

Performance of NaClO in selective oxidation of salix microcrystalline cellulose

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By oxidizing primary hydroxyl on surface of the salix microcrystalline cellulose with NaClO, we studied the effects onto performance of salix microcrystalline cellulose resulted from oxidant in different amounts. Performance of salix microcrystalline cellulose having been oxidized takes on attributes including lower degree of polymerization, stronger hydrophilicity due to increased carboxyl, which also resulted in larger water retention values; oxidation at paracrystalline areas began to oxidize crystallization areas, making the oxidized cellulose have higher pyrolysis temperature, significantly smaller granularity and increased specific surface, which caused some damage to superficial and internal structures, so that changes occurred in form of the cellulose.

Keywords: Salix Cellulose, Selective Oxidation, Performance

INTRODUCTION

During selective oxidation of the cellulose, intramolecular hydroxyl will be oxidized into carboxylic acid group, which will enhance cellulose's reactive activity and adsorptive capacity for ion. In the process of preparing composite material in the solution, dispersion degree of carboxylic acidified cellulose has also been improved, which greatly expanded the application range of cellulose in different fields. Together with biocompatibility and degradability, cellulose has been under the spotlight in fields of nanophase materials and biomedicine [1, 2, 3, 4, 5]. Richard K. Johnson used to utilize TEMPO to oxidize cellulose and study the application of cellulose in the field of nanocomposites, where content of carboxyl group reached up to 1.1 mmol/g after cellulose having been carboxylic acidified. Youssef Habibi [6, 7] carboxylic acidified the nano-cellulose, microcrystalline cellulose and cellulose whiskers they have prepared. Flocculation didn't appear in those cellulose having been treated and birefringence occurred in the cellulose whiskers under polarizing microscope. He also prepared nano-composite materials with those carboxylated cellulose. After the study, he found that carboxylic acidification could greatly improve adsorptive capacity of the fiber, which serves as the best template for nanocomposites. T. Saito et al [8] conducted attribute analysis on aldehyde content and carboxylic acid group of the carboxylated cellulose with different cellulosic feedstocks and oxidation processes and studied changes of

performance index with polymerized degree, pattern, crystal structure, crystallinity, water retention value and so on. A. Isogai et al [9] oxidized cellulose materials with the TEMPO / NaClO / NaBr oxidation system. A lot of experiments showed that amount of TEMPO had great impact onto polymerization degree of the product. Both regenerated fiber and mercerized fiber can be completely oxidized. However, natural cellulose can't realize complete selective oxidation, mainly due to high crystallinity of native cellulose affects the oxidation effect..

EXPERIMENTAL

Disperse the prepared salix microcrystalline cellulose in deionized water to make 2.0% solution of microcrystalline cellulose, add TEMPO (0.1 mmol/g) and NaBr (1 mmol/g) to make stable solution for later use, adjust PH to 10.75 with sodium carbonate/sodium bicarbonate solution as a buffer, add a certain amount of 9% NaClO solution, adjust PH to be constant with ammonia, and then finish the preparation of salix cellulose with different levels of carboxylic acid groups. As PH value keeps unchanged during reaction, add a certain amount of absolute ethanol to terminate the reaction. Stir for 10 minutes, centrifuge at high speed and then obtain the carboxylated salix cellulose. Repeatedly wash with deionized water, add 0.1 mol/L AgNO₃, test to make sure no presence of chloride ions, dry at low temperatures for later use.

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To Determine Content of Carboxylic Acid Group in Salix Cellulose

Obtain carboxylic acid in free state by the replacement reaction between calcium acetate and carboxylic acid group on the salix cellulose, and then use standard NaOH solution to titrate. The principle as follows:



Weigh 1 g of the sample mentioned above, soak the sample with 50 ml of 0.1 mol/L newly-prepared calcium acetate in a 100 ml iodine flask, place for 24 hours with stirring. Take 10ml of solution mentioned above and place in a 250 ml conical flask, add mixed indicator of cresol red - thymol blue, select 0.1 mol/L standard NaOH solution as the titration reagent, observe colour of the solution changing from yellow to purple, record consumption volume of NaOH solution as V, take another 10ml of solution mentioned above for blank test, titrate with standard NaOH solution at $c = 0.1 \text{ mol/L}$, and record volume of the standard NaOH solution as V_0 .

Formula for calculating content of the carboxylic acid group as follows:

$$\text{Carboxyl group content (mmol} \cdot \text{g}^{-1}) = (V - V_0) \times 5c / W$$

Where, W is the absolutely dry mass of test sample under accurate weighing.

To Determine Polymerization of Salix Cellulose with Carboxylic Acid Group

Adopt the Uno Viscosity Method to calculate the degree of polymerization. Dissolve 0.05 g of salix microcrystalline cellulose and 0.05 g of oxidation product respectively in 1 M of copper ammonia solution and 0.1 M of NaCl solution, and analyze viscosity of the solution in a thermostat. Draw 15 ml of the prepared solution and inject into the viscometer, keep temperature of the viscometer constant, let the solution flow from end opening of the viscometer, and record the time for solution to flow through the viscometer with a stopwatch. Repeat the test for three times, ensuring time difference among the three tests to be 0.2 s. Determine relevant value at T2 with the same method, adding 5 ml, 15 ml and 25 ml of copper ammonia solution respectively. And then determine relevant values at T3, T4 and T5. Obtain viscosity of the salix cellulose at 25°C -- $[\eta]$. In the same way, obtain viscosity of the carboxylated salix cellulose at 25°C -- $[\eta]$.

To Determine Water Retention Value of the Salix Cellulose with Carboxylic Acid Group

Weigh 0.25 g of absolutely-dry cellulose with carboxylic acid group, put into stainless-steel strainer, and make absorption at 25°C for 30 minutes. Put the strainer with sample into high speed centrifuge at 6000 rev / min for 15 minutes. Take out the sample and weigh, and record the weight as W1. Place the sample in a vacuum drying oven at 105°C for 4 hours, weigh the sample and record the weight as W2. Use the following formula to calculate the water retention value (WRV%):

$$WRV = 100(W1 - W2) / W2$$

RESULTS AND DISCUSSION

Effect of the Amount of NaClO onto Carboxyl Content of Salix Cellulose

Figure 1 showed that carboxyl content of salix cellulose increased along with the amount of NaClO getting larger. As amount of NaClO increased to 5.0 mmol/g from 1.0 mmol/g, content of carboxylic acid group in the salix cellulose increased to 0.90 mmol/g from 0.21 mmol/g, indicating that larger amounts of NaClO could break crystalline areas on the surface of salix cellulose and thus enhance the degree of oxidation in crystalline areas of the salix cellulose. A small amount of hemicellulose contained in the salix cellulose may serve as another reason, because hemicellulose has the lower molecular weight whose pentosan can be easily carboxylated.

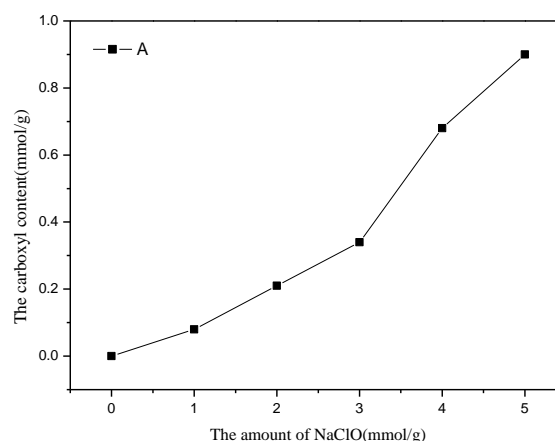


Fig. 1. Effect of the amount of NaClO onto carboxyl content of salix cellulose.

Effect of The Amount of NaClO onto Polymerization of Salix Cellulose

In general, water retention value of the cellulose is related to length of the cellulose, swelling resistance of the cellulose, fibrillation and other factors.

As having been oxidized, amount of small pieces in the cellulose will increase. However, water retention value of the oxidized cellulose gets larger due to increased amount of carboxyl group which has the hydrophilicity. Therefore, as amounts of NaClO changing, salix cellulose will change and water retention value will get larger. As shown in the figure 2, water retention value increased for 198% as amount of NaClO reached to 5 mmol/g, which was one time larger than the water retention value of non-oxidized cellulose.

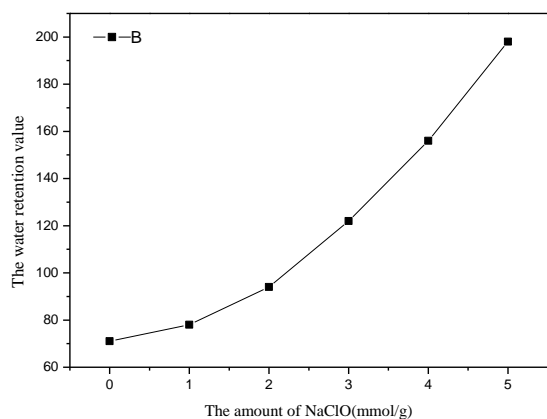


Fig. 2. Effect of the amount of NaClO onto water retention value of salix cellulose.

Ultra-Red Adsorption Spectroscopy on NaClO Amounts Used for Salix Cellulose

As shown in Figure 3, increased amount of NaClO enhanced the oxidizing power of the oxidation system for salix microcrystalline cellulose. Along with changing amounts of NaClO, oxidized salix microcrystalline cellulose showed strengthened absorption peak at 1650 cm^{-1} site, which was mainly the carbonyl absorption peak. Because carboxyl groups were introduced onto macromolecule chain of the salix cellulose having been oxidized. Content of carboxylic acid group increases along with increased amounts of NaClO, where absorption strength and width of the peak also enhanced. There were no changes at other major absorption peaks, which indicated that other functional groups had no changes and congruous chemical structures during the oxidation. However, stretching peaks of the secondary hydroxyl group at sites of 1110 cm^{-1} and 1175 cm^{-1} showed significantly decreased vibration, because secondary hydroxyl groups at C2 and C3 on macromolecular chains of salix cellulose had been oxidized into aldehyde groups. Therefore, it indicated that selective oxidation mainly occurred in the oxidation process which produced the dialdehyde-oxidized salix cellulose. Also shown in the figure, absorption peak at the 1650 cm^{-1} site had

no obvious changes as amounts of NaClO increasing from 1 mmol/g to 3 mmol/g. Changes on absorption peak at the 1650 cm^{-1} site became obvious as amounts of NaClO increasing from 3 mmol/g to 5 mmol/g. Because NaClO at the amount between 1 mmol/g and 3 mmol/g mainly oxidized paracrystalline areas of the microcrystalline cellulose. As the amount continued to grow, oxidation in the paracrystalline area finished and began to occur in the crystalline area, which caused enhanced absorption peak at 1650 cm^{-1} site and increased exposure of secondary hydroxyl group in the crystalline area, where stretching peaks of the secondary hydroxyl group at sites of 1110 cm^{-1} and 1175 cm^{-1} showed enhanced vibration.

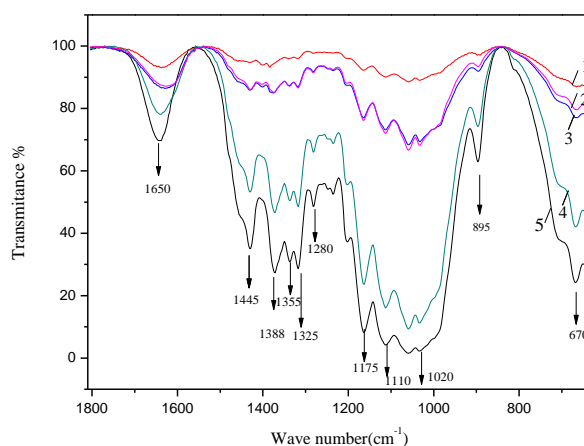


Fig. 3. Ultra-red adsorption spectroscopy on different NaClO amounts used for salix cellulose.

Thermo-Gravimetry for Salix Cellulose Based on NaClO Amounts

Figure 4 to Figure 8 showed that heat resistance of the carboxylated cellulose changed along with the amounts of NaClO going as 1 mmol/g, 2 mmol/g, 3 mmol/g, 4 mmol/g and 5 mmol/g. Free water contained in the carboxylated cellulose acts as the reason for weight loss at 150°C. In an amount of 1.0 mmol/g NaClO, weight loss started at 215°C and ended at 408°C. When the amount of NaClO reached to 2.0 mmol/g, initial temperature for weight loss had no obvious changes and termination temperature was at 443°C. In an amount of 3.0 mmol/g NaClO, termination temperature for weight loss was at 476°C. In an amount 4.0 mmol/g NaClO, termination temperature for weight loss was at 528°C. When the amount reached to 5.0 mmol/g, termination temperature for weight loss was at 551°C. Strengthened oxidation in the salix microcrystalline cellulose caused the thermal decomposition temperature presenting an upward trend. As oxidation in the microcrystalline cellulose getting

deepened, non-crystalline areas on the surface will be oxidized and degraded. As a result of oxidation getting into the crystalline area, amount of cellulose will get larger and thus termination temperature will get higher. In addition, absorption peaks on thermal decomposition became significantly moderate, which was mainly caused by a large amount of oligosaccharides produced during oxidation.

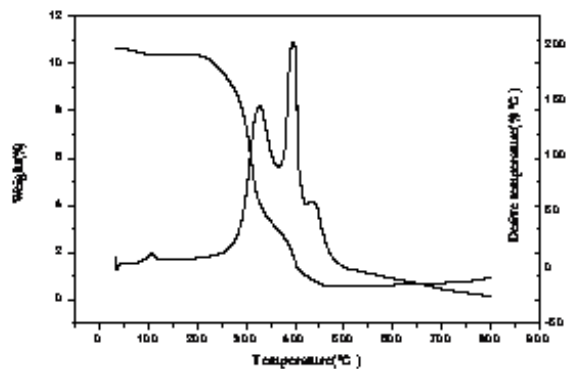


Fig. 4. TG diagram under 1.0 mmol/g NaClO.

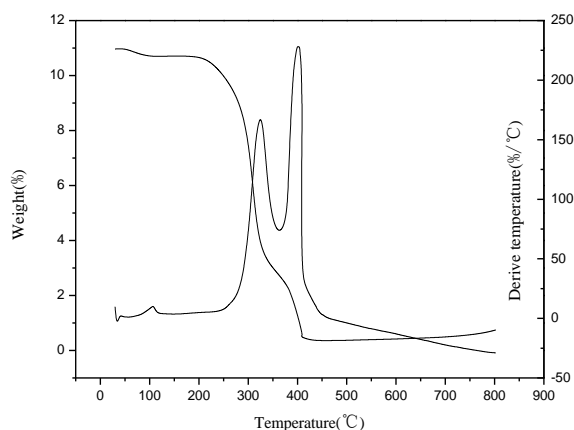


Fig. 5. TG diagram under 2.0 mmol/g NaClO.

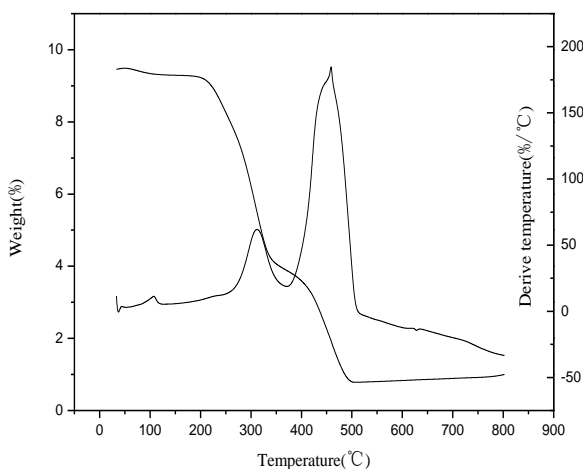


Fig. 6. TG diagram under 3.0 mmol/g NaClO.

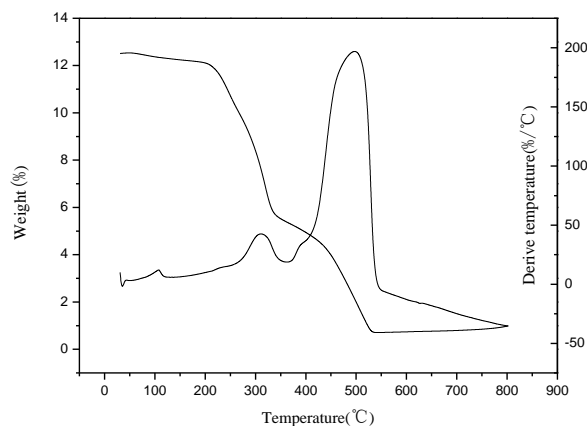


Fig. 7. TG diagram under 4.0 mmol/g NaClO.

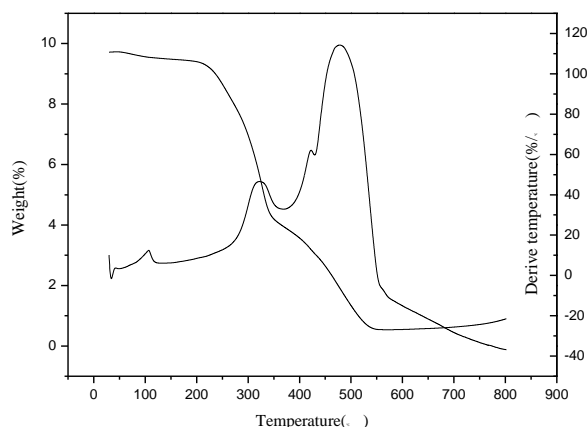


Fig. 8. TG diagram under 5.0 mmol/g NaClO.

Sem Analysis for *Salix* Cellulose Based on *Nacl*o Amounts

As seen from figure 9-13, changes occurred on surface of the cellulose with continuous adding of NaClO. When NaClO added in an amount of 1.0 mmol/g, surface of the cellulose having been carboxylated became rough, interface on the surface became blurred and began to show coarseness. When NaClO added in an amount of 3.0 mmol/g, orientation of the cellulose deteriorated. When NaClO added in an amount of 4.0 mmol/g, orientation of the cellulose disappeared. When NaClO added in an amount of 5.0 mmol/g, cavities began to appear on the surface, which mainly because larger amounts of oxidant continuously got into crystalline areas of the cellulose and resulted in oxidation. Meanwhile, granularity of the cellulose became significantly small and specific surface became larger, which indicated that increasing amounts of oxidizer were liable to cause some damage for surface and internal structures of the suit fiber, making forms of the cellulose change.

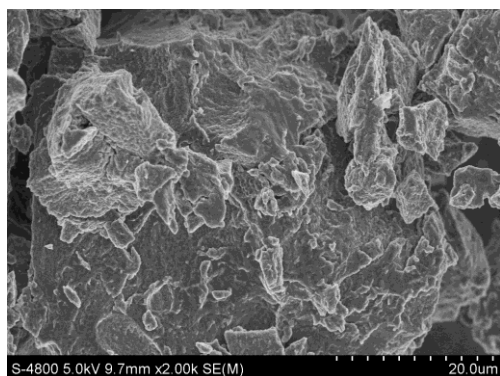


Fig. 9. Scanning electron micrograph under 1.0 mmol/g NaClO.

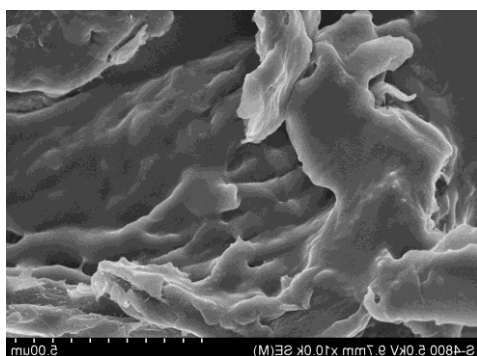


Fig. 10. Scanning electron micrograph under 2.0 mmol/g NaClO.

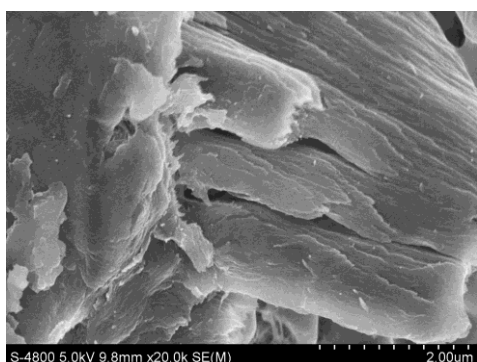


Fig. 11. Scanning electron micrograph under 3.0 mmol/g NaClO.

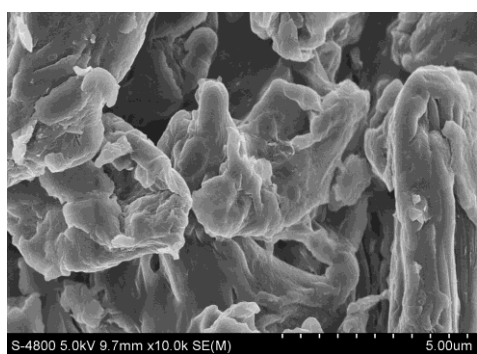


Fig. 12. Scanning electron micrograph under 4.0 mmol/g NaClO.

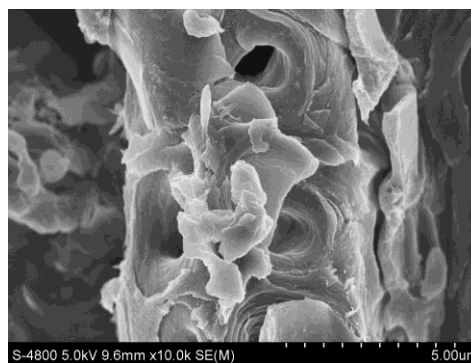


Fig. 13. Scanning electron micrograph under 5.0 mmol/g NaClO.

CONCLUSION

1. With the increasing amounts of NaClO, number of carboxylic acid groups becomes larger during selective oxidation of salix cellulose, changing from 1.0mmol/g to 5.0mmol/g. On the contrary, increasing amounts of NaClO can decrease polymerized degree of the salix cellulose, which indicates that carboxylicly acidified degree of the salix cellulose is related to the polymerized degree. After cellulose having been oxidized, content of carboxyl groups will get larger, leading to stronger hydrophilicity. As amounts of NaClO changing, salix cellulose will change and water retention value will get larger accordingly. Water retention value increased for 198% as amount of NaClO reached to 5 mmol/g, which was one time larger than the water retention value of non-oxidized cellulose.

2. NaClO at the amount between 1 mmol/g and 3 mmol/g mainly oxidized para-crystalline areas of the microcrystalline cellulose. As the amount continued to grow, oxidation in the para-crystalline area finished and began to occur in the crystalline area, which caused enhanced absorption peak at 1650cm⁻¹ site and increased exposure of secondary hydroxyl group in the crystalline area, where stretching peaks of the secondary hydroxyl group at sites of 1110 cm⁻¹ and 1175 cm⁻¹ showed enhanced vibration.

3. As amount of NaClO added in larger amounts, strengthened oxidation in the salix microcrystalline cellulose will cause the thermal decomposition temperature presenting an upward trend. Along with oxidation in the microcrystalline cellulose getting deepened, non-crystalline areas on the surface will be oxidized and degraded. As a result of oxidation getting into the crystalline area, amount of cellulose will get larger and thus termination temperature will get higher. Absorption peaks on thermal decomposition became significantly moderate, which was mainly caused

by a large amount of oligosaccharides produced during oxidation.

4. Larger amounts of oxidant continuously will get into crystalline areas of the cellulose and result in oxidation. Meanwhile, granularity of the cellulose became significantly small and specific surface became larger, which indicated that increasing amounts of oxidizer were liable to cause some damage for surface and internal structures of the suit fiber, making forms of the cellulose change.

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