

A METHOD OF PREPARING SPHERICAL NANO-CRYSTAL CELLULOSE WITH MIXED CRYSTALLINE FORMS OF CELLULOSE I AND II*

Xiao-fang Li^a, En-yong Ding^{a, b**} and Guo-kang Li¹

^a Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry,
Chinese Academy of Sciences, Guangzhou 510650, China

^b College of Material Science and Engineering, South China University of Technology, Guangzhou 510641, China

Abstract A new kind of nano-crystal cellulose (NCC) prepared from natural cotton fiber has been obtained by the method of acid hydrolysis. Compared to most other nanophase materials that derive from inorganic materials, our products are prepared from natural cotton fibers. The products are of spherical shape with mixed crystal forms of cellulose I and II. The preparation conditions determine the properties of the products. Prior treatment is a critical procedure. The properties of the products are also strongly affected by such conditions as the kinds of acids used, the ratio of the acid mixture, the acid concentration, the ultrasonic agitation time and hydrolysis temperature. The number average molecular weight of NCC is determined by gel permeation chromatography (GPC). The particle size and shape were determined by transmission electron microscopy (TEM). X-ray diffraction was used to detect the crystallinity and average crystallite size of the particle.

Keywords Spherical nano-crystal cellulose, Mixed crystal forms of cellulose I and II, Ultrasonic agitation

INTRODUCTION

Cellulose is the most abundant and renewable natural resource on earth^[1]. Suitably prepared celluloses in the forms of powders such as microcrystalline cellulose (MCC) and microfibrillated cellulose (MFC) are very useful products^[2-6]. They have been applied in pharmaceutical, food, ceramic, paint, iron and many other industries^[5-9]. Such a wide application is attributed to their special properties: (1) the micron dimensional particle size, (2) large specific area, (3) inertness to many organic or inorganic substances.

There has been great progress in recent years in the field of cellulose degradation^[10-14]. Some articles mentioned such special properties as aggregation or liquid crystalline state of nano-cellulose with cellulose I crystal form^[15, 16].

Nanophase materials, which have been called miracles of the century, have attracted great interest in recent years. Their special properties have predestined them for use in many high-tech fields. Most of the nanophase materials are prepared from inorganic materials and few are reported to be obtained from natural products.

We have successfully prepared a new kind of NCC by degrading cotton fibers. This NCC has spherical shape and mixed crystal forms of cellulose I and II that are totally different from the conventional NCC. In this paper, transmission electron microscopy (TEM), GPC, electron diffraction and X-ray diffraction will be used to characterize this new NCC.

The continuous progress of materials science today needs to meet the requirement of various properties^[17] such as regenerative, "smart", environmentally compatible^[18] and energy conservative. Because the highly crystalline regions of cellulose have been greatly disrupted, it can be predicted that there are more exposed reactive groups in NCC than in other forms of cellulose because of its extremely fine particles and larger specific

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** Corresponding author: En-yong Ding (丁恩勇), E-mail: dingey@mail.gic.ac.cn

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area, which enable it to be made into some new nano-composite materials. NCC can be used for pharmaceutical applications, such as high quality packing material, suspension stabilizer, water container, a flow characteristic controller in the system used for final products. It can also be used as the carrier of biocatalysts for the same purpose mentioned above. We can expect that NCC will be a promising product in the future, especially in the high-tech fields of biochemistry.

EXPERIMENTAL

Sample Preparation

Short-staple cotton was used as raw cellulosic material. DMSO and sodium hydroxide were used for prior treatment^[19, 20]. Inorganic acids such as sulfuric acid and hydrochloride acid were used as catalysts. Ultrasonic apparatus was the reaction instrument.

The short-staple cotton was subjected to some prior treatments before it reacted with catalysts. Sodium hydroxide solution of 5 mol/L and DMSO were used as prior treatment reagents. The cotton fiber was first reacted with NaOH at 75°C for 4 h. Then the cotton was washed with distilled water until the pH value reached 8 or lower. After being dried in an oven, the fiber treated with DMSO at 75°C for another 4 h.

Sodium hydroxide and hydrochloric acid were mixed in a ratio of 3:1. The optimal concentration of the mixed acids is 40% (V/V), and the ratio of cotton to hydrolyst was determined at 1 g/40 mL.

After the prior treatment, cotton fibers and acids were proportionally mixed and put to ultrasonic agitator (New Power, Guangzhou, Power: 400 W) at 75°C for more than 8 h. White or ivory yellow suspension colloid can be obtained after this process. The final products (shown in Fig. 1) were obtained after the sequential processes of filtering, washing and centrifuging.

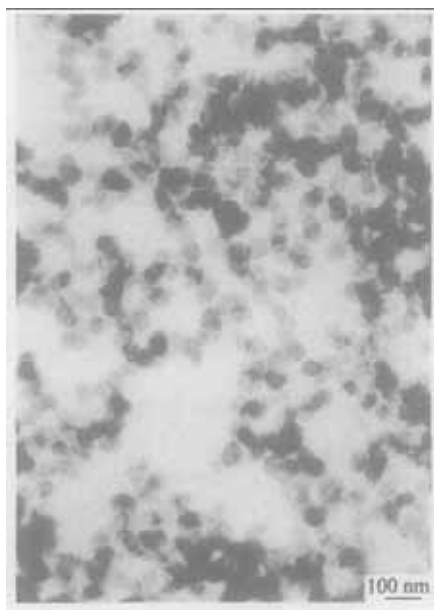


Fig. 1 The TEM photo of nano-crystal cellulose

Characterization

The crystal form, crystallinity and crystallite size of NCC were measured using X-ray diffraction (Rigaku, Japan)^[21]. The measurement was performed with CuK α radiation ($\lambda = 0.154$ nm) and Ni filter, at a voltage of 40 kV and a current of 30 mA. The crystallinity was calculated by the method of peak separation. The weight average crystalline size was calculated by using the Scherrer equation on the basis of the X-ray intensity

distribution versus 2θ .

The molecular weight of NCC was determined by GPC (Waters 991, GPC, USA). The NCC sample was converted into diacetate cellulose and was then dissolved in THF • $\overline{DP}$ was calculated from the MW data.

The particle shapes and sizes of NCC were determined by TEM (JEM-1010, Japan). The TEM sample was prepared by drying a drop of the diluted suspension on a copper grid. The particle dimensions were measured by manual counting from the TEM micrographs at a magnification of 100,000 times.

RESULTS AND DISCUSSION

Effect of Preparation Conditions on the Properties of Nano-Crystal Cellulose

The acid hydrolysis of cotton fibers was carried out in a heterogeneous system. This process depends on the prior treatment process, acid species, acid concentration, reaction temperature, hydrolysis time and many other factors.

The purpose of DMSO and sodium hydroxide treatment is to swell the cotton so that the hydrolyst can diffuse into the fibers more easily. Without this process, only rod-like large microcrystalline cellulose can be obtained no matter how long the cotton has been treated.

The hydrolysis conditions must be sufficiently strong to ensure the fibers can be degraded to nanometer dimensions. But they also must be appropriately mild to avoid complete hydrolysis of fiber into glucose or even carbonization. Properly mixed acids can avoid such extremes. A mixture of sodium hydroxide and hydrochloric acid proved to be a good choice. When the ratio of sodium hydroxide to hydrochloric acid is higher than 4:1, the cotton fibers will degrade into glucose after being hydrolyzed for more than 2 h. With the increase of hydrochloric acid content, the hydrolysis degree decreases. The optimal ratio was 3:1. The effect of the ratio of acids on the physical properties of fiber was shown in Table 1.

Table 1. Relationship between acid ratios and physical properties of the products

Sample	H ₂ SO ₄ :HCl (V/V)	Degradation degree	Stability after 48 h	Particle shape	Particle size distribution
1	3:1	Ivory yellow suspension colloid	Stable, without stratification	Spherical particles	Uniform particle size
2	2:1	Ivory yellow suspension colloid	Stable, without stratification	Spherical and some large particles	Uniform particle size
3	1:1	White suspension colloid	Stratified with supernatant layer at above	Spherical and some large particles	Non-uniform particle size
4	1:2	White suspension colloid	Stratified with supernatant layer at above	Spherical and some large particles	Non-uniform particle size
5	1:3	White suspension colloid	White precipitate	Mainly large particles	Non-uniform particle size

Table 2. Relationship between acid concentration and the physical properties of the products

Sample	Acid concentration (%)	Degradation degree	Stability after (48 h)	Particle shape	Particle size distribution
6	10	White precipitate	White precipitate	Large particles	Non-uniform particles
7	20	White precipitate	White precipitate	Large particles	Non-uniform particles
8	30	White suspension colloid	Stratified with supernatant layer at above	Spherical and some massive particle	Non- uniform particles
9	40	Ivory yellow suspension colloid	Stable, without stratification	Spherical particles	Uniform particle size
10	45	The cotton fiber was dissolved after 2h of ultrasonic treatment			
11	50	The cotton fiber was dissolved immediately			

Table 3. Relationship between the time of ultrasonic treatment and physical properties of the products

Sample	Degradation time (h)	Degradation degree	Particle shape	Degree of scatter
12	2	White precipitate	Mainly large particles	Agglomerated spherical particles
13	4	White precipitate	Mainly large particles	Agglomerated spherical particles
14	6	White suspension colloid	Non-uniform particle shape	Agglomerated spherical particles
15	8	Ivory yellow suspension colloid	Uniform particle shape	Scatter dispersion
16	10	Ivory yellow suspension colloid	Uniform particle shape	Scatter dispersion

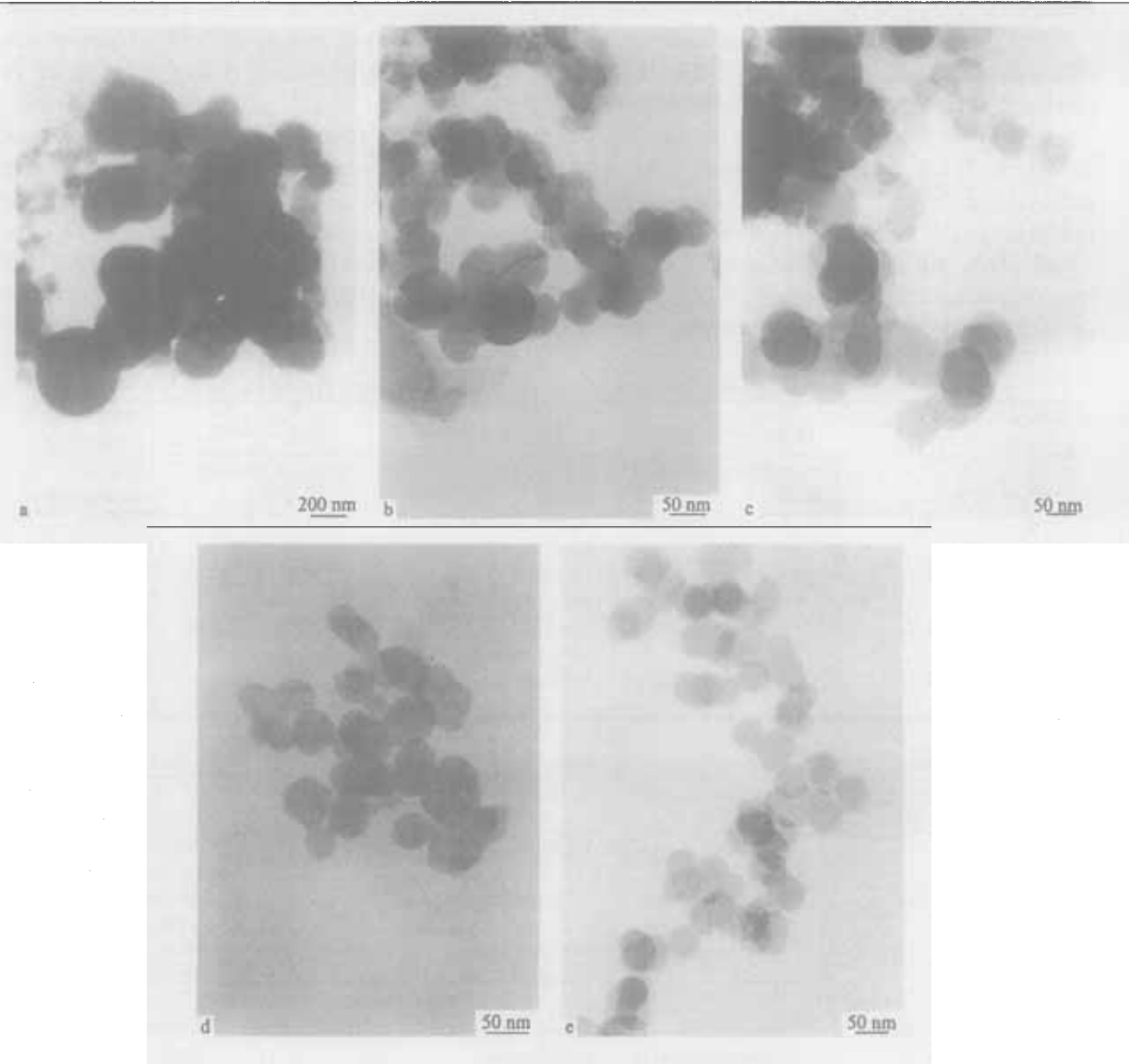


Fig. 2 (a) TEM microphotograph of the sample after 2 h ultrasonic agitation
(b) TEM microphotograph of the sample after 4 h ultrasonic agitation
(c) TEM microphotograph of the sample after 6 h ultrasonic agitation
(d) TEM microphotograph of the sample after 8 h ultrasonic agitation
(e) TEM microphotograph of the sample after 10 h ultrasonic agitation

After prior treatment, the cotton fibers will dissolve when the acid concentration (V/V) is above 50%. At a concentration of 45%, the cotton fibers will degrade into glucose after hydrolysis for a few hours. But when the acid concentration is below 25%, the hydrolysis effect is far from enough. The optimal concentration is between 30%~40%, as shown in Table 2.

The reaction temperature is also an important factor. It is difficult to control the hydrolysis degree at a high temperature. But when the temperature is below 60°C, the reaction proceeds very slowly. Our experimental temperature was fixed at 75°C.

Ultrasonic agitation conditions is another important factor. It can be inferred from Table 3 that during the first 5 or 6 h, ultrasonic agitation determines the extent of particle size. The particle size reaches a balance by then. Further action can change it only slightly. However, the longer the treatment, the more uniform the spherical particles were. This trend can be observed in Fig. 2 and 3.

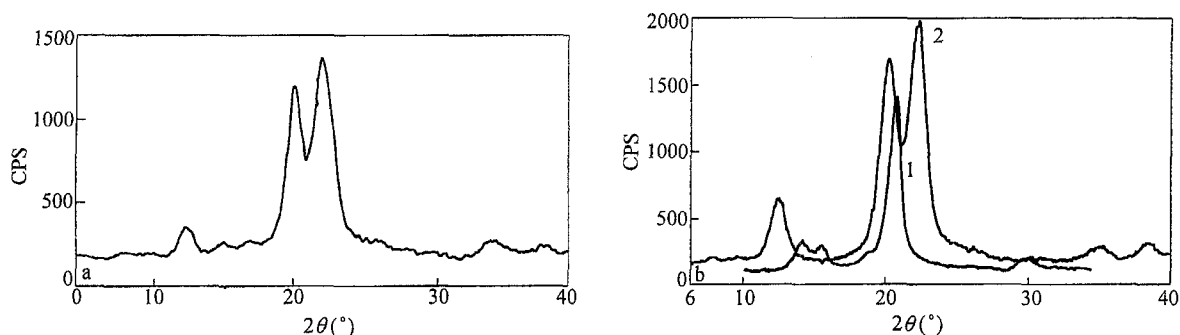


Fig. 3 (a) X-ray diffraction pattern of NCC; (b) X-ray diffraction pattern of cellulose I and cellulose II crystallites

Crystallinity and Crystallite Size

Before the X-ray diffraction examination, the NCC samples were dried in an oven at 100~105°C, a temperature much lower than its pyrolysis temperature. After the water had been removed, the dried products became dark brown or even black in color. This may be due to the strong absorption of broad band of the NCC, which is a characteristic of nanophase materials. MCC still maintains its white color when treated under the same conditions.

The X-ray diffraction pattern of the products is shown in Fig. 3(a). On contrast to Fig. 3(b), the shape of the curve in Fig. 3(a) clearly shows that after the prior treatment, the sample has the crystal lattice of cellulose I and cellulose II. The value of the average crystallite size of the cellulose I parts is 8.3 nm and that of the cellulose II parts is 7.2 nm. It is apparent that the average crystallite size of cellulose II is smaller than that of cellulose I. The results also show that the crystallinity of the cellulose I is 0.17 and that of the cellulose II is 0.59.

Number Average Molecular Weight and $\overline{DP}$

The polymerization degree of natural cellulose is very high. For example, the lowest $\overline{DP}$ of cotton fibers is between 13000~14000. $\overline{DP}$ of the commercial MCC is between 130~180 and of MFC is above 700. This result shows that the molecular weight of diacetate NCC is normally distributed. M_n of diacetate NCC is 3398, so the M_n of NCC is calculated to be 2844, and $\overline{DP}$ is 17.5.

CONCLUSIONS

A method of preparing nano-crystal cellulose was found to be highly sensitive to the reaction conditions. Prior treatment was essential here. DMSO and sodium hydroxide was used as prior treatment reagents and mixtures of sulfuric acid and hydrochloric acids were used as hydrolysts. Suitable hydrolysis conditions after prior treatment are: ratio of sulfuric acid to hydrochloric acid: 3:1; acid concentration: 40% (V/V); cotton fibers to acid ratio:

1 g/40 mL; ultrasonic agitation: over 8 h; reaction temperature: 70~80°C. Finely dispersed spherical NCC with mixed crystal form of cellulose I and II can be obtained in this processes.

REFERENCES

- 1 Gao, J. and Tang, L.G., Cellulose Science (Chinese), Science Press, Beijing, 1996, p.1-12
- 2 Song, J. and Hou, Y.F., Journal of Cellulose Science and Technology (Chinese), 1995, 3(3): 1-9
- 3 Pan, S.H., Li, G.K., Wang, Z.Z. and Wang, Z., Xianweisu Kexue Yu Jishu (Chinese), 1996, 4(2): 19-24
- 4 Cleopatra, V.O. and Jeana, N., Cellulose Chem. and Technol., 1994, 28: 115-119
- 5 Hogen, J., Shue, P.I. and Podczek, F., Pharm. Res., 1996, 36(6): 944-949
- 6 Plonka, A.M., Cellulose Chem. Technol., 1982, 16: 473-484
- 7 Zograf, G., Kontny, M.J., Yang, G.S. and Brenner, A., Int. J. Pharmaceut., 1994, 18: 99-116
- 8 Ardizzome, S., Dioguardi, F.S., Mussini, T. and Mussini, P.R., Cellulose, 1999, 6: 57-69
- 9 Hirofumi, O., Miki, I. and Kunihiro, O., Cellulose, 1997, 4: 57-73
- 10 Klaus, G., Cellulose Chem. Technol., 1996, 30: 3-12
- 11 Younis, H.S. and Raymond, A.Y., Cellulose Chem. Technol., 1988, 22: 3-15
- 12 Cleopatra, V.O., Oita, N. and Badiu, S., Cellulose Chem. Technol. 1993, 27: 145-153
- 13 Mushtaq, A., David, C. A., Christian, D.E., Alan, M.E. and Robin, K.H., Cellulose, 1996, 3: 77-90
- 14 Seves, A.M., Sora, S.N., Testa, G. and Rossi, E., Cellulose Chem. Technol., 1998, 32: 197-209
- 15 Li, G.K. and Pan, S.H., Chinese Pat., 1994, 2L9415873.X
- 16 Xue, M.D., Revol, J.F. and Gray, D.G., Cellulose, 1998, 5: 19-32
- 17 Guo, J.S., Chemistry Today (Chinese), Beijing University Press, Beijing, 1995, p.367-368
- 18 Valentin, I.P. and Breaban, I.G., Cellulose Chem. Technol., 1995, 29: 575-587
- 19 Isogai, A. and Atalla, R.H., Cellulose, 1998, 5: 309-319
- 20 Kroon-Batenburg, L.M.J., Bouma, B., and Kroon, J., Macromolecules, 1996, 9: 5695-5699
- 21 Majdanac, L.D., Poleti, D. and Teodorovic, M.J., Acta Polymerica, 1991, 42: 351-357