World Scientific Research Journal (WSRJ) ISSN: 2472-3703
www.wsr-j.org

Preparation and Characterization of Cellulose Nanocrystals via Acid Hydrolysis

Yanan Hu [a], Mengchao Zhang [b], Lichun Zhang [c], Meihong Tang [d] and Yan Wang [e]

College of Mechanical and Electronics Engineering, Shandong University of Science and Technology, Qingdao 266590, China

[a]1249091282@qq.com, [b]1521229044@qq.com, [c]2085360203@qq.com

[d]1598535270@qq.com, [e]1366100566@qq.com

Abstract: Cellulose nanocrystals (CNCs) are a new kind of biomass-based nanomaterials with high purity, crystallinity, strength and other characteristics, and they are light, biodegradable and renewable. In this paper, sulfuric acid hydrolysis method was used to prepare cellulose nanocrystals using microcrystalline cellulose as raw material. The ultrastructure of cellulose nanocrystals was characterized by field emission scanning electron microscopy, infrared spectroscopy, X-ray diffractometry and thermogravimetric analysis, and their size distributions were analyzed.

Keywords: Cellulose nanocrystals; morphological analysis; performance characterization.

---

1. INTRODUCTION

With the increasing depletion of chemical resources and the continuous deepening of people's pursuit of environmental protection, sustainable development and circular economy, the world has begun to focus on the use of natural renewable biomass resources. Cellulose is the most widely distributed natural polymer material today. It is not only rich in source, but also non-toxic and renewable. Because of its nano-scale size, it's often referred to as Cellulose nanocrystal [1]. Cellulose nanocrystals have been given more properties through chemical functional modification of the surface and hybridization with inorganic functionalized nanomaterials, and have also shown great application prospects in many fields.

Cellulose is a linear homopolymer compound composed of D-dehydrated pyran glucose anhydride (AGU) units linked to each other by β-(1→4)-D-glycosidic bonds, and the molecular formula is (C6H10O5)n. The contents of carbon, hydrogen, and oxygen were 44.44%, 6.17%, and 49.39% respectively [2]. The molecular structure of cellulose is shown in Fig.1 [2]. The hydroxyl groups on each anhydroglucose unit are located in the C2, C3 and C6

positions, with the typical properties of primary and secondary alcohols, which have an absolute effect on the properties of the cellulose.

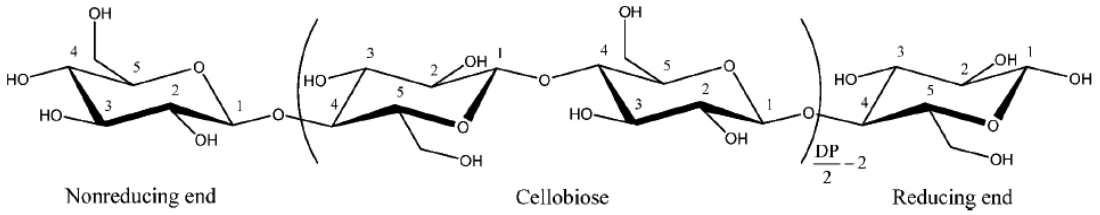

Fig.1 The chemical structure of cellulose

2. EXPERIMENTAL SECTION

2.1 Material

Microcrystalline cellulose(MCC) was purchased from Sinop-harm Chemical Reagent Co, Sulfuric acid (H2SO4, ≥99.0%) was purchased from Shanghai Pilot Chemical, Deionized water.

2.2 Preparation of CNCs

First configure 64% concentrated sulfuric acid with sulfuric acid and deionized water. Cellulose nanocrystals (CNCs) were prepared by 5g MCC using 87.5mL 64% (w/w) sulfuric acid at 44℃ for 180 min. The suspension was diluted 10-fold with deionized water, then centrifuged at 8000 rpm for 10 min to concentrate the cellulose and to remove excess aqueous acid, and recentrifuged. The resulting precipitate was placed in regenerated cellulose dialysis membranes (Union Carbide Corporation) having a molecular weight cut off of 12,000-14,000 and dialyzed against deionized water for 3 days until the value of pH remained constant. Finally, freeze and dry with a freeze-dryer.

2.3 Characterization

The surfaces of the specimens were observed using an Inspect field emission SEM with 15 kV accelerating voltage to study the dispersion of fillers.

FTIR Spectrometer with an attenuated total reflection (ATR). The cellulose nanocrystalline solution was cast into the infrared spectrum with a resolution of 4cm-1, and the scanning frequency was 32 times/s.

The measurement range was 400-4000cm-1 Wide Angle X-ray Scattering (WAXS) experiments were performed using a DMAX-II diffractometer. Diffraction patterns were obtained under the following conditions: 40 kV, 40mA, soller slit 0.04 rad and antiscatter slit 0.5°.

The thermal stability of the micro-injection molded specimens were evaluated by thermogravimetric analysis (TGA). It was performed by heating the specimens (5-7mg) from 100℃ to 600℃ at a heating rate of 10℃/min in nitrogen flow.

3. RESULTS AND DISCUSSION

3.1 SEM analyses

Fig.2(a) shows the field emission scanning electron micrograph of MCC. It can be observed from the graph that the MCC presents a stick structure with a length of about 20-100 microns and a diameter of 10-25 microns. Fig.2(b) shows the field emission scanning electron micrograph of CNCs that prepared by hydrolysis of sulfuric acid hydrolysis. It can be observed from Fig.2(b) that cellulose nanocrystals obtained by hydrolysis of sulfuric acid are filamentous, about 10-50nm in diameter, and are about hundreds of nanometers long.

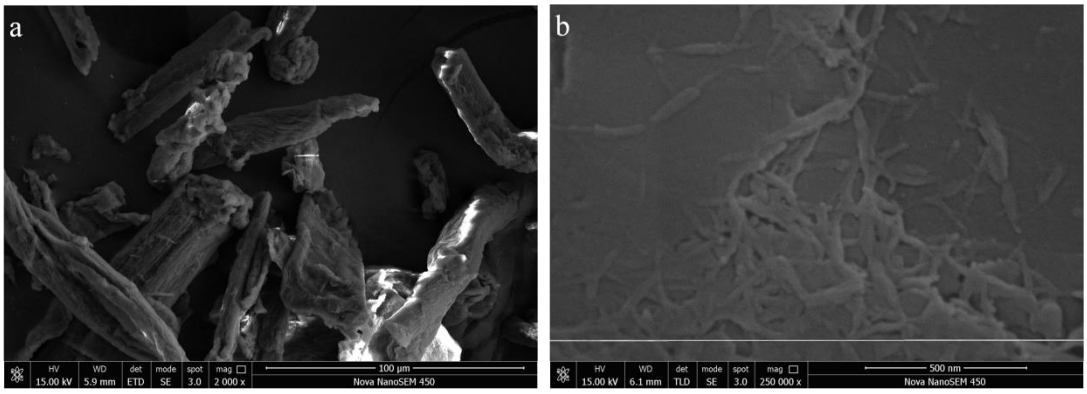

Fig.2 SEM morphology of (a) MCC and (b) CNCs

3.2 FT-IR analyses

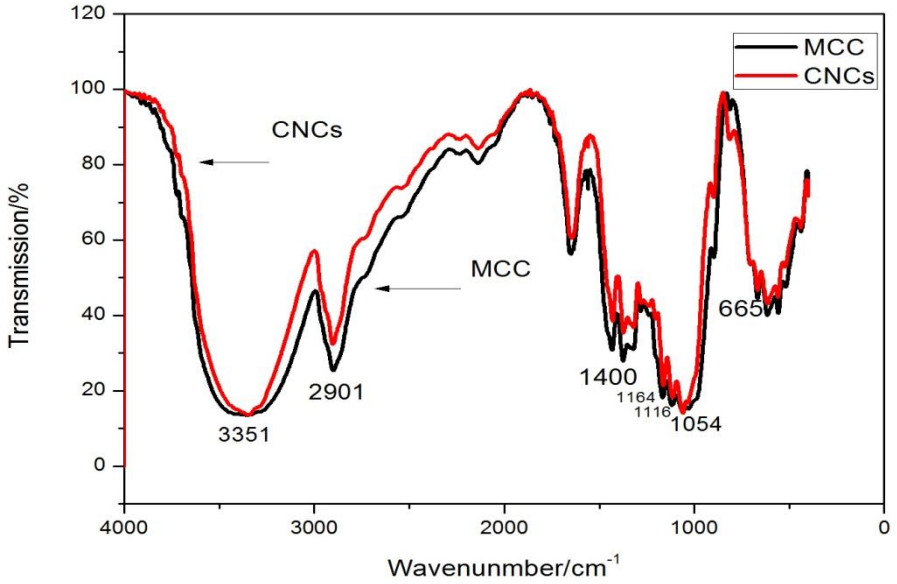

Fig.3 Infrared spectrogram of MCC and CNCs

Fig.3 shows the infrared spectra of MCC and CNCs. There is a major peak near 3351cm-1 in the spectrogram, indicating the presence of hydroxyl. In the vicinity of 2901cm-1 corresponds to the C-H symmetric stretching vibration peak of methylene (-CH2-). Another major absorption peak near 1054 cm-1, corresponding C-O stretching vibration of cellulose, alcohol, and there is a lot of near its weaker shoulder peak, near 1116 and 1164cm-1 respectively corresponding to the cellulose molecules within the ether of C-O stretching vibration and C-C skeleton stretching vibration absorption[4].

This thesis sulfuric acid hydrolysis of CNCs prepared by the MCC, compared the characteristic peak on the chromatogram and no obvious change, shows that the CNCs is still the basic chemical structure of cellulose, on the other hand also illustrates the particularity of CNCs show originated in the nano size effect.

3.3 XRD analyses

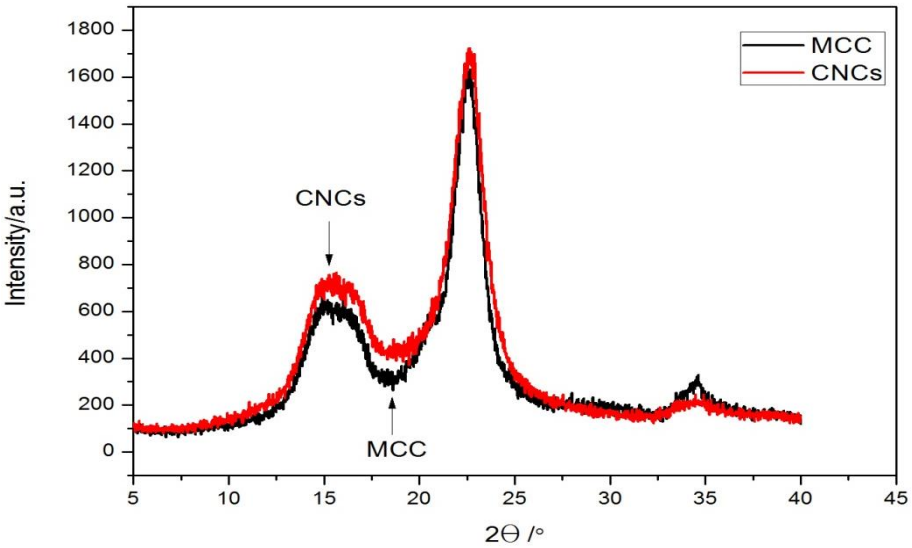

Fig.4 XRD diagram of MCC and CNCs

Fig.4 shows that the position of several important diffraction peaks in the XRD spectra of CNCs prepared by sulfuric acid catalytic hydrolysis is the same as that of MCC. The results show that the crystalline form of CNCs has not changed in the process of sulfuric acid swelling, and the swelling process occurs in the crystal zone, not in the crystal region. The hydrolytic reaction has no effect on the crystalline structure of cellulose. The spectra of CNCs crystals moved up a certain distance from the MCC, indicating that the crystallinity of CNCs is higher than that of MCC.

3.4 TAG analyses

After the acid treatment of cellulose, the surface groups of the crystal have changed, and these changes have a certain effect on the thermal stability of cellulose. In this paper, the thermal stability of CNCs was studied by thermogravimetric analysis.

Fig.5 is for MCC and CNCs thermogravimetric analysis diagram, can be seen from the diagram, the initial degradation temperature of MCC is in the vicinity of 288℃, the degradation of CNCs is near the starting temperature of 185℃. Cellulose nanocrystals prepared by sulfuric acid hydrolysis can be grafted on its surface with a lot of sulfonate substrates, which greatly reduces the thermal decomposition temperature. But after acidification, the non-cellulosic components in the raw material microcrystalline cellulose will be removed by acid. Therefore, the final residual amount of CNCs is about 21%, which is more than 2% of the final residual amount of MCC.

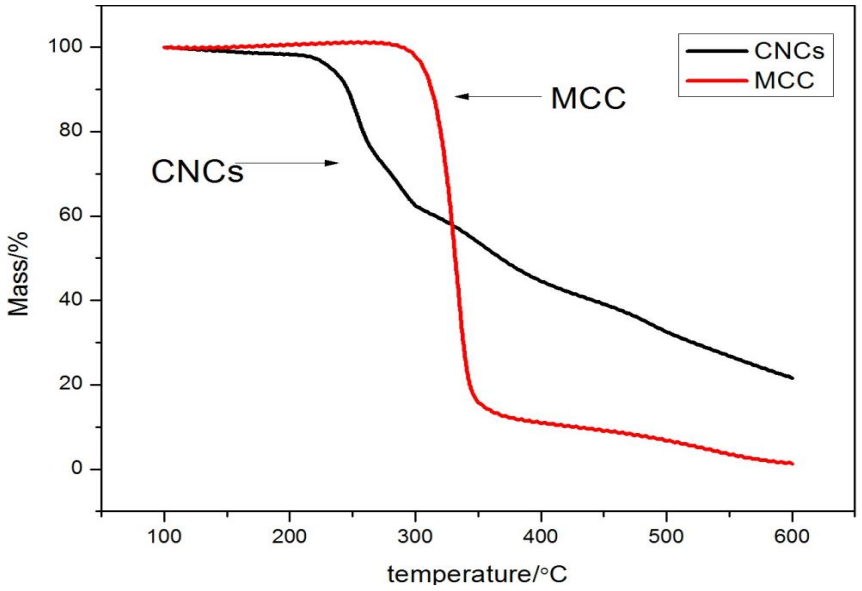

Fig.5 Thermogravimetric analysis of MCC and CNCs

4. CONCLUSION

In this work, the particles of CNCs were prepared by the hydrolysis method with MCC, and the size range was 10~50nm wide and hundreds of nanometers long. The concentration was too low, and the swelling and hydrolysis of MCC were not sufficient. High concentration, excessive hydrolysis of cellulose, lead to carbonation reaction occurs.

In the process of the preparation of cellulose nanocrystals, as a result of the sulphuric acid hydrolysis of cellulose nanocrystals, will be grafted on the surface on many foundation sulfonic acid group which make its stability than the initial thermal stability of microcrystalline cellulose.

REFERENCES

[1] Y Habibi, L A Lucia,O J Rojis. Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications[J], Chemical Reviews, 2010, 110(6):3479-3500

[2] A Sturcova,I His, D C Apperley, et al. Structural Detail of Crystalline Cellulose from Higher Plants[J], Biomacromolecule, 2004, 5(4):1333-1339

[3] D Fengel and G Wegener. Wood [M], Berlin: Walter de Gruyter, 1989

[4] Alemdar A, Sain M. Isolation and characterization of nanofibers from agricultural residues-wheat straw and soy hulls[J], Bioresource Technology, 2008, 99(6):1664-1671

[5] Worarin Meesorn,Anuja Shirole, Dimitri Vanhecke.A simple and versatile strategy to improve the mechanical properties of polymer nanocomposites with cellulose nanocrystals[J],Macromolecules,2017