

Dissolution and Structure Change of Bagasse Cellulose in Zinc Chloride Solution

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The dissolution of sugarcane bagasse cellulose (SBC) in zinc chloride solution was studied at elevated temperatures. Based on single factor experiments, the effects of zinc chloride mass fraction, dissolution time, temperature, and bagasse cellulose mass fraction were investigated by an orthogonal experiment, and the optimal dissolution conditions were obtained. The dissolution process of bagasse cellulose was observed under a microscope. Additionally, the original SBC and regenerated SBC were both characterized by Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Temperature was found to be the most important factor affecting dissolution time. The best dissolving process took place at 85 °C to dissolve 2% SBC in 85% zinc chloride for 210 min. It was shown that the zinc chloride was a direct solvent for SBC. After regeneration of cellulose in zinc chloride, the crystallinity of cellulose was decreased greatly, from 77% to 54%, its crystalline form was transformed from cellulose I to cellulose II, its thermal decomposition temperature was reduced, its thermal stability was slightly decreased, and its internal structure was disrupted.

Keywords: Sugarcane bagasse cellulose; Zinc chloride solution; Solubility; Structure analysis

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INTRODUCTION

Because of climate change, dwindling fossil fuel resources, and increasing environmental pollution, the development of renewable resources has attracted increasing attention (Pacala and Socolow 2004; Ragauskas *et al.* 2006; Tan and MacFarlane 2010). Bagasse is a typical agricultural waste that is derived from sugar cane and consists of the fibrous residue that remains after crushing to remove sugar from sugar cane stalks. Generally, bagasse is composed of 32% to 48% cellulose, 19% to 24% hemicelluloses, and 23% to 32% lignin (Adsul *et al.* 2004). Bagasse cellulose is an ideal natural polysaccharide polymer material because it is a cheap, renewable, environmentally friendly, biocompatible material that can be degraded in the natural environment. It is considered to have great potential for development in the 21st century.

Cellulose, one of the most abundant renewable resources in the world, and its derivatives are now widely utilized in areas such as pharmaceuticals, chemical synthesis, and papermaking (Vermerris and Abril 2015). The market for cellulose has been experiencing steady growth for the past several years, driven by increased usage of the

product in various end-use capacities, and these demands drive the development of technology for cellulose production (Klemm *et al.* 2005). Regenerated cellulose of high molecular weight can be prepared as a kind of membrane material with great potential. It has shown great value in wastewater treatment, depending on how it has been modified.

However, because of the complexity of the cellulose network, the partial crystalline structure, and the extended noncovalent interactions among molecules, chemical processing of cellulose is rather difficult. Cellulose is neither meltable nor soluble in common solvents; water and typical organic solvents fail in this respect. Philipp *et al.* (1986) changed these classifications to derivatizing, non-derivatizing, aqueous, and non-aqueous systems. Additionally, the number of components in the solvent system has been considered in these classifications (Heinze and Liebert 2001). From an organic chemistry perspective, categorizing cellulose solvents as non-derivatizing or derivatizing systems is the most appropriate (Medronho and Lindman 2014). The derivatizing solvent group comprises all systems where cellulose dissolution occurs *via* covalent modification, resulting in an unstable ether, ester, or acetal intermediate. The term “non-derivatizing solvent” comprises systems capable of dissolving cellulose *via* physical intermolecular interactions alone.

A ZnCl_2 aqueous solution provides a new platform for utilization of cellulose because of its excellent dissolution capacity for cellulose. Compared with traditional solvents, it can be regarded as green, stable, cheap, and easy to recycle; furthermore, the dissolving process does not need activation, in addition to the advantage of simple operation (Cao *et al.* 1994). ZnCl_2 aqueous solutions dissolve cellulose in two steps: the solution penetrates the cellulose interior, then Zn^{2+} and Cl^- break the hydrogen bonds. The cellulose's intermolecular and intramolecular hydrogen bonding breakage promotes the dissolution of cellulose (Yang *et al.* 2011). Xiong *et al.* (2010) found out that ZnCl_2 aqueous solutions cannot dissolve cellulose unless the salt mass fraction is higher than 65%. The intramolecular hydrogen bond of regenerated cellulose appears to become weakened in the course of dissolution.

The aim of the present work was to investigate the ability of ZnCl_2 aqueous solution, a molten salt hydrate, to serve as a solvent for bagasse celluloses. A further aim was to investigate changes in the structure and properties of the regenerated bagasse cellulose in this solvent.

EXPERIMENTAL

Materials

Bagasse pulp (bleached kraft pulp) was obtained from Guangxi Guitang Co., Ltd. (China), and the sugarcane bagasse cellulose (SBC) applied in this study contained 83.92% cellulose, 9.34% hemicelluloses, and 5.13% lignin. Anhydrous zinc chloride (ZnCl_2 , analytical grade) was purchased from Tianjin Dibo Chemical Co., Ltd. (China). All solutions were prepared with distilled water.

Methods

Anhydrous ZnCl_2 was added to a 250-mL beaker with an electric stirrer to obtain ZnCl_2 aqueous solutions with concentrations of 65%, 70%, 75%, 80%, 85%, and 90%. The ZnCl_2 solution was then mixed with sugarcane bagasse cellulose (SBC) (1%, 2%, 3%, 4%, 5%, and 6%). Then, the system was stirred at various temperatures (50, 60, 70, 80, 90, and

100 °C). Regenerated SBC was obtained from the above solutions by adding about 150 mL of distilled water into the solution, which was allowed to stand for 48 h. The regenerated cellulose was collected *via* filtration, followed by thorough washing with distilled water and dried at 60 °C for 24 h. Additionally, during the dissolution process, the solution was sampled at intervals and observed under a light microscope (Nikon ECLIPSE 50i, Japan). The solubility (*S*), characterized by the quantity of cellulose dissolved, is expressed as,

$$S = [W_1/(W_1+ W_2)] \quad (1)$$

where W_1 is the weight of the dissolved cellulose and W_2 is the combined weight of the gel and insoluble cellulose isolated by centrifugation.

Fourier transform infrared spectroscopy analysis

The NICOLET iS50 FTIR spectra for native and regenerated SBC were obtained in the range of 500 to 4000 cm^{-1} (Thermo Fisher Scientific, USA). The scan speed was 0.2 cm/s , and 32 scans were taken per sample. The samples were mixed with KBr and ground before being pressed into wafers.

Wide-angle X-ray diffraction analysis

The crystalline structure of the samples was examined using a DX-2700A wide-angle X-ray diffractometer (HaoYuan Corporation, China). The radiation was Ni-filtered Cu-K α radiation of wavelength 0.1542 nm operating at 40 kV and 20 mA. The scanning range and rate were 5° to 65° and 0.04° s^{-1} , respectively.

Thermo-gravimetric differential thermal analysis

A TG instrument (Setaram STA, France) was used in this study to determine the changes in material mass loss and heat release with temperature. Samples were heated from 30 to 600 °C at 10 °C /min.

Scanning electron microscopy analysis

Images of the regenerated cellulose were acquired by SEM to observe the morphology and microstructure of the nascent cellulose. For SEM analysis, the fabricated materials were examined with an S-3400N scanning electron microscope (Hitachi, Japan), operated at 20 kV.

RESULTS AND DISCUSSION

Effect of ZnCl₂ Concentration on Dissolution Time

The effect of ZnCl₂ concentration on dissolution time was evaluated from 65% to 90% ZnCl₂ concentrations. As Fig. 1 shows, when the ZnCl₂ mass fraction increased from 65% to 90%, the cellulose dissolution time decreased from 360 to 253 min. The Zn²⁺ ions could penetrate the inner structure of bagasse cellulose, weakening the intramolecular and intermolecular hydrogen bonds and disrupting the crystalline region.

Effect of Temperature on Dissolution Time

It can be seen from Fig. 2 that with an increase in the solution's temperature, the solution time decreased. At 50 °C, 660 min are required to dissolve the cellulose, and when the temperature reached 100 °C, the cellulose was dissolved within 90 min.

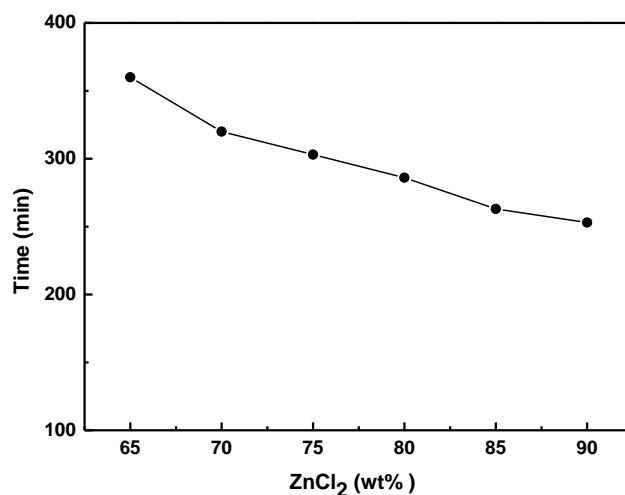


Fig. 1. Effect of ZnCl₂ content on concentration time (at 80 °C, cellulose concentration 1%)

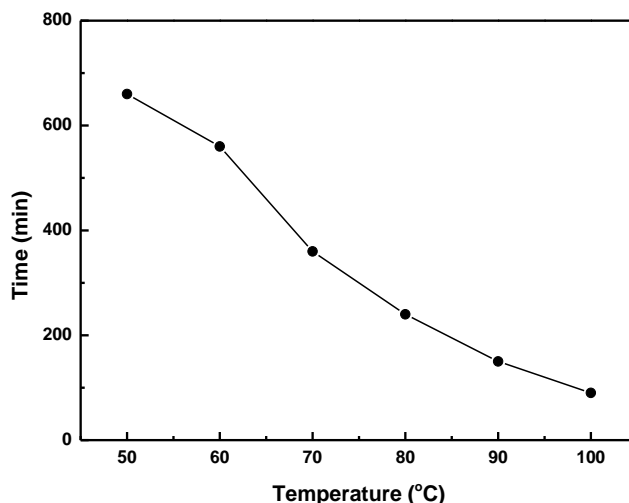


Fig. 2. Effect of temperature on dissolution time (at cellulose concentration 1%, ZnCl₂ 90%)

Temperature's influence on the properties of cellulose dissolution is three-fold: first, the endothermic reaction of cellulose is due to the stronger hydrogen bonding, so a high temperature can promote the dissolution of cellulose; second, a high temperature can aggravate the thermal motion of Zn²⁺ and Cl⁻ ions, which can make the cellulose fibers easier to aggregate together with solvent at high temperatures, which provide more energy for the dissolving process; third, high temperatures can reduce the viscosity of the solution, distributing the cellulose more evenly in the ZnCl₂ aqueous solution and promoting the dissolution of the cellulose in the ZnCl₂ solution completely. However, it was discovered that when the temperature was greater than 90 °C, the bagasse cellulose solution turned yellow, which indicated that cellulose may have degraded because of the high temperature (Heinze and Liebert 2001; Medronho and Lindman 2014).

Effect of Cellulose Content on Dissolution Time

The effect of cellulose content on the solubility of bagasse cellulose in zinc chloride solutions was tested. It can be seen in Fig. 3 that with an increase in cellulose content, the

dissolution time increased. When cellulose content was below 3%, it responded more gradually to changes in dissolution time. But after 3%, the dissolution time became longer. This was attributed to increased viscosity of the mixture.

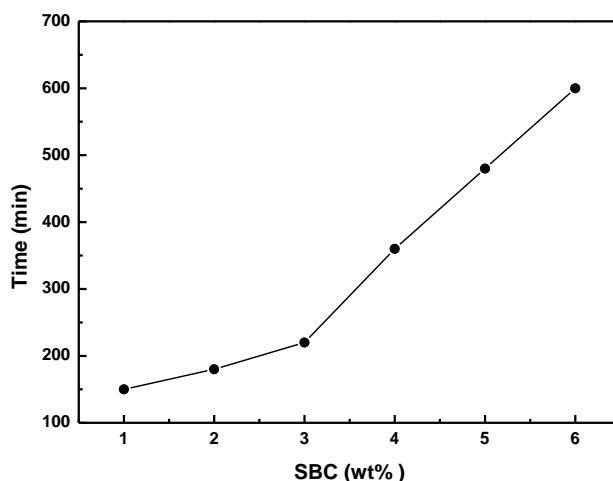


Fig. 3. Effect of cellulose contents on dissolution time (at 90 °C, ZnCl₂ 90%)

Table 1. The Best Solution Process with Zinc Chloride Aqueous Solution

Factors Samples	A ZnCl ₂ (w%)	B Cell (w%)	C T (°C)	D t (min)	S
1	80	1	80	180	84.2
2	80	2	85	210	92.3
3	80	3	90	240	88.3
4	85	1	85	240	93.8
5	85	2	90	180	91.5
6	85	3	80	210	88.5
7	90	1	90	210	92.3
8	90	2	80	240	89.3
9	90	3	85	180	91.2
K ₁ ^a	88.2	90.1	87.3	88.9	
K ₂	91.2	91.0	92.4	91.0	
K ₃	90.9	89.3	90.7	90.5	
K _{1/3}	29.4	30.0	29.1	29.7	
K _{2/3}	30.4	30.3	30.8	30.3	
K _{3/3}	30.3	29.8	30.2	30.2	
R ^b	3.0	1.7	5.1	2.1	
					C>A>D>B C ₂ A ₂ D ₂ B ₂

^a K₁, K₂, and K₃ stand for the sum of indicatrix which corresponds with the relevant grade of factor j. (j=A,B,C,D)

^b R reflects the effect of different levels of factor on the estimated index. If the R of one factor is big, it means different levels of this factor have the great effect on the estimated index value.

Orthogonal Experimental Design

An orthogonal experiment was employed to detect the influence of the zinc chloride mass fraction, dissolution time, dissolution temperature, and cellulose content on the dissolving mass fraction properties. Table 1 shows that the dissolution temperature was the largest influencing factor, ZnCl_2 mass was second, and dissolution time was the third most important factor. Cellulose content was the least influencing factor. The best dissolving process took place at 85 °C to dissolve 2% cellulose in 85% ZnCl_2 in 210 min.

Bagasse Cellulose Process of Dissolution

Figure 4 shows the changes in bagasse cellulose during dissolution in an aqueous ZnCl_2 solution.

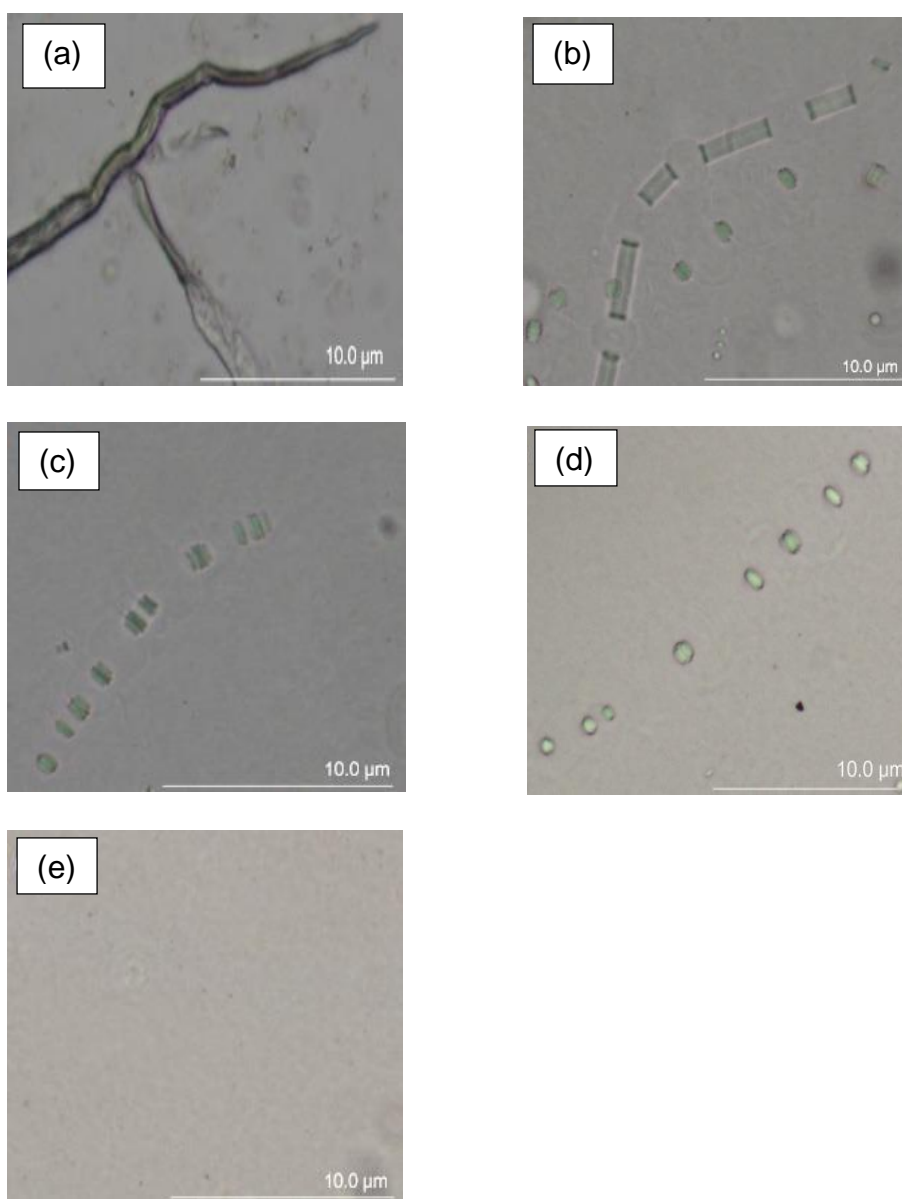


Fig. 4. Images for bagasse cellulose dissolution in aqueous ZnCl_2 solution for (a) 0 min, (b) 90 min, (c) 150 min, (d) 180 min, and (e) 210 min

It can be seen that the bagasse cellulose exhibited a clear image initially after mixing (Fig. 4a). Then a ballooning phenomenon became apparent, as shown in Fig. 4b. The ballooning can be attributed to solvent-induced changes in the molecular order of the native polymer. These changes take place to a variable extent, affecting the intermolecular interactions among the macromolecules. These interactions also would be modified by any chemical derivatization of the biopolymer. When placed in a swelling agent or a solvent, natural cellulose fibers can show non-regular swelling along the fiber. With increasing time, the size of bagasse cellulose particle decreased. After an even longer time (Fig. 4e), the visual field gradually disappeared, indicating that the bagasse cellulose became completely dissolved (Medronho and Lindman 2014).

FTIR Spectra for Native and Regenerated SBC

The FTIR spectra of native SBC and regenerated SBC are shown in Fig. 5. The spectrum of regenerated SBC was quite similar to its native counterpart and no new characteristic peaks were found, indicating that no chemical changes had occurred to the glucosides in the regenerated SBC. Thus, the aqueous ZnCl_2 solution can be considered to be a non-derivatizing solvent for SBC.

Nevertheless, there were also some differences in band wavenumbers between native and regenerated cellulose. As seen from Fig. 5, the adsorption band between 3320 and 3297 cm^{-1} indicates the interactions of hydrogen bonds. The peak at 1115 cm^{-1} was shifted to 1094 cm^{-1} and the one at 895 cm^{-1} was shifted to 887 cm^{-1} . According to Ahmad *et al.* (2011) and Ma *et al.* (2006), the peak at the lower wave number was a result of strong hydrogen bonds, which drag the relative groups to a lower vibration frequency, and the peaks at the higher wave numbers are due to the weak interaction of hydrogen bonding. Thus, the changes in wave numbers indicated less hydrogen bonding in the regenerated SBC.

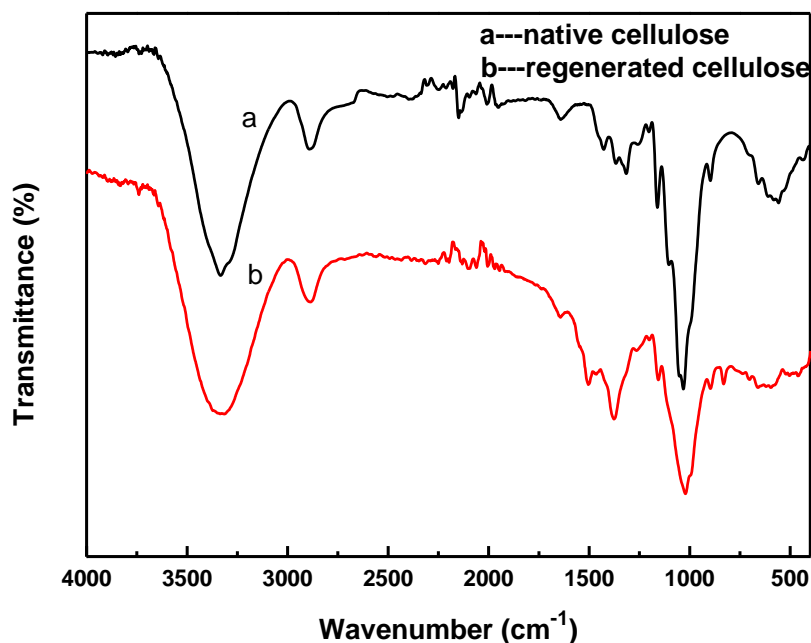


Fig. 5. FTIR spectra for (a) native cellulose and (b) regenerated cellulose

XRD Analysis of Native and Regenerated SBC

Native SBC and regenerated SBC after treatment with aqueous ZnCl_2 solutions were examined by XRD, and the results are shown in Fig. 6. Native SBC exhibited a typical A-type XRD pattern, giving strong reflections at approximately $2\theta = 16^\circ$ and 24° , which is a typical cellulose I type. It was also found that regenerated SBC exhibited strong reflections at approximately $2\theta = 14^\circ$ and 22° , which is a typical cellulose II type.

According to peak separation fit (Liu *et al.* 2015), the degree of crystallinity of the regenerated cellulose was 54%, which was lower than the original SBC (77%). This result showed that the crystalline region of native SBC was damaged during dissolution. The loss of crystallinity could be attributed to Zn^{2+} ion penetration into SBC, which weakened the inter- and intra-molecular hydrogen bonds (Lin *et al.* 2015). These results were in agreement with the shifts observed by FTIR.

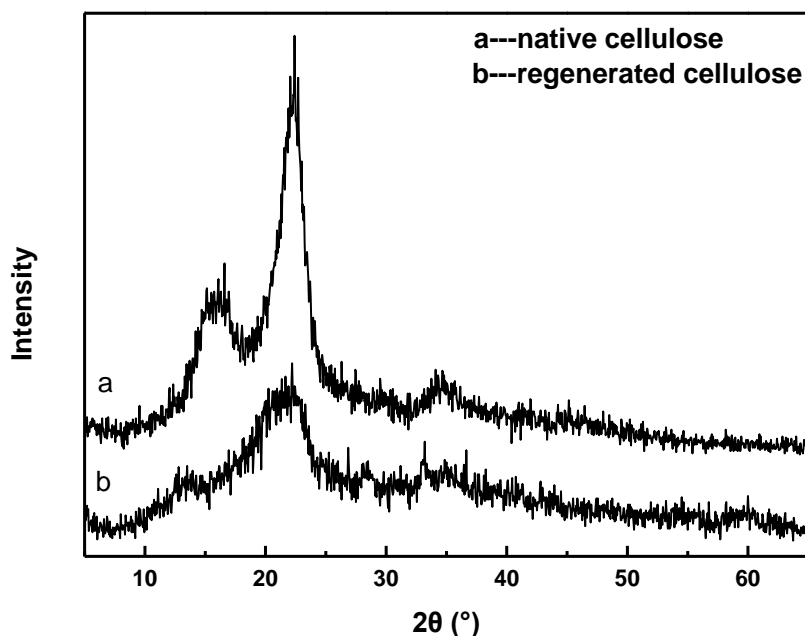


Fig. 6. XRD patterns of (a) original cellulose and (b) regenerated cellulose

Thermal Decomposition of Native and Regenerated SBC

The thermal behavior of the native cellulose and regenerated cellulose is shown in Fig. 7. The mass losses within 150°C of the initial temperature were related to water evaporation on the surface of cellulose. From 150 to 240°C , the mass was almost unchanged. Further weight loss from 240 to 380°C was relatively fast because of the dehydration and decomposition of the molecules of cellulose. From 380 to 600°C , the mass losses were slower (Lu and Shen 2011).

The maximum degradation and initial degradation temperatures were 346.1 and 245.5°C , respectively, for cellulose, and 326.10 and 232.2°C , respectively, for regenerated cellulose. These results indicate that the thermal stability of the regenerated cellulose was slightly worse than that of the original cellulose.

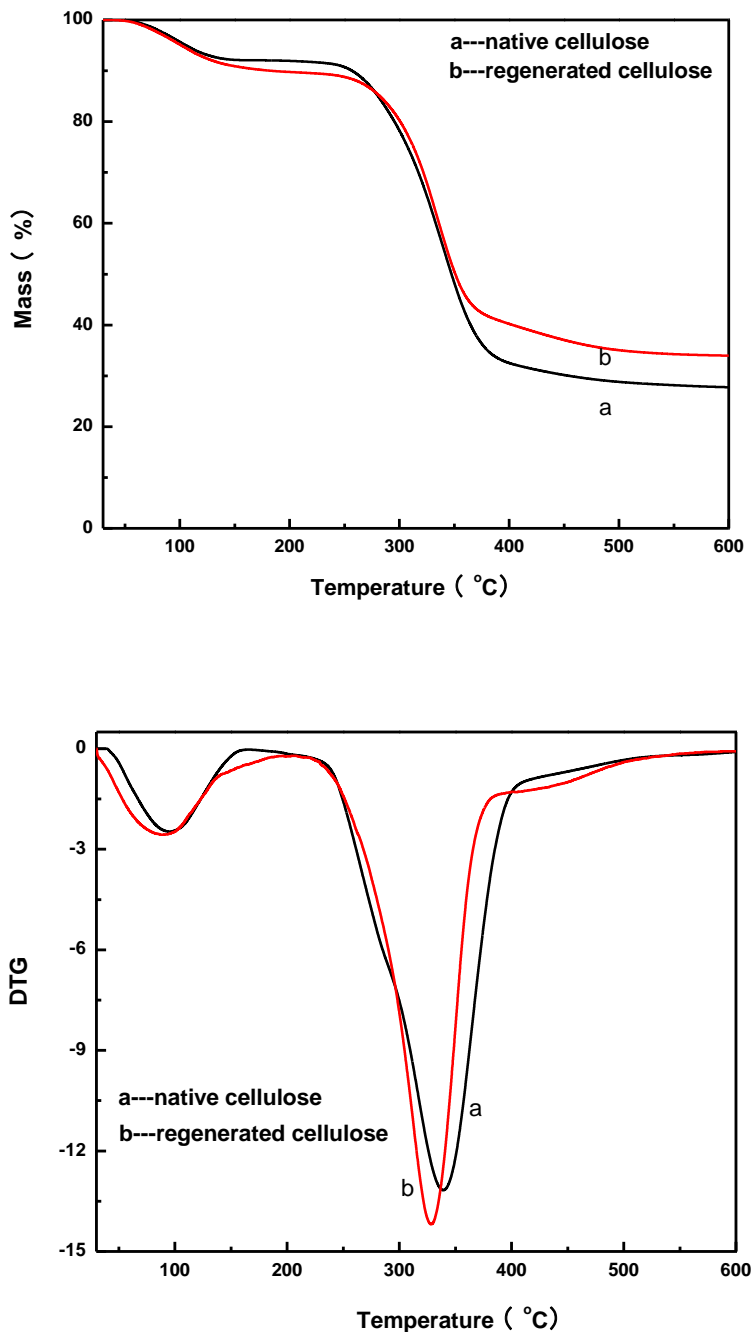


Fig. 7. TGA and DTG curves of original cellulose and regenerated cellulose

Morphology of Native and Regenerated SBC

SEM analysis was used to characterize the structures on the surface of the original and regenerated cellulose. The native cellulose (Figs. 8a and 8b) had a smooth and homogeneous nonporous structure, indicating a dense architecture. However, the surface of regenerated cellulose (Figs. 8c and 8d) exhibited a very rough surface, and a new compact cortex appeared in the regenerated cellulose.

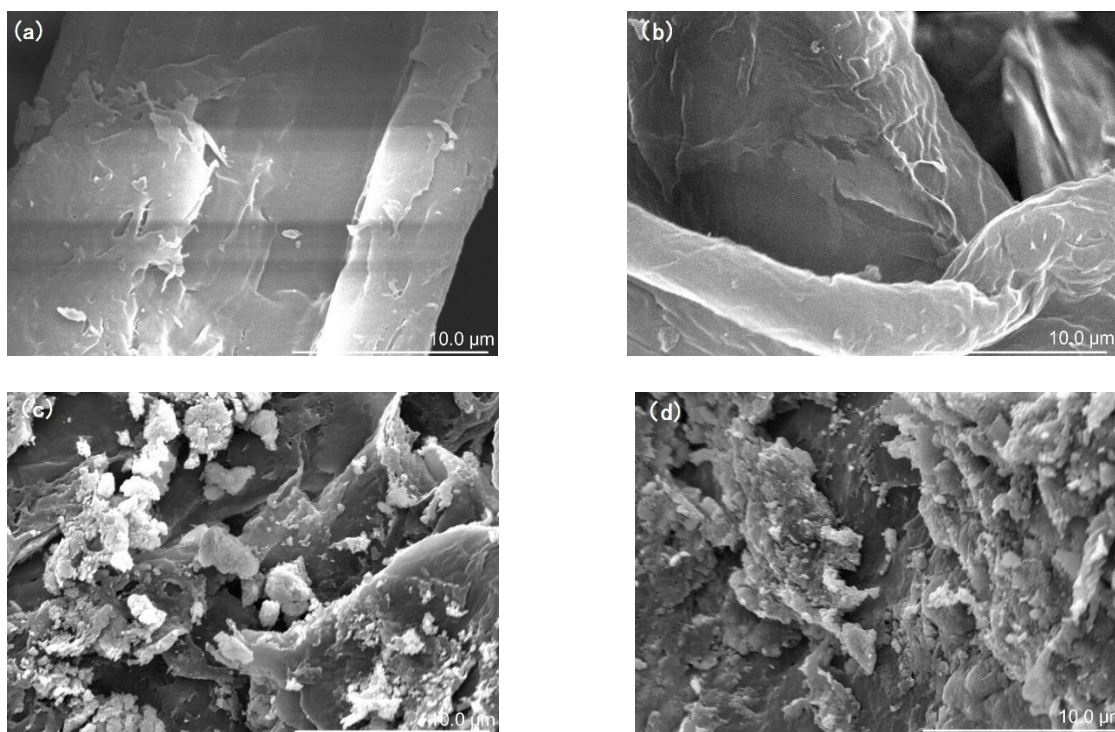


Fig. 8. SEM images of (a, b) original cellulose and (c, d) regenerated cellulose

CONCLUSIONS

1. An orthogonal experiment was designed to detect the influence of zinc chloride mass fraction, dissolution time, dissolution temperature, and cellulose contents on the bagasse cellulose dissolution. It was discovered that the dissolution temperature was the greatest influencing factor, zinc chloride mass fraction was second, and dissolution time was third. Cellulose content was the least influencing factor. The best dissolution process was at 85 °C to dissolve 2% cellulose in 85% zinc chloride in 210 min.
2. With increasing zinc chloride mass fraction and temperature, dissolution was enhanced. However, an aqueous zinc chloride solution cannot completely dissolve cellulose when the cellulose content is beyond 6%.
3. By characterizing the structure and properties of regenerated SBC, the aqueous $ZnCl_2$ solution was found to be a non-derivatizing solvent for bagasse cellulose, whose crystalline form transformed completely from type I to type II after regeneration directly from the $ZnCl_2$ solution. The combination of dissolution and regeneration destroyed the inter- and intra-molecular hydrogen bonds of cellulose and converted the crystalline structure to an amorphous state. The regenerated cellulose had a lower degree of crystallinity and thermal stability than the original cellulose.

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