

Accessibility and Morphology of Cellulose Fibres Treated with Sodium Hydroxide

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Cellulose fibres were treated with sodium hydroxide (NaOH) to improve the accessibility of chemical reagents and the roughness of fibre surface at low temperatures. The accessibility, supermolecular structure, morphology, and physical properties of fibres were investigated using solid-state cross polarisation/magic angle spinning ¹³C nuclear magnetic resonance (CP/MAS ¹³C NMR), wide-angle X-ray diffraction (WAXD), and scanning electron microscopy (SEM). The results showed that in low temperature (-16 °C), the iodine sorption value of cellulose fibres is 145.2 mg. The shift from the C6 signal of the molecular structure to the amorphous area indicated a decrease in the crystallinity of the material from 66% to 8%, and the transformation from cellulose I to II occurred. The SEM revealed fold shapes in the fibre surface, which increased the fibre surface area.

Keywords: Cellulose; Sodium hydroxide; Accessibility; Morphology

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INTRODUCTION

Natural cellulose is one of the cheapest and most abundant renewable resources in nature. A promising energy material, natural cellulose has excellent biodegradability and environmentally friendly properties (Kaplan 1998) and can replace existing petroleum-based plastics and chemicals that cause severe environmental pollution and the overuse of resources (Teeri *et al.* 2007; Wu *et al.* 2009). Fibres, films, and other products produced by cellulose have good biocompatibilities and mechanical properties (Kalia *et al.* 2011).

The accessibility of cellulose concerns the degree of difficulty with which reagents are able to reach the hydroxyl groups of cellulose. When the fibres have high accessibilities, the chemical reagents easily permeate them. The accessibility of several kinds of fibres are shown in Table 1. From the table, one can see that the natural fibres of cotton and wood pulps have lower accessibilities than those of rayon. The accessibility of impact rayon can reach up to 86%, and this excellent penetration is beneficial for chemical treatment and dyeing. Therefore, disrupting the fibres' primary walls and exposing the microfibrils would improve the utilisation of cellulose. During a heterogeneous reaction, some activating treatments are necessary to improve the accessibility and reactivity of cellulose.

Table 1. The Accessibility of Fibres (Zhili Yang *et al.* 1981)

Types of Fibres	Cotton	Wood Pulps	Rayon	Impact Rayon
Accessibility (%)	40	50-56	68	86

Adsorption of various solutes onto fibre occurs mainly on the amorphous regions and usually to a lesser degree on the surfaces of crystallised areas. The transport of chemical reagents to the reaction sites can occur within the less-ordered (amorphous) regions. The fibre accessibility is therefore dependent on the crystalline-amorphous structure.

To improve accessibility, overcome the non-uniform tendency reaction internally, and improve reaction performance, cellulose is usually swelled or activation-pretreated before the multiphase reaction (Le Moigne and Navard 2009). Swelling of the fibre structure may help to increase the degree of fibre accessibility (Roy *et al.* 2009). The pretreatments can disrupt the primary walls of the fibres and damage the intra- and intermolecular hydrogen bonds, thus freeing up hydroxyl groups and transforming the fractional crystallisation area into an amorphous area (Gupta *et al.* 2013). Alkali metal hydroxides such as sodium hydroxide are commonly used for the various modifications of cellulose materials (*e.g.*, mercerisation, a conventional technique used to improve the dimensional stability, strength, luster, and dye ability of cotton using highly concentrated sodium hydroxide), the preparation of rayon fibres (Wilkes 2001; Meng *et al.* 2013), and the introduction of distinct chemical substances into the cellulose materials to alter their properties (Okubayashi and Bechtold 2005). Swelling pretreatment can break cellulose molecular hydrogen bonds with chemical reagents, high-concentration NaOH aqueous solutions, and organic bases (amine). Sodium hydroxide aqueous solutions and cellulose form a Na⁺/water and cellulose system, which chemically forms stable hydrogen bonded network structures capable of splitting the tight packing of the cellulose chains, while blocking the polymerisation of cellulose. The alkali treatment shortens the molecular chains, and the uniform cell structures and crystallinity and crystal grains are slightly reduced after processing. Those changes allow chemical reagents to penetrate cellulose fibres more easily while preserving the chemical composition of the fibres. With a decrease in temperature, the degree of cellulose swelling increases. Also, the grafting rate of cellulose increases significantly compared with the untreated samples. Therefore, alkali pretreatment helps to obtain high grafting rates for products under mild conditions.

In this study, NaOH solutions were used to pretreat plant cellulose fibres. In addition, the processing conditions and the accessibility, supermolecular structure, morphology, thermal stability, and physical properties of the cellulose fibres were assessed. Compared with the previous researchers' works, the integrated and systematic study was focused on detecting the crystal structure of cellulose by using solid-state CP/MAS ¹³C NMR method and analyzing the accessibility of alkali cellulose, which have important significance for the further study of the chemical reactions of cellulose.

EXPERIMENTAL

Materials

Bleached hardwood sulphate pulp sheets were provided by Tianjin Zhong Chao Paper Industry Co. (China) as an experimental material. Sodium hydroxide (NaOH; analytical reagent), used as a solute, and iodine, potassium iodide, sodium thiosulfate, sodium sulfate, nitric acid, dichloromethane, and methanol (analytical reagents) were obtained from Tianjin Jiang Tian Chemical Reagent Co. (China). The water used in the experiments was deionised in the lab.

Methods

Alkaline pretreatment

Bleach broad leaf pulp cellulose fibres (5 g) were predried in a -0.1 MPa vacuum at 70 °C for 24 h and then immersed in 100 mL of a NaOH solution (0, 8, 12, 15, 18, 20, or 25% w/v) with vigorous stirring at ambient, -16 °C, and 100 °C for 24 h. The alkaline-treated fibres were subsequently washed with running tap water and then distilled water until no alkali was present in the wash, and then dried under vacuum to a constant weight. The alkali wash was recycled to avoid environmental pollution.

Molecular weight determination of cellulose samples

Gel permeation chromatography (GPC) is a very effective method for determining the molecular weight distribution of large polymers, and it can be used to measure cellulose degradation after alkali treatment. Dry cellulose fibres and alkali-treated cellulose fibres were dissolved in 1 to 2 mg/mL of tetrahydrofuran, and the molecular weight of the samples was measured by GPC (Agilent 1100, USA) with tetrahydrofuran as leachate.

Accessibility

Iodine adsorption measurements can be effectively used to determine adsorption in cellulose materials and its fabric. Consistent with the earlier discussion, the adsorption is assumed to take place in the amorphous and the surface of microcrystalline regions of cellulose, and not into the crystalline region, so it can be used to test the accessibility of cellulose. 0.3 g of dry novel fibrils and alkali cellulose samples were put into the brown glass bottles respectively. And 50 mL of iodine solution (0.1 mol/L) and 50 mL of saturated sodium sulfate solution were added accurately in the above bottles, mixing, and then put in 20 °C water for 1 h, followed by removal of 50 mL filtrates. Sodium hyposulphite standard solution (0.01 mol/L) was used in the titration, and 1% starch developing agent served as the indicator. The blank experiment was carried out with the same operation. The iodine adsorption value (mg) was calculated as,

$$V_{IS}/\text{mg} = \frac{(a - b) \times c \times 254}{2w} \quad (1)$$

where a is the consumable sodium hyposulphite solution with control groups (mL), b is the consumable sodium hyposulphite solution with samples (mL), c is the molar concentration of sodium hyposulphite solution (mol/L), and w is the dry weight of the sample (g).

CP/MAS ¹³C NMR measurements

The structure of natural fibres and alkali-treated cellulose fibres was determined with solid-state CP/MAS ¹³C NMR measurements conducted at room temperature on a Bruker AV300 spectrometer (Bruker, Germany) equipped with a CP MAS probe operating at 300 MHz. The rotational speed was around 5 KHz.

X-ray diffraction measurement

X-ray diffraction was carried out with a Riguka D/max-C X-ray diffractometer (Riguka, Japan) using Cu K α radiation ($\lambda = 0.154$ nm), and the diffraction patterns were collected in the 2θ range of 5~50°. The degree of crystallinity (X_c) of the samples was calculated using the ratio of the area in a diffractogram corresponding to crystalline (S_c) and amorphous regions (S_a) as follows (Zhili Yang *et al.* 1981):

$$X_c = \frac{S_c}{(S_c + S_a)} \quad (2)$$

Morphology analysis

To determine the surface texture of samples and evaluate changes in the surface that were provoked by the chemical treatments, natural and treated fibres were analysed using a scanning electron microscope (SEM) (SU1510, Hitachi Ltd.; Japan) at an accelerating voltage of 8 kV. All samples were attached to aluminum stubs and gold-coated to avoid electrostatic charging for improved image resolution (El Oudiani *et al.* 2012).

RESULTS AND DISCUSSION

The molecular weight of cellulose through alkali treatment can be measured by GPC after nitrating in an agent composed of nitric acid and methylene chloride at a weight ratio of 1:1, as shown in Table 2. The degree of polymerization of the neutral fibre was 1130, and the average polymerisation degree of alkali cellulose was measured as 521 with this method. Thus, cellulose was degraded after alkali treatment.

Table 2. Molecular Mass of Cellulose

Sample	M_w	DP
Cellulose Fibres	183200	1130
Alkali Cellulose Fibres	84540	521

Although cellulose fiber is a porous polymer with a wide pore size distribution, the coiling hierarchical and aggregated structures cause low accessibility and poor reactivity of cellulose with chemical reagents. Through swelling, the hydroxyl binding force would be weakened; this would improve the diffusion velocity of the reagent to the inside of cellulose. Figure 1 shows the iodine adsorption values for cellulose at low, high, and room temperatures and with 0%, 8%, 12%, 15%, 18%, 20%, and 25% sodium hydroxide concentrations. From the diagram it can be seen that the iodine adsorption value of cellulose after cryogenic alkali treatment was greater than in the room- and high-temperature samples. The results show that the iodine adsorption value first increased and then decreased slowly with increasing NaOH concentration, and the value of iodine adsorption reached a maximum when the NaOH concentration was 15%. The reaction of NaOH with cellulose releases ample heat, and a low reaction temperature is beneficial for the formation of alkali cellulose. High temperatures slow the reaction rate; therefore, a low temperature clearly increases the processing of cellulose.

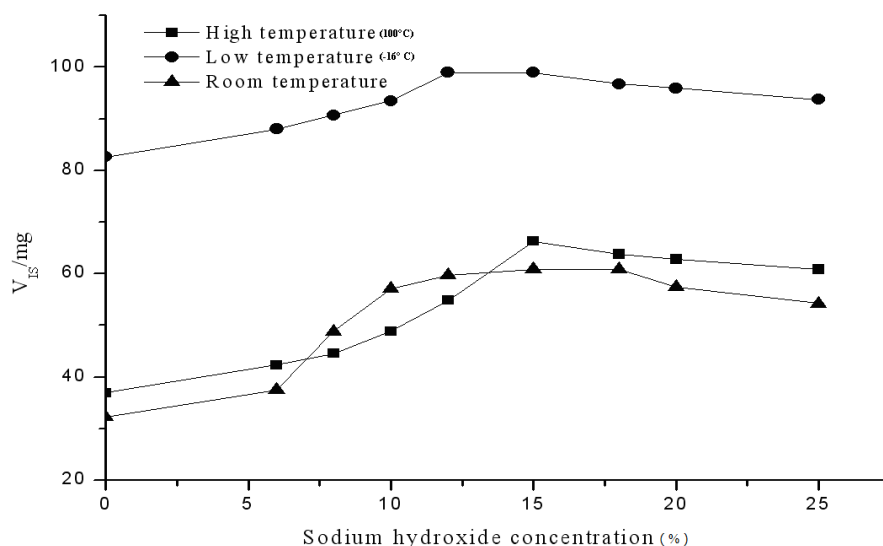


Fig. 1. Iodine adsorption values of cellulose with different temperatures and sodium hydroxide concentrations

There are three characteristic peaks of cellulose in X-ray diffractions, and these are located at approximately $2\theta = 14^\circ$, 16° , and 22° (cellulose I), and the positions of the (101), ($10\bar{1}$), and (002) crystallographic plane reflect natural cellulose (Khalifa *et al.* 1991; Davidson *et al.* 2004; Ouajai and Shanks 2005; El Oudiani *et al.* 2011). The diffractogram peaks are typical of the cellulose II polymorph, and are located at $2\theta = 11^\circ$, 20° , and 21° , corresponding to the diffraction of the (101), ($10\bar{1}$), and (002) crystallographic plane reflections in regenerated cellulose, respectively (Raymond *et al.* 1995; Oh *et al.* 2005; Ouajai and Shanks 2005; Assa *et al.* 2006; El Oudiani *et al.* 2011; Yue *et al.* 2013).

The wide-angle X-ray diffraction traces with corrected intensities and the crystalline parameters of treated cellulose with different sodium hydroxide concentrations are shown in Fig. 2 and Table 3. All of the diffractograms of the treated and untreated samples exhibit considerable overlap of the diffraction peaks. Thus, peak resolution is the only valid method for obtaining reliable parameters to measure crystallinity and apparent crystallite size. In this study, crystalline scattering is excluded from unidentified phases of non-cellulosic origin from the contribution to the total cellulose crystalline scattering. The diffractogram of fibres (0% (w/v) NaOH) shows a pattern quite similar to peaks characteristic of native cellulose (cellulose I), and the calculated degree of crystallinity was 66%. While the degree of crystallinity of cellulose fibres first decreased and then increased when treated with various concentrations of NaOH solutions from 8% to 25%, the diffraction traces were transformed from crystal I to II. The alkali treatment of cellulose, which induces irreversible transformation of the crystalline structure from native cellulose (cellulose I) to mercerised cellulose (cellulose II), goes through different crystalline complexes called soda celluloses (Na Cell) (Kayoko *et al.* 2011). The crystal packing of chains initially aligned in parallel for native cellulose I was rearranged into anti-parallel chains characteristic of cellulose II (Akira *et al.* 2003). During this

transformation, the alkali solution penetrated the amorphous regions located among the crystallites. The penetration of the alkali solution in the less ordered regions led to the formation of soda cellulose II, which had little effect on the chain conformation and crystalline regions. Nevertheless, the formation of soda cellulose II with anti-parallel chains is thermodynamically favorable and results in the gradual decrease of cellulose I crystalline regions, which further leads to the formation of soda cellulose II crystallites. Following the first step, cellulose I becomes able to absorb more alkali solution and is then converted into soda cellulose II, which has a helical structure. By washing Na-cellulose, all NaOH is eliminated, and the final structure of cellulose II is obtained by drying.

The crystallinity of 8% alkali cellulose was 61%, and the crystallinities of alkali cellulose decreased notably with an increase in NaOH. The minimum degree of crystallinity was 8% with 15% NaOH. These results indicate that alkali treatment has a decrystallising effect on cellulose. This is because of the interaction between sodium, cellulose, and Na^+ in the hydrated ion. Along with the increase in the alkali concentration, the crystal binding force is overcome by the hydration of the sodium ion. This causes a degree of change in the lattice, which is an irreversible swelling. At the same time, the intensity of the inter- and intra-hydrogen bonds of cellulose decreases with increasing amorphous areas, which leads to a loss in crystallinity. However, the degree of crystallinity showed an upward trend when the concentration of alkali subsequently increased. This is because part of the amorphous region was dissolved; the degree of crystallinity is 81% with 25% NaOH. Finally, it can be determined that the concentration of alkali-pretreated cellulose fibres was 15% and the crystallinity was 8%.

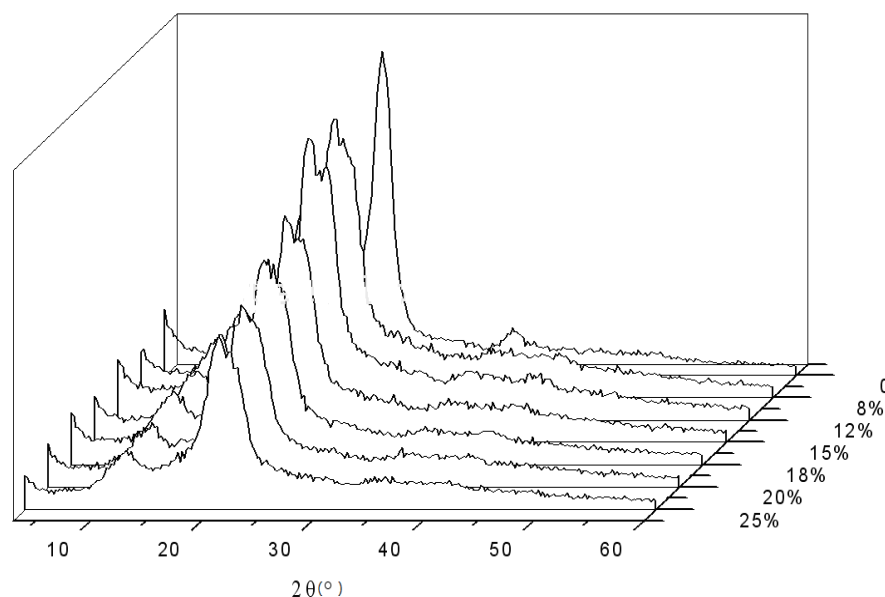
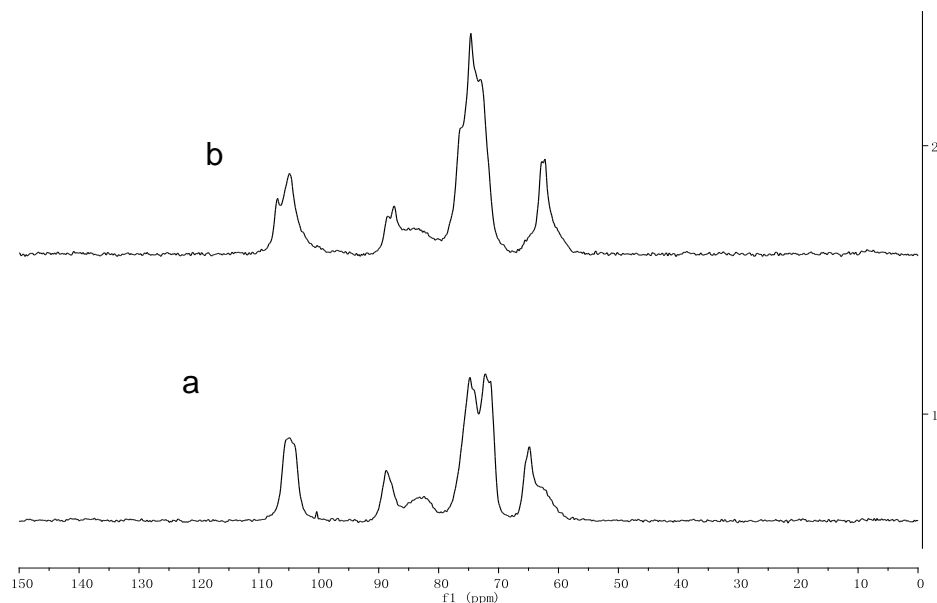


Fig. 2. The wide angle X-ray diffraction of cellulose with different sodium hydroxide concentrations

Table 3. Crystalline Parameters of Cellulose with Different Sodium Hydroxide Concentrations

Concentrations of NaOH	2θ (°)	d/A	h	k	l	Crystallinity (%)
0%	15.28	5.7939	1	0	1	65.96
	16.63	5.3265	1	0	-1	
	22.64	3.9242	0	0	2	
8%	12.38	7.1438	1	0	1	61.3
	20.52	4.3246	1	0	-1	
	22.13	4.0135	0	0	2	
12%	10.882	8.1238	1	0	1	23.79
	20.34	4.3625	1	0	-1	
	22.02	4.0333	0	0	2	
15%	11.44	7.7288	1	0	1	8.29
	20.46	4.3372	1	0	-1	
	22.21	3.9993	0	0	2	
18%	11.6	7.993	1	0	1	32.97
	20.26	4.3795	1	0	-1	
	22.329	3.9781	0	0	2	
20%	11.5	7.6685	1	0	1	74.72
	20.54	4.3205	1	0	-1	
	22.32	3.9798	0	0	2	
25%	11.74	7.5317	1	0	1	80.84
	20.28	4.3752	1	0	-1	
	22.16	4.0081	0	0	2	

The evidence for the molecular structures of native and soda cellulose is provided by the CP/MAS ^{13}C NMR spectra shown in Fig. 3.

**Fig. 3.** The CP/MAS ^{13}C NMR spectra of (a) native and (b) alkali cellulose

The strong peaks in the range of 60 to 110 ppm are all carbon signals. In the native spectrum, 104.90 ppm is the C1 signal, 88.78 ppm is the C4 signal (which belongs

to the crystalline region), and C2, C3, and C5 signals are found at 74.36 ppm. The peak at 65.06 ppm comes from the C6 signal of the crystalline region. However, in the Na cell spectrum, the peak at 65.06 ppm due to the C6 signal shifted to 62.3 ppm, which was in the amorphous region. This means that most of the cellulose crystal structure was broken and turned into amorphous cellulose after dissolving.

To improve the accessibility of cellulose for reagents, which is important for obtaining a high-quality product, the surface of the fibre can be pretreated using chemical methods (El Oudiani *et al.* 2012). Analysis by SEM was used to characterise any changes in the surface morphology of the cellulose. The SEM images were obtained for parent and alkali cellulose fibres. Figure 4 depicts the transformation in surface morphology of native fibres subjected to soda cellulose with 15% NaOH at -16 °C for 24 h. The untreated cellulose fibres exhibits a relatively smooth surface compared with the alkali fibres. Moreover, through erosion with NaOH, obvious erosion and grooves on the Na cell surface and in the intercellular region of the alkali fibre are clearly visible.

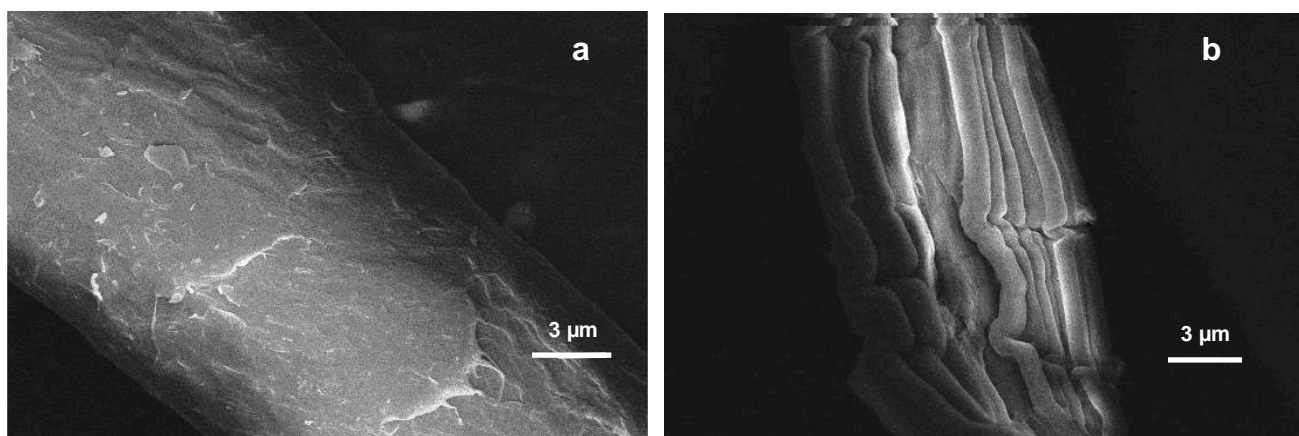


Fig. 4. The surface structure of (a) native and (b) alkali cellulose fibres

CONCLUSIONS

1. After pretreating cellulose with NaOH, the morphology of the fibre showed great variations in the primary wall of cellulose fibres and was extremely damaged; the fibre surfaces presented a folded shape.
2. The supermolecular structure of cellulose was transformed from the cellulose I crystalline form to cellulose II.
3. The shift of the C6 signal to the amorphous region signifies reduced crystallinity.
4. The reaction properties of cellulose fibres improve with increasing accessibility of cellulose and the exposed hydroxyl of cellulose inner layers, which is beneficial to graft or replace the modification of cellulose.

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