



## Modification of Bioscoured Cotton Cellulose by Grafting and Hydrolysis Process

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### ABSTRACT

The gray single jersey knitted cotton fabric was bioscoured with pectinase enzyme and grafted with acrylonitrile monomer by potassium permanganate/citric acid redox system. The grafted cotton was hydrolyzed with alkali and acetone solvent in presence of a mild alkali solution separately. FTIR analysis was performed to study the changes that were imparted by the chemical modification. The absorption peak observed at  $2259\text{ cm}^{-1}$  corresponds to the stretching vibration of  $\text{C}\equiv\text{N}$ , which confirms the grafting. Changes in the surface morphology were observed through the SEM studies. Because of more swelling nature of the fibres after hydrolysis process by 1.5N sodium hydroxide the sample image shows slightly bulkier than the other samples. TGA-DTA thermal analysis shows that the thermal stability was not much affected by the chemical modification. The solvent induced hydrolysis process shows good results than the alkali treatments. The grafted cotton shows higher thermal stability than the bioscoured fabric. The modified fabric shows higher degradation temperature than the grafted fabric. Dyeing was carried out with different salt concentrations. The acetone and alkali treated samples show 130% and 20-30% increase in dye uptake than the grafted and sodium hydroxide alone treated samples. Acetone treatment has brought some chemical changes to an alkali treated fabric in its structure and increases the affinity of the modified cotton towards reactive dye.

### Key Words:

bioscouring;  
grafting;  
cotton cellulose;  
SEM;  
dyeing.

### INTRODUCTION

Textile industrial sector utilizes the cotton fibres for the production of various end use materials by weaving and knitting processes. With latest technology development in knitting process, most of the garments are made from the knitted cloth because of their easy wear and handling properties. Cotton fibres have certain limitations such as poor crease resistance, poor dimensional stability, and their tendency to wrinkle [1]. These

drawbacks have directed attention towards improving the properties through changing the physical and chemical structures of cellulose. Several researchers have found that graft copolymerization of cotton with different vinyl monomers improves the strength, toughness, flex-abrasion resistance, and thermoplasticity. Among the various graft copolymerization methods available, redox-initiated grafting offers advantages because

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in the presence of redox systems, grafting can be carried out under milder conditions with minimum side reactions. Hence, grafting of synthetic polymers on cellulose eliminates these drawbacks and allows the acquisition of the additional properties of grafted polymers without destroying its own properties [2].

However the graft copolymerized cotton shows poor moisture absorption and dyeability, because of high degree of hydrophobicity of the vinyl groups attached onto cellulose end chain due to grafting. To increase the hydrophilicity, monomers containing hydrophilic groups must be grafted onto cellulose. A study [3] deals with modifying the chemical structure of cellulosic cotton fabrics by introducing amino groups as a new active centre. The modification succeeded in increasing the extent of fixation of several dye classes by strengthening the bond formed between the dye and the chemically modified fabrics. The stronger the bond formed the greater is the fastness of the dyed substrate [4,5]. Blackburn et al. [6] reported the treatment of cellulose with cationic or nucleophilic polymers to enable reactive dyeing at neutral pH. Recently, a study was conducted to introduce an amide group in the cellulose structure for neutral dyeing [7].

Generally, knitted cotton material is used as inner wear garments and it should have more hydrophilic nature. In the present work, an attempt was made to modify the cellulose structure of knitted cotton fabric by grafting process after bioscouring. For this reason, the grafted cotton cellulose was hydrolyzed with a mixture of acetone and alkali and characterized by FTIR techniques. The dyeing behaviour was studied at different salt concentrations.

## EXPERIMENTAL

### Materials

Single Jersey knitted cotton fabric with 130 GSM (40s Combed) used in this study was kindly supplied by Hitech Garments, Tirupur. All the chemicals used were of Analar grade. The enzyme pectinase was kindly supplied by Rossari India Pvt. Ltd. Acrylonitrile was used without any further purification. Deionized water was used for all the chemical treatments and final washing of samples.

### Bioscouring

The gray knitted cotton fabric was cut into pieces (30 cm width and 30 cm length). The bioscouring was carried out in a programmable HTHP beaker-dyeing machine using pectinase enzyme (2 gpl) with liquor to material ratio of 10:1. The pH was maintained at 4.5 using citric acid/sodium acetate buffer. The temperature was slowly raised to 50°C and maintained for 1 h. Then the fabric was taken out and washed well with water and the residual enzymes were deactivated by increasing the temperature to 80°C for 10 min. They were then cooled and washed well with deionized water and air-dried [8].

### Graft Copolymerization

The grafting operation is carried out using a potassium permanganate/citric acid redox system with acrylonitrile monomer as reported by Hafiz et al. [9]. The bioscourd knitted cotton fabric was impregnated in an aqueous solution containing specific concentrations of potassium permanganate (0.25 gpl). The treatment was carried out for 15 min at 30°C with continuous and vigorous shaking to avoid uneven manganese dioxide deposition on the fabric surface. The liquor to material ratio was kept at 10:1. The treated fabric was then washed well with cold water and squeezed between two papers before immersing in the polymerization solution.

The permanganate treated cotton fabric was put in a 500-mL stoppered round bottomed flask containing an aqueous solution of acrylonitrile monomer (20% OWM) and citric acid (0.25 gpl) at 80°C for 60 min. The liquor to material ratio was 20:1 and the reaction was carried out with vigorous and continuous shaking. At the end of the reaction, the sample was removed and washed several times with cold water and then rinsed with deionized water and air-dried.

### Sodium Hydroxide Treatment

The grafted fabric is treated with sodium hydroxide (1.5% and 3%) with liquor to material ratio of 10:1 for 30 min and then washed well with water, finally neutralized with a dilute solution of acetic acid to remove traces of sodium hydroxide then rinsed with deionized water and air-dried. The 1.5% and 3.0% sodium hydroxide treated samples are designated as 1.5N and 3.0N samples, respectively.

### Sodium Hydroxide and Acetone Treatment

The grafted fabric was treated with a mixture of 1.5% aqueous sodium hydroxide and with equal amount of acetone for 30 min at liquor ratio of 1:10. The fabric was washed well with water and neutralized with a dilute solution of acetic acid to remove traces of sodium hydroxide and finally rinsed with deionized water and air-dried. The same experiment was carried out using 3% aqueous sodium hydroxide under similar conditions. These samples were designated as 1.5A and 3.0A samples, respectively.

### Dyeing

The bioscoured, grafted, and modified cotton fabrics were dyed with Drimarene Red HE3B 1% shade (1 g of dye/100g of fabric) according to the conventional method using NaCl (10 g/L), sodium carbonate (12 g/L), and 1:20 liquor ratio. Dyeing temperature was raised from 40°C to 80°C after which the dyeing was carried out for further 45 min. The dyed samples were taken out, washed with cold water, soaped at boil, rinsed thoroughly in hot water, washed again with cold water, and finally air-dried. The same method of dyeing was repeated with addition of salt (20, 30, and 40 g/L).

### FTIR Analysis

For Fourier transform infrared (FTIR) spectroscopic analysis, the modified sample was ground and the fine powder sample was mixed with dry potassium bromide (KBr). It was then made into a film and analyzed by a Perkin-Elmer FTIR spectrophotometer (Spectrum RX1 model).

### SEM Studies

Surface morphology of bioscoured and the modified cotton fabrics were analyzed with a Joel scanning electron microscope (JSM8404) after gold coating by sputtering method.

### Thermal Analysis

Dynamic thermogravimetric analyses were performed using a Diamond TGA-DTA thermal analyzer, Perkin-Elmer. Temperature programmes for dynamic testes were run from 30°C to 800°C at a heating rate of 10°C/min. TG/DTG tests were carried out under nitrogen atmosphere (300 mL/min) to prevent any

thermooxidative degradation. The sample was contained in a sample pan made of platinum. Typically 10 mg to 12 mg of sample was spread evenly over the floor of the sample pan. Pans were kept under programme control for 2 min at the temperature of the first isothermal when the temperature was stabilized. TG-DTG-DTA curves were simultaneously recorded. Thermogravimetry is widely used as a method for the determination of kinetic parameters such as activation energy, frequency factors to elucidate the thermal degradation mechanisms and the thermal stability of materials [10].

### Colour Measurement

The colour values of the dyed fabrics were measured using a Gretag Macbeth spectrophotometer (2180 UV). Color iMatch was according to the CIELAB colour difference concept at standard illuminant D65/10° observer in the wavelength range of 360 nm to 750 nm at 10 nm intervals. The reflectance values were recorded at 2 points on each face of the folded fabric (8 points) at an interval of 1 cm from each other.

## RESULTS AND DISCUSSION

The recorded FTIR spectra of all the treated samples with their exact position and their possible assignments [11] are presented in Table 1. Bands at different places in the spectra of the treated and untreated cotton fabric in the region 1464 cm<sup>-1</sup> to 1050 cm<sup>-1</sup> are almost similar. These are due to various characteristics of specific groups like CH<sub>2</sub>- bending in gluco-pyranose of cellulose, -OH in plane bending, aliphatic C-H bending, interaction between -OH bending and C-O stretching, asymmetric C-O-C stretching and C-O/C-C stretching vibrations (Figure 1).

The bioscoured knitted fabric when subjected to permanganate treatment, a large amount of manganese dioxide is deposited on the fabric. In the presence of citric acid, carboxyl radicals are formed as a result of the action of citric acid on the deposited manganese dioxide [12]. Once these free radical species (R.) are created, they produce reactive sites located along the cellulose backbone (cellulose macroradical) through direct abstraction of a hydro-

**Table 1.** FTIR spectral data of chemically modified cotton fabric.

Assigned peaks	Bioscoured	Grafted	1.5N	3.0N	1.5A	3.0A
C=O Str	1735	1732	-	-	-	-
C – C Str	-	1241	-	-	-	-
-C≡N Str	-	2259	2259	2259	-	-
-NH <sub>2</sub> Str	-	-	-	-	3446	3489
-NH Str	-	-	-	-	3336	3330
C=O Str	-	-	-	-	1874	1842
-CONH <sub>2</sub> -	-	-	-	-	1650	1655
C–N–H Str	-	-	-	-	1238	1243
C–N Str	-	133	1330	1363	1336	1334

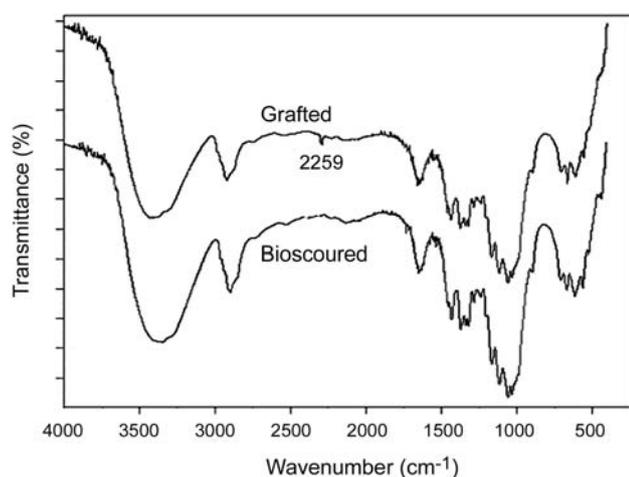
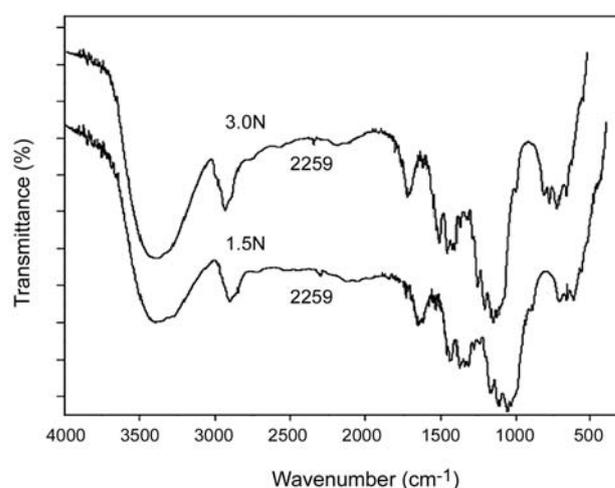
gen atom from the hydroxy groups present in the cellulose. Cellulose macroradicals are immobile themselves and for grafting to occur, the monomer molecules have to be in their vicinity. In presence of acrylonitrile monomer, these sites were added to the double bond of acrylonitrile resulting in a covalent bond between the monomer and the cellulose.

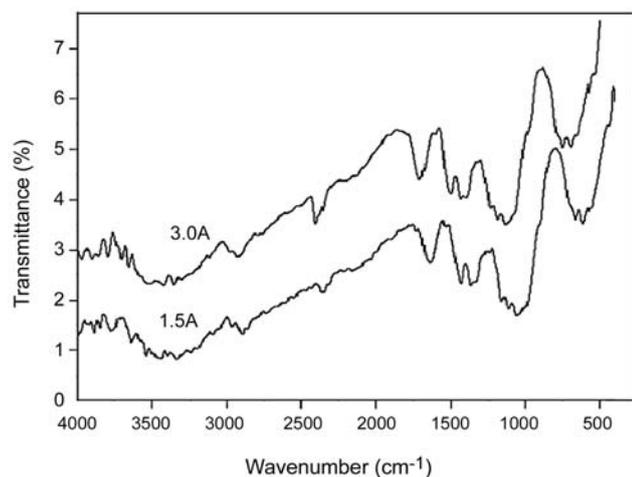
The FTIR spectra of the bioscoured and grafted fabrics are shown in Figure 1. The -OH stretching vibration of the bioscoured fabric occurs at 3434.10 cm<sup>-1</sup>. In the grafted cotton this band has undergone a shift towards 3390.47 cm<sup>-1</sup>. It can also be observed that the hydroxyl band intensity of the grafted cellulose was considerably less than that of the pure cellulose. This may be an indication of the possible participation of the hydroxyl groups in the

modification. Further absorption peak observed at 2259.32 cm<sup>-1</sup> corresponds to the stretching vibration of C≡N. The presence of nitrile group could be regarded as a strong evidence for the grafted cellulose.

Strong bands occurred at 1602 cm<sup>-1</sup> may be attributed to the presence of absorbed water for the bioscoured fabric. Bioscoured cotton knits were comparable to those of conventionally alkaline scoured cotton knits [13]. However, shift in the band to higher wavenumber 1618.48 cm<sup>-1</sup> followed by reduction in intensity was observed in the case of grafted fabric. This may be due to the poor moisture regain of the grafted fabric.

The FTIR spectra of alkali treated fabrics with 1.5% and 3.0% concentrations of alkali are shown in

**Figure 1.** FTIR spectra of bioscoured and grafted samples.**Figure 2.** FTIR spectra of 1.5N and 3.0N samples.



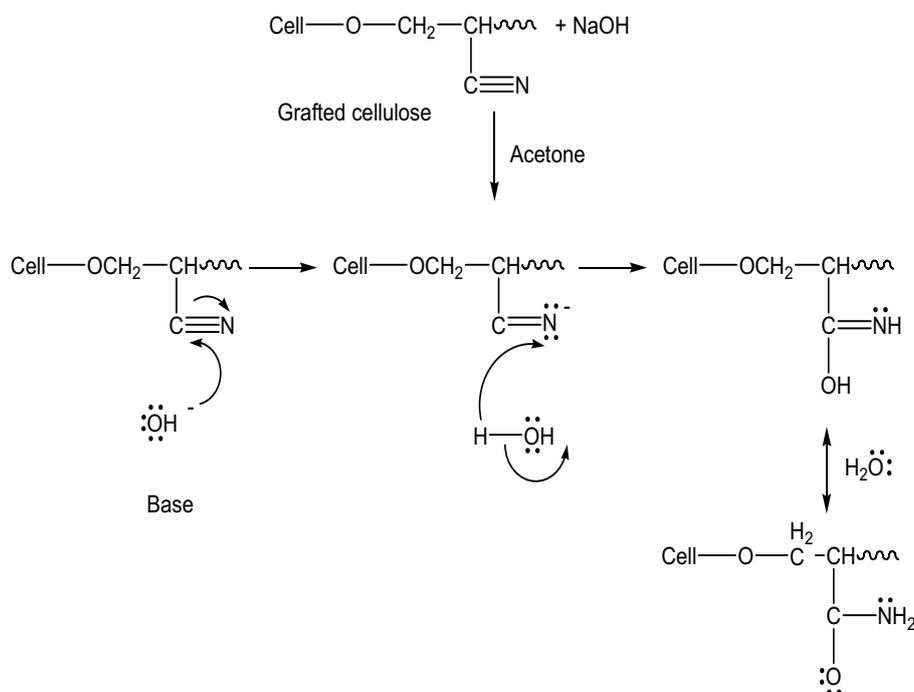
**Figure 3.** FTIR spectra of 1.5A and 3.0A samples.

Figure 2. Treatment with alkali has made no marked impact on the structural changes of the grafted cotton. However, the intensification of the band peak for absorbed water with increase in alkali concentration is noted. The peak intensity is higher than the grafted cotton but similar for 1.5N treated and 3.0N fabric samples. This shows that there is no chemical modification in the case of alkali treatment.

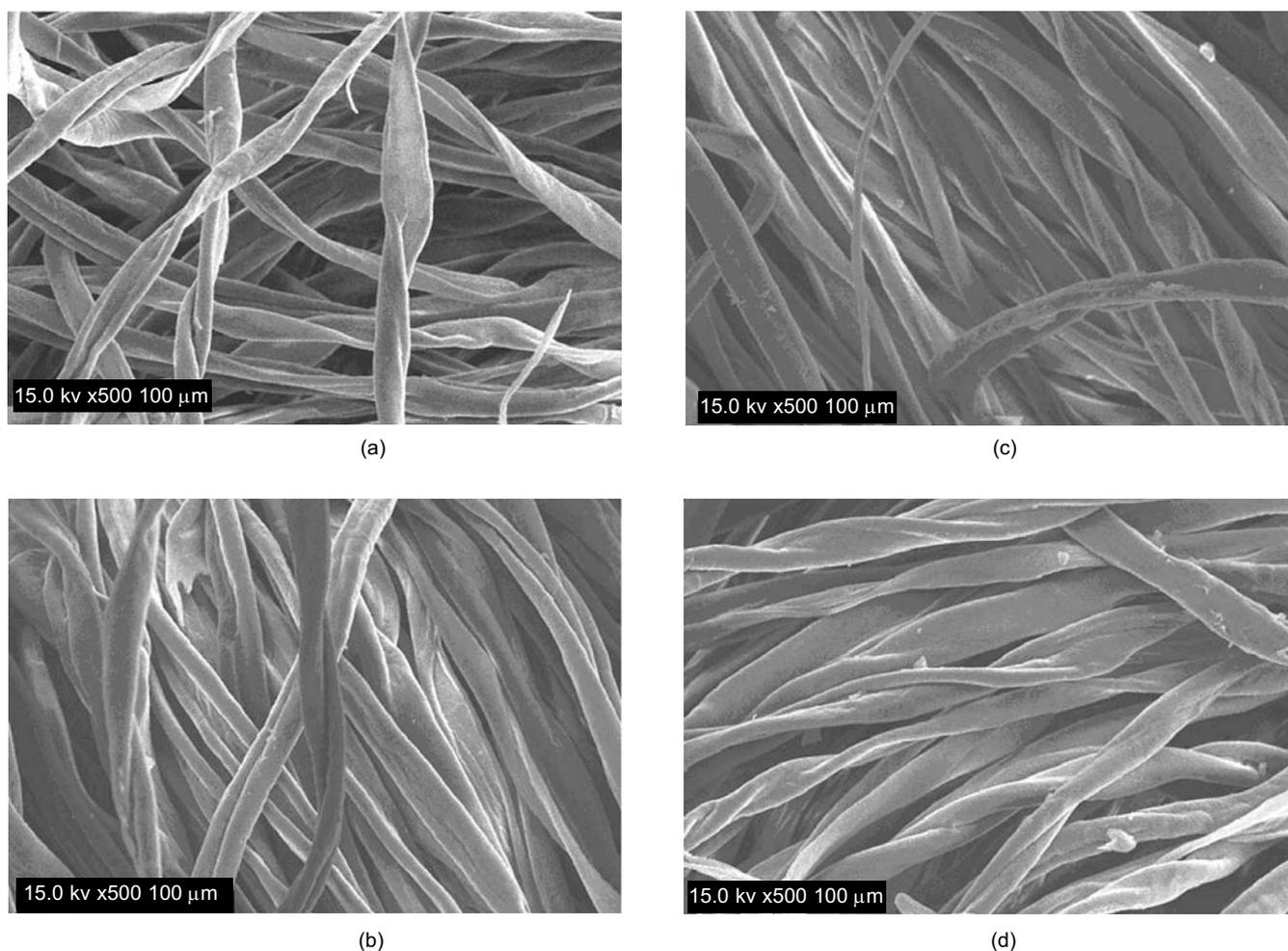
The IR spectra of 1.5A and 3.0A fabrics show some vibrational changes in their respective spectrum

due to the addition of acetone to the alkali treated fabric (Figure 3). Further occurrence of a broad peak in the region between  $3570\text{ cm}^{-1}$  and  $3200\text{ cm}^{-1}$  is noted. The peak observed in similar regions for bioscourced and grafted cottons is narrow and is a characteristic of  $-\text{OH}$  stretching vibration. For 1.5A fabric this region is split into multiple peaks. The appearance of such peak is characteristic of  $\text{N}-\text{H}$  stretching vibrations. This may be due to inter- or intra-molecular hydrogen bonding or may be the fact that the point of reaction is at the  $-\text{C}\equiv\text{N}$  which is hydrolyzed to form amide. The disappearance of the peak for nitrile group at  $2259\text{ cm}^{-1}$  supports the above argument. Hence it may be resolved that cyano end group of the grafted cotton is hydrolyzed by acetone in the presence of alkali.

The hydrolysis may yield both  $-\text{NH}_2$  and  $=\text{NH}$  as proposed in the mechanism. This can be confirmed by the occurrence of peaks at  $3446\text{ cm}^{-1}$  (1.5A) and  $3489\text{ cm}^{-1}$  (3.0A) for  $-\text{NH}_2$  group. The peaks formed at  $3336\text{ cm}^{-1}$  (1.5A) and  $3330\text{ cm}^{-1}$  (3.0A) are due to the  $=\text{NH}$  group. This clearly shows that in acetone and alkali treated samples the hydrolyzed nitrile groups exist in two resonance forms as shown in the mechanism. An additional peak for  $-\text{C}=\text{O}$  is also observed at  $1874\text{ cm}^{-1}$  and  $1842\text{ cm}^{-1}$ . The  $\text{C}-\text{N}$  stretching frequency is observed at  $1330\text{ cm}^{-1}$  and  $1363\text{ cm}^{-1}$



**Scheme I.** Reaction mechanism for hydrolysis of grafted cellulose.



**Figure 4.** SEM photographs of: (a) bioscoured, (b) grafted, (c) 1.5N, and (d) 1.5A samples.

for 1.5N and 3.0N samples and at  $1336\text{ cm}^{-1}$  and  $1334\text{ cm}^{-1}$  for 1.5A and 3.0A samples, respectively.

From the FTIR studies the following reactions might happen and the possible mechanism is shown in Scheme I.

In the proposed reaction mechanism, the acetone solvent induces the hydrolysis reaction favourably in treated fabrics compared to sodium hydroxide alone.

The surface morphologies of the bioscoured, grafted, 1.5N and 1.5A samples are examined using the scanning electron microscope. The bioscoured fabric is clear and the convolutions of the cellulose fibres are fairly visible (Figure 4a). The surface of the grafted cotton appears to be bulkier and the interfibre spaces are very much reduced (Figure 4b). There is no difference between the grafted (Figure 4b) and 1.5N treated sample (Figure 4c). Sample image of 1.5A (Figure 4d) shows slightly bulkier than the other samples.

This may be due to the more swelling nature of the fibres after hydrolysis process.

Thermal parameters of the modified samples are reported in Table 2. The values of initial decomposition temperature ( $T_i$ ) and maximum degradation temperature ( $T_{max}$ ) are noted from the onset of decomposition process and maximum of DTG curve, respectively [14]. The  $T_i$  is  $327^\circ\text{C}$  for the bioscoured and  $330^\circ\text{C}$  for the grafted fabric. After initial loss of moisture the rapid weight loss of the cellulosic fabrics occurs. This loss is attributed to actual pyrolysis reaction. The peak temperature for major degradation stage is  $358^\circ\text{C}$  for bioscoured and  $364^\circ\text{C}$  for the grafted fabric. The grafted fabric has the highest major decomposition temperature (charring temperature) than the bioscoured. This can be due to the fact that in case of grafted cellulose, the poly(acrylonitrile) chains ( $-\text{CH}_2-\text{CH}_2-\text{CN}-$ ) attached to cellulose

**Table 2.** Thermodynamical parameter of modified cotton.

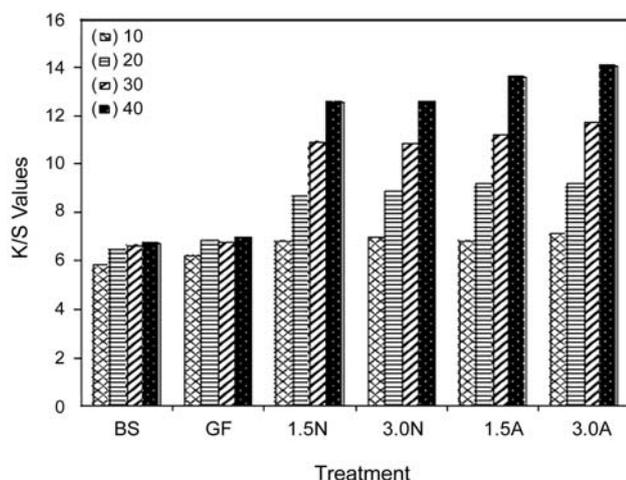
Sample	$T_i$ (°C)	$T_{max}$ (°C)	DTG peak height (%/min)	Temperature range (°C)	
				Initial	Final
BS	327	358	14.58	295-330	332-382
Grafted	330	364	20.90	301-335	336-384
1.5N	324	358	22.69	307-333	333-382
3.0N	321	360	23.59	298-330	331-382
1.5A	322	359	26.05	301-332	333-383
3.0A	323	360	17.63	299-330	333-384

**Table 3.** Percent increase of K/S values of modified samples with bioscourd fabric.

Salt concentration (g/L)	Grafted	1.5N	3.0N	1.5A	3.0A
10	7	17	20	17	22
20	7	49	52	58	57
30	1	87	86	92	101
40	4	115	116	133	142

probably forms a ring structure during pyrolysis. This ring structure of acrylonitrile has a higher charring temperature than the linear polymer [15]. There is no change in the case of alkali and acetone treated samples.

The bioscourd sample shows low K/S value than the all other treated samples (Figure 5). As the salt concentration increases the dye uptake increases in each modified samples. The increase in K/S values

**Figure 5.** K/S values of the modified fabrics at different salt concentrations.

with respect to bioscourd samples is shown in Table 3. The grafted sample shows a marginal increase (7%) at lower salt concentration. A better increment in the K/S values is noticed with both 1.5% and 3.0% sodium hydroxide treated samples compared to bioscourd samples. But there is no significant difference between these two fabric samples. In the case of 1.5A and 3.0A samples, there is a marginal increase in the percentage of K/S values at higher salt concentrations. A maximum of 142% increase is obtained with 3.0A sample dyed with 40 g/L salt concentration. This shows that the acetone treatment has brought some chemical changes to an alkali treated fabric in its structure and increases the affinity of the modified cotton towards reactive dye [16].

## CONCLUSION

FTIR study confirms the presence of  $-C\equiv N$  group as a result of graft copolymerization reactions with the appearance of peaks at  $2259\text{ cm}^{-1}$ . The characteristic amide group peak at frequency between  $1642\text{ cm}^{-1}$  to  $1656\text{ cm}^{-1}$  indicates the possible hydrolysis of the grafted cellulose due to the presence of acetone. SEM

study confirms that, the hydrolysis of grafted cellulose in presence of alkali and acetone improves the fibre swellability. The grafted cotton shows higher thermal stability than the bioscoured fabric. The value of K/S is higher for the 1.5A and 3.0A samples than the 1.5N and 3.0N treated samples at each salt concentration.

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