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Effect of low energy ion beam implantation on the microstructure of cellulose

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ABSTRACT

The changes of cellulose microstructure after being implanted by low energy N^+ were studied by infrared (IR), X-ray diffraction (XRD) and scanning electron microscope (SEM). The results showed that the cellulose intramolecular and the intermolecular hydrogen bonds have broken after being implanted by N^+. With the increase in implantation doses, the cellulose relative degree of crystallinity reduced gradually, when the implantation doses increased to 1500×10^{14} N^+ cm^{-2}, the relative degree of crystallinity decreased 6.84% than the control sample. Furthermore, the average diameter of cellulose powder reduced gradually as well, and many tiny fragments were visible on the surface of cellulose powder.

1. Introduction

Cellulose is the most abundant renewable resource in the biosphere, but this resource has not been fully utilized at present. This resulted in a huge waste of resource and energy. In order to make better use of cellulose and avoid causing environmental pollution, more and more researchers started to study cellulose degradation and application, and look forward to transform the most abundant and cheapest renewable resource into fuel form that can be used directly (Tang et al., 2008; Xu and L, 2009)

The ion beam implantation technology could control the implantation strength and dose precisely, and has been widely used in the study of material modification. After over 20 years of development, significant achievements have been obtained in many fields such as improvement of crops and micro-organisms, plant gene transfer, life origin and evolution, environmental radiation and human health and so on, and also remarkable economic and social benefits have been achieved. Studies have shown that the low energy ion implantation has a more profound mechanism than γ-rays and other ionizing radiation, it has effects of mass deposition and charge transfer besides the energy process of ionizing radiation (Cui and Li, 2005; Liang, 2007; Yu, 1995). In this paper, the change of cellulose microstructure after being implanted by low energy N^+ was studied.

2. Material and methods

2.1. Material

Experimental cellulose powder was supplied by the Aladdin Reagent Company. It was microcrystalline cellulose and the average diameter was 90 μm. The cellulose powder was dried at 105 °C until the weight became constant.

2.2. Methods

2.2.1. Low-energy ion implantation

Ion beam implantation was carried out at the Nanjing University of Technology with the ion implantation facility. The cellulose powder was fixed on a sterilized Petri dish by twin adhesive and dried in the hood. The dishes were placed on the sample holder, which was designed specifically for ion implantation. The ion source was nitrogen ions (N^+). The implantation energy was 10 keV, the pulse current was 25 mA, the pulse time was 5 s, the interval was 30 s and the operating pressure in the target chamber was about 10^{-3} Pa. After implantation, the samples were harvested and dried at 105 °C until the weight became constant.

2.2.2. IR analysis

The changes in cellulose chemical structure were detected using Nicolet is10 infrared spectrometer. The scanning wave number range was in 4000–500 cm^{-1}. The relative intensity of the absorption peak was calculated by the ratio of the transmittance of the corresponding absorption peak at 1372 cm^{-1}, which

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appeared only in the crystalline structure of cellulose, it was related to the degree of crystallinity (Yang et al., 2009). The results were the average of three experiments.

2.2.3. XRD analysis

The changes in cellulose relative degree of crystallinity were detected using ARL-X'TRA X-ray diffractometer produced by US National Thermal Power Corporation. The test was carried out with radiation of wavelength $\lambda=0.154$ nm, the grazing angle (2θ) ranging from 5° to 50° with an angle resolution of 0.02°, and the voltage was 40 KV with the electrical current of 20 mA. The relative degree of crystallinity was calculated according to the crystallization formula proposed by Segal et al. (1959).

$$C_{rI}(\%) = [(I_{002} - I_{am})/I_{002}] \times 100$$

Crl(%) is the percentage of the relative degree of crystallinity, I_{002} is the large intensity (arbitrary units) of (0 0 2) lattice diffraction angle and I_{am} is the scattering intensity of the non-crystalline background diffraction when the 2θ angle was near 18° (with the same units of I_{002}). The results were the average of three experimental data.

2.2.4. SEM analysis

The cellulose microstructure was observed using a Hitachi 3400-N scanning electron microscope. The samples were observed with magnification of 120 and 5000 times (Lu et al., 2005).

3. Results

3.1. IR analysis

The IR spectra of those implanted by 250×10^{14}–1000×10^{14} N^+ cm^{-2} doses and those that were not implanted are shown in Fig. 1. The corresponding structures of IR absorption peaks are shown in Table 1, and the relative intensities of the absorption peaks are shown in Table 2.

3400 and 2900 cm^{-1} were absorption peaks of intramolecular hydrogen bonds and intermolecular hydrogen bonds, respectively. With the increase in implantation doses, the relative intensities of the two absorption peaks all decreased gradually (Table 2). This indicated that in the implantation range of this study, the N^+ implanted caused the intramolecular and intermolecular hydrogen bonds to rupture. From Fig. 1 we can see that there was a carbonyl absorption peak at near of 1730 when the implantation dose increased to 1500×10^{14} N^+ cm^{-2}. This indicated that six ring alicyclic ketones or six ring grease was likely formed in cellulose molecules after being implanted by N^+.

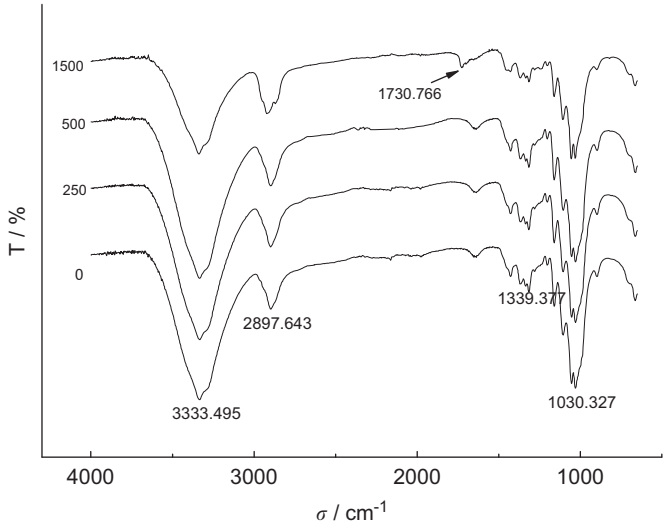

Fig. 1. IR spectra of cellulose implanted by low-energy N^+ with different doses.

Table 1
Absorption peaks of IR spectra and its structure ascription.

Wave number (σ/cm^{-1})	Response peak
3400	Intramolecular –OH bond stretching vibration
2900	Intermolecular –OH bond stretching vibration
1432	Cellulose-CH_2 bending vibration and shear vibration
1372	Cellulose and hemicellulose –CH bending vibration
1163	Cellulose and hemicellulose C–O–C stretching vibration
1058~1060	Cellulose and hemicellulose C–O stretching vibration
898	β-glucoside bond vibration

Table 2
Relative intensities of absorption peaks in IR spectra.

Wave number (σ/cm^{-1})	Implantation doses (10^{14} N^+cm^{-2})			
	0	250	500	1500
3400	0.670	0.655	0.648	0.576
2900	0.904	0.902	0.893	0.882
1432	1.029	1.030	1.030	1.021
1372	1.000	1.000	1.000	1.000
1163	0.933	0.935	0.934	0.946
898	1.023	1.022	1.025	1.027

Table 3
Effect of different implanted doses on the displacement of –OH absorption peaks in IR spectra.

Implantation doses (10^{14} N^+cm^{-2})	0	250	500	1500
Intramolecular –OH peak position	3333.5	3334.5	3336.4	3338.3
Intermolecular –OH peak position	2897.6	2898.1	2907.6	2920.3

We know that the strength of the hydrogen bonds directly affects the –OH peak position, the stronger the hydrogen bonds, the lower the wave number of –OH peak will shift to, and vice versa. From Fig. 1 and Table 3 we can see that the –OH peaks of the cellulose powder gradually shifted to higher wave number after being implanted by N^+. This indicated that the implanted N^+ damaged the cellulose intermolecular and intramolecular hydrogen bonds, that is, the crystalline structure of cellulose powder was damaged.

1432 and 1164 cm^{-1} are the characteristic absorption peaks of cellulose macromolecule structure. These two absorption peaks changed little after implantation in this experiment, and this indicated that the N^+ implanted does not change the structure of cellulose macromolecules. 898 cm^{-1} is the absorption peak of β-glycosidic bond vibration, and the peak did not change either after implantation, and we can say that the N^+ implanted did not affect the structure of β-glycosidic bond.

3.2. XRD analysis

In this paper, the changes in cellulose powder crystalline structure implanted by low-energy N^+ were detected by X-ray diffraction. Results are shown in Fig. 2. As the implantation dose increases, the wave trough near $2\theta=18°$ was the diffraction