular weight (M_η) was determined to be 10.2×10^4g/mol by viscometry according to Equation 1 (11):

$$[\eta] = 3.85 \times 10^{-2} M_n{}^{0.76} (mLg^{-1}) \quad (1)$$

Polyethylene glycol (PEG) reagents were purchased from Tianjin Tiantai Chemical Company Ltd. (Tianjin, China), and their average molecular weights are 200, 400, 600, 800 and 1000 g/mol, coded as PEG 200, PEG 400, PEG 600, PEG 800, PEG 1000, respectively. All chemical reagents were purchased from commercial resources in China and were of analytical grade.

2.2 Apparatus

1. An ultrasound generator: JY88—II type bio-cell disrupter (manufactured by Shanghai Xin Zhi Biology Research Institute, and Ningbo Xin Zhi Science and Equipment Institute, China).
2. A centrifugal apparatus: TDL-5 type (manufactured by Shanghai Anting Centrifugal Apparatus Factory, China).

2.3 Pre-treatment Process

The pre-treatment of cellulose was measured according to the following process. 0.30 g cotton linter was immersed in 20 mL PEG solution (0.30 g/mL) for 5 min, and then the suspension slurry was treated by ultrasonification under a certain experimental condition. The ultrasound treatment was performed in a way of treating 2 s with 2 s cooling intervals to avoid overheating. The above pre-treatment was repeated until the expected experimental time occurred. Next, the pretreated cotton linters were washed by PEG solution (0.10 g/mL) and distilled water successively. Finally, the pretreated cotton linters were dried at room temperature for 12 h, and then vacuum-dried at 40°C for 8 h.

2.4 Selection of Factors and Their Levels

According to the basic knowledge of ultrasonification treatment, ultrasonic power, ultrasonic time, and PEG molecular weight are the key influence factors affecting on the final crystallinity of the cellulose fiber. These parameters were varied at five levels as shown in Table 1. The applied ranges of the variables were chosen based on the literature and our preliminary experiments.

2.5 Selection of Orthogonal Array and Assignment of Factors

Standard tables known as orthogonal arrays (OA) are used to design the experiments using the Taguchi method. An OA with three factors and five levels are shown in Table 2. This OA is particularly designed with the symbol of L25. Each row in the array represents a trial condition with the factor levels, which are indicated by the numbers in the

Table 1. Experimental influence factors and their levels

Influence Factors	*Level 1*	*Level 2*	*Level 3*	*Level 4*	*Level 5*
PEG M_w/g/mol (F1)	200	400	600	800	1000
Ultrasonic time /s (F2)	30	60	90	120	150
Ultrasonic power/W (F3)	300	400	500	600	700

Table 2. Experimental layout of an L25 orthogonal array according to Taguchi's method

	Factors and their levels		
Trial number	*F1*	*F2*	*F3*
1	1	1	1
2	1	2	2
3	1	3	3
4	1	4	4
5	1	5	5
6	2	1	2
7	2	2	3
8	2	3	4
9	2	4	5
10	2	5	1
11	3	1	3
12	3	2	4
13	3	3	5
14	3	4	1
15	3	5	2
16	4	1	4
17	4	2	5
18	4	3	1
19	4	4	2
20	4	5	3
21	5	1	5
22	5	2	4
23	5	3	1
24	5	4	2
25	5	5	3

row. The columns correspond to the factors specified in this study, and each column contains five level 1, five level 2, five level 3, five level 4, and five level 5 conditions (a total of 25 conditions). Therefore, the evaluation of results has been standardized by this method. The contribution of influence factors were analyzed statistically by ANOVA method.

2.6 Measurement of Swelling Rate in Distilled Water

The water absorbency of the pretreated cellulose was measured at room temperature according to the following process. A tea bag was made of 200 mesh stainless steel. The tea bag containing sample (0.30 g) was immersed entirely in excess distilled water for 10, 15, 20, 25 and 30 min. Then, the swollen sample was placed in a centrifuge tube and centrifuged at the speed of 30 r/s for 15 min. The centrifuge tube was equipped with a sintered glass filter to allow excess water to drain away from the sample. During centrifugation, the tube was sealed with aluminum foil to prevent evaporation of water. After the centrifugation, the samples without the excess water was collected and weighed. The water absorbency in distilled water of samples, Q_t, was calculated by:

$$Q_t = (m_2 - m_1)/m_1 \quad (2)$$

Where m_1 and m_2 are the weights of the dry sample and the swollen sample, respectively. Q_t is calculated as grams of water per gram of sample. Parallel measurements in triplicate were carried out for every sample.

2.7 Measurement of Water Retention Value (WRV) in Distilled Water

The water retention value (WRV) was measured by a centrifugation technique in which cellulose sample of 0.30 g was swollen with excess distilled water for 30 min before being subjected to centrifugation. The measurement condition of centrifugation method is the same as that mentioned above. The weight of a sample was recorded as m_{wet} after the centrifugation, and the oven-dried weight (m_{dry}) of the sample was then determined after vacuum-dried to a constant weight at 70°C. The WRV value was calculated as follows:

$$WRV(wt\%) = [(m_{wet} - m_{dry})/m_{dry}] \times 100\% \quad (3)$$

Three parallel measurements were carried out for every sample.

2.8 Characterization

Wide-angle X-ray diffraction (WAXD) patterns were recorded on an X'PertPRODY2198 X-ray diffractometer, by using Cu Kα radiation (λ =1.5406) at 30 kV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 5 to 45°. The crystallinity was calculated by the method of peak separation with a peak resolution program using Scherrer's equation (12).

Thermogravimetric analysis (TGA) of the specimens with 1 mm length and 1 mm width were carried out with a thermobalance (STA409, Netzsch, Germany) under air atmosphere, at a heating rate of 10°C/min. The temperature is increased from 25 to 105°C, containing the test condition until the weight percent achieves the flat level.

The images of samples were observed by environmental scanning electron microscopy (ESEM, JSM-35CF, NEC, Japan). The free surface of the samples in dry state were observed and photographed.

3 Results and Discussion

3.1 Optimized Experimental Condition of Fiber

There are many influence factors affecting the ultimate crystallinity of cellulose fiber. To optimize the affecting variables on the crystallinity of the cellulose fibers, Taguchi method was used in this paper (6). The effects of ultrasound treatment conditions on crystallinity of cellulose fiber were examined in terms of PEG molecular weight, treatment time and ultrasound power. These parameters and the related levels are presented in Table 1. After selecting the

Table 3. Experimental layout of the influence factors and related crystallinity data of cellulose fiber

Trial	*PEG* M_w*/g/mol*	*Ultrasonic time /s*	*Ultrasonic power/W*	*Crystallinity/%*
1	200	30	300	67.02
2	200	60	400	70.90
3	200	90	500	67.72
4	200	120	600	61.79
5	200	150	700	61.07
6	400	60	300	60.70
7	400	90	400	51.90
8	400	120	500	58.80
9	400	150	600	60.53
10	400	30	700	59.05
11	600	90	300	78.84
12	600	120	400	54.82
13	600	150	500	42.95
14	600	30	600	70.53
15	600	60	700	43.03
16	800	120	300	77.55
17	800	150	400	60.81
18	800	30	500	44.46
19	800	60	600	62.29
20	800	90	700	75.88
21	1000	150	300	68.95
22	1000	30	400	70.45
23	1000	60	500	59.20
24	1000	90	600	72.25
25	1000	120	700	69.18

mentioned influence factors, an OA table was formed in Table 2. The experimental layout after assigning the values of the parameters and observed crystallinity values are shown in Table 3. According to Table 3, 25 experiments were carried out and the resulting crystallinity of pretreated cellulose fibers was measured. It should be emphasized that the interaction between the variables were neglected. From Table 3, the optimized values of the ultrasonic powder, ultrasonic time, PEG molecular weight for trial 13 are 500 W, 150 s, and 600 g/mol, respectively. The crystallinity of pretreated cellulose fiber is 42.95% accordingly.

The contribution of three influence factors with five levels related to the average values of crystallinity for pretreated cellulose fiber are obtained by ANOVA analysis in Table 4 and illustrated in Figures 1–3. The effects of molecular weight of PEG on crystallinity of cellulose fiber are shown in Figure 1. From the Figure, the PEG reagents with medium molecular weight (400 and 600 g/mol) can effectively decrease the crystallinity of cellulose fiber. However, the PEG reagents with the relatively higher and lower molecular weight did not exhibit the strong capability to destroy the crystal behavior of cellulose, which attributed to the relatively lower dispersion level or weak intermolecular interaction with cellulose. The above results imply that PEG reagents with medium molecular weight can form relatively stronger intermolecular interaction with cellulose to interrupt the crystal domain of cellulose fiber, resulting in a relatively lower crystallinity accordingly. Influence of ultrasound treatment time on the crystallinity of cellulose is shown in Figure 2. The lowest crystallinity of 58.86% can be achieved when the ultrasound treatment time is 150 s. The lower crystallinity for ultrasound wave treated sample may be attributed to the structural changes, i.e., accessibility improvement and more porous morphology created by ultrasound treatment. The power of ultrasound is a very important parameter that has also great influence on acoustic cavitation and the efficiency of the ultrasound treatment. It is shown in Figure 3 that the crystallinity of cellulose fiber decreased to a minimum value of 54.62% when the power is increased to 500 W. However, it is noted that there is no linear relationship between the crystallinity and the power of ultrasound wave. This finding supports the relevant theory of sonochemistry that cavitation intensity has a maximum value at the proper power of ultrasound (13). Moreover, the most effective factor is ultrasonic powder according to Table 4. It can be seen from the results that the crystallinity reached the minimum average value (54.62%) when ultrasound power attains level three.

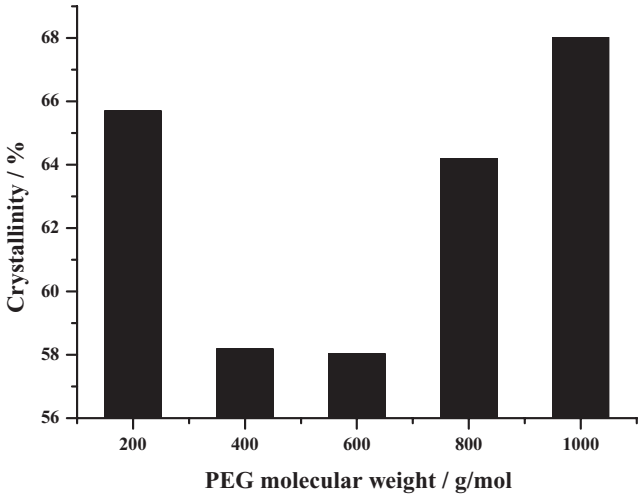

Fig. 1. PEG molecular weight (g/mol) dependence of crystallinity (%) for the pretreated cellulose fibers.

Table 4. The contribution of factors with five levels related to the average values of crystallinity data for cellulose fiber by analysis

Control factors	*Level 1*	*Level 2*	*Level 3*	*Level 4*	*Level 5*
PEG M_w/g/mol	65.70	58.19	58.03	64.19	68.01
Ultrasonic time /s	62.30	59.22	69.32	64.43	58.86
Ultrasonic power/W	70.61	61.77	54.62	65.47	61.64

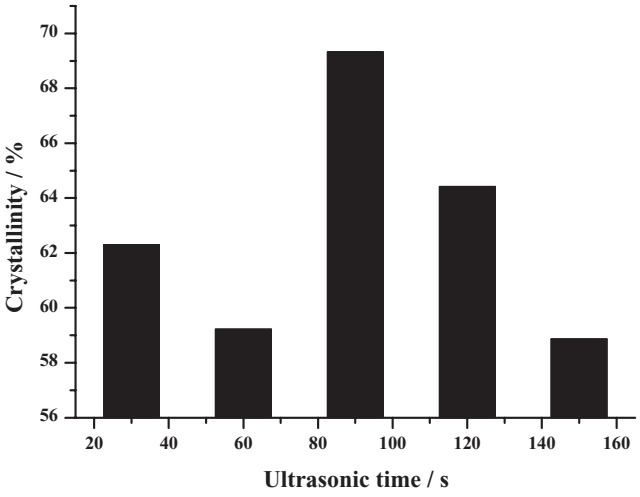

Fig. 2. Ultrasonic time (s) dependence of crystallinity (%) for the pretreated cellulose fibers.

3.2 Crystal Structure and Morphology of the Pretreated Fiber Under Optimized Conditions

In order to confirm that there is no water influence for the resulting structure, morphology and swelling property, thermogravimetric analysis (TGA) method was used to measure the water content of the pretreated cellulose fibers in dry state. There is almost no weight loss can be observed when the test temperature increased from 25 to 105°C, even though the test condition was contained at 105°C for 10 min. Three parallel measurements were carried out for every sample. Observed slight errors can be attributed to the apparatus for the operation.

X-ray diffraction technique was employed in this work to investigate the crystalline structural changes of cellulose brought about by the ultrasound assisting PEG treatment.

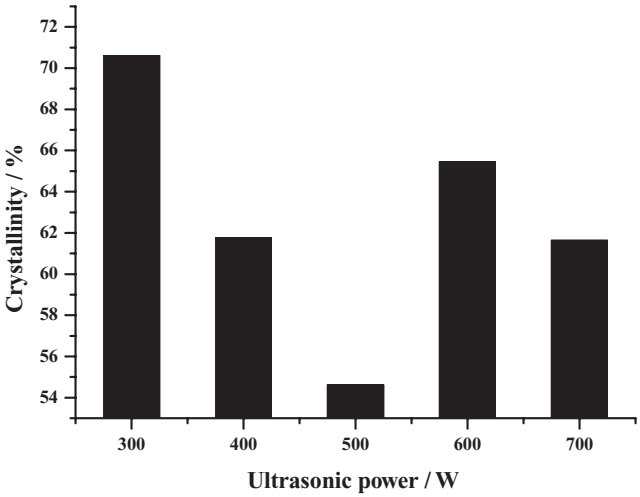

Fig. 3. Ultrasonic power (W) dependence of crystallinity (%) for the pretreated cellulose fibers.

The X-ray diffraction patterns of the native and pretreated cellulose fibers are shown in Figure 4. For cellulose fiber, 2θ angles at 14.8, 16.3, 21.6, 22.6 and 35° were assigned to (101), (10$\bar{1}$), (021), (002), and (040) planes, respectively. The diffraction peaks at 2θ = 14.8, 16.3, and 22.6° are characteristic for cellulose I crystal, and those at 11.8, 19.9, and 21.6° are characteristic for cellulose II crystal (14). In this study, the natural cotton linter (trial 0) exhibited a sharp peak at 2θ = 22.6° (002), and two broadened peaks within the range 2θ = 16.4–14.7, corresponding to the crystallographic form of cellulose I. The pretreated cellulose fiber under the optimal condition (trial 13) showed the sharp peak around 2θ = 22.6°, corresponding to (002) plane. Moreover, the crystallinity for the (101), (021), (002), and (040) planes were obviously lower than those of the cotton linters, indicating that the crystal structure of the treated cellulose fibers is weakened. Accordingly, the crystallinity of cellulose fiber decreased obviously from 72.16 to 42.95%. Zhang et al. reported that the change of cellulose I into cellulose II occurred in the regeneration process of cellulose (15). Sreenivasan et al. also found that the native cellulose fibers can be swollen in KOH aqueous solution and partly conversed to cellulose II (16). On the contrary, the crystal type of pretreated cellulose fiber (not shown all) in this study is the same as that of cellulose I. Therefore, it is confirmed that the ultrasonification assisting PEG treatment did not change the original crystal structure of cellulose fiber, which is completely different from those chemical treatment. In view of WAXD analysis for pretreated cellulose fiber, the relatively strong intermolecular interaction between PEG and cellulose fiber occurred to interrupt and weaken the crystal domains of cellulose, resulting in the decrease of crystallinity.

SEM observation can give information of the crystallization behavior and morphological change (17). Figure 5 shows the ESEM photographs of the free surfaces of the original cellulose fiber (trial 0) and pretreated cellulose fiber under optimal condition (trial 13) with different magnification scales. From Figures (b) and (d), the cellulose fibers are straight and uniform. The pretreated cellulose fiber is swollen slightly, which did not show any obvious change compared with the natural cotton linter. However, as is evident from the photographs (a) and (c) with higher magnification, compared to the untreated native cellulose, the morphology structure of ultrasound wave treated cellulose sample becomes more rough, amorphous and loose. An ultrasound treatment has an alternating rarefaction and compression half-cycle. During the compression process, certain sizes of cavities (bubbles) in the liquid medium are suddenly collapsed, creating powerful shock waves, and generating a large amount of mechanical and thermal energy in the liquid (18). Tang et al. reported that the morphology and structure of cellulose fibers have changed after ultrasound treatment, peeling of S1-layer in the form of large pieces or in the form of smaller flakes and partial fibrillation are observed in cellulose fibers under 400 W

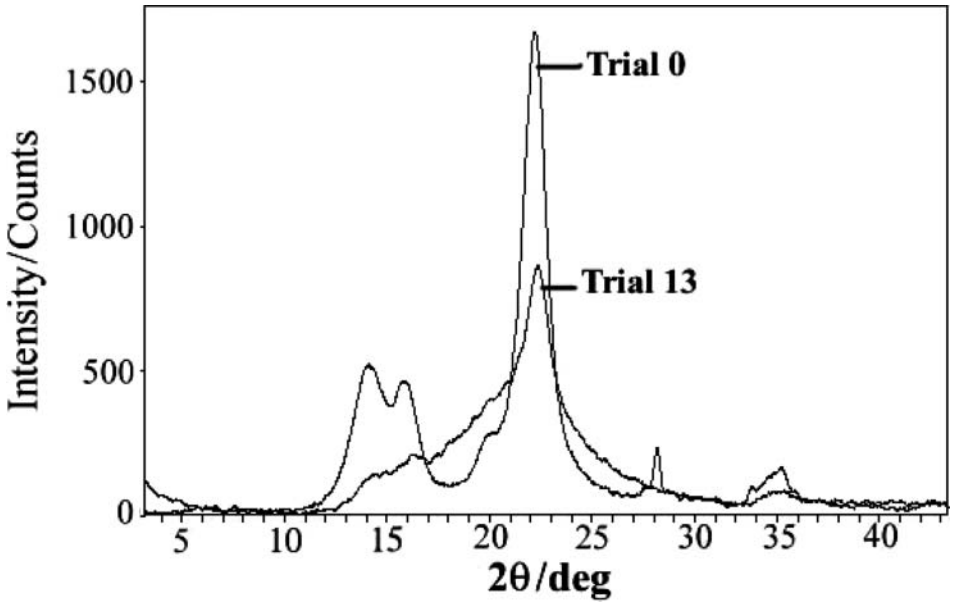

Fig. 4. WAXD spectra of native cellulose fiber (trial 0) and pretreated cellulose fiber (trial 13).

and 360 s (7). On the contrary, the morphology of cellulose fiber did not change thoroughly using ultrasound assisting PEG method under 500 W and 150 s in this study. The difference is hypothesized to the important role of PEG in pre-treatment process to decrease the crystallinty of cellulose fiber. The results imply that PEG was dispersed in cellulose network with ultrasound treatment to weaken the original inter- and intra-macromolecular hydrogen bonds without breaking the surface morphology of cellulose, resulting in the relatively lower crystallinity. These findings supported the conclusion obtained by WAXD.

3.3 Accessibility of the Pretreated Fiber Under Optimized Conditions

Accessibility of cellulose can be measured by a variety of techniques in the dry, as well as wet, states. It is generally recognized that the accessibility (accessible pore volume and accessible surface area) of cellulose can be characterized by the determination of some easily obtainable reactivity-relevant parameters like the water retention value (WRV) or the crystallinity index (X_c) (19, 20). The water absorbency and WRV values of native and pretreated cellulose fibers are summarized in Table 5. The absorbency time dependence of the absorbency (Q_t) for the native cellulose and

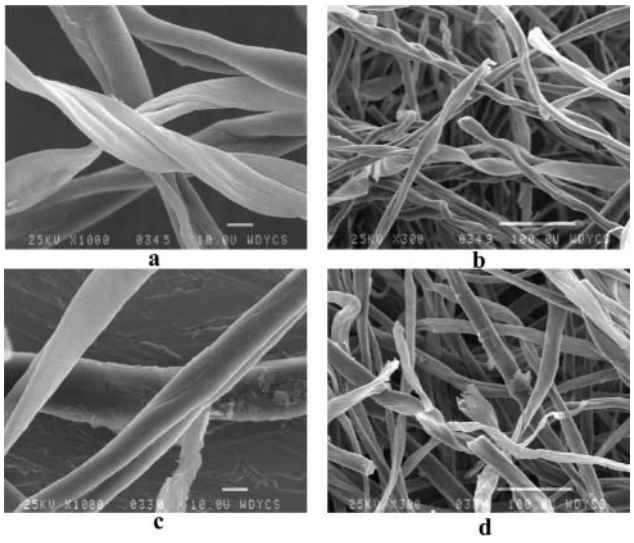

Fig. 5. Environmental scanning electron microscopy images of native cellulose fiber (a, b) and pretreated cellulose fiber (c, d) in dry state (a, c: ×1000; b, d: ×300).

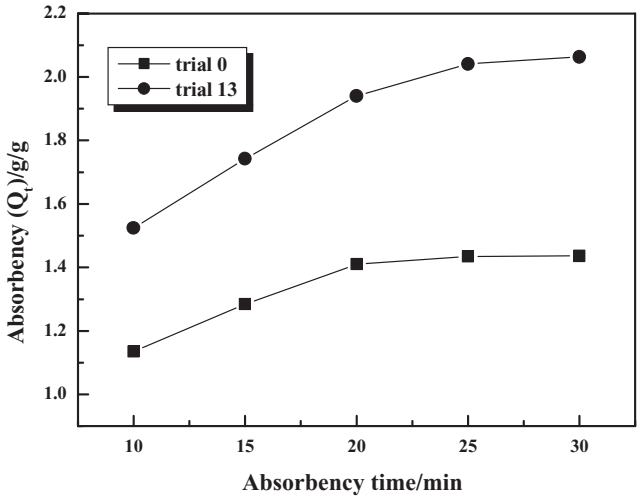

Fig. 6. Water absorbency time (min) dependence of absorbency (Q_t) of native cellulose fiber (trial 0) and pretreated cellulose fiber (trial 13).

Table 5. Water absorbency (Q_t) and WRV values of cellulose fibers

Samples	Q_t *(10 min) / g/g*	Q_t *(15 min) / g/g*	Q_t *(20 min) / g/g*	Q_t *(25 min) / g/g*	Q_t *(30 min) / g/g*	*WRV / %*
Native cellulose fiber (trial 0)	1.135	1.284	1.410	1.435	1.436	47.21
Pretreated cellulose fiber (trial 13)	1.524	1.742	1.940	2.041	2.063	113.5

ultrasound wave assisting PEG treated cellulose are shown in Figure 6. From the Figure, both cellulose fibers have similar behavior. The absorbency values increased with an increase of absorbency time from 10 to 30 min. The Q_t values for the native cellulose fiber increased from 1.135 to 1.436 g/g with an increase of absorbency time from 10 to 30 min. Similarly, the absorbency of the pretreated cellulose fiber increased with increasing absorbency time from 1.524 to 2.063 g/g. Therefore, the absorbency capacity of the pretreated cellulose fiber is significantly higher than that of the native cotton linter. The improvement in the absorbency could have resulted from an enhancement in accessibility and reactivity of cellulose by ultrasound wave assisting PEG pre-treatment. Table 5 also shows the accessibility (in terms of WRV) changes of the ultrasound treated cellulose samples. WRV value for the untreated native cellulose is 47.21%. After cellulose is treated by ultrasound assisting PEG for 150 s, the WRV value increased to 113.5%.

Based on the results mentioned above, the ultrasound wave assisting PEG pre-treatment method has excellent effect on decreasing the crystallinity of cellulose fiber and increasing the accessibility of cellulosic bonds. In fact, the resulting very small quantity of PEG can act as pore-forming agent and improve the water absorbency capacity for the grafting cellulosic super-absorbent polymer. Further experiments will be performed in order to synthesize and characterize the grafting cellulosic super-absorbent polymer based on pretreated cellulose, and compare with the traditional counterparts.

4 Conclusions

The novel ultrasound wave assisting polyethylene glycol (PEG) pre-treatment method was successfully used to decrease the crystallinity and increases the accessibility of cellulose fiber. The effects of ultrasonification assisting PEG method on the crystallinity and swelling capacity of cellulose fiber were investigated in this research. The Taguchi method was applied to optimize the experimental condition using standard L25 orthogonal array with three factors and five levels. The research results revealed that, under the optimal experimental condition (ultrasonic powder, 500 W; ultrasonic time, 150 s; PEG molecular weight, 600 g/mol), the crystallinity of cellulose fiber decreased from 72.16 to 42.95%. Accordingly, the absorbency of cellulose fiber increased from 1.436 to 2.063 g/g, and the water retention value increased from 47.21 to 113.4%. However, the morphology of cellulose fiber did not change thoroughly compared with the original cellulose fiber. The significant increase in accessibility with significant decrease in crystallinity for cellulose fiber was attributed to the strong intermolecular interaction between PEG and cellulose network brought about by ultrasound wave treatment. These results can give better understanding of the effect of pretreatment and conduct the chemical functionalization of cellulose fiber.

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