CHAPTER VII

MODIFICATION OF JUTE AND ITS DYEING BEHAVIOR WITH DISPERSE DYE
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7.1. Introduction

There has been a worldwide awareness and realization about the urgency and necessity of environmental protection and preservation which forced introduction of legislation in many countries to ban or curb the use of non-biodegradable substances like plastic bags to prevent further degradation of the environment. Hence, awareness and urge to use biodegradable substances to manufacture articles of daily necessity has arisen. Jute is an ideal choice for this. The golden fibre "jute" is once again regaining its dominant position as packaging material along with increasing application in diversified [1] and value added utility articles like table mats, sling bags, carry bags, school bags, laminated shopping bags, soft luggage's, blankets, carpets, sacking and Hessians [2].

Jute is very sensitive to alkali [3,4]. The extent of damage depends on the concentration, time and temperature. Jute has higher affinity towards basic dyestuff than others do [5]. Different investigators [6-11] have described the general methods of dyeing with different types of dyestuffs on jute. Farouqui et al [12-15] carried out research on jute dyeing using basic, acid, direct and
mordant dyes. Disperse dyeing on jute [16], resin treatment on enzymated jute fabric [17], characterization of chemically modified jute fibres by FT-IR spectra [18], Ceric-induced grafting of 2-hydroxyethyl methacrylate on jute [19] have been reported in literature.

7.2. Benzoylthioglycollate

The preparation and characterization of sodium benzoylthioglycollate (BTG) have been described [20]. Model reactions indicated that BTG readily undergoes nucleophilic substitution reactions with amines. Cotton was benzoylated using BTG [21]. Effects of pad liquor additives and thermosol temperatures on the extent of cotton benzoylation have been reported [22].

Based on the modification investigation on cotton using BTG, it was aimed to study similar type of modification on jute. The effect of padding and thermosol treatment on jute by benzoylation and subsequent dyeing with a disperse dye have been studied and presented.

7.3. Experimental details

Jute fibres (Corchorus capsularis) were obtained from Ahmedabad Textile Research Association, Ahmedabad and cut into small bundles of about 3 inch length. These fibres were then subjected to bleaching. Bleached jute
fibres were used in this study. Sodium benzoylthioglycollate (BTG) was used as modifier. Sodium acetate, sodium hydroxide, sodium carbonate and urea were used in modification steps. A disperse dye, Disperse Orange 13, was used in dyeing experiments.

7.3.1. Benzoylation on jute using BTG

Many number of pad liquors containing different concentration of BTG with sodium acetate, sodium bicarbonate, sodium carbonate, sodium hydroxide and urea were prepared. Jute fibres were padded using Konrad Peter Padding Mangle at 85% wet pickup with these solutions and dried at room temperature for 24 hours. Then the fabrics were baked (thermosol) in a Werner Mathis AG Laboratory Steamer unit for different temperature and time. The modified jute fabrics were thoroughly washed with cold water and dried at 110°C. Samples of the modified fabrics were extracted 5 times with distilled water at 50°C for 15 min. The solution thus obtained was made up to 250 ml and measured on a Jasco V-530 UV-Visible spectrophotometer at $\lambda_{	ext{max}}$ 239 nm for absorbance. The percentage fixation of BTG on jute was calculated as

\[
\text{Fixation \%} = 100 - \left(\frac{A_2}{A_1}\right) \times 100,
\]

where $A_1$ and $A_2$ are the absorbency of extract before and after thermosol process respectively.
7.3.2. Determination of the degree of substitution (DS) of BTG modified jute

The weight gain of the modified jute fibres were measured and the degree of substitution of the modified fibres were calculated using the equation:

\[ DS = \frac{\text{Actual weight gain}}{\text{Theoretical weight gain}} \]

Theoretical weight gain = \((484/172) \times \text{weight of fabric} - \text{weight of fabric}\)

(484 is the molecular weight of the tribenzoylated anhydroglucoside residue in jute and 172 is the molecular weight of the original anhydroglucoside residue).

7.3.3. Differential scanning colorimetric measurement

Differential Scanning Colorimetry (DSC) measurement was carried out for both unmodified and BTG modified jute fibres using a Dupont 1090 Thermal Analyzer. The temperature was increased at a rate of 10°C per min.

7.3.4. FT-IR spectroscopy measurement

The FT-IR Spectra of unmodified and BTG modified jute fibres were obtained on a Perkin-Elmer 1725 Spectrometer using the diffuse reflectance DRIFTS attachment. 5-mg of the sample was mixed with 200-mg potassium bromide and pressed into discs. The difference in spectrum was obtained by
computer subtraction of the unmodified jute spectrum from that of the modified jute fabric.

7.3.5. Dyeing

The modified (benzoylated) and unmodified jute fibres were dyed with 2% (owf) Disperse Orange 13 dye at a pH of 6.5. The pH was maintained using a 0.1M citric acid / 0.2M disodium hydrogen phosphate buffer. A liquor ratio of 1:20 was used and the dyeing was carried out in closed tubes housed in a rotadyer. The dye bath temperature was raised to 100°C over 20 min and maintained at this temperature for 1 hour. The dyed fabric was thoroughly washed with water and dried. Wash fastness values of all dyed samples were measured by ISO2 [23] and ISO3 test methods.

7.4. Results and discussion

7.4.1. Differential Scanning Colorimetry

The DSC plot for untreated jute revealed that exothermic enthalpy changes at temperatures of 348 and 387°C and an endothermic enthalpy changes at 378°C. The corresponding DSC plot for BTG modified jute contained only an endothermic enthalpy change at 385°C. The exothermic changes obtained in the DSC plot for jute are associated with decomposition processes, which may occur within the substrate during heating. The
endothermic peaks obtained in the DSC plots for both untreated and BTG modified jute fabrics are possibly due to local changes either in the crystalline regions of natural jute or a breakdown in the hydrophobic interactions in the BTG modified jute on heating. The shift in the position of the endothermic peak to 385°C is likely to be due to changes occurring in the physical structure of the polymer.

The DSC plots for unmodified and BTG modified jute fabric also contained endothermic peaks at temperatures of 118 and 115°C respectively. The area of the endothermic peak in the DSC plot for untreated jute was greater than that obtained in the DSC plot for BTG modified jute (Figure 7.1). These endothermic peaks are probably associated with the removal of water from the cellulose polymer chains. The lower peak area obtained in the DSC plot of BTG modified jute is probably due to a decrease in the amount of water trapped within the polymer chain, which is brought about by changes in the physical and hydrophobic nature of the polymer after benzoylation.

7.4.2. FT-IR measurement

Infrared spectral analysis is a powerful tool to identify the nature of bonding and different functional groups present in a sample by monitoring the vibrational energy level of the molecules, which are essentially the fingerprint of different molecules. In general, the energy of molecule can be separated into three parts (i) rotational energy of the molecule as a whole, (ii) vibrational
energy of the constituent atoms and (iii) electronic energy levels due to the motion of electrons.

The FT-IR spectrum obtained by subtracting the DRIFTS spectrum of modified and unmodified jute from the DRIFTS spectrum of BTG modified jute showed a very strong absorption peak at 1720 cm\(^{-1}\). This absorption peak corresponds to the stretching absorption of the carbonyl group in the resulting benzoyl ester derivative of jute (Figure 7.2). This spectrum also showed absorption peaks at 1605 and 1450 cm\(^{-1}\) which correspond to the IR stretching vibrations of the C=C bonds in the benzene ring of the benzoyl ester modified jute.

7.4.3. Esterification of jute

DSC indicated that important changes associated with increased hydrophobicity have occurred on benzoylation. Since BTG is a water-soluble active ester, its use would allow the formation of benzoyl esters of cellulose. The esterification of jute by BTG was confirmed from the FT-IR spectrum.

The reaction of BTG with jute may be represented as follows:

\[
\text{Jute-OH} + \text{C}_6\text{H}_5\text{-CO-SCH}_2\text{COO}^+\text{Na}^+ \rightarrow \text{C}_6\text{H}_5\text{CO-O-Jute} + \text{HSCH}_2\text{COO}^+\text{Na}^+
\]
7.4.4. Dyeing

On thermosol treatment of jute impregnated with BTG and disperse orange 13, the liberated thioglycollate interacts with the selected disperse dye giving a weaker hue to the dyed modified fabric. The visible absorbance spectrum of Disperse Orange 13 dye showed a wavelength of maximum absorption at 422 nm. The addition of sodium thioglycollate to the dye solution produced in the formation of two absorption peaks in the spectrum of the dye, one at a wavelength of 415 nm and second at 610 nm. As more thioglycollate was added to the dye solution, the peak at 610 nm was gradually shifted to a wavelength of 600 nm, the peak at 415 nm being unaffected. It is likely that many disperse dyes would be prone to reduction with thioglycollate and thus 'all-in' processes using pad liquors containing dye and fibre arylating agent together are not possible in the case of BTG.

When 2% BTG was applied from a neutral pad liquor and fixation step (200°C, 60 sec), very low K/S values in dyeing were recorded, which indicated that these conditions were inadequate to achieve esterification.

7.4.5. Effect of sodium bicarbonate

As 2% BTG (16% owf) was applied to jute in the presence of sodium bicarbonate and fixed at 200°C for 60 sec, the dye uptake of the subsequent disperse dyeing increased as the concentration of sodium bicarbonate in the
pad liquor increased. The dye uptake begins to fall above 0.4% sodium bicarbonate (Figure 7.3), which may be due to the competing hydrolysis reaction of hydroxyl ions with BTG to form sodium benzoate.

7.4.6. Effect of sodium carbonate

When 2% BTG (16% owf) was applied to jute in the presence of sodium carbonate, the high dye uptake was achieved with a sodium carbonate concentration of 0.2%. Application of 3% BTG (24% owf) required a sodium carbonate concentration of 0.4% to obtain the highest dye uptake (Figure 7.4).

7.4.7. Effect of sodium hydroxide

BTG application to jute in the presence of sodium hydroxide gave very promising dye uptake, especially when lower levels of alkali were used (Table 7.1). At higher levels of jute benzoylation, good color yield and wet fastness properties of the resulting disperse dyeing may be achieved.

7.4.8. Effect of urea

Addition of urea to the pad liquor containing 2% BTG and 0.2% sodium carbonate were expected to increase the extent of benzoylation followed by thermo fixation at 200°C for 60 sec. The subsequent dyeing results indicate that
additional urea has an adverse effect on the reaction (Table 7.2). Urea decomposition provides ammonia and it is likely that BTG reacts rapidly with ammonia to produce benzamide, which does not react with jute.

7.4.9. Effect of time and temperature

As thermal time was increased from 15 to 90 sec, higher levels of BTG fixation were achieved, resulting in modified jute fabrics with higher D.S values. D.S. and covalent fixation of BTG to jute also increased as higher temperature was used during thermosol treatment (Figure 7.5).

The increased values in D.S. gave rise to disperse dyeing of improved dye uptake, when longer thermosol times or higher temperatures were used. The BTG fixation results versus thermosol time and temperature produced a maximum fixation value of 80.4%, which represents a D.S. of about 0.1. Notwithstanding the relatively large amount of BTG applied (16% owf), the fixation indicates that the acyl thioglycollate is a remarkably efficient reactive group in the alkaline pad thermosol treatment of jute.

7.4.10. Effect of sodium carbonate concentration on D.S.

When jute was modified with BTG (2%) and sodium carbonate (0.2%), the highest D.S. value was achieved (Figure 7.6).
As the weight gain of the benzoylated jute increased, the dye uptake of the resulting disperse dyeing also increased. Weight gain was converted to D.S. values and plotted against K/S. A linear plot (Figure 7.7) was obtained which indicates that as the level of benzoylation of the jute increases, dye uptake increases.

Similar linear plots of disperse dyeing color yield versus extent of benzoylation were obtained on wool modified with benzoic anhydride was reported in literature [24]. These effects demonstrate that aromatic interactions between the disperse dye and the benzoyl groups covalently incorporated in the modified fibres are the source of the disperse dye substantives [25].

7.5. Conclusion

Generally natural fabric jute has very little substantivity for disperse dyes and resulting disperse dyeing show poor response to the ISO2 and ISO3 wash fastness tests. This investigation has demonstrated that a water soluble benzoylating agent, BTG, can be applied to jute in the presence of alkali via a pad thermosol process to produce a modified fabric for which disperse dye has improved substantivity. The results obtained in dyeing were of good color yield and showed good results to ISO2 and ISO3 wash fastness tests.
References


Table 7.1: Effects of alkali and BTG in dyeing and wash fastness.

<table>
<thead>
<tr>
<th>BTG Conc. (%)</th>
<th>NaOH conc. (%)</th>
<th>K/S (422 nm)</th>
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<th>ISO3</th>
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Table 7.2: Effect of urea

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Figure 7.1: DSC of modified and unmodified jute

![DSC graph showing modified jute and original jute](image)

Figure 7.2: FT-IR Spectrum of modified and unmodified jute

![FT-IR spectrum graph](image)
Figure 7.3: The effect of sodium bicarbonate on color yield

Figure 7.4: The effect of sodium carbonate on color yield
Figure 7.5: The effect of time and temperature on the fixation of BTG (2% of BTG, 0.2% of sodium carbonate) on jute

Figure 7.6: Effect of sodium carbonate concentration on D.S
Figure 7.7: Effect of D.S. on color yield

- D.S.
- K/S (422 nm)