Study surface modified nanocellulose whiskers in coconut shell

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Abstract. The nanocellulose whiskers degraded by coconut shell were modified by silane coupling agent (KH-570). The structure, morphology and dispersibility of modified nanocellulose whiskers were characterized and analyzed by infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electron microscope (TEM) and sedimentation. The results showed that the modified nanocellulose whiskers have been changed from hydrophilic to hydrophobic, and could be dispersed uniformly in ethanol without agglomeration because silane coupling agent reacts with hydroxyl groups on the surface of nanocellulose whiskers. The study showed that the crystallinity of nanocellulose whiskers were decreased with the increase of the content of coupling agent. Experiment also indicated that both of dispersibility and crystallinity could reached optimism when the amount of coupling agent is 2%. Finally, the mechanism of chemical reaction of coupling agent modified nanocellulose whisker in coconut huskwas established by comparison of molecular structure of KH-570, modification process and the infrared spectrum of nanocellulose whiskers.

1. Introduction

As main component in the cell walls of all plants, cellulose is a fibrous, tough, water-insoluble substance and widely considered to be the most abundant biodeived polymer on the planet. Nanocellulose whiskers (NCWs) are nanocrystalline fibers obtained from natural fibers. NCWs have been applied widely in optical and electronic devices [1,2], molecule biology [3] and composite materials [4,5] due to its optimum properties of low density, high modulus, high strength, high surface area, biocompatible and biodegradability [6,7,8,9], and etc. So, its applications have attracted more and more attention in over the year.

Coconut shells (CS) are an agricultural byproduct that are often considered to be a hard wood [10]. CS with a plentiful lignocellulosic are considered to be waste in the tropical areas of many countries. In recent years, only a few CS have been used in research, such as the preparation of activated carbon [11,12,13], handicrafts [14,15], lignocellulosic filler [16], adsorbent [17], concrete [18,19], briquettes [20] and polymer composites [20], etc. Thus, the disposal of CS causes huge environmental problems [22]. For example, approximately 23 million coconuts are produced annually in Hainan Island, China [23]. In general, the resource of CS is very rich while its comprehensive utilization rate is very low. Therefore, the preparation of NCWs from coconut shell fiber is an environment friendly research program.

The surface of NCWs is rich in hydroxyl groups, which is hydrophilic and not easy to disperse in organic solvents. Because of its high specific surface area and surface energy, NCWs will gather together to form aggregates in order to maintain a stable state and reduce the surface energy. In order
to increase the comprehensive properties of the materials, the dispersion of NCWs have been improved [24]. In the present study, the surface modification of NCWs was carried out with silane coupling agent KH-570 to improve dispersivity and reduce hydrophilicity. The surface modified NCWs were characterized by TEM, XRD, FTIR respectively. The properties and mechanism of modified NCWs were discussed.

2. Experimental

2.1. Materials
Nanocellulose whiskers (NCWs) were prepared in our laboratory. KH-570 was obtained from Nanjing Chuangshi Chemical Co., Ltd (China). Ethanol (95%, AR grade) and Acetic acid (AR grade) were purchased from Xilong Scientific Co., Ltd (China). The water used in this experiment was distilled.

2.2. Preparation of modified NCWs
KH-570 is dissolved in 95% ethanol to obtain 0.5%, 1.0%, 2%, 3% solution respectively, shown in Table 1. After adjusted pH to 4-5 with acetic acid, the solution was heated at 50°C on magnetic stirrer for 5 hour, the modified NCWs were obtained and then dried by vacuum freezing drier.

| Sample number | Content of KH-570(%) | Quality of nanocellulose whiskers(g) |
|---------------|----------------------|-------------------------------------|
| 1             | 0                    | 0.05                                |
| 2             | 0.5                  | 0.05                                |
| 3             | 1.0                  | 0.05                                |
| 4             | 2.0                  | 0.05                                |
| 5             | 3.0                  | 0.05                                |

2.3. Characterization
FTIR analyzer (Perkin-ElmerSpectrum-400, USA) was employed to analyze the samples treated and untreated NCWs.

XRD patterns were obtained with an X-ray diffractometer (D/max 2200VPC, Rigaku, Japan) with graphite monochromatized Cu Ka radiation at the scan rate of 4°/min in a 2θ range of 5~50°. The crystallinity index (CrI) of samples was calculated from the X-ray diffraction patterns according to the following equation:

\[ Cr = \left[ \frac{I_{002} - I_{am}}{I_{002}} \right] \times 100\% \]  \[ (1) \]

where Cr is relative crystallinity; \( I_{002} \) is the diffraction intensity of (002) crystal plane; \( I_{am} \) is the diffraction intensity of amorphous region. For cellulose type I, \( I_{am} \) is the intensity of the amorphous background diffraction at about 18.0°.

The microphology of modified NCWs were observed with JEM-1010 transmission electron microscopy (TEM) (JEOL Ltd., Japan) at 200 kV accelerating voltage. A droplet of diluted modified NCWs suspension was put on a Cu-grid and the excess liquid was removed by blotting with a piece of filter paper.

3. Results and Discussion

3.1. Fourier-Transform Infrared Spectroscopy (FTIR)
The infrared spectrum of NCWs before and after KH-570 modification is shown in Figure 1. The effects of chemical grafting and the surface functional groups were analyzed. The Figure 1(a) shows the infrared spectra in the scanning range of 4000-500cm\(^{-1}\). The Figure 1(b) shows the partial infrared spectra in the scanning range of 2500-700 cm\(^{-1}\).

The curve 1 shows the infrared spectra of NCWs. The band at 3317cm\(^{-1}\) is indicative of -OH stretching vibrations, and the peak at 2891 cm\(^{-1}\) is attributed to C-H stretching vibrations. The peak at
1593 cm\(^{-1}\) can be assigned to bending vibration peak of hydroxyl group. They are all characteristic absorption peaks of nano cellulose [26,27]. The curves 2-5 in the Figure 1 are the infrared spectra of NCWs modified by silane coupling agent KH-570. Compared with the unmodified nano cellulose whiskers, the absorption peak of 3317 cm\(^{-1}\) narrowed and blue shifted with the increase of KH-570 content, which indicated that -OH on the surface of NCWs reacts with KH-570, and the surface hydroxyl is reduced. The characteristic peaks at 1634 cm\(^{-1}\) and 1715 cm\(^{-1}\) are the stretching vibration absorption peaks of C=C and C=O respectively. The absorption peaks at 1295 cm\(^{-1}\) and 1321 cm\(^{-1}\) are the characteristic peaks of coupling agent KH-570[28,29], which indicates that KH-570 reacted with NCWs. The purpose of surface modification of NCWs by KH-570 is achieved.

![Figure 1. Fourier transform infrared spectroscopy (FTIR) spectra of NCWs.](image)

3.2. X-ray diffraction (XRD) analysis

Figure 2 shows the XRD patterns of NCWs with different KH-570 contents. The crystalline peaks appeared near at 17° and 20° of 2\(\theta\), correspond to the crystal planes of 101 and 002, which were cellulose type I structures [30,31]. The crystallinity of NCWs sample 1, 2, 3, 4 and 5 calculated according to Eq. (1)[25] were 35.4%, 26.2%, 28.6%, 29.8% and 28.7%, respectively. The X-ray diffraction spectrum analysis showed that both of the intensity of characteristic peaks and relative crystallinity of NCWs treated by KH-570 were decreased. The reasons could be that the introduction of KH-570 onto NCWs backbone reduced the hydrogen bonding forming ability of NCWs and damaged original structure and the regularity. When the concentration of coupling agent KH-570 was more than 2%, the crystallinity and characteristic peak strength were increased instead of decreasing, which suggested that the NCWs can be completely connected or coated when the concentration of coupling agent KH-570 is less than 2%. The part connected with the NCWs is likely to hydrolyze and condense with each other in the solution, forming a quasi crystallization when the coupling agent content KH-570 is excessive over 2%.
3.3. Dispersion of modified nano cellulose whiskers

The suspension of NCWs treated with different concentrations of KH-570 for 24 hours was shown in Figure 3, which can be seen that most of NCWs without KH-570 (sample 1) are deposited at the bottom, the NCWs with 3% KH-570 (sample 5) are partially precipitated, and NCWs with 0.5% KH-570 (sample 2) and 1.0% KH-570 (sample 3) are slightly precipitated. KH-570 is hydrolyzed to form silanol, and the OH group of silanol reacts with OH group on the surface of NCWs, which show that the surface of NCWs grafted with KH-570 and further blocked the hydrogen bonding form of NCWs. In addition, due to the steric hindrance effect of the KH-570 structure of NCWs, the precipitation phenomenon caused by the aggregation of NCWs has been greatly reduced. The NCWs treated with 2% KH-570 (sample 4) remained uniform suspension after standing for 24 hours, indicating that the NCWs and KH-570 were well grafted.

3.4. Morphology analysis of NCWs

To confirm the size and morphology of NCWs, a dilute suspension was observed using TEM, shown in Figure 4. It can be also seen from Figure 4 that the length of NCWs distributes between 150 and 330 nm. They are whisker like. Although the unmodified NCWs were treated by ultrasonic dispersion, the agglomeration still existed as shown in Figure 4 (a). It may be that NCWs are rich in hydroxyl groups[27] and have high surface energy, which leads to poor dispersion. Figure 4 (b) shows that the NCWs modified by coupling agent KH-570 were distributed uniformly without aggregation. It is
possible that KH-570 was adsorbed on surface and formed chemistry bond which prevented NCWs from reuniting. Therefore, hydrogen bonding and surface tension have been reduced significantly. Then the modified NCWs liquids dispersed were obtained.

3.5. Modification mechanism
There are abundant hydroxyl groups on the surface of NCWs, which are easy to agglomerate due to the action of hydrogen bond and van der Waals force. Thus the hydroxyl stretching vibration absorption peak of the modified NCWs is weakened, and the characteristic peak of KH-570 appears at 1295 cm\(^{-1}\), 1321 cm\(^{-1}\), 1634 cm\(^{-1}\), 1715 cm\(^{-1}\), 2883 cm\(^{-1}\), 2949 cm\(^{-1}\) shown in Figure 1. The results demonstrated that the hydroxyl groups on the surface of NCWs in coconut shell modified by KH-570 react with the silicon hydroxyl groups and formed a new covalent bond. On the one hand, the modification process of KH-570(CH=CH\(\text{COOC}_3\text{H}_6\text{Si(OCH}_3\text{)}_3\) is that the methoxy - (OCH\(_3\)) \(_3\) is hydrolyzed, and then silanol and CH=CH\(\text{COOC}_3\text{H}_6\text{Si(OCH}_3\text{)}_3\) are obtained. On the other hand, the solvent molecules enter the surface of the modified NCWs and prevent the aggregation of cellulose whiskers. So, the NCWs suspension are evenly dispersed. It can be clearly observed from the transmission electron microscope that the modified NCWs in coconut shell are whisker like. The chemical reaction mechanism of coupling agent modified coconut shell can be illustrated by infrared spectrum and molecular structure formula of KH-570. Figure 5 shows the reaction process. Figure 6 shows the surface modification and dispersion of cellulose whiskers after coupling agent KH-570.

Modified NCWs connect the silane coupling agent monomer through the hydroxyl groups on its surface, so that the structure of the composite is similar to a "brush", and the polarity of the cellulose whiskers is changed at the same time. When the modified cellulose whiskers enter the solvent medium, the contact and aggregation of nanofibers are blocked due to the steric hindrance effect of the structure and the change of polarity. Thereafter, the aggregation of suspension is inhibited [33]. After modification with KH-570, the hydroxyl groups on the surface of NCWs interact with KH-570, resulting in the change of spatial structure, and the formation of large steric hindrance on the surface of NCWs, which effectively prevent the agglomeration of whiskers and significantly improve the dispersion of NCWs in solvent.
6

4. Conclusions
The surface of NCWs in coconut shell was modified and dispersed evenly by silane coupling agent KH-570. The infrared spectrum showed that KH-570 grafted onto the surface of NCWs effectively formed chemical bond with the surface of NCWs, and reduced the surface hydroxyl groups and hydrophilicity. The three-dimensional structure of modified NCWs showed good hydrophobicity. So the dispersion stability of NCWs suspension was improved significantly. The size of NCWs before and after modification was 150-330 nm, but the crystallinity of NCWs decreased.

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