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Thermal degradation behaviors of spherical cellulose nanocrystals with sulfate groups

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Abstract

A kind of spherical cellulose nanocrystals was prepared by hydrolysis of microcrystalline cellulose with mixed acid. In order to improve the thermal stability, two methods were used: diminishing the acid sulfate groups by desulfation and neutralizing them by using NaOH solution. The thermal degradation behaviors were characterized by thermogravimetric analysis and differential scanning calorimetry at nitrogen current. The results indicated that the degradation of cellulose nanocrystals with acid sulfate groups started at lower temperature and showed two remarkable pyrolysis processes. Profile analysis of the derivative thermogravimetric curves showed that each pyrolysis process was composed of multi-step reactions. When neutralized by NaOH solution, the degradation shifted to the higher temperature and occurred within a narrow temperature range. The influence of particle size of cellulose on degradation was also investigated. The results indicated that the degradation of cellulose with small size took place at lower temperature and facilitated the char residue formation.

Keywords: Thermal degradation; Cellulose nanocrystals; Particle size

1. Introduction

The stable suspension of cellulose nanocrystals (CNCs) can be prepared by acid hydrolysis of native cellulose [1,2]. It has gained much attention due to the suspension formation of the chiral nematic phase above critical concentration [3–8]. In recent years, the application of CNC as reinforcing filler in polymer composites has attracted wide interest because of their the renewable nature and the high mechanical properties [9–14]. The thermostability of cellulose nanocrystals is important for these applications, especially for thermoplastics because the processing temperature often exceeds 200 °C [15].

The native cellulose was usually hydrolyzed by sulfuric acid to obtain the stable suspension of CNC because the negative sulfate groups were introduced into the outer surface of cellulose during the hydrolysis process [3,16]. However, the presence of acid sulfate groups would decrease the thermal stability by the dehydration reaction [17]. Usually, the higher acid sulfate groups content in cellulose leads to a lower temperature of thermal degradation of cellulose. If hydrochloric acid is used instead of sulfuric acid to hydrolyze the native cellulose, the thermal stability of the prepared nanocrystals would improve, while the nanocrystals inclined to aggregate due to lacking of the electrostatic repulsion force between crystal particles [18]. In the present work, a kind of mixed acid of sulfuric acid and hydrochloric acid was used to prepare the spherical CNC. In this case, smaller content of acid sulfate groups was introduced into the surface of CNC, on the other hand, the suspension still kept stable.

In order to improve the thermal stability of CNC with acid sulfate groups, two methods were usually adopted: diminishing the acid sulfate groups by desulfation and neutralization by alkaline solution. In the present work, these two methods

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were used to treat the spherical CNC and the differences of their thermal degradations were investigated. This work elucidated the relationship between the acid sulfate groups, the sodium sulfate groups, and the thermal degradation behaviors of CNC. Moreover, the degradation behaviors of the raw materials, microcrystalline cellulose (MCC), were also investigated and compared with the behaviors of CNC to study the influence of particles' size on the thermal degradation of cellulose.

2. Experimental section

2.1. Sample preparation

A commercial MCC (particle size: 20 μm) was purchased from the Gaoli Regent Company (Guangzhou, China). Both the sulfuric acid (98% w/w) and the concentrated hydrochloric acid (37% w/w) were of analytical grade.

MCC was treated by ultrasonic (NP-B-33-400, Newpower Ultrasonic Equipments Co. Ltd., China) for 10 h at 68 °C with mixed acid composed of 30% (v/v) sulfuric acid and 10% (v/v) hydrochloric acid. The ratio of mixed acid to MCC was 25.7 (mL g^{-1}). After hydrolysis, the suspension was cooled to room temperature and then repeatedly washed with distilled water until the pH of suspension reached up to about 3. The supernatant and the agglomerated micro-cellulose particles were separated by centrifugation. The supernatant was transferred into the dialysis membranes having a molecular weight cutoff of 8000 and dialyzed against distilled water for several days until the pH of outside membrane water reached neutrality. However, pH of the inner suspension was around 5 which was coded as sample CNC-a. The CNC-b was obtained by repeated washing of CNC-a with distilled water for more than 1 month until the suspension was about neutrality. Then 1.0% (w/w) NaOH solution was added to the CNC-a suspension with stirring to adjust the suspension pH to about 9.0 and then stood for 48 h at room temperature. Afterwards the suspension was washed with distilled water to neutrality to obtain the sample CNC-c. Some definite volume of CNC-a suspension was added to the 20-fold 1.0% NaOH solution with stirring, stood for 48 h at room temperature and washed with distilled water to neutrality to obtain the sample CNC-d.

Some commercial MCC powders were immersed into the 0.1% H_2SO_4 (w/w) solution for 8 h. In this concentration of H_2SO_4 solution, small amounts of sulfuric acid molecules would absorb into the surface of MCC. On the other hand, the structure of MCC would maintain and was not damaged by sulfuric acid. The impregnated MCC was filtered by Buchner funnel with distilled water until the filtrate reached up to pH ≈ 4.0 and the sample named as MCC-a. The sample MCC-a was treated by same methods corresponding to CNC samples to obtain a series of MCC samples, coded as MCC-b, MCC-c and MCC-d.

All samples were dried at 80 °C in vacuum drying oven for 48 h and then cooled to constant weight in the desiccator at room temperature.

2.2. Instrumental analysis

The surface charge of CNC particles was determined by the method described by Araki et al. [2]. Forty-five milliliters of the suspensions (about 0.1%) was mixed with 5 mL of 0.01 M NaCl before measurements. The aqueous NaOH solution (0.01 M) was added dropwise from a microburette with continuous stirring. The change in conductivity was recorded by a conductometer after each step.

In order to exactly determine the surface charge of MCC samples, about 0.5 g of dried MCC was pre-immersed in 45 mL distilled water in conical flask for 48 h. The resulting suspension was mixed with 5 mL of 0.01 M NaCl and was determined as CNC suspension.

Thermogravimetric analysis (TGA 2050, TA) was carried out to determine the thermal stability of samples at nitrogen current of 80 mL min^{-1}. The sample was heated to 550 °C with the heating rate of 20 °C min^{-1}. Derivative TG (DTG) curves expressed the weight-loss rate as a function of time. Profile analysis of DTG curve was done with peak fitting program of Peakfit Software [19] using Beta line shape. The baseline was corrected by non-parametric model with 0.5% tolerance and the deconvolution peakfit model was used to fit the DTG data.

Differential scanning calorimetry (DSC) was carried out with DSC-2C, PE. About 10 mg of sample was transferred into the aluminum DSC crucible and sealed by aluminum lid. The sample was first heated to 120 °C and kept at the temperature for 5 min to remove the moisture. After cooled to room temperature, the sample was heated again to the appropriate temperature at which the weight loss of sample was lower than 10% to protect the furnace from being contaminated. The heating rate was 5 °C min^{-1} at nitrogen current.

The crystal structures of CNC and MCC samples were studied by X-ray diffractometer (D/MAX-1200, Rigaku, Japan), and the diffraction angle 2θ was from 6° to 40°. Profile analysis was carried out with peak fitting program using Gaussian line shapes to determine the crystallinity of samples. The crystallinity was taken at the ratio of the sum of areas under the crystalline diffraction peaks to the total area under the curve between $2\theta = 6°$ and 40°.

The shape and size of both MCC and CNC samples were investigated by transmission electron microscopy (TEM, JEM-100CX II). The cellulose suspensions were diluted by distilled water to about 0.1% concentration and sonicated for 3 min. One drop of suspension was transferred on a copper grid, dried for 24 h at room temperature and then observed by TEM at 100 kV.

3. Results and discussion

3.1. Sulfate content and the appearance

While preparing CNC by hydrolysis with mixed acid, some negatively charged acid sulfate groups were introduced into the surface of CNC, so that the suspension could be kept stable. Although the hydrochloric acid also took part in the

Table 1
The shape, the acid sulfate content, and the crystallinity for CNC and MCC samples

Sample	Shape	Acid sulfate content (mmol kg^{-1})	Crystallinity (%)
MCC-a	Rodlike	13.9	83
MCC-b	Rodlike	–	83
MCC-c	Rodlike	–	83
MCC-d	Rodlike	–	83
CNC-a	Spherical	16.7	80
CNC-b	Spherical	<2.0	81
CNC-c	Spherical	–	82
CNC-d	Spherical	–	78

hydrolysis reaction, the chloride ions were easily eliminated by repeated washing with distilled water [2]. However, some acid sulfate groups still remained due to the formation of ester groups with cellulose. The acid sulfate contents of samples were determined by conductometric titration method. The results are listed in Table 1.

The acid sulfate content of sample CNC-a ($\rho = 1.56\ \mathrm{g\ cm^{-3}}$) was 16.7 mmol kg^{-1}, and the content of acid sulfate of sample CNC-b was less than 2.0 mmol kg^{-1}, distinctly smaller than that of CNC-a. After repeated washing for more than 1 month, small content of acid sulfate groups still remained in sample CNC-b. This observation indicated that the desulfation of CNC was a very slow process at room temperature. The sulfuric acid content of MCC-a was 13.9 mmol kg^{-1}, which was similar to that of CNC-a, while the sulfuric acid in MCC-b was non-detectable. The explanation was that the sulfuric acid molecules were just absorbed on the surface of MCC, so it was easily eliminated by washing with distilled water.

The TEM images of the commercial MCC and CNC samples with different treatments are shown in Fig. 1. It was observed that the commercial MCC particles were rodlike shape. The average particle length of MCC was about 20 μm. After hydrolysis, not only the particle size of MCC obviously decreased but also the shape of the particles remarkably changed. From Fig. 1, it was clearly observed that all CNC particles were spherical particles in nano-dimension and that the particle size of CNC sample with different treatments did not obviously change. The CNC particles aggregated to some extent in TEM images probably due to the evaporation of water. The average diameter of spherical CNC obtained from TEM images was about 60 nm, which was noticeably smaller than the size of MCC. The shape of CNC particles prepared in the present work was remarkably different from the rodlike shape of cellulose whiskers reported in the previous work [1,16,20–22]. The results of a series of experiments indicated that two reasons should be attributed to this difference. In this experiment, the mixed acid was used to hydrolyze the cellulose materials, compared with the single acid in the previous work. The composition and the proper ratio of mixed acid were the important factors to form the spherical CNC particles. On the other hand, the ultrasonic treatment played an important role in forming the spherical CNC. Without the ultrasonic treatment, the spherical CNC could not be obtained. A paper about the mechanism of the spherical CNC formation is under preparation.

3.2. Thermogravimetric analysis

The TG and DTG curves of CNC are shown in Fig. 2. All CNC samples had a small weight loss in low temperature (<120 °C) range, corresponding to the evaporation of absorbed water. In the high temperature range (>150 °C), the degradation behaviors of CNC samples were different with each other as shown in the TG and DTG curves.

For CNC samples with detectable acid sulfate groups (CNC-a and CNC-b), the degradation occurred within a wider temperature range and showed two well separated pyrolysis processes in the DTG curves. One process occurred between 150 and 290 °C and the other between 320 and 500 °C. When the acid sulfate groups of CNC were neutralized by NaOH solution, their thermal decomposition considerably shifted to the higher temperature and occurred within a narrow temperature range. Although sample CNC-c still showed two pyrolysis processes, the first process between 220 and 260 °C was so small that the second process dominated the overall pyrolysis. After treatment by the higher content NaOH solution (1.0%), the degradation of CNC-d just showed one pyrolysis process.

The TG and DTG curves of MCC samples are shown in Fig. 3. In the case of MCC-a with similar content of sulfuric acid to CNC-a, the degradation also started at lower temperature and occurred within a wider temperature range. However, only one pyrolysis process was observed in the DTG curve, compared with the two processes in CNC-a. When the sulfuric acid was eliminated by washing with distilled water or neutralized by NaOH solution, the degradation of MCC samples shifted to the higher temperature in turn. This trend was similar to the CNC samples.

Because CNC was prepared by hydrolysis with the 40% (v/v) mixed acid at 68 °C for 10 h, process which probably destroyed the crystalline structure of cellulose and resulted in the change of the degradation behaviors [23]. The X-ray diffractometer was used to investigate the crystalline structure of samples and the X-ray curves of commercial MCC and CNC samples are shown in Fig. 4. From the X-ray curves, it was clearly observed that the X-ray diffraction patterns of CNC samples and commercial MCC were similar [24]. This observation indicated that the crystalline structure of cellulose I of MCC had been maintained [25] after hydrolysis with mixed acid. The degree of crystallinity (see Table 1) also confirmed this result. The crystallinity of CNC samples was slightly lower than that of MCC. An explanation was that the ratio of surface amorphous was high in CNC due to their high specific surface area. Therefore, the difference of thermal degradation behaviors in CNC was arising from the differences in outer surface structure of nano-crystalline particles including the presence of sulfate groups.

The water content and the char residue at 500 °C obtained from the TG curves of each sample are listed in Table 2. The amounts of char residue at 500 °C in samples with acid sulfate groups were remarkably larger than that of samples

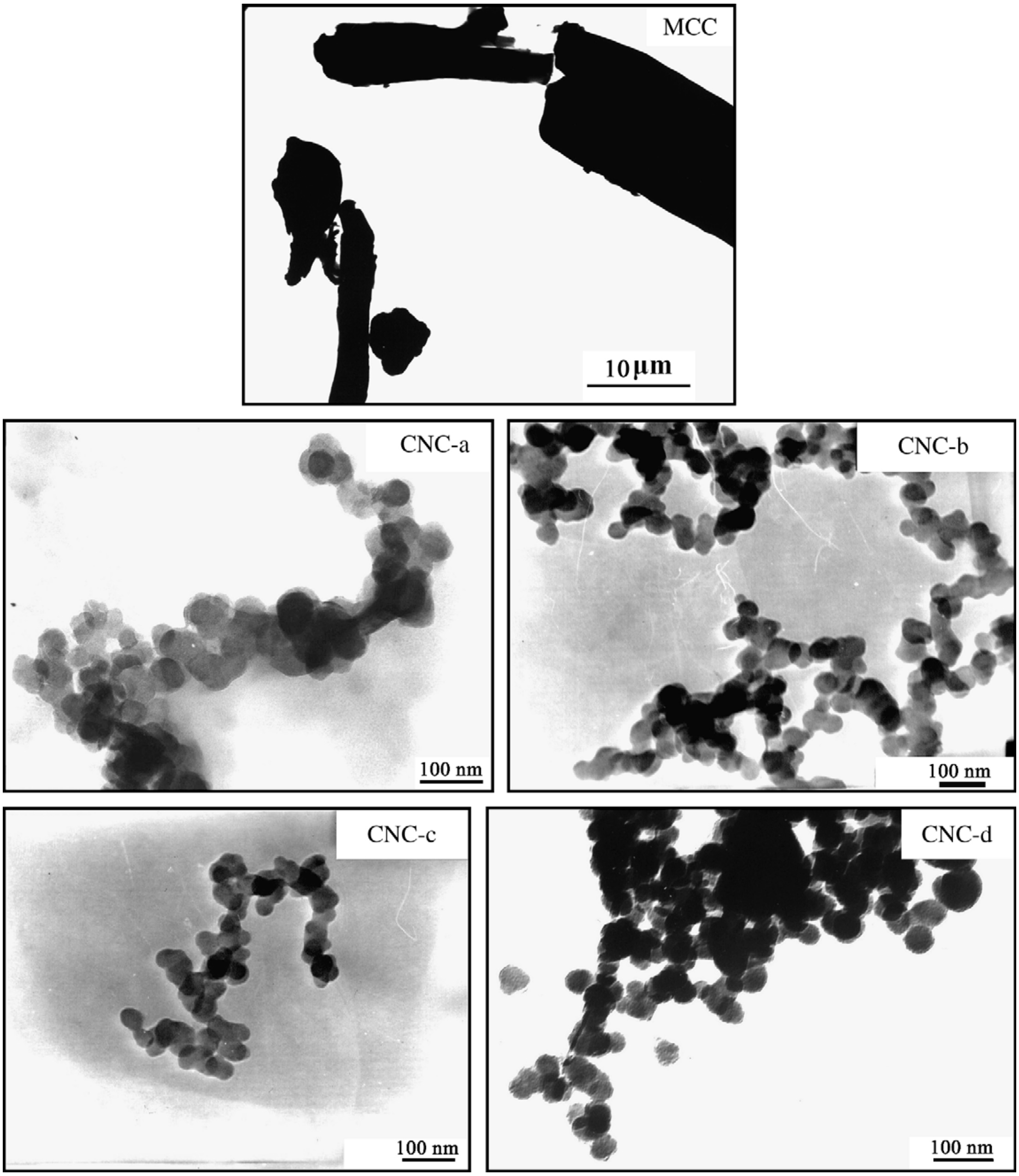

Fig. 1. TEM images of commercial microcrystalline cellulose (MCC) and spherical cellulose nanocrystal (CNC) samples with different treatments.

neutralized by 1.0% NaOH solution. Sulfuric acid was a well-known dehydration catalyst and facilitated the char residue formation [26–28]. When the alkaline ion (Na^+) replaced the hydrogen ion (H^+), the dehydration catalyzed by acid was inhibited. Moreover, alkaline ions with highly polar field could act as catalyst for complete degradation of glycosidic units by hemolytic mechanism [29,30] which brought about the decrease of char residue yield.

The amount of char residue in CNC samples ranging from 23% to 34% was noticeably larger than that of corresponding MCC samples which ranged from 1.3% to 8.7%. A reasonable explanation was that CNC particles had a great number of free end chains due to their small particle size. The end chains started decomposition at lower temperature [31], consequently, facilitated the increase of the char yield of CNC [30]. Furthermore, compared with MCC, the thermal stability of CNC decreased. The drying process of CNC suspensions at 80 °C probably played the role as preheating or activation cellulose in low temperature and thus leading to the increase of char yield.

Between 150 and 500 °C, the pyrolysis of samples CNC-a, CNC-b and CNC-c showed two apparent processes, while the rest of the samples showed one pyrolysis process. The onset temperature, the temperature at maximum weight-loss rate ($T_{\max}$), the maximum weight-loss rates ($\mathrm{WLR}_{\max}$) and the weight loss (WL) of every process are listed in Table 3.

For CNC samples with detectable acid sulfate groups, associated with the temperature range, we considered the lower

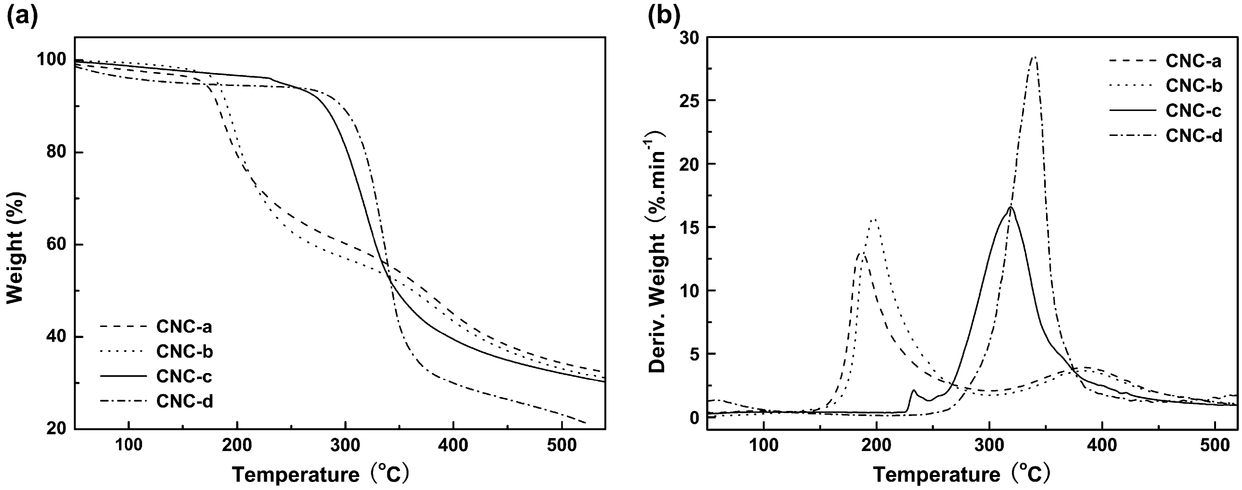

Fig. 2. The TG (a) and the DTG (b) curves of spherical CNC samples.

temperature process (termed "first process" in Table 3) corresponding to the primary pyrolysis of CNC catalyzed by acid sulfate groups, and the higher temperature process (termed "second process" in Table 3) relating to the slow charring process of the solid residue. From Table 3, it was observed that the difference of the weight loss between the first and the second process was not obvious in the CNC samples with acid sulfate groups. When the acid sulfate groups neutralized by the lower content NaOH solution, the first process in CNC-c only had about 1.5% weight loss, however, the weight loss in the second process reached up to 58%. This result indicated that the second process was the primary pyrolysis of CNC-c. After neutralized by the higher content NaOH solution, CNC-d just showed only one pyrolysis process with about 66% weight loss.

Kim and his co-workers [27] had observed the two pyrolysis processes in TGA curves of cotton cellulose with high sulfuric acid content (above 2.3%). This result was in agreement with our observation that MCC-a showed only one pyrolysis process because the content of sulfuric acid was smaller (only 0.14%). However, CNC-a had the similar amount of acid sulfate groups as MCC-a, the thermal degradation behavior showed two well separated pyrolysis processes and was clearly different from the behavior of MCC-a. On the other hand, even with smaller content acid sulfate groups, the degradation behavior of CNC-b also showed two pyrolysis processes, similar to that of CNC-a. This observation indicated that the characteristics of cellulose particles dominated the whole thermal degradation behaviors when the particles size of cellulose was in the nano-dimension range [32].

Winter and Roman [17] had studied the effect of acid sulfate groups of rodlike cellulose whiskers on the thermal degradation behaviors in air. They observed that only one DTG peak between 150 and 350 °C formed for all cellulose whiskers and their decomposition behaviors were different with the various contents of acid sulfate group. However, in the present work, although the difference of the content of acid sulfate groups between CNC-a and CNC-b was great, their degradation behaviors were similar and showed two apparent DTG peaks. Several reasons should be attributed to the distinction between Winter's and our observations. Compared with nitrogen current in the present work, the experiment of Winter was carried out under air current. The different experimental condition

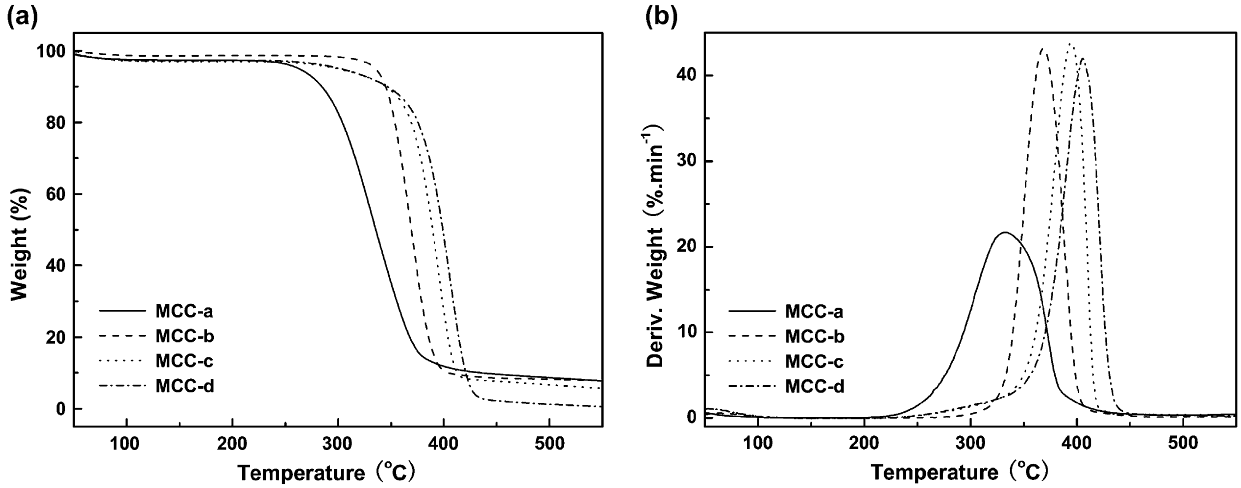

Fig. 3. The TG (a) and the DTG (b) curves of MCC samples.

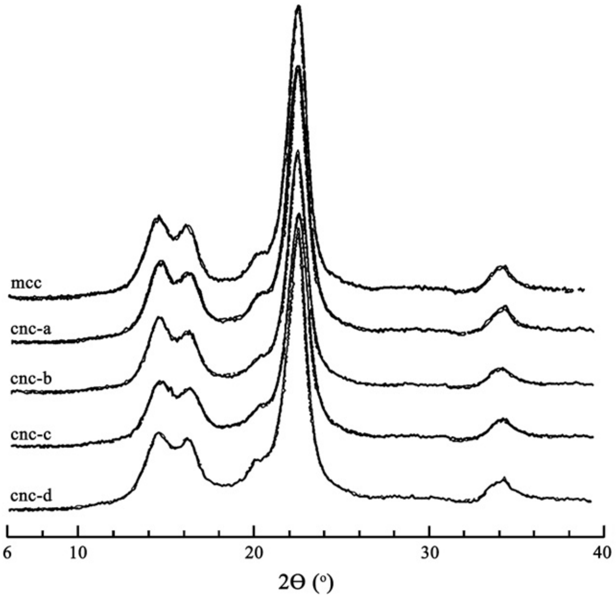

Fig. 4. The X-ray curves of commercial MCC and CNC samples with different treatments.

would cause the cellulose pyrolysis behaviors different. The different shape of CNC and the native source of cellulose also played important roles in the different degradation behaviors. The further related study is going on.

3.3. Profile analysis of DTG data

In order to gain further insight into the thermal degradation behaviors of CNC, profile analysis of DTG curves of CNC has been done with a peak fitting program using Peakfit software. According to the common experience, the curve of MCC-b or MCC-c was considered as a single regular DTG peak. So these two peaks were fitted respectively by each of the line shapes for Gaussian, Gaussian–Lorentzian, Pearson VII, asymmetric logistic, asymmetric double Gaussian cumulative and Beta shapes. The best fitting results were obtained in the case of Beta line shape, and the reliability values of r^2 for both curves were over 0.999. Therefore, the Beta line shape was used to fit the DTG curves of CNC samples and the fitting curves with the partial peaks are shown in Fig. 5.

Table 2
The water content and char at 500 °C of CNC and MCC samples obtained from TG curves

Sample	Water content[a] (%)	Char at 500 °C (%)
CNC-a	2.4	34.4
CNC-b	0.8	33.2
CNC-c	1.5	32.1
CNC-d	4.2	23.2
MCC-a	2.5	8.7
MCC-b	1.4	8.2
MCC-c	2.8	6.7
MCC-d	2.7	1.3

[a] Weight loss at 110 °C.

Table 3
Onset temperature, degradation temperature, T_{max}, maximum weight-loss rate, WLR_{max}, and weight loss, WL, in the thermal degradation processes of MCC and CNC samples obtained from the DTG curves

Sample	Onset temp (°C)	First process			Second process		
		T_{max} (°C)	WLR_{max} (% min^{-1})	WL (%)	T_{max} (°C)	WLR_{max} (% min^{-1})	WL (%)
CNC-a	172	187	13.3	36.2	385	3.91	25.7
CNC-b	178	198	15.78	41.3	385	3.65	24
CNC-c	228	234	2.13	1.5	318	16.57	58.2
CNC-d	298	339	28.5	65.9	–	–	–
MCC-a	270	332	21.69	87.8	–	–	–
MCC-b	336	370	43.14	90.3	–	–	–
MCC-c	359	394	43.86	88.3	–	–	–
MCC-d	367	406	41.98	95	–	–	–

For the observed DTG data in the case of sample CNC-a, the best fit was obtained for five Beta line shapes with maxima at 181, 194, 246, 371 and 428 °C, respectively. The former three peaks contributed to the primary process in the thermal degradation and the following two peaks contributed to the second pyrolysis process. The fit of DTG data of CNC-b was similar to that of CNC-a and also lead to the formation of the five peaks with maxima at 193, 204, 276, 376 and 435 °C. For the DTG data of CNC-c, three peaks were assumed to achieve the excellent fit with maxima at 232, 317 and 367 °C, respectively. The deconvolution of CNC-d DTG data lead to the formation of two peaks with maxima at 334 and 349 °C, respectively, with predominance of the first one.

The thermal degradation of cellulose with acid catalyst was usually hypothesized including two consecutive reactions [26,29]. Under the catalysis of acid sulfate groups, the dehydration reaction firstly took place at cellulose chain units directly containing these groups at lower temperature. The consecutive degradation reaction occurred at the cellulose chains which were not in direct contact with the catalyst or in the cellulose crystal interior [29], probably accompanied by some char residue formation. Our fitting results of primary pyrolysis in CNC-a and CNC-b were in good agreement with the hypothesis. The first and second peaks were corresponding to the decomposition of cellulose chains in direct or indirect contact with acid sulfate groups, respectively, and the third peak represented the accompanied decomposition of solid residue. The second pyrolysis process was related to the slow decomposition of solid residues to form the char products. Since CNC with acid sulfate groups could be decomposed by more pathways in the action of acid, the intermediate products which could further decompose to the char were more complex than that of cellulose without acid. Therefore, their thermal degradation presented the second pyrolysis processes with multiple reactions. So in the case of CNC-a and CNC-b, the fits of second pyrolysis showed two peaks. When the acid sulfate groups were neutralized by NaOH solution, the primary thermal degradation of CNC becomes simple and showed typical two-step reactions of cellulose with some inorganic salts [29,33]: the first peak corresponded to the pyrolysis of cellulose macromolecules followed by a flat tailing (the second

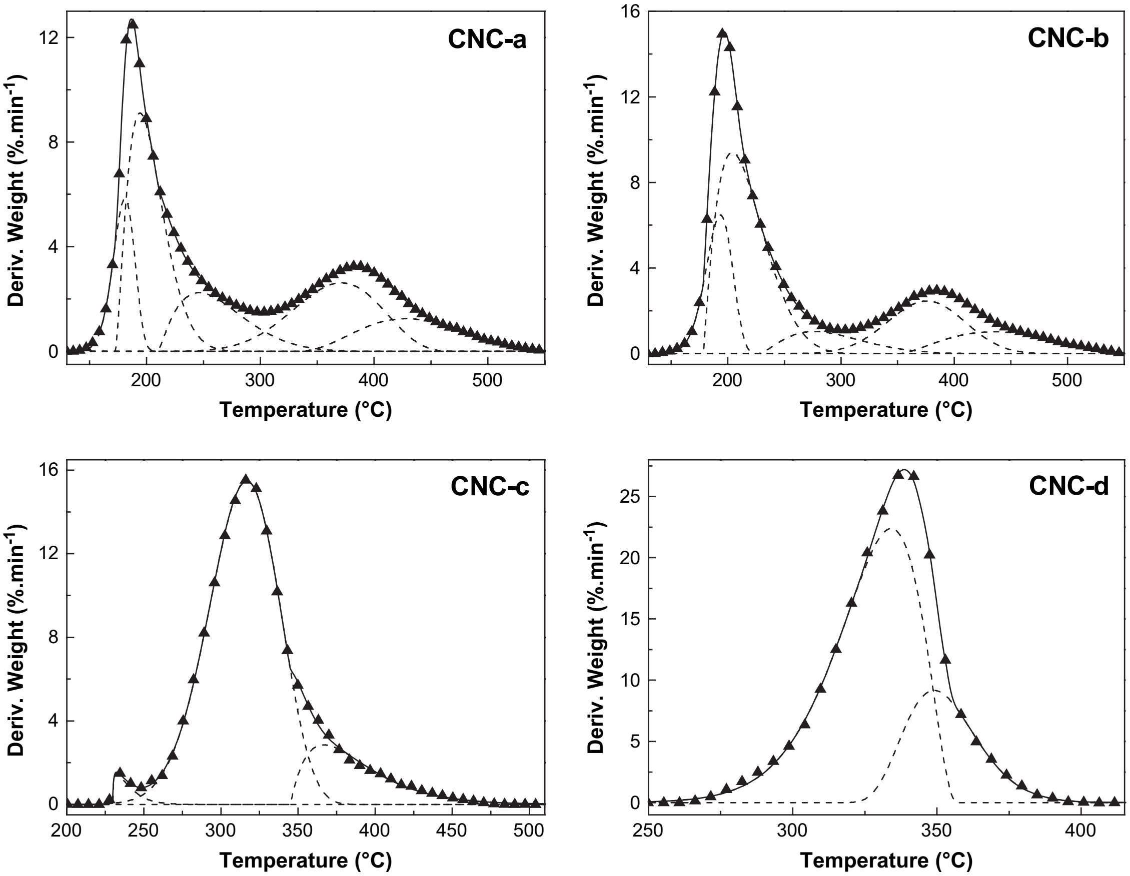

Fig. 5. The fitting results of DTG curves of CNC samples by using Beta line shape. The solid triangle (▲), solid line, and dash line represent the experimental data, the fitted data and the contributions of the partial peaks, respectively.

peak) relating to a slow step-by-step decomposition of the solid residue.

3.4. Differential scanning calorimetric analysis

The differential scanning calorimetry (DSC) curves of CNC samples are shown in Fig. 6. It was observed that CNC-a and CNC-b had similar DSC curves and decomposed at lower temperature. The endothermic peak with maximum at about 185 °C coincided with the first fitting peak of primary pyrolysis, corresponding to the dehydration reaction catalyzed by acid sulfate groups [27]. When acid sulfate groups were neutralized by NaOH solution, so that the decomposition of CNC in DSC curves considerably shifted to the higher temperature indicated that their thermal stability remarkably increased. In the case of CNC-d, the DSC curve showed an endothermic peak over 300 °C corresponding to the pyrolysis process. It was noticeable that sample CNC-c showed two small endothermic peaks between 230 and 240 °C which was in good agreement with the first process of DTG curves in Fig. 5. This observation confirmed that the subtle decomposition indeed occurred before the primary pyrolysis process.

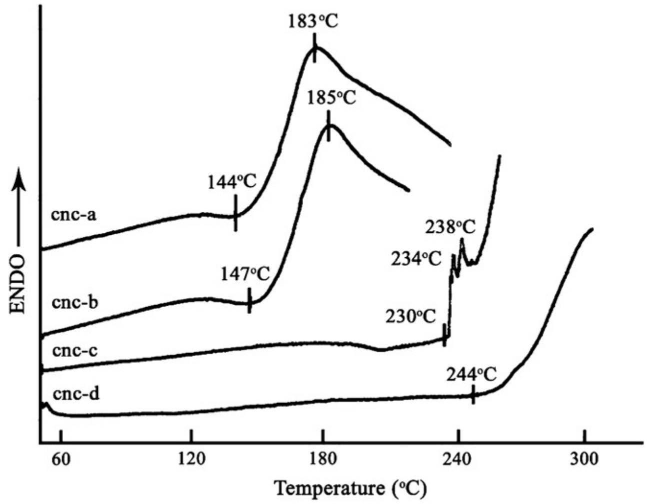

Fig. 6. The DSC curves of CNC samples.

4. Conclusion

In the present work, the thermal degradation behaviors of spherical cellulose nanocrystals (CNCs) and microcrystalline cellulose (MCC) were investigated. Comparing with MCC, the decomposition of CNC started at lower temperature and the char yield obviously increased. This distinction was mainly caused by the significant difference in the particle size between CNC and MCC. CNC had a great number of free end chains in surface due to the small particle size and the high specific surface area, these end chains started to decompose at low temperature. The decomposition of cellulose at low temperature usually facilitated the formation of char residue. Furthermore, because of the small particles' size, the CNCs were sensitive to the outer surface structure including the presence of sulfate groups. Therefore, with similar amount of acid sulfate groups, the overall degradation behavior of CNC was more complex and different from the behavior of MCC. When the acid sulfate groups of CNC surface were neutralized by NaOH solution, their thermal degradation considerably shifted to the higher temperature. This observation indicated that the method of using NaOH solution neutralized the acid sulfate groups to improve CNC thermal stability was efficient.

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