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Radiation effect of Apocynum fiber

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Abstract Changes of surface shape, aggregate state, and microstructure of Apocynum fiber before and after irradiation were studied by XRD, IR, SEM, ESR, and solid state ^{13}C CP/ MAS NMR. The results show that the surface shape and microstructure were not spoiled under 50 kGy gamma irradiation, while the crystallization of Apocynum fiber changed under 280 kGy . It also shows that different free radicals appear after irradiation and their concentration increases with the increase of irradiation dose.

Key words XRD, IR, SEM, ESR, CP/ MAS, Hydrogen bond, Free radical
CLC number O63

1 Introduction

Apocynum fiber is known for its softness, luster, coolness, good moisture absorption, and air permeability. Still, it has some faults such as smooth on surface, less curves, and inferior quality for spinning. The physical properties of Apocynum fiber was studied by Zhang Yi et al,[1] and Ce^+ induced graft Apocynum fiber was studied by Chen Bowen et al.[2] Hassanpour and coworkers studied the modification of the cellulose.[3,4] We primarily focused on the concentration and stability of the free radicals in grafting Apocynum fiber. To study the radiation effect of Apocynum fiber and the form of free radicals, we have used various methods such as XRD, SEM, IR, ESR, and ^{13}C CP/ MAS NMR.

2 Experimental

2.1 Materials and irradiation

The Apocynum fiber used in this study was purchased from Yuli County of Xinjiang. After extracting the enzyme the samples were distilled for 24 h by acetone. And after being dried in a vacuum drying oven and degasified by N_2, they were irradiated by a ^{60}Co source of 1.85×10^{11} Bq at room temperature at a dose rate of 6.7 kGy/h. The doses were 0, 50 , and 280 kGy, respectively.

2.2 Instruments and methods

The samples were characterized by IR spectrophotometer (Bruker Eqinox55), X-ray diffractometer (M18XHF22) with Cu K_α radiation ($\lambda=1.54056$ Å), and Type LEO1430VP environment scanning electron microscope with a magnification of 5000.

Solid state ^{13}C cross polarization magic-angle spinning (CP/MAS) NMR experiments were performed on Varian Inova 600 MHz NMR spectrometer at 298.0 K. Magic-angle spinning rate was 4.0 kHz. To avoid peak split, total sideband suppression (TOSS) technique was not used. Methothrin with chemical shift of 17.35×10^{-6} was used as an external reference for ^{13}C chemical shifts.

The ESR spectra were recorded with a Bruker ER 200D-SRC spectrometer using 90 G/min scan speed,

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5 G modulation amplitude, and 5 mW microwave power.

3 Results and discussion

3.1 Analysis of surface shape of Apocynum fiber

The SEM photographs of Apocynum fiber before and after irradiation are shown in Fig. 1. It could be observed that Apocynum raw fiber was smooth on the surface, had less curves and some knots on its body. It was a kind of highly directed and rigid fiber with the average diameter of 14 μm. There were some small blocks on the Apocynum fiber after extracting, showing that the impurity of pectin had not been extracted completely from the Apocynum fiber. The average diameters of the Apocynum fiber are 18 μm, 28 μm, and 24 μm, respectively, therefore the diameter expanded after ^{60}Co gamma irradiation. There was a great amount of hydrogen bonds in native cellulose; parts of these hydrogen bonds that were probably destroyed by extracting and gamma irradiation. Meanwhile the effect of the hydrogen bonds was weakened by them, so the fasciculuses were loosened; the probable result was the expansion of the average diameter. The irradiation of excessive dose would destroy the crystal structure of fiber, shorten the distance between molecules, and heighten the density.[5] This is the possible reason for the fact that the Apocynum exposed to 280 kGy is (24 μm) thinner than that (28 μm) exposed to 50 kGy.

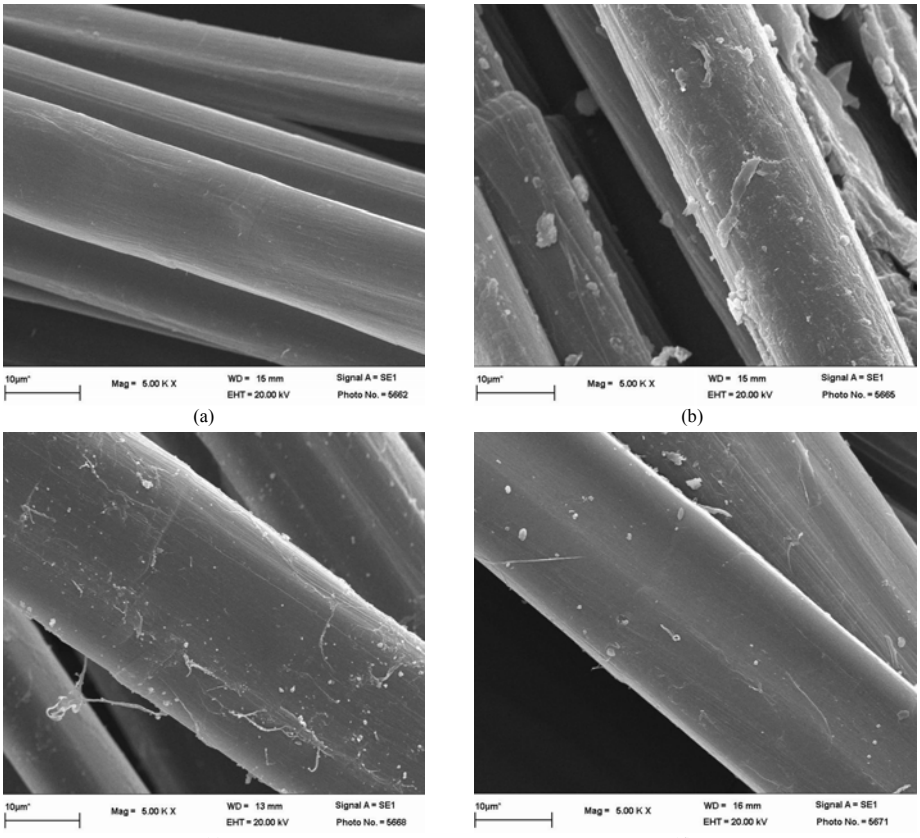


Fig.1 The SEM photographs of Apocynum fiber before and after irradiation.
(a) 0 Gy (raw fiber), (b) 0 Gy (extracting fiber), (c) 50 kGy, (d) 280 kGy

3.2 Analysis of IR and XRD spectra

The IR spectra of Apocynum fiber before and after gamma irradiation are shown in Fig.2. The absorption peaks of 3345 cm^{-1} in Fig.2(a) and 3338 cm^{-1} in Fig.2(b) were assigned to the primary alcohol group, while that of 2922 cm^{-1} in Fig.2(a) and 2901 cm^{-1} in Fig.2(b) were attributed to the C-H bonds. As the figure shows, the primary difference between Fig.2(a) and Fig.2(b) was in the fingerprint segments (800–1400 cm^{-1}); the Apocynum raw fiber containing

benzenoid materials like pectin and lignin caused the fingerprint segments in Fig.2(a) to be more complex than in Fig.2(b). The absorption peak of 1696 cm^{-1} in Fig.2(c) was associated with carbonyl. It was also shown that the intensity of the peak of carbonyl under 280 kGy gamma irradiation was higher than that under 50 kGy. It indicated that part of the alcohol group was oxidated into carbonyl under gamma irradiation and its concentration increased with the irradiation dose's increase. It has been elucidated in some documents that the intensity of hydrogen bonds between molecules affects the wavenumber of the absorption peak of the alcohol group. The stronger the intensity of hythe drogen bond, the lower the wavenumber of the alcohol group and vice versa. [6] The absorption peaks of alcohol in Fig.2(c) and (d) were broader than those in Fig.2(b), which was attributed partly to the decrease of the hydrogen bonds, because the effect of the decrease made the alcohol peak region broaden toward the lower wavenumber.

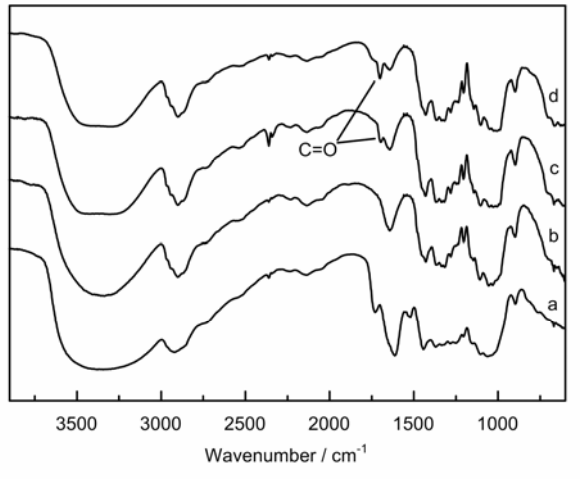


Fig.2 The IR spectra of Apocynum fiber before and after gamma irradiation.

(a) 0 Gy (raw fiber), (b) 0 Gy (extracting fiber), (c) 50 kGy, (d) 280 kGy

The XRD spectra are shown in Fig. 3 and there were three crystal peaks at spectrum(a), which were 23°, 15° and 17°, respectively. But these peaks fall off and disperse widely in Fig.3(b), (c), and (d). It indicates that the extracting and gamma irradiation could change the aggregate state of Apocynum fiber and decrease their crystallinity. As shown in IR spectra, the carbonyl appeared after irradiation, and its existence not only destroyed the orderly structure but also weakened the hydrogen bonds between fasciculuses. It also verified the fact of Apocynum fiber's broadening as mentioned above (3.1).

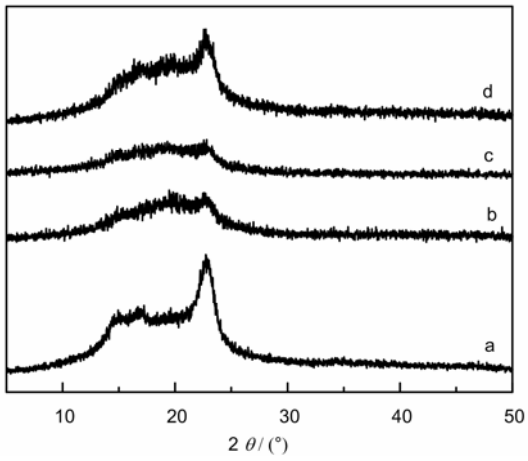


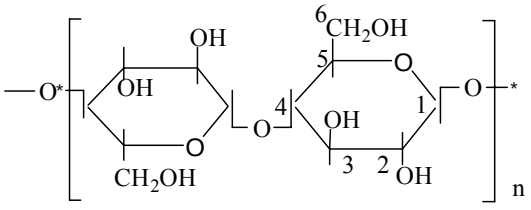
Fig.3 The XRD spectra of Apocynum fiber before and after gamma irradiation

(a) 0 Gy (raw fiber), (b) 0 Gy (extracting fiber), (c) 50 kGy, (d) 280 kGy

But compared with the lower dose, the intensity of the three crystal peaks increased under a higher dose, showing that gamma irradiation of a higher dose may break the macromolecular chain into shorter chains which move more quickly than longer chains. And the shorter the macromolecular chain, the easier it is to order Apocynum fiber and to heighten the crystal peaks.

3.3 Solid state ^{13}C CP/ MAS NMR spectra

The ^{13}C CP/ MAS NMR spectra of Apocynum fiber before and after gamma irradiation are shown in Fig. 4. Atalla and coworkers analyzed cotton linters, ramie and other celluloses by ^{13}C CP/ MAS NMR.[7,8] As we know, the main component of the most native fiber of plants is cellulose, just as it is in Apocynum. The chemical structure of cellulose is shown below:



Beginning at the high field part of the spectrum, the chemical shift of 66.7×10^{-6} was assigned to C6, and the region between 72.7×10^{-6} and 76.1×10^{-6} was attributed to C2, C3, and C5, respectively. The 90.4×10^{-6} was associated with C4 and the 107.1×10^{-6} with C1. Comparing the spectra before and after gamma irradiation, we did not find the region of chemical shifts and the shape of the peaks change noticeably. It showed that the main component of Apocynum fiber was cellulose exactly, and its structure was not spoiled by irradiation. We found that in NMR spectra no new types of carbon were created, though the carbonyl absorption peak appeared in IR spectra. It was probably strained by solid state ^{13}C NMR solution so that a few carbonyl peaks did not appear in NMR spectra. We could also see the peak's broadening after irradiation. This indicates that strong interactions existed between molecules in solid, so the resolution became worse. On the other hand, the increase of the concentration of free radicals within Apocynum fiber, as paramagnetic substance, would make the shape of peaks broader and the NMR solution lower.

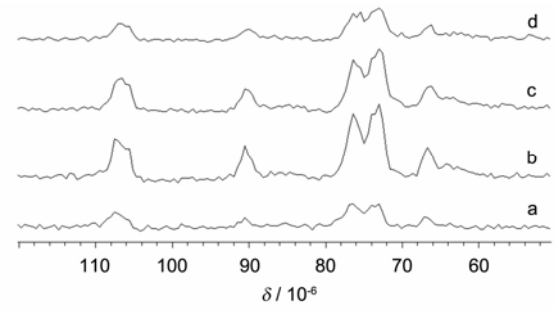


Fig.4 The CP/MAS NMR spectra of Apocynum fiber before and after irradiation.

(a) 0 Gy (raw fiber), (b) 0 Gy (extracting fiber), (c) 50kGy, (d) 280kGy.

3.4 ESR analysis

The ESR spectra are shown in Fig. 5. The ESR spectrum of the sample before irradiation was almost a beeline, indicating that the concentration of free radicals before irradiation pointed to zero. The samples after irradiation were kept unanalyzed for two months, but the double resonance signals in ESR spectra still appeared, which proved that the free radicals were stable. Its shape was judged to be Gaussian line type through the differential slope method and its *g* factor was 2.0009, and the isotropic nitrogen hyperfine coupling constant is 20 G. The ESR intensity increased with the dose increasing, showing that the concentration of free radicals in Apocynum increased with the increasing dose.

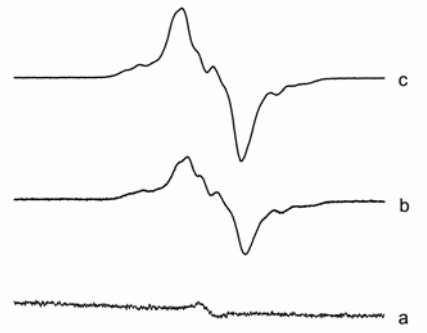


Fig.5 The ESR spectra of the Apocynum fiber before and after irradiation.

(a) 0 Gy (extracting fiber), (b) 50kGy, (c) 280kGy.

On average, the ESR spectrum is symmetrical, but it is unsymmetrical and there appears more than one peak in Fig. 5. This is probably due to the fact that Apocynum fiber has more than one kind of interacting free radicals after irradiation and these free radicals are anisotropy. The dissymmetry of ESR spectrum and the change of the half-high width indicate that after irradiation Apocynum fiber has more than one kind of blending free radicals.

4 Conclusions

The structure of Apocynum fiber was not changed noticeably by gamma irradiation; the production of free radicals and their stability were the important basis for our study on the Apocynum grafting. Our other articles expound the copolymerization of Apocynum grafting with monomer.

Acknowledgment

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