EFFECTS OF SUPERCRITICAL CARBON DIOXIDE ON MORPHOLOGY OF APOCYNUM VENETUM FIBERS

by

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This paper investigated the structures and compositions of apocynum venetum fibers treated with pectinase and mixture of sodium hydroxide and hydrogen peroxide in supercritical carbon dioxide fluid. The apocynum venetum fibers were analyzed by Fourier transform infrared spectrometry, X-ray diffraction, and scanning electron microscopy. Fourier transform infrared analysis indicated that pectinase could remove the pectin and hemicellulose and the mixture of sodium hydroxide and hydrogen peroxide could extract the lignin in supercritical carbon dioxide. Meanwhile, the results of X-ray diffraction showed that cellulose crystallinity index and crystallite sizes of treated fibers increased in comparison with that of untreated fibers. The studies of scanning electron microscopy also revealed a complete removal of non-cellulosic gummy material from surface of treated apocynum venetum fibers. Small gummy on the surface of apocynum venetum fibers would be removed by supercritical carbon dioxide, which can be verified by bubble dynamics.

Key words: *apocynum venetum, supercritical carbon dioxide, structure, bubble*

Introduction

Apocynum venetum (AV) is one type of wild plants. The AV fibers contain up to 50-60% non-cellulosic gummy material. The plant gum on the fiber must be eliminated for further industrial utilization. Traditionally, degumming is achieved by classical chemical process with sodium hydroxide, which poses serious environmental threats [1]. Besides, biotechnological degumming process is another way to remove the plant gum involving polysaccharide degrading microorganisms and enzymes [2]; however, the biotechnological degumming process is not stable. Thus, a new degumming method should be proposed. As an environmental medium, supercritical carbon dioxide (SC-CO_2) fluid has been developed rapidly in recent years and obtained numerous achievements in many fields [3, 4]. Here, the aim of this work is to investigate the new degumming method of AV fibers with pectinase, mixture of sodium hydroxide and hydrogen peroxide ($NaOH/H_2O_2$) utilizing SC-CO_2 as solvent. The basic information that the influence of pectinase, mixture of $NaOH/H_2O_2$ in SC-CO_2 on the chemical compositions, crystal structures, and surface morphology of the AV fibers was obtained. These characteristics were assessed by means of the combinations of Fourier transform infrared (FT-IR) spectrometry, X-ray diffraction (XRD), and scanning electron microscopy (SEM).

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Experimental

The AV fibers without tension were placed into a treatment kettle (500 mL). Carbon dioxide in a gas cylinder filtered with a purifier was liquefied through a refrigerator. The liquefied CO_2 mixed with pectinase, mixture of $NaOH/H_2O_2$ was pressurized to above critical pressure using a high-pressure pump and heated to above critical temperature by a heat exchanger. SC-CO_2 fluid was then injected to the kettle in which the AV fibers would be treated. Then the AV fibers were analyzed by FT-IR, XRD, and SEM.

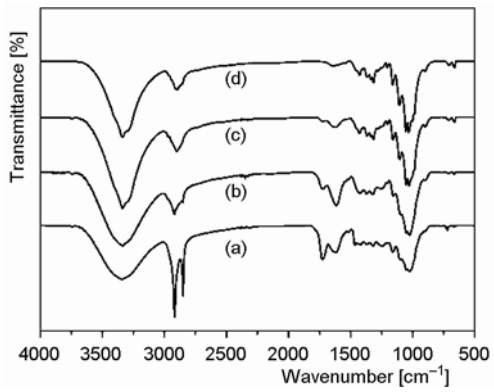

Figure 1. FT-IR spectra of AV fibers; (a) untreated AV fibers, (b) treated in SC-CO_2, (c) treated with pectinase in SC-CO_2, and (d) treated with $NaOH/H_2O_2$ in SC-CO_2

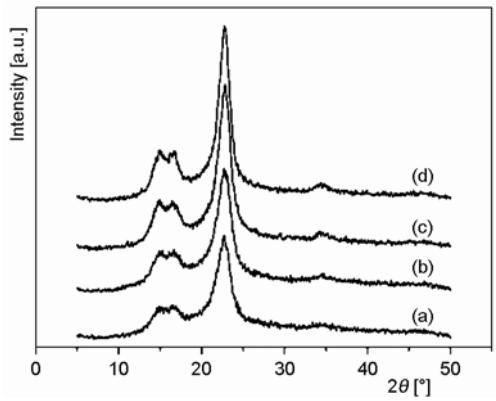

Figure 2. X-ray diffractogram of AV fibers; (a) untreated AV fibers, (b) treated in SC-CO_2, (c) treated with pectinase in SC-CO_2, and (d) treated with $NaOH/H_2O_2$ in SC-CO_2

Results and discussions

The FT-IR spectra for untreated and treated fibers are shown in fig. 1, the main FT-IR absorption spectra of all AV fibers were similar. Therefore, the treated fibers can keep their cellulose structures [5]. The disappearance of the absorption at 2852 cm^{-1} and decrease of the peak at 2916 cm^{-1} in the treated fibers indicated that the SC-CO_2 can remove the waxes. The peak at 1732 cm^{-1} disappeared after the treatment by pectinase or mixture of $NaOH/H_2O_2$ in SC-CO_2. The reason could be the removal of pectin and hemicelluloses. After treatment by the mixture of $NaOH/H_2O_2$ in SC-CO_2, the absorption band at 1626 cm^{-1} was weakened, indicating the removal of lignin.

X-ray diffractograms of the treated and untreated fibers are shown in fig. 2. When the content of cellulose was large, as the AV fibers treated with pectinase and mixture of $NaOH/H_2O_2$, two peaks could be observed at 2θ angles of 15.2° and 16.3°. However, these two peaks were smeared since the untreated fibers contained large amount of amorphous materials, thus, appearing one broad peak [6]. The crystallinity index of fibers was 72.9%, 75.3%, 80.9%, and 82.5%, respectively. Meanwhile, the crystallite sizes were 41.4 Å, 43.7 Å, 47.6 Å, and 50.8Å. For the increase of crystallinity index and crystallite sizes after treated, one reason is that the amorphous non-cellulosic compounds have been removed; the other reason is that CO_2 could swell the AV fibers in the supercritical state. Both of the reasons contributed to the interaction and movement of the macromolecular chains of AV fibers which causes the macromolecular chains to rearrange.

As shown in fig. 3(a), AV fibers are covered heavily with non-cellulosic components. From fig. 3(b), the residual gummy materials could be still observed on the surface of

the AV fibers treated in SC-CO_2 while the wax-like substances evidently decreased. The phenomenon could be explained by the bubble explosion [7, 8]. Many bubbles were formed on the surface of the AV fibers during the treatment in SC-CO_2. Once the pressure of CO_2 exceeds the critical value of bubbles surface tension, the bubble would be broken. The small gummy would be removed. The surface of AV fibers treated with pectinase or mixture of $NaOH/H_2O_2$ in SC-CO_2, figs. 3(c) and 3(d), became smoother in comparison with that of untreated, which could be attributed to the removal of some gummy materials covered on the surface of fibers. However, as shown in fig. 3(c), a certain number of residual gums still existed which restrained the isolation of fibers completely and the result was also evidenced by the results of FT-IR.

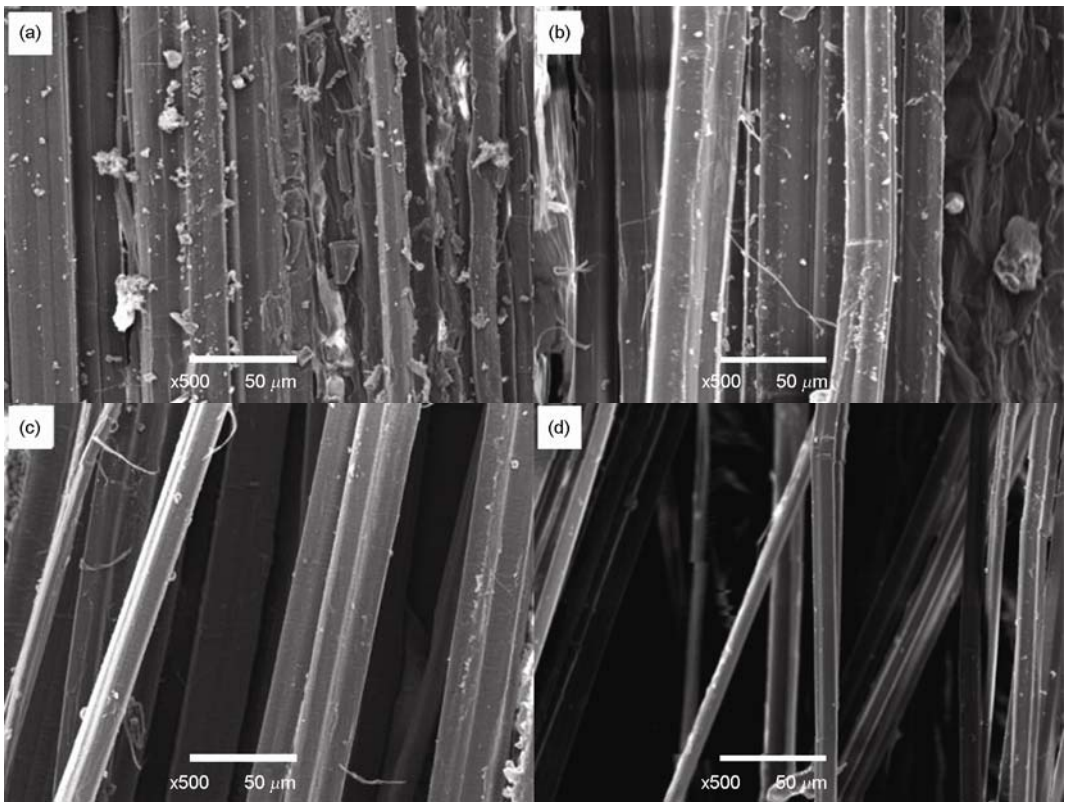

Figure 3. SEM examination micrographs of AV fibers; (a) untreated AV fibers, (b) treated in SC-CO_2, (c) treated with pectinase in SC-CO_2, (d) treated with $NaOH/H_2O_2$ in SC-CO_2

Conclusions

This paper reported the structures and compositions of AV fibers treated in SC-CO_2. The results showed that non-cellulosic components could be remarkably removed by pectinase or mixture of $NaOH/H_2O_2$ in SC-CO_2 from FT-IR. The crystallinity indexes and crystallite sizes of the treated fibers increased slightly in comparison with those of the untreated fibers. The results of SEM indicated that the surface of AV fibers treated with pectinase or mixture of $NaOH/H_2O_2$ became smoother and non-cellulosic components would be eliminated in SC-CO_2. The existence of water resulted in the formation of bubbles on the surface of the AV

fibers. Small gummy on the surface of AV fibers would be removed by SC-CO_2 when bubbles broke, which can be explained by bubble explosion.

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