Effect of Hydrogen Peroxide Bleaching onto Sulfonated Jute Fiber

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ABSTRACT: Bleaching of raw and sulfonated jute fiber with hydrogen peroxide were carried out in an aqueous medium. To obtain the optimum condition for bleaching, the effects of hydrogen peroxide concentration, temperature, time, pH, and fiber–liquor ration were studied. Bleaching affected the whiteness and tenacity, and the optimum whiteness index (76) and tenacity (13.7 g/tex) for the bleached sulfonated jute fiber were obtained with 2.1% hydrogen peroxide at pH 11, temperature 95°C, treatment time 110 min, and fiber–liquor ratio 1 : 7. The photo-oxidative degradation of bleached sulfonated jute fiber was characterized by

UV light exposure and compared with that of bleached raw jute fiber. It has been observed that the photo-oxidative degradation as well as loss in tenacity and yellowness of the bleached sulfonated jute fiber was 63 and 40% lower than that of bleached raw jute fiber. Bleached sulfonated jute fiber had excellent impact on color fastness with reactive dyes. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3603–3607, 2006

Key words: bleaching; sulfonation; photo-oxidative degradation; color fastness; jute; sulfonated jute

INTRODUCTION

Hydrogen peroxide is widely used in the textile industry as a bleaching agent particularly for whitening cotton fabric or yarn.¹ One advantage of delignification with hydrogen peroxide when compared with delignification using chlorine is that the effluent from peroxide stage being freed from chlorine atom, which decreases plant pollution and improves the product quality. The disadvantage of hydrogen peroxide is its high cost, but hydrogen peroxide can partially replace bleaching powder or calcium hypochlorite in bleaching the textile fiber. It also functions as a replacement for hypochlorite either partially or wholly. The pH as well as the concentration of hydrogen peroxide ions play a significant role in alkaline peroxide bleaching.² For hydrogen peroxide to be able to give maximum bleaching efficiency, an alkaline medium is essential.³ Presence of iron, manganese, and copper are generally considered undesirable during bleaching operations because it leads to the decomposition of the peroxide and reduces its availability for bleaching.⁴ However, stabilizing agents including sodium silicate⁵ and complexing agents such as EDTA^{6,7} are commonly used to limit the decomposition of the hydrogen peroxide and inhibit the catalytic decomposition by transition metals.⁸ This can be explained by buffer action⁴ and complex formation between these additives and an active metal ion.⁹Also sodium silicate disrupts the chain reaction decomposition by reacting with hydroxyl radicals, the resultant peroxysilicate may also act as a bleaching agent.¹⁰

In the present study, hydrogen peroxide bleaching of sulfonated jute fiber has been investigated. The optimum levels of bleaching variables, e.g., hydrogen peroxide concentration, time, temperature, pH, and fiber–liquor ratio, have been determined. An assessment of whiteness and tenacity of bleached sulfonated jute fiber has been done. The results have been compared with that of bleached raw jute fiber.

EXPERIMENTAL

Materials

Raw and sulfonated jute fibers were used as materials for the investigation. Reagent grades of Hydrogen peroxide (Mallinckrodt), sodium silicate (TITRI STAR), sodium sulfite (MERCK), soda ash (MERCK), EDA (J.T.BAKER), and detergent (AATCC) was used.

Sulfonation

Raw jute fiber was sulfonated with 12.0% sodium sulfite, 0.3% EDA (ethylendiamine) and 4.0% soda ash (owf) at 170 °C for 3 h.¹¹

Optimization of bleaching method

The treatment of raw and sulfonated jute fibers were carried out in a 100 mL stoppered Erlenmeyer flask.

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Figure 1 Effect of hydrogen peroxide concentration on whiteness index and tenacity of jute fiber (\bullet : whiteness of bleached raw jute, \blacktriangle : whiteness of bleached sulfonated jute, \bigtriangleup : tenacity of bleached sulfonated jute, \bigcirc : tenacity of bleached raw jute).

Bleaching was done with 0.3–2.7% H_2O_2 and 5% sodium silicate based on the weight of fiber at 5–13 pH, 40–100 °C for 40–120 min in the fiber–liquor ratio of 1:5–1:11. At the end of the desired reaction period, both the fibers were thoroughly washed with distilled water and dried in air oven.¹²

Testing

Tenacity, whiteness index, and weather resistance of the bleached sulfonated jute fibers were tested according to ASTM method D 2524–94 and AATCC test methods 110–95 and 169-2003.

RESULTS AND DISCUSSION

Effect of hydrogen peroxide concentration

Figure 1 shows that the whiteness of both fibers increases up to 2.1% and then slightly increases with the increase of hydrogen peroxide concentration. Conversely, the tenacity of both fibers decreases with the increase of hydrogen peroxide concentration. This can be explained on the basis that increase in the hydrogen peroxide charge lowers the initial pH, which stoichiometrically becomes unfavorable. So, low peroxide charge has a pronounced effect on the stoichiometry, which shows that a low peroxide charge is favorable.¹³ Also, an increase in the hydrogen peroxide charge gives not only increase of hydrogen peroxide consumption but also in some case produces greater reduction in the light absorption coefficient because of oxidation in the cellulose chain.¹⁴It is also observed from the Figure 1 that the whiteness index of bleached sulfonated jute fiber was 45% higher than that of bleached raw jute fiber with 2.1% H₂O₂.

Effect of temperature

Figure 2 shows that whiteness of both fibers increases with the increase of temperature up to 95°C and then slightly decreases with the further increase in temperature. But tenacity of both fibers decreases with the increase in temperature. This can be confirmed to the increase in the temperature of more than 90–95°C, which produces a greater drop in hydrogen peroxide concentration, and consequently hydrogen peroxide appears to decompose without bleaching effect. On the other hand high temperature is not desired, since it creates the risk of whiteness reversion.¹⁵ The presence of hydrogen atoms in the polymer molecule greatly decreases the energy of the C–C bond. When the fiber is heated the energy of thermal motion causes fluctuation of the chemical bond, which causes the weaking of bond in the cellulose chain. As a result, the tenacity of the fiber decreases.

Effect of time

It can be seen from the Figure 3 that the whiteness of both the fibers increases with the increase in reaction time upto 110 min and then decreases. However the tenacities of both fibers decrease with the increase in time. Hydrolysis and oxidation degradation are the main causes for this. The loss in tenacity due to hydrolysis cannot be attributed to losses in the fiber substance or weight of the fiber.¹⁶ The removal of lignin will result in the disintegration of the fiber with a great reduction in tenacity.¹⁷



Figure 2 Effect of temperature on whiteness index and tenacity of jute fiber (\bullet : whiteness of bleached raw jute, \blacktriangle : whiteness of bleached sulfonated jute, \triangle : tenacity of bleached sulfonated jute, \bigcirc : tenacity of bleached raw jute).



Figure 3 Effect of time on whiteness index and tenacity of jute fiber (\bullet : whiteness of bleached raw jute, \blacktriangle : whiteness of bleached sulfonated jute, Δ : tenacity of bleached sulfonated jute, \bigcirc : tenacity of bleached raw jute).

Effect of pH

It is observed from the Figure 4 that whiteness and tenacity of both the fibers increase with the increase of pH up to 11 and decrease with further increase in pH. This can be attributed to the fact the hydrogen peroxide is too stable at high pH,¹¹ which effect in liberating per hydroxyl ions $(HOO^-)^{18}$ as represented in the following equation

$$H_2O_2 \to H^+ + HOO^- \tag{1}$$

The formation of HOO^- is favored by alkali medium as shown in eq. (2)



Figure 4 Effect of pH on whiteness index and tenacity of jute fiber (\bullet : whiteness of bleached raw jute, \blacktriangle : whiteness of bleached sulfonated jute, Δ : tenacity of bleached sulfonated jute, \bigcirc : tenacity of bleached raw jute).



Figure 5 Effect of fiber–liquor ratiotime on whiteness index and tenacity of jute fiber (\bullet : whiteness of bleached raw jute, \blacktriangle : whiteness of bleached sulfonated jute, \triangle : tenacity of bleached sulfonated jute, \bigcirc : tenacity of bleached raw jute).

$$H_2O_2 + HO^- \rightarrow H_2O + HOO^-$$
 (2)

Decreasing the pH causes the peroxide to become unstable as shown in eq. (3)

$$H_2O_2 + HOO^- \rightarrow H_2O + O_2 + HO^- \qquad (3)$$

The liberated molecular oxygen, however has no bleaching action and causes loss of bleaching power. So, the pH 11 is found to be convenient to obtain high final whiteness by minimizing hydrogen peroxide decomposition and chromophores forming reaction.¹⁹

Effect of liquor ratio

Figure 5 shows that the whiteness of both fibers increases with the increase in the fiber–liquor ratio of up to 1:7 and beyond which it decreased. Conversely, the tenacity of both fibers increases with the increase in fiber–liquor ratio. It may be explained that a decreased liquor ratio gives an increased peroxide concentration at constant peroxide charge. The lower fiber–liquor ratio below 1:7 decreases the distance between the cellulose and active oxygen, and hence increases the possibility of some short-lived active species migrating from the sample.²⁰ Increase in fiber–liquor ratio of more than 1:7 did not improve the bleaching response of hydrogen peroxide. This may be related to the presence of radicals that are produced by peroxide decomposition.²¹

It is observed from the Table I that the percent loss in tenacity of both bleached raw and sulfonated jute fiber decreases with the progress of time. At the end of 180 AFU tenacity the loss of bleached raw jute fiber was 67% and bleached sulfonated jute fiber was 24.6. This happens, probably, because of the presence of

TABLE I Loss in Tenacity of Bleached Raw and Sulfonated Jute Fiber on Exposure to UV Light

Exposure period (AFU)	Loss in tenacity (%)	
	Bleached raw jute fiber	Bleached sulfonated jute fiber
5	18.50	5.20
10	32.25	9.56
20	43.00	12.00
40	51.80	14.90
80	59.00	18.10
180	67.00	24.60

higher amount of lignin content in bleached raw jute fiber than that of bleached sulfonated jute fiber. The high reactive groups present in lignin are phenolic and alcoholic hydroxyl groups.²² Lignin is highly sensitive to the action of light. The photo-oxidative degradation is initiated by lignin, which acts as a sensitizer and causes degradation of cellulose in all possible manner through the formation of hydrogen peroxide.²³ The reaction involved in the photo-chemical degradation of jute fiber is mainly oxidative in nature, and with prolonged exposure to light, the constituent of cellulose chains are gradually attacked and ultimately broken down into smaller fragments. As a result, the tenacity of jute fiber is decreased. In polymeric materials, usually strength is contributed not only by the crystalline region but also by the amorphous region because lignin acts as a cementing material that forms encrustants with cellulose. On exposure to light in presence of atmospheric oxygen these encrustants are broken down because of the involvement of lignin in the reactions, and therefore the loss in tenacity. In other words, When UV light falls upon jute fiber the rupture of cellulose chains involves either carbon–carbon or carbon–oxygen single bonds,²³ thus causing fission of cellulose chains and hence, tenacity is lost. It is seen from the Table I that the tenacity of bleached raw jute fiber decreases rapidly than that of bleached sulfonated jute fiber with the progress of exposure time. It may be explained that the bleached sulfonated jute contains minor amounts (4.8%) of lignin. More than 60% phenolic groups of lignin were blocked by ⁻HSO₃ groups. After sulfonation, when the fiber is subjected to light in presence of atmospheric oxygen degradation cannot be accelerated as much as bleached raw jute fiber, which indicates that lignin is mainly responsible for the photooxidative degradation of jute fiber.

Characteristics

The yellow index of bleached sufonated jute fiber after the exposure of UV light (180 AFU) was 40% lower than that of bleached raw jute fiber. When UV light

TABLE II Wash Fastness of Bleached Sulfonated Jute Fibers Dyed with Reactive Dyes

	Gray scale rating
Reactive orange ME2R	2–3
Bleached raw jute Bleached sulfonated jute	4–5
Reactive Red ME8B Bleached raw jute Bleached sulfonated jute	2 3–4

falls upon bleached raw jute fiber, the phenolic hydroxyl group of lignin in bleached raw jute creates free radicals. These radicals undergo transformation into quinoid structures, which are the origin of the yellowing on the surface of bleached raw jute.

The bleached sulfonated jute fibers were dyed (2.5%) dye) with Reactive Red ME8B and Reactive Orange ME2R at 70°C for 60 min in the fiber:liquor ratio of 1:20. The bleached sulfonated jute fiber had excellent wash and light fastness than that of bleached raw jute. This can be explained by the fact that (i) the covalent bonds between the dyes and sulfonated jute fiber were stronger than the bonds in raw jute fiber, (ii) lower amount of lignin in bleached sulfonated jute fiber, and (iii) less effect of UV light on bleached sulfonated jute than that of bleached raw jute. When UV light fell upon dyed, bleached raw jute fiber, the phenolic hydroxyl groups of lignin created free radicals. These free radicals oxidized the dye molecule, thus causing easy fading of dyed, bleached raw jute.²⁴ The results are listed in Tables II and III.

CONCLUSIONS

The raw and sulfonated jute fibers were bleached with hydrogen peroxide under different conditions such as varying pH, treatment time, temperature, hydrogen peroxide concentration, and fiber–liquor ratio. The optimum whiteness index (CIE) and tenacity (g/tex) were 76 and 13.7 for bleached sulfonated jute and 42 and 12.9 for bleached raw jute with 2.1% (owf) hydrogen peroxide at pH 11, temperature 95°C, treatment time of 110 min, and 1:7 fiber–liquor ratio. The photo-oxidative degradation

TABLE III Light Fastness of Dyed, Bleached Sulfonated Jute Fibers on Exposure (40 AFU) to UV Light

	Gray scale rating
Reactive orange ME2R	1–2
Bleached raw jute Bleached sulfonated jute	3–5
Reactive Red ME8B Bleached raw jute Bleached sulfonated jute	1 3

of bleached sulfonated jute fiber was characterized by UV light exposure at 180 AFU and compared with that of bleached raw jute fiber. It has been observed that the photo-oxidative degradation as well as percent loss in tenacity of the bleached sulfonated jute fiber was 24.60 and bleached raw jute was 67. The yellow index of bleached sulfonated jute was significantly lower than that of bleached raw jute. The color fastness (e.g., light and wash fastness) of bleached sulfonated jute fiber with reactive dyes had excellent impact than that of bleached raw jute.

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