

Alkali Resistance of a Casein-Acrylonitrile Graft Copolymer Fiber

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ABSTRACT: The casein-acrylonitrile graft copolymer fiber was treated in sodium hydroxide, sodium carbonate, and sodium bicarbonate solutions to evaluate its alkali resistance which was very important for wet processing. The weight loss and whiteness of the treated fibers were examined. UV spectra of the alkaline treatment solutions and IR spectra of the treated fibers were analyzed. The study showed that the fiber exhibited poor alkali resistance. Treating temperature, alkali concentration, and strength affected the weight loss and whiteness of the treated fibers. A high

weight loss was found even at low alkali concentration, and the obvious yellowing was observed at higher alkali concentration and temperature. The weight loss was primarily due to the hydrolysis of casein, whereas the yellowing was caused by the hydrolysis of nitrile groups and induced formation of C=N conjugated system. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1195–1200, 2008

Key words: graft copolymers; polyacrylonitrile; proteins; fibers; alkali resistance

INTRODUCTION

Polyacrylonitrile fiber is one of the most important synthetic fibers. It has been widely used in the textile industry and replaced wool in many respects because of its outstanding physical and chemical properties, such as soft, wool-like hand, good elastic resilience, excellent resistance to sunlight, and good antibacterial property. However, it also suffers from some shortcomings such as low moisture absorption and high collection of static charge. There have been many attempts to improve its inferior behaviors. A lot of studies have been focused on the combination of acrylonitrile-based polymers and natural polymers. The strategies reported are mainly classified into two ways: (a) graft-polymerization of acrylonitrile onto casein,^{1–7} silk fibroin,^{8–10} wool keratin,^{11,12} soybean protein,^{13,14} gelatin¹⁵ etc., and (b) blending of polyacrylonitrile and silk fibroin,^{16–18} chitosan and its derivative.^{19–22}

In the 1960s, Toyobo Co. in Japan invented a method to make the casein and acrylonitrile copolymer and exploited a new type of filament whose

trade name was Chinon.^{1,2} The filament was commercially produced in 1969.^{1,2} In recent years, a casein-acrylonitrile graft copolymer staple fiber has been put into commercial production.⁶ The commercial casein-acrylonitrile graft copolymer fiber is virtually composed of a mixture of grafted copolymer, homopolyacrylonitrile, and unreacted casein.²³ Its tensile and thermal properties are similar to those of polyacrylonitrile fiber, and its hydrophilic property is intermediate between polyacrylonitrile and natural fibers.^{2,23} In spite of extensive studies on the fine structure and mechanical properties of the fiber made from acrylonitrile-grafted casein,^{3–5,23–25} little attention has been paid to the analysis of the chemical behaviors in the wet processing of the fiber and its textiles.

For the wet processing of textiles, the alkali resistance is one of the most important properties in determining the successful processing of a fiber as the pretreatment, and reactive dyeing process are usually carried out under alkaline medium. Therefore, this study is mainly concerned with the alkali-resistant properties of casein-acrylonitrile graft copolymer fiber. Sodium hydroxide, sodium carbonate, and sodium bicarbonate solutions of different alkali concentrations were used to treat the fiber, and the weight loss and whiteness of the treated fiber were measured. The functional groups in the fiber before and after the alkaline treatment were examined through IR spectra. The hydrolyzed casein in alkaline solutions was also analyzed through UV spectra.

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EXPERIMENTAL

Materials

The casein-acrylonitrile graft copolymer fiber containing about 25% casein was kindly supplied by Shanghai Zhengjia Milk Fiber Sci and Tech Co. Its linear density and length were 1.67 dtex and 38 mm, respectively. To remove the finish oils added during fiber spinning, the fiber was washed with a nonionic surfactant solution of 0.5 g dm⁻³ at 70°C for 60 min, then completely rinsed, and dried in the open air. The weight loss of the fiber during this washing was 5.17%.

Sodium hydroxide, sodium carbonate, and sodium bicarbonate were of analytical reagent grade. The nonionic polyoxyethylene ether surfactant, Leveler O, was currently a commercial product.

Alkaline treatment

The fiber was immersed in a glass tube containing the required amount of different alkali solution, in which the nonionic surfactant (0.5 g dm⁻³) was added. The tube was subsequently placed in a water bath maintained at a constant temperature of 60 or 80°C for 120 min. The ratio of the solution to the fiber was 100 : 1. After treatment, the fiber was washed with distilled water, dried in the open air, and finally kept in the desiccator.

Weight loss estimation

The fibers before and after alkaline treatment were dried at a room temperature for 24 h in the desiccator with silica gel, and then weighed. The weight loss (%WL) of the treated fibers was calculated using eq. (1):

$$\%WL = 100 \times (W_0 - W_1)/W_0 \quad (1)$$

where W_0 and W_1 are the weights of the dried fibers before and after alkaline treatment.

Whiteness index determination

The color space coordinates (L , a , and b) were measured with an UltraScan XE spectrophotometer (Hunter Associates Laboratory) using illuminant D65 and 10° standard observer. An average of eight readings was taken each time. The whiteness index (WI) of samples was calculated using eq. (2):

$$WI = 100 - [(100-L)^2 + a^2 + b^2]^{0.5} \quad (2)$$

where L is an illuminance index, and a and b denote chromaticness indices (color indices), respectively.

FTIR analysis

Infrared spectra were recorded with a Nicolet 5700 FTIR spectrometer (Thermo Fisher Scientific) using potassium bromide pellets. The fibers were cut into powder with a pair of scissors, and the fiber powders were then used as samples. All of the IR data were collected from 32 scans with a resolution of 4.0 cm⁻¹.

UV spectrum analysis

UV absorption spectra of alkaline treatment solutions were obtained with a UV-2550 UV-Vis spectrophotometer (Shimadzu Co.).

RESULTS AND DISCUSSION

Weight loss of treated fibers

The alkaline treatment of the fibers was performed for 120 min at 60 and 80°C using alkali concentrations in the range of 0–10 g dm⁻³. The weight loss of treated fibers is presented in Figure 1.

In the absence of alkali, the weight loss of the fibers was 0.9 and 2.7% at 60 and 80°C, respectively, indicating that a small quantity of casein could be lost during this warm or hot washing. In addition, the weight loss of the fibers had reached to 5.17% during the first washing at 70°C before these washing, as described in the Materials section. The reason for the weight loss during the warm and hot washing is that some casein could be not grafted with acrylonitrile and has low molecular weight caused by the acid hydrolysis during the preparation of copolymer in zinc chloride solution and certain solubility in hot water.

After the fibers were treated in sodium hydroxide, sodium carbonate, and sodium bicarbonate solutions using a concentration of 0.5 g dm⁻³ at 60°C, the weight loss around 10.0%, 8.4%, and 5.0% was reached respectively, whereas the corresponding values were about 13.3%, 13.1%, and 10.2% respectively, at the same alkali concentration at 80°C. The high weight loss at low alkali concentration might be ascribed to the special fiber structure and the low molecular weight of casein. The commercial casein-acrylonitrile graft copolymer fiber usually consists of graft copolymer, homopolyacrylonitrile, and ungrafted casein.^{23,26} Furthermore, the major part of casein in graft copolymer is amorphous,^{3,4} and the ordered domains or the crystal structure of polyacrylonitrile component are similar to those of polyacrylonitrile fiber and relatively unchanged upon protein component in copolymer.^{3–5,16} Although the polyacrylonitrile fiber has the poor resistance to alkali, it undergoes the low weight loss around 3% after the alkaline treatment in 2.5% (w/w) sodium hydroxide

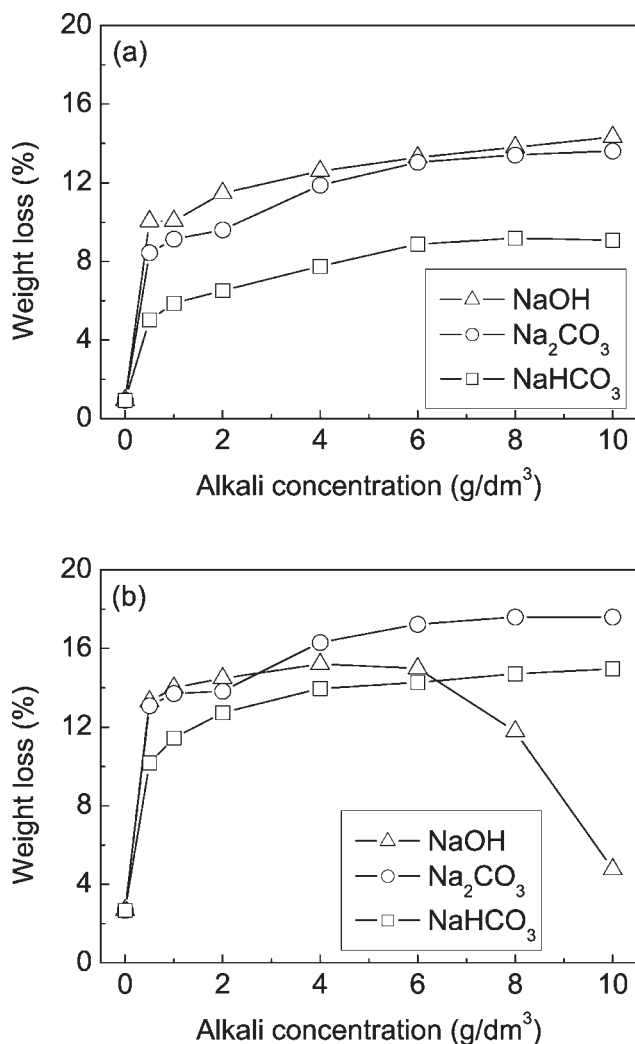


Figure 1 Weight loss of the fibers treated by alkalis at (a) 60°C and (b) 80°C.

solution at 95°C, as observed in an earlier study.²⁷ So, it is obvious that the weight loss of the fiber at low alkali concentration is a consequence of the loss of casein component. A certain quantity of the ungrafted casein and the amorphous casein in graft copolymer are easily attacked by alkali, and what is more, casein has relatively low molecular weight. Therefore, the hydrolyzed casein proteins in the fiber are easily dissolved into alkaline solution, and the corresponding high weight loss is reached.

It is interesting to find that the weight loss of the fiber increased gradually with an increase in alkali concentration when the concentration was higher than 0.5 g dm⁻³. The increment in weight loss at the alkali concentration exceeding 0.5 g dm⁻³ might be caused by the hydrolysis of the casein of high molecular weight in graft copolymer as well as the hydrolysis of the polyacrylonitrile in graft copolymer and the cross-blended homopolyacrylonitrile.

Besides, It should be mentioned that the fiber became gelatinous owing to the hydrolysis of polyacrylonitrile when the concentration of sodium hydroxide reached 6–10 g dm⁻³ at 80°C. The gelatin was able to wrap the hydrolyzed casein, and hence the weight loss of the fiber decreased dramatically.

Whiteness of treated fibers

The whiteness indices of treated fibers are shown in Figure 2. The changes in whiteness varied with alkali concentration and strength as well as temperature. The whiteness index of the fiber treated with sodium hydroxide decreased remarkably with increasing alkali concentration at 60 and 80°C. As for the alkaline treatment by sodium bicarbonate and sodium carbonate, the whiteness index exhibited a slight decrease at 60°C and a gradual decrease at 80°C with increasing alkali concentration. When sodium carbonate concentration exceeded 6 g dm⁻³ at 60°C and 2 g dm⁻³ at 80°C, and sodium

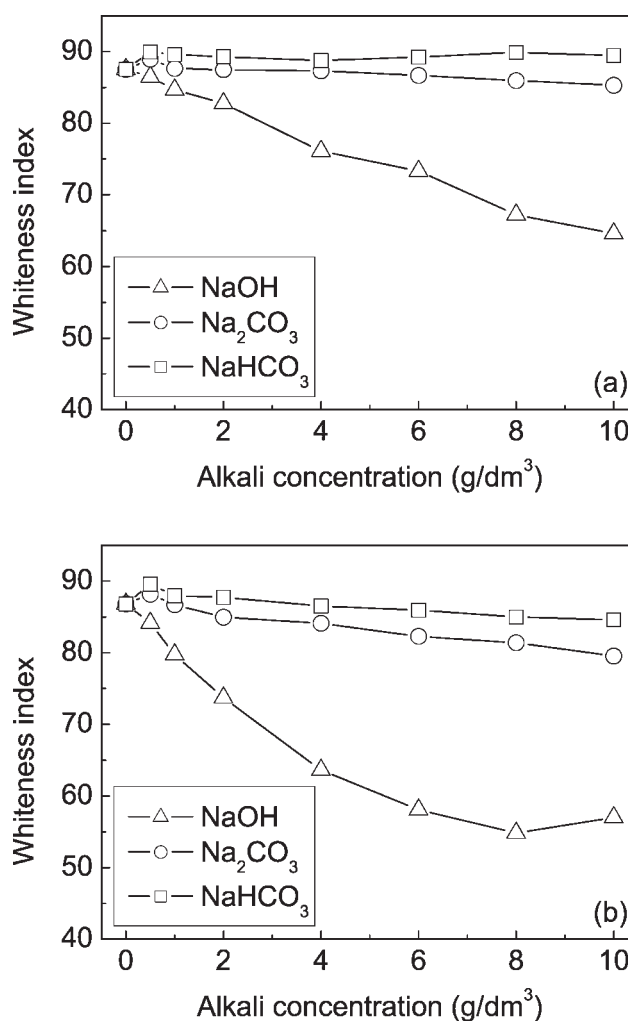


Figure 2 Whiteness of the fibers treated by alkalis at (a) 60°C and (b) 80°C.

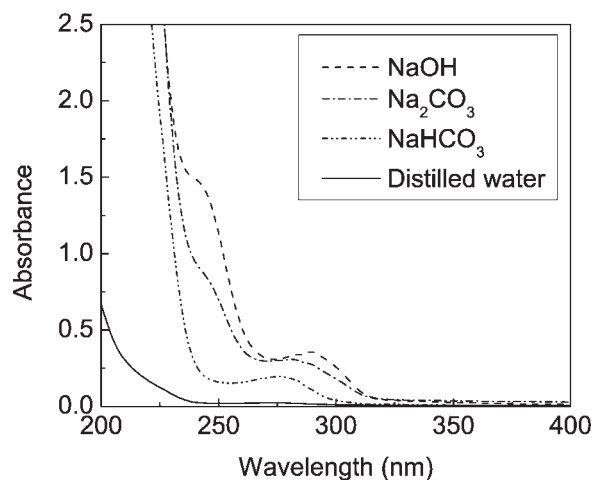


Figure 3 UV absorption spectra of alkaline treatment solutions. Treating conditions: alkali concentration 6 g dm^{-3} , temperature 60°C , time 120 min.

bicarbonate concentration exceeded 6 g dm^{-3} at 80°C , the treated fiber exhibited yellowish appearance. These observations reveal that the alkali strength and concentration have a profound effect on the whiteness of the treated fiber.

The treatment with alkalis, especially with sodium hydroxide, produced a yellowing effect on the fiber. The yellowing might be attributed to the cyclization reaction of nitrile groups during the hydrolysis of polyacrylonitrile component in the fiber.^{28–30}

UV spectra of alkaline treatment solutions

In UV absorption spectra, most of the proteins have characteristic maximum absorption at about 280 nm ³¹ because proteins contain tyrosine, tryptophan, and phenylalanine. To understand whether the hydrolyzed casein exists in alkaline treatment solutions, the UV absorption spectra of the residual solutions were examined.

As shown in Figure 3, the absorption peaks of the alkaline treatment solutions of sodium bicarbonate, sodium carbonate, and sodium hydroxide were at about 276, 282, and 290 nm, respectively. These maximum absorption wavelengths are consistent with those of amino acids containing aromatic rings, indicating the existence of the hydrolyzed casein in alkaline treatment solution. The maximum absorption wavelength had a red shift effect with increasing alkali strength due to the greater extent of the ionization of phenolic hydroxyl groups in hydrolyzed casein protein.

Figure 3 also showed that the absorption intensities of sodium hydroxide and sodium carbonate treatment solutions were obviously higher than that of sodium bicarbonate solution, suggesting that the extent of casein hydrolysis was greater and the

quantity of the hydrolyzed casein became larger in stronger alkali solution. These findings are consistent with the fact that the higher weight loss of the fiber treated in stronger alkali solution occurred as shown in Figure 1.

FTIR analyses

The FTIR spectra of casein-acrylonitrile graft fibers treated with and without alkalis are shown in Figures 4 and 5. The IR spectrum of the original fiber shows the characteristic peaks of polyacrylonitrile at 2244 ($\nu\text{C}\equiv\text{N}$), 1454 ($\delta\text{C}\text{H}_2$), 1385 ($\delta\text{C}\text{H}$), and 1252 cm^{-1} ($\gamma_{\text{C}}\text{C}\text{H}$), and those of casein at 1662 ($\nu\text{C}=\text{O}$, amide I) and 1537 cm^{-1} ($\delta\text{N}-\text{H}$, amide II), in agreement with the literatures.^{4,9,28–30,32}

As for the fibers treat with distilled water, sodium bicarbonate and sodium carbonate at two alkali concentrations and temperature, the intensities of the peaks at 2244 and 1454 cm^{-1} increased obviously, and those at 1537 cm^{-1} decreased clearly with increasing alkali strength. Moreover, this tendency was intensified at higher alkali concentration and temperature. The phenomena resulted from the

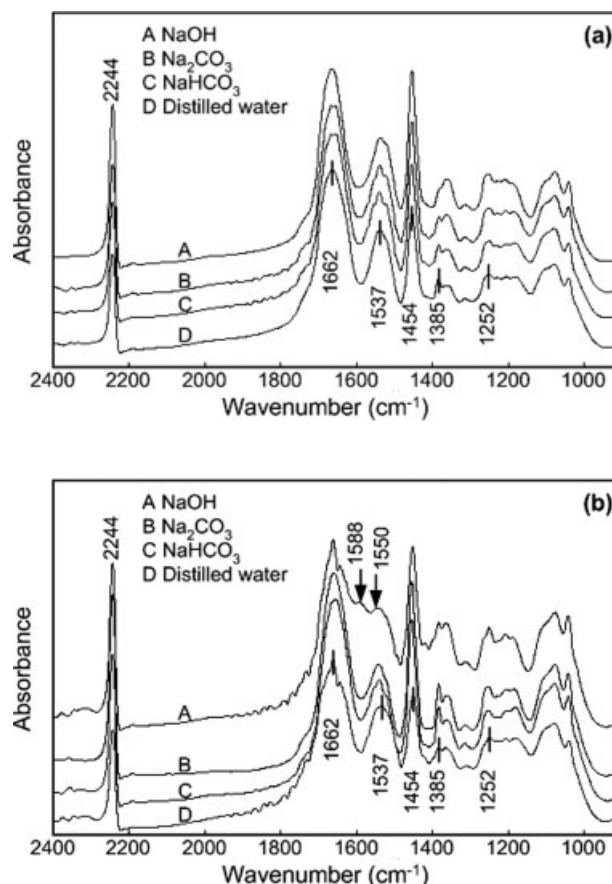


Figure 4 FTIR spectra in the range of $900\text{--}2400 \text{ cm}^{-1}$ of the fibers treated in 2 g dm^{-3} alkali solution at (a) 60°C and (b) 80°C .

during the alkaline treatment was primarily caused by the hydrolysis of casein. Besides, FTIR analyses indicated that the hydrolysis of nitrile groups and induced formation of C=N conjugated system were responsible for the yellowing effect of the fiber treated under strongly alkaline medium.

The weight loss and yellowing of the casein-acrylonitrile graft copolymer fiber under alkaline medium would become two serious problems when it is processed in textile factories. As the pretreatment and reactive dyeing of textiles are usually carried out under alkaline medium, some effective measures should be taken to reduce the loss of casein, yellowing of the scoured and bleached fiber, and color change of the palely dyed fiber.

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