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Carbohydrate Polymers 61 (2005) 393–398

Carbohydrate Polymers

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Investigations of the effects of glyoxal cross-linking on the structure and properties of chitosan fiber

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Received 6 November 2004; revised 22 April 2005; accepted 30 April 2005
Available online 25 July 2005

Abstract

The effect of glyoxal cross-linking on the structure and properties of chitosan fiber has been studied using different techniques. Swelling results showed that the cross-linking process can be described by a formula such as: $S=79.24-5.05C+0.24C^2$ (S, swelling degree; C, glyoxal concentration). WAXD indicated that the cross-linking affects on the chitosan fibers at reducing of its crystallinity, e.g. from 34.7 to 27.2% for this case prepared fiber. Comparing to uncross-linked chitosan fiber, DSC and polarizing microscopy further indicated that the change of the crystal structure for cross-linked chitosan fiber is exactly affecting to the thermal properties. Additionally, SEM photographs showed that the cross-linking seems to play a role to smooth the surface of fiber due to the surface of original chitosan fiber observed roughly.

Keywords: Chitosan fiber; Glyoxal; Cross-linking; Structure; Property

1. Introduction

Chitosan fiber was early developed by Austin and Brine (1981) and Peniston and Johnson (1977). With respect to the bio-properties of chitosan (Adusumilli & Bolton, 1991; AlAngary, AlHelw, AlDardiri, & Mahrous, 1998; Aly 1998; Elcin, Dixit, & Gitnick, 1998; Kifune, Yamaguchi, & Tanae, 1987; Mattiolibelmonte et al., 1995; Naseema, Padayatti, & Paulose, 1995; Richardson, Kolbe, & Duncan, 1999; Su et al., 1999), it was noted that chitosan fiber has been further fabricated to other medical products (Malette & Quigley, 1985; Tsurutani, Kifune, & Nakamura, 1993). However, it is generally known that this bio-fiber has visible shortages in its dimension unstably and mechanical properties weakly as comparing to other natural polymeric fibers. Hence, it was observed that several researchers have tried to apply different reagents to cross-link chitosan fiber to improve the tenacity (Knaul, Hudson, & Creber, 1999; Lee, Park, & Choi, 2004; Suye & Mizusawa, 1999). Recently, we have also prepared a chitosan fiber and studied of the use of glyoxal as a reagent to cross-link obtained fiber obtained positive results (Yang, Dou, Liang, & Shen, 2005). Of that case, though the cross-linking related mechanism has been principally known to be due to the occurrence of acetalization and Schiff base reaction (Yang et al., 2005), it was clearly known and proposed that further studies of the influence of cross-linking on the changes of the crystal structure for chitosan fiber is required in coming studies. This is because that the chitosan is considerable to be easily crystallized with respect to its regular and rigid molecular chain, and strong polarity (Ogawa, Yui, & Okuyama, 2004).

Following previous study (Yang et al., 2005), the aim of this paper is thus proposed to investigate the effects of cross-linking on the crystal structure of chitosan fiber, the effect of swelling degree on the tenacity of chitosan fiber and the effect of cross-linking on the surface of chitosan fiber.

In addition to previously used FTIR (Yang et al., 2005), experimentally, several other methodologies were employed in this case, e.g. wide-angle X-ray diffraction, WAXD, differential scanning calorimeter, DSC, polarizing microscopy and scanning electron microscope, SEM.

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doi:10.1016/j.carbpol.2005.04.017

2. Experimental

2.1. Chitosan fiber

The samples of both cross-linked and uncross-linked chitosan fibers were prepared as the same as previously described by means of the wet spinning technique (Yang et al., 2005). Briefly, commercial chitosan powder with known viscosity, e.g. of about 625 mPa S and degree of deacetylation, e.g. 91.2%, respectively, was used as received.

The reagent used for cross-linking was analytic glyoxal.

2.2. Swelling

In order to understand the swelling behavior for cross-linked chitosan fiber, the diameter of fiber before and after soaking in a 5% (v/v) acetic acid solution for 24 h, 25 °C, respectively, were taken as a measure by means of an optical microscope and Eq. (1)

$$S(\%) = (1 - D_0/D_S)100\% \quad (1)$$

where S and D represent the swelling degree and fiber diameter, respectively; the subscripts, e.g. 0 and S, represent the diameter of fiber pre- and after swelling, respectively.

2.3. Fiber analysis and characterization

The WAXD curves were recorded by Rigaku D-MAX-B type wide-angle X-ray Diffractometer using Ni-filtrated Cu–K radiation at 35 kV and 40 mA with a scanning rate of 6 °C/min.

The crystallinity of the chitosan fiber sample was estimated based on literature (Mo, Zhou, & Sun, 1993) suggested formula (2)

$$f_c = \int_{x_1}^{x_2} I_c(x)\mathrm{d}x \Big/ \int_{x_1}^{x_2} I(x)\mathrm{d}x \quad (2)$$

where:

$f_c$the crystallinity of chitosan fiber,
$I(x)$the gross diffraction intensity of chitosan fiber,
$I_c(x)$the diffraction intensity from crystal part of chitosan fiber, and
$x2\theta$ value.

DSC thermogram of chitosan fiber was obtained using a Mettler Differential Scanning Calorimeter, DSC822e, with a heating rate of 5 °C/min under nitrogen stream condition.

The polarizing microscope of the chitosan fiber was recorded using a BX51 Polarizing Microscope (Japan) with a hot stage at different temperatures. In this case, the rate for temperature heating was pre-set at about 6 °C/min and each photo was recorded by an online camera with a shift of about 10 s.

The SEM photographics of the chitosan fibers were obtained using a JSM-5600LV Scanning Electron Microscope.

3. Results and discussion

3.1. Effect of glyoxal cross-linking on the degree of swelling for chitosan fiber

The effect of cross-linking on the degree of swelling was showed in Fig. 1. Observed that the increase of the glyoxal concentration is visible to decrease the swelling degree indicating that the cross-linking reaction is exactly taken place as previous found (Yang et al., 2005). Since Fig. 1 showed swelling behavior has been found in good agreement with Uragami and Takigawa (1990), meanwhile to support our previous conclusions (Yang et al., 2005), it is evidently that this case adopted method for description of the cross-linking is capable.

According to Fig. 1, it is therefore confirmed that the cross-linking process is capable for enhancement of the tenacity for chitosan fiber. Additionally, Fig. 1 presented swelling behavior suggests that the use of glyoxal as a reagent to cross-link chitosan fiber may follow a regulation such as: $S = 79.24 - 5.05C + 0.24C^2$. Of which, S and C represents the swelling degree and the concentration of glyoxal, respectively.

3.2. Influence of cross-linking on the crystal structure of chitosan fibers

Because chitosan has two crystal types, e.g. α and β, both belong to the monoclinic system in resulting of molecular chain in regular, rigid, polar and crystallization (Ogawa et al., 2004), and such properties further causing chitosan fiber to have different cell parameters (Jiang, 2001;

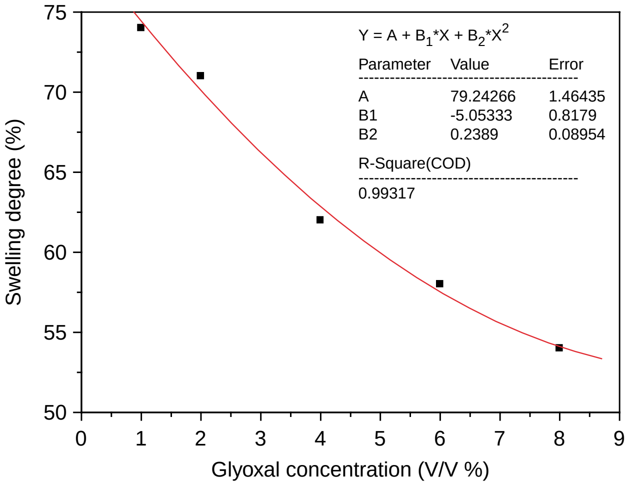


Fig. 1. Influence of the glyoxal concentration on the swelling degree for cross-linking of chitosan fiber.

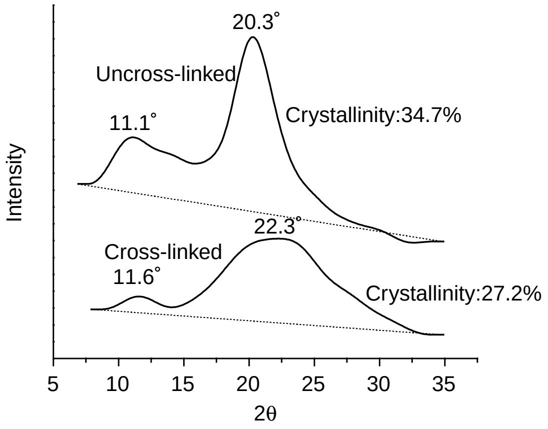


Fig. 2. A comparison of X-ray diffraction diagrams for chitosan fiber cross-linked and uncross-linked.

Urbanczyk & Lippsymonowicz, 1994), it is principally considered that those crystal structure of chitosan fiber might be influenced by employed cross-linking reaction. Therefore, to understand the influence of cross-linking on the structure of chitosan fiber is expected. A comparison of the X-ray diffraction spectra for chitosan fibers before and after cross-linking with glyoxal was thus presented in Fig. 2. Clearly, two intense diffraction peaks were visibly located at 11.1 and 20.3°, respectively, for original sample to indicate that these are typical characteristics for chitosan fiber. Moreover, according to Jiang (2001), it is further known that these two intense peaks in relation to the α crystal of chitosan. Taking this in mind to characterize the cross-linked chitosan fiber (Fig. 2), hence these two peaks visibly reduced or shifted for cross-linked chitosan fiber would be considered that the crystal structure of cross-linked chitosan fiber might be changed from α to β type (Jiang, 2001). Obviously, this finding is important for understanding the mechanism of cross-linking for chitosan fiber. Because Jiang (2001) has found that the β type crystal structure for chitosan fiber may cause its thermal stability decreasing due to such crystal molecules comprise more amorphous structure than that of α crystal molecules, and the acting forces among β crystal molecules weaker than that of α crystal molecules, it was re-considered that this case found crystal behavior for cross-linked chitosan fiber seems to be a good explanation for supporting our previous conclusion that the cross-linking process with glyoxal caused the occurrences of the Schiff base reaction and acetalization (Yang et al., 2005). Based on Eq. (2), the crystal structure change for chitosan fiber was also known quantitatively, i.e. the cross-linking seems to reduce the crystal component for this fiber from 34.7 to 27.2%. In fact, the formation of the imperfect β-crystal was ascribed to the deterioration of the crystallization for chitosan after cross-linking is in good agreement with Monteiro and Airoldi (1999) and Uragami, Matsuda, Okuno, and Miyata (1994).

Since the appearance of β-crystal for chitosan fiber should influence on the thermal properties (Jiang, 2001), DSC was performed and a comparison of two chitosan fibers pre- and after cross-linking was presented in Fig. 3. Of which, the dehydration phenomenon was initially observed for two samples, e.g. at about 75 °C for uncross-linked and at about 78 °C for cross-linked chitosan fiber, respectively. Probably, these cross-linking induced phenomena are due to the hydroxyls of chitosan fiber that resulted in hydrogen bonds in connection with the molecules of water (Jiang, 2001). Assuming this is correct, therefore, the visible shift, e.g. 3 °C, for cross-linked chitosan fiber that was higher than that of uncross-linked sample might be taken as an indication for understanding the network resulted in chitosan fiber and probably due to the embedding of moisture. Since Fig. 3 further presented two small endothermic peaks consistency at 162 or 163 °C, respectively, for chitosan fibers pre- and after cross-linking, and both seem to be related to the finding of Ahn, Choi, and Cho (2001) and Ko, Jo, Lee, and Kim (1997). It was further known that the chitosan fiber may keep its α-crystal structure at this temperature. In other words, this suggests that the crystal change for chitosan fiber may need a more high temperature, e.g. at least higher than 162 °C. Obviously, this relationship between the crystal structure and thermal property for chitosan fiber is important. According to Fig. 3, the evidence for resulting of the β-crystal structure for chitosan fiber relating to the temperature seems to be visible because the curve for cross-linked fiber has been found obviously raised after 162 °C in comparison with uncross-linked sample. However, the detailed temperature seems to be impossible from Fig. 3 indicating other techniques required. The decompose temperature for both chitosan fibers was observed at about 294 °C for uncross-linked sample and about 279 °C for cross-linked sample. With respect to above mentioned difference between two chitosan fibers, clearly, this indicated that the cross-linking process would reduce

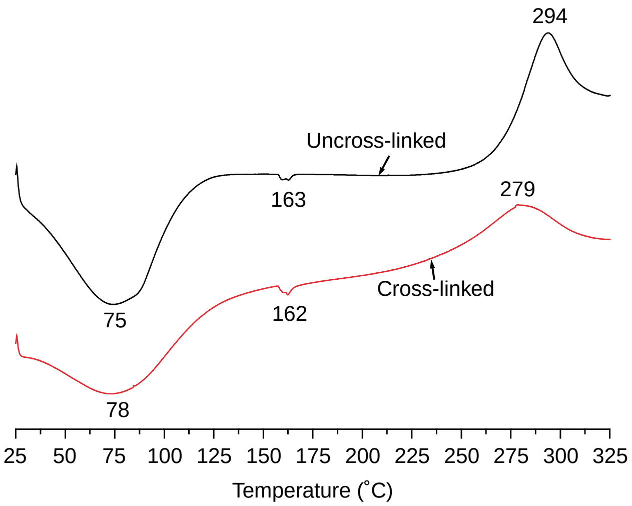
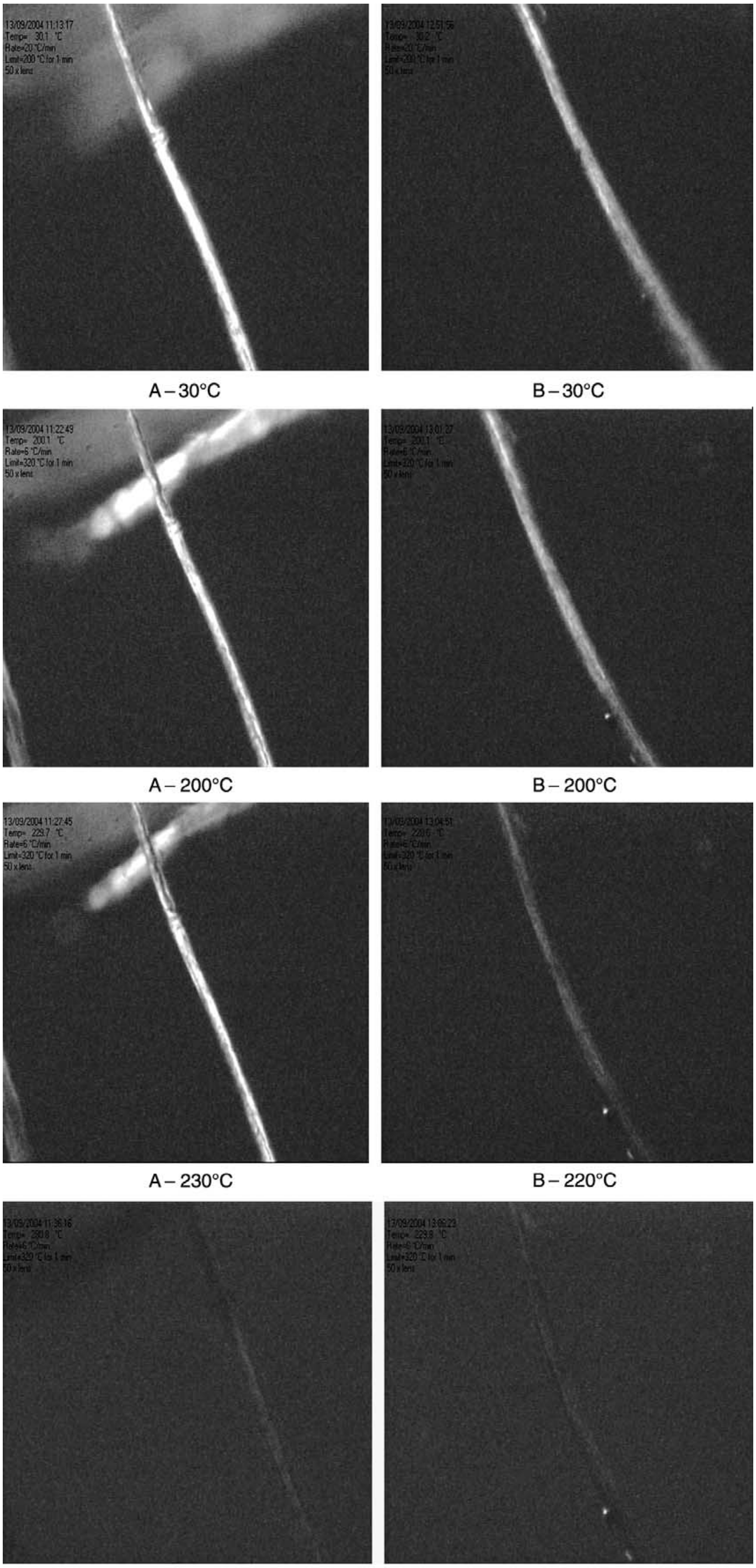


Fig. 3. A comparison of DSC curves for chitosan fiber cross-linked and uncross-linked.



A – 30°C

B – 30°C

A – 200°C

B – 200°C

A – 230°C

B – 220°C

A – 281°C

B – 230°C

Fig. 4. Polarizing microscopy of chitosan fiber cross-linked and uncross-linked. A, uncross-linked; B, cross-linked.

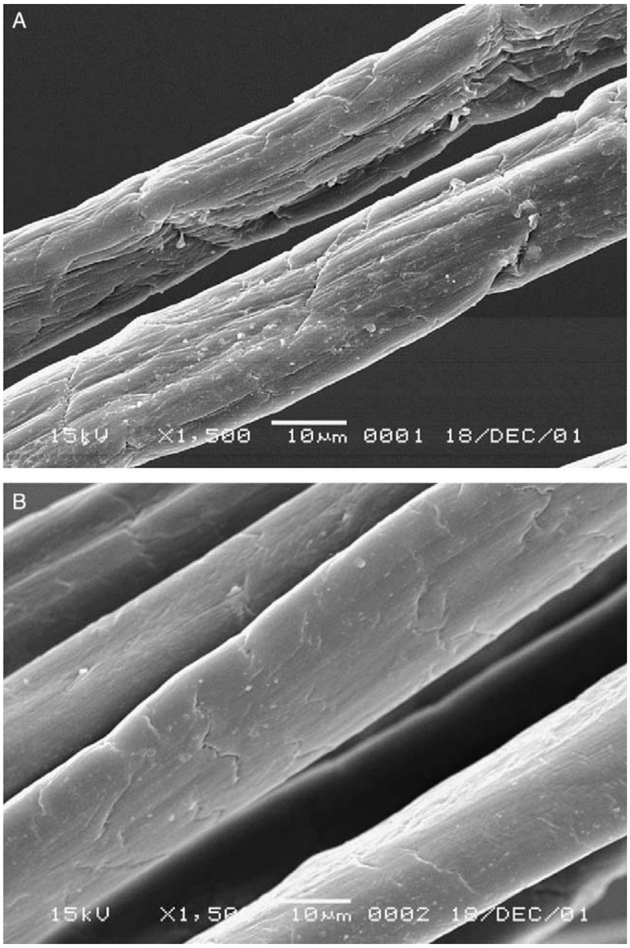


Fig. 5. SEM photomicrographs of chitosan fiber uncross-linked and cross-linked. A, uncross-linked; B, cross-linked.

the degree of crystallization for chitosan fiber to support the finding from literature (Jiang, 2001).

In addition to the use of DSC, the change of the crystal structure for chitosan fiber by cross-linking was furthermore investigated by application of a hot stage polarizing microscope. Relying on observed light intensities, the thermal phenomena for two chitosan fiber samples obtained from polarizing microscope was compared in Fig. 4. Due to the light intensity observed stronger for uncross-linked fiber and weaker for cross-linked sample, it is clearly that the cross-linking is indeed to reduce the thermal properties for chitosan fiber. Additionally, since the light intensity observed strongly for uncross-linked chitosan fiber corresponding to a temperature range, e.g. from 30 to 230 °C, then gradually darken until disappeared at a temperature of about 281 °C, meanwhile the disappearance of light intensity for cross-linked chitosan fiber to be at about 230 °C (Fig. 4), it indicates that the original chitosan fiber may start melting since 230 °C and decomposing since 281 °C, while for cross-linked sample these two temperatures changed. In principal, this means that chitosan fiber changes its α-crystal structure to β-crystal structure during the melting process.

The influence of cross-linking on the surface of chitosan fiber was investigated by SEM. Fig. 5 indicated that the cross-linking might play a role to coat the surface of chitosan fiber due to the uncross-linked sample presented rough surface, e.g. with a lot of visible grooves, while the surface of cross-linked sample is obviously in smooth. Since the same phenomenon was also observed by Hirano et al. (1999), it is known that one may apply the cross-linking technique to modify the surface of chitosan fiber to fit different requests in coming application cases.

4. Conclusion

Following the studies previously (Yang et al., 2005), this paper further studied the chitosan fiber after cross-linking with glyoxal using different methods, e.g. swelling, WAXD, DSC, SEM and polarizing microscope. Results showed that the cross-linking reaction may cause chitosan fiber to change its crystal structure from α- to β-type meanwhile to reduce the degree of crystallization, and this change might be corresponding to the melt temperature. Therefore, the influence from cross-linking on thermal properties of chitosan fiber is visible. Based on SEM, it was known that the cross-linking process may also smooth the surface for chitosan fiber.

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