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Performance of Salix Cellulose in the Process of Micro/Nano

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Abstract: The results obtained from the micro-nanometers process of nitrocellulose indicate the trend of moving toward lower wave numbers in the vibration peak of microcrystalline cellulose and nanometer cellulose. It also has an absorbance larger than the one of nitrocellulose. The hydrogen bonds both inner molecule and between molecular are strengthened. Hydroxyl of cellulose is observed to be acid-oxidized. The crystal structure of cellulose is found to keep the cellulose I type during the process of micronanometers. At same time, crystallinity of cellulose is improved and the opposite thermal stability is wrecked and leads to possibility of carbonization in lower temperature.

Key words: Nitrocellulose, microcrystalline, nanocrystalline, performance

INTRODUCTION

Cellulose is a kind of natural high molecular polymer and it is the smallest physical structure unit of cellulose. When it is converted into superfine fiber it will have excellent properties including high crystallinity, high purity, high Young modulus, high strength, high hydrophilic, high fine structure and high transparency, etc. As a kind of natural fiber it is widely applied in various aspects for its outstanding properties of light, degradability, great biocompatibility and renewability. It has attracted the attentions of many scholars. Turbak *et al.* (1983) used 4% prehydrolysis wood pulp as the raw material and made up the melamine faced chipboard. Dufresne (Li *et al.*, 2010) purified beet fiber through high-pressure homogenization treatment and produced the MFC (Melamine Faced Chipboard). MFC is also adopted here to ensure the destruction of all its cell walls. When dried, MFC is put for the preparation of high strength fiber sheet. Zimmermann *et al.* (2010) adopts different raw materials and through using mechanical dispersion and high pressure homogenization, MFC with maximum length and diameter smaller than 100 nm was obtained. Analysis shows that agglomeration in the micron size of cellulose has poor uniformity of network structure. Using sulfuric acid hydrolyzed cotton, wood pulp and other raw materials. They also studied the self-assembly properties and the synthesis conditions of cellulose liquid crystal. In 2006, (Bondeson *et al.*, 2006) optimized the conditions of the sulfuric acid hydrolysis of Norway spruce preparation Nano fibers and found the rapidly and high yields method of preparing Nano cellulose colloid.

Ding Enyong (Qin *et al.*, 2011) used cotton fiber as raw material to produce spherical or ellipsoidal Nano fibers, in size range of 5-100 nm, through ultrasonic dispersion and acid hydrolysis. N crystal type of cellulose was identified on the particles' out layers. Zhong-Yan Qin (Bai *et al.*, 2009) adopted the cotton pulps as raw material, fabricated Nano fibers NCC with diameter of 5-10 nm and length of the 100-400 nm, through the ultrasonic treatment. Nano fibers synthesized by this method have particular properties of both high crystallinity and yield stability.

MATERIALS AND METHODS

Preparation of nitrocellulose: Salix wood powder and nitric acid-ethanol (1:4) with a liquid ratio of 1:25 are mixed in a reactor equipping with a reflux-condensing device. The mixture is put in the water 100°C for about one hour, then repeat above operations for three to five times, till cellulose turns white. Then residue is washed by ethanol nitrate and then hot water, until its pH value reached neutral. The finally use anhydrous ethanol washing for twice and then drains filtrate.

Preparation of MCC: Salix psammophila cellulose is divided on 6% hydrochloric acid, (Salix cellulose): (hydrochloric acid) =1:20, hydrolyzing temperature is 95 degrees Celsius. The time of hydrolysis is set to 25 min. After though rinsing and washing to neutral pH value, samples are dried at low temperature.

Preparation of nanometer cellulose: The Microcrystalline Cellulose (MCC) is dissolved into a quantity of 64%

H₂SO₄ solution. Then microcrystalline cellulose solution is dispersed by microwave analyzer and then subject it in 45centigrade water bath for 2 h. The solution is transferred to a dialysis bag for dialysis until it reached neutral. The bag containing Nan-crystalline cellulose is put for drying in the freezes dryer.

TESTS OF SAMPLES' PROPERTIES

Measurement of ATR-FTIR: ATR-FTIR means Attenuated total reflectance-Fourier transform infrared spectrometry. The infrared spectrums of nitrocellulose, microcrystalline cellulose and cellulose Nanowhiskers are tested by Pekin-Elmer Fourier transform total reflection infrared spectroscopy. Each sample is scanned for 16 times. Middle infrared spectral region is refined to 650 ~ 4000 cm⁻¹ with the resolution of 2 cm⁻¹.

Measurement of X-ray diffraction: The X-ray diffract meter is applied in the test, Cu-Ka radiographic source is 40 kV and 250 mA. The scan rate is 5° min⁻¹, the scanning range is 2θ between 5 to 60°.

Thermo-gravimetric analysis: Differential thermal scanning calorimeter was employed here to measure the fibers Thermo Gravimetric (TG) curves. The tests are conducted in nitrogen atmosphere, the nitrogen flow printed mUmin, heating rate of 10°C min⁻¹. The test temperature is ranged from 25 to 600°C.

RESULTS AND DISCUSSION

From Fig. 1 it can be seen that cellulose molecules of the H and the adjacent hydroxyl groups of the O are linked to the formation of hydrogen bonds on the

cellulose. These hydrogen bonds' stretching vibrations, however, are concentrated at about 3400 cm⁻¹. The hydrogen bonding found among molecules are included but not limited to HO (3) O (2) HO (6), O (3) HO (5) O (6). The vibration peak of both microcrystalline cellulose and Nano-cellulose are observed to be with the trend of moving to the lower wave number. The absorbance of Nanocellulose and microcrystalline cellulose are significantly greater than that of the nitrocellulose, indicating that both intermolecular and intermolecular hydrogen bonds are strengthened. It is caused by the existence of alcohol hydroxyl groups of cellulose during the preparation the microcrystalline cellulose and nanometer cellulose. The cellulose of the alcohol hydroxyl groups is in a pattern of acid-oxidized. Smaller absorption peaks at 1710 cm⁻¹ are only found in nitrocellulose samples, produced by the ester group. For the micro-nano sample of cellulose, the corresponding peak is not found in the spectrum. The stretching vibration of C = O fell in the band of 1598 cm⁻¹. It is easy to find the band of nitrated cellulose, microcrystalline cellulose in Fig. 1 without much change. The absorption peaks of Nano-cellulose are broadened, as the result of the oxidation, during the preparation of Nano -ellulose by sulfuric acid. The characteristic peaks of cellulose fell with in 1368-1361 cm⁻¹. The other peaks between 1160-1000 cm⁻¹ are corresponding to a cyclic C-O-C asymmetric plane stretching vibrations. 11060 cm⁻¹ stood for the circular C-O-C's C-C's stretching vibration. All C-C bonds are obviously oxidized through the nanometer of the cellulose. Other peaks found on the spectrum include the cyclic C-O-C asymmetric plane stretching vibration/CH₂ (CH₂OH) on 898 cm⁻¹ and the OH surface deformation vibration on 700-666 cm⁻¹.

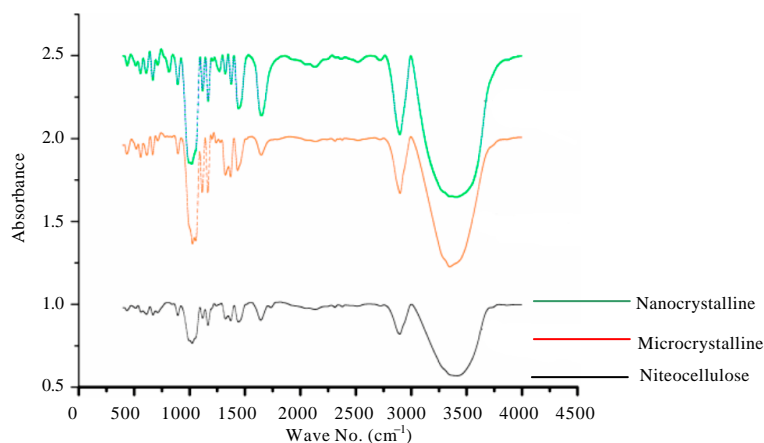


Fig. 1: Nitrocellulose, microcrystalline cellulose, nano cellulose infrared spectrogram

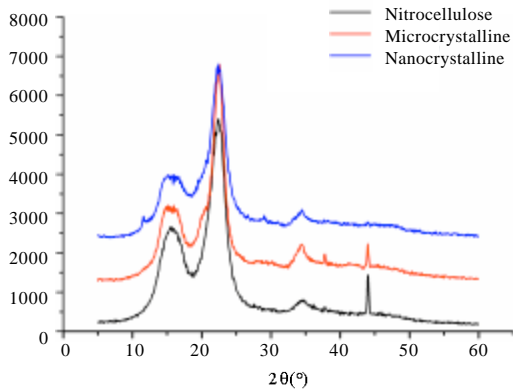


Fig. 2: Nitrocellulose, microcrystalline cellulose, nano cellulose X-ray spectrum diagram

Figure 2 is the X-ray patterns of nitrated cellulose, microcrystalline cellulose and cellulose Nanocrystal. From the figure, one can conclude that the difference between their each individual characteristic peaks remains mainly consistent. The strongest peak located at 14.8, 16.1 and 22.4°, respectively. Each of them is in correspondence to the cellulose crystal of 101, 10T and 002. So from this phenomenon it is quite sure that the cellulose maintains itself in the form of type I during the process of micro-Nano preparation. Compared to the cellulose samples, crystallinity is increased from 76.2 to 87.6%. The diffraction peak represents for a mixture with the process of micro Nano cellulose, is located at 22.4° and is sharper and higher in relative peak strength. However, the dispersion of non-crystalline is decreased, as in the opposite zone of crystalline. In the process of acid-hydrolyzation, hydrogen ions entered the amorphous regions of cellulose and accelerate the hydrolysis of the glycoside bond cleavage. Thus the cellulose crystal is finally obtained. For the amorphous regions of cellulose, reactivity activity is scored higher than the crystallization zone. In the hydrolysis reaction, amorphous regions of cellulose reacted quickly while the crystal fiber zone restricted its own reactions to the surface areas. Therefore, crystallization among nitrocellulose, microcrystalline cellulose and cellulose Nano-crystal comparison of Nano-crystalline Cellulose are all greatly improved.

The polymers such as Cellulose will start its degradation as dehydrated and aromatized when heated. From Fig. 3 and 4, they show the identical distribution of the decomposition temperature of nitrated cellulose and microcrystalline cellulose. The pyrogenation temperature of the nitrocellulose is obviously higher, when compared with the Nanocrystalline Cellulose. Seen from the figure,

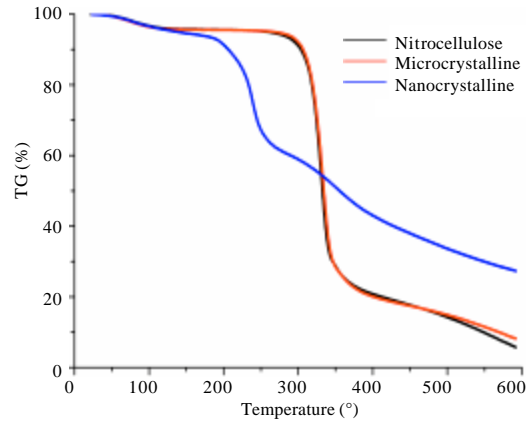


Fig. 3: Nitrocellulose, microcrystalline cellulose, Nano-cellulose thermal analysis curve

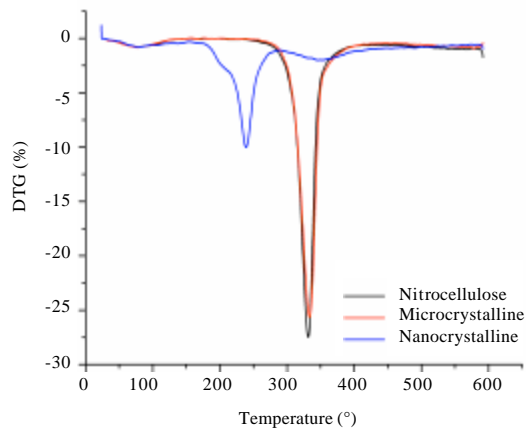


Fig. 4: Nitrocellulose, microcrystalline cellulose, Nano cellulose thermal gravity analysis curve

a smaller absorption peak will appeared when the temperature is among 25-150°C. When the temperature is added to 300-400°C, another strong absorption peak is appeared. As to the nitration cellulose and microcrystalline cellulose, there are no obvious absorption peaks at 150-240°C while Nano cellulose produces an opposite peak under the effects from thermal behavior. A strong absorption peak is found at about 240°C and later is verified to be the Nano cellulose. Figure 3 and 4 show the smaller absorption peak of Nano-cellulose and indicated by the figures, the heat of Nanocrystalline Cellulose is considerably smaller than nitrocellulose, thus has worse in thermal stability. Due to the small sizes, Nano cellulose absorbs heat faster than nitrocellulose molecules with increasing temperature. It also show that the Nano-cellulose possess a good heat dissipation effect, due to the

exposure of Nano cellulose molecular chain function groups, followed by activity strengthening and carbonization under lower temperature. The Nanocrystalline cellulose's como water and C2, C4 hydroxyl are removed at the same time.

CONCLUSION

The emerging regions of both vibration peak of microcrystalline cellulose and cellulose Nanocrystal have the trend of moving towards lower wave numbers. The absorption of Nano cellulose and microcrystalline cellulose are greater than that of nitrocellulose. Intermolecular hydrogen bond is strengthened while at the same time the cellulose of hydroxyl is oxidized.

During the process of preparing micro-nano cellulose its crystal structure remains keep to type I. Compared with the nitrocellulose, the crystallinity of cellulose is increased from 76.2-87.6%. In the same process, the diffraction peak at 22.4° is sharpened while the relative peak strength is increased significantly but the non-crystal zones are decreased.

Nano cellulose has a better dissipation effect than the microcrystalline cellulose, or cellulose in the process of micro nanometer. When the section group of cellulose molecular chain is exposed, activity intensity will be increased. The carbonization is then achieved under low temperature. Cellulose's como water and C2, C4 hydroxyl are removed at the same time.

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