

# Crosslinking of chitosan fiber by a water-soluble diepoxy crosslinker for enhanced acid resistance and its impact on fiber structures and properties



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## ABSTRACT

Chitosan fiber for functional textile applications has drawn great attention due to its naturally occurring antibacterial activity, moisture-retaining and no allergenic reaction. However chitosan fiber has the weight loss defect under acidic processing conditions and during peroxide bleaching, which restricts its application and decreases its functionalities. In the present work, chitosan fiber was crosslinked by a water-soluble diepoxy compound with the aim of enhancing its acid resistance. The effects of crosslinking conditions (sodium carbonate dosage, crosslinker dosage and temperature) on the weight loss of crosslinked chitosan fiber in acid solution were studied. Additionally, the effects of crosslinking on the structures, resistance to peroxide bleaching, tensile strength, thermal stability and dye adsorption properties of chitosan fiber were also discussed. The results showed that the crosslinking by the diepoxy crosslinker was able to greatly reduce the weight loss of chitosan fiber in acid solution, and slightly reduce the weight loss during hydrogen peroxide bleaching. Crosslinking treatment slightly improved the thermal stability of chitosan fiber, and had no impact on the crystalline structure and dye adsorptions of chitosan fiber. However, the dry tensile strength of chitosan fiber decreased linearly with increasing diepoxy crosslinker dosage.

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## 1. Introduction

Chitosan—the *N*-deacetylated derivative of chitin as one of the most promising biological macromolecule polymers has been widely studied and used because of its distinctive biomedical properties such as biocompatibility, biodegradability, antibacterial activity, and nontoxicity [1–5]. In the field of fiber manufacturing, acidic chitosan solution can be used to produce textile fiber using a wet spinning technique. Chitosan fiber has various merits including no allergenic reaction, low antigenicity, high safety, organism compatibility, gentleness to the body, antibacterial and deodorizing effects, wound-healing, and moisture-retaining [6]. In recent years, the application of chitosan fiber for the development of functional textiles such as underwear, sleepwear, and hospital clothing has aroused great attention [6–9]. In view of the production cost of functional textiles, chitosan fiber is usually applied in the form of blending with other staple fibers such as wool, cotton and viscose.

Like other textiles, the blends containing chitosan fiber must also be scoured, bleached, dyed and finished prior to becoming end products. In these procedures, they are inevitably subjected to the processing under acidic conditions, the processing under alkaline conditions followed by acid neutralization, and peroxide bleaching. However, it is well known that chitosan polymers have poor resistances to acid and hydrogen

peroxide [1,2,10,11]. Hydrogen peroxide treatment can lead to the depolymerization of chitosan polymers [10,11]. Because of the good solubility of chitosan polymers in acidic solution, the treatment under acidic conditions can also cause the weight loss of chitosan fiber in the blends, which is bound to exert a negative impact on the functional properties of the blends. Therefore, it is essential to enhance the resistances of chitosan fiber to acid and hydrogen peroxide.

In order to enhance the stability of chitosan fiber under aqueous environments, regulate its functional properties and improve its mechanical strength, various chemical crosslinking treatments have been widely used [12–17]. The typical crosslinkers reported earlier include glyoxal, glutaraldehyde and epichlorohydrin. Usually, these crosslinkers are applied in the post-treatment stage after wet spinning. After crosslinking treatment, chitosan fiber showed an obviously decreased solubility under a wide pH range, and a reduced extent of swelling in acid solution [16–18]. Apart from epichlorohydrin, ethylene glycol diglycidyl ether was used to crosslink the electrospun chitosan fiber membranes [19]. However, both epichlorohydrin and ethylene glycol diglycidyl ether have poor solubility in water, and they are not very suitable for the crosslinking of chitosan fiber textiles using the aqueous wet processing approach.

In the present work, chitosan fiber was crosslinked using a water-soluble diepoxy crosslinker in alkaline solution with the aim of enhancing its acid resistance and decreasing its weight loss when processed under acidic conditions. The main conditions of crosslinking treatment were discussed. In addition, the effects of crosslinking on the structures,

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resistance to peroxide bleaching, tensile strength, thermal stability and dye adsorption properties of chitosan fiber were also studied.

## 2. Experimental

### 2.1. Materials

The 2.22 dtex  $\times$  38 mm staple chitosan fiber was purchased from Shandong Weifang Youngchito Bio. Co. Ltd. To remove the spin finishes added to the fiber during post-spinning treatments, fiber samples were scoured in the solution containing 0.5 g/L sodium bicarbonate and 0.5 g/L Leveling Agent O (polyoxyethylene alkyl ether) at 80 °C for 40 min using a 50:1 liquor ratio (the ratio of liquor volume to fiber weight). The scoured fibers were then rinsed thoroughly in tap water, and allowed to dry in the open air.

Crosslinker EH was provided from Shanghai Tiantan Auxiliaries Co. and used as received. The structure of Crosslinker EH is shown in Fig. 1. Two direct dyes (Everdirect Supra Yellow RL and Blue BRR) and two reactive dyes (Everzol Yellow ED-R and Navy ED) were purchased from Everlight Chemical Industrial Co. and used as received. Leveling Agent O was provided by Jiangsu Hai'an Petrochemical Plant, China. Sodium carbonate, sodium bicarbonate, sodium silicate, sodium sulfate, sulfuric acid and 30% (w/w) hydrogen peroxide were of analytical reagent grade.

### 2.2. Crosslinking treatment

The crosslinking treatment of chitosan fiber was carried out in the sealed and conical flasks immersed in the XW-ZDR low-noise oscillated dyeing machine (Jiangsu Jingjiang Xingwang Dyeing and Finishing Machinery Factory, China) using a liquor ratio of 100:1 for 60 min. The solution was prepared with Crosslinker EH and sodium carbonate. After crosslinking reaction, the crosslinked fiber was rinsed thoroughly in distilled water and then allowed to dry in open air.

To assess the effect of sodium carbonate dosage on the crosslinking of chitosan fiber, crosslinking treatment was carried out at 60 °C using 6 g/L Crosslinker EH and  $X$  g/L ( $X = 0, 2, 4, 6, 8$  and  $10$ ) sodium carbonate. To evaluate the effect of Crosslinker EH dosage on the crosslinking of chitosan fiber, crosslinking treatment was performed at 60 °C using  $Y$  g/L ( $Y = 0, 2, 4, 6, 8$  and  $10$ ) Crosslinker EH and 2 g/L sodium carbonate. For the study of the temperature dependence of the crosslinking of chitosan fiber, 6 g/L Crosslinker EH, 2 g/L sodium carbonate and six temperatures (30, 40, 50, 60, 70 and 80 °C) were used. In the experiments of dyeability tests, wide angle X-ray diffraction (XRD) measurements, Fourier transform infrared (FTIR) spectral analyses, and thermogravimetric (TG) analyses, the crosslinked fiber samples were obtained using three Crosslinker EH dosages (0, 2 and 8 g/L), 2 g/L sodium carbonate and a temperature of 60 °C.

### 2.3. Measurements

#### 2.3.1. Stability tests

The acid resistance of the crosslinked chitosan fiber was characterized by its weight loss in acidic solution. The sample was immersed in 0.5 mol/L sulfuric acid solutions using a liquor ratio of 100:1, and treated at 80 °C for 60 min. The acidic treatment was carried out in the sealed and conical flasks immersed in the oscillated dyeing machine. After this treatment, the fiber residue was obtained by filtering the solutions. During the process of filtering, the fiber residue was fully washed with distilled water. In order to obtain the dry weight of fiber samples, the

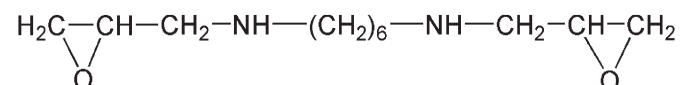


Fig. 1. Chemical structure of Crosslinker EH.

original fiber and the fiber residue from acidic treatment were first dried in an oven at 60 °C for 40 min, and then at 105 °C for 120 min. The weight loss of the crosslinked chitosan fiber during acidic treatment was calculated using Eq. (1).

$$\text{Weight loss (\%)} = 100 \times \frac{W_0 - W_1}{W_0} \quad (1)$$

where  $W_0$  is the dry weight of the original fiber, and  $W_1$  is the dry weight of the fiber residue after acidic treatment.

Taking into account the facts that the stability of chitosan polymer to oxidants is poor [10,11] and hydrogen peroxide as an oxidation bleaching agent is widely used in the wet processing of textiles [20,21], the stability of the crosslinked chitosan fiber to hydrogen peroxide bleaching was also tested. The sample was immersed in the solution containing 12 g/L 30% hydrogen peroxide, 4 g/L sodium carbonate, 1.5 g/L sodium silicate and 0.5 g/L Leveling Agent O using a liquor ratio of 100:1, and bleached at 90 °C for 60 min. After bleaching, the fiber residue was collected by filtration. The weight loss of the crosslinked chitosan fiber during bleaching was calculated according to the difference of the dry weight between the original fiber and the fiber residue from bleaching.

#### 2.3.2. Dyeability tests

Two direct dyes (Everdirect Supra Yellow RL and Blue BRR) and two reactive dyes (Everzol Yellow ED-R and Navy ED) were used to test the dyeability of the crosslinked chitosan fiber. Dyeing was carried out in the sealed and conical flasks immersed in the oscillated dyeing machine using a liquor ratio of 50:1.

For the dyeing experiments of direct dyes, the dyebath contained 8% o.w.f. (on the weight of fiber) dye, 0.4 g/L Leveling Agent O, and 10 g/L sodium sulfate. The dyeing started at 30 °C, the temperature was raised at a rate of 2 °C/min up to 90 °C, and at this temperature the dyeing continued for 60 min. In order to evaluate the exhaustion of dyes, the Shimadzu UV-1800 UV-vis spectrophotometer (Shimadzu Co., Japan) was used to measure the absorbance of the dye solution at the maximum absorption wavelength. The exhaustion percentage of direct dyes was calculated using Eq. (2).

$$\text{Exhaustion (\%)} = 100 \times \frac{A_0 - A_1}{A_0} \quad (2)$$

where  $A_0$  and  $A_1$  are the absorbance of the dyebath before and after dyeing, respectively.

For the reactive dyeing experiments, the initial dyebath contained 4% o.w.f. dye, 0.4 g/L Leveling Agent O, and 60 g/L sodium sulfate. After the fiber was immersed in the dyebath at 30 °C, the temperature was increased to 50 °C at 1 °C/min. At 50 °C, 8 g/L sodium carbonate was added into the dyebath and the dyeing continued for 60 min. After dyeing, the sample was removed and rinsed thoroughly in distilled water. The final soaping was performed in a solution of 2 g/L soaping agent at 95 °C for 15 min. The exhaustion percentage of reactive dyes was calculated using Eq. (2). The fixation percentage of reactive dyes was calculated using Eq. (3).

$$\text{Fixation (\%)} = 100 \times \frac{A_0 - A_1 - A_2}{A_0} \quad (3)$$

where  $A_0$  and  $A_1$  are the absorbance of the dyebath before and after dyeing, respectively;  $A_2$  is the absorbance of the soaping solution.

#### 2.3.3. Tensile strength

The dry tensile strength of chitosan fiber was measured with an electronic single fiber strength tester (Nantong Hongda Experiment Instruments Co. Ltd., China). A gauge length of 10 mm and a crosshead

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