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Analysis of Structural Changes and Dye Uptake Properties of Alkali Treated and Strain Hardened Regenerated Cellulosic Yarns

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ABSTRACT

Mercerization is an important process applied to cellulosic fibers for improving the properties like dimensional stability, luster and dye uptake. Strain hardening is a technology for strengthening materials by realigning of atoms in crystal lattice and is generally used in metallurgy and is being tried on yarns. In the present study, four types of regenerated cellulose fibers namely lyocell, modal bamboo and viscose were subjected to swelling by alkali (4% NaOH) treatment and Strain hardening by stretching device with the objective of studying mechanical properties, structural properties and dye uptake properties. It is observed that tenacity was lowered below that of corresponding controls due to alkali treatment in case of all the four yarns. The strain hardening immediately after the alkali treatment enhanced strength of Bamboo and Modal up to 125% and 105% of the corresponding control yarns , whereas it was only 98% and 85% strength of corresponding untreated yarns in the case of Lyocell and Viscose. The MTC values of alkali treated – strain hardened yarns were lesser than that of control and this is indicative of increase in inter fiber cohesion. Interestingly there was a tremendous improvement in dye uptake property of all four regenerated cellulosic yarns. This paper reports the impact of alkali treatment followed by stretching on essential properties of regenerated cellulosic yarns.

Keywords: cellulosic fibers, bamboo fiber, Lyocell, Mercerization

INTRODUCTION

The generations of regenerated cellulose fibers, such as viscose, modal and lyocell fibers are among the most important fibers from the point of textile and environmental aspects due to the natural structures and properties [1]. New regenerated cellulosic fibers like lyocell are produced by a more environmentally friendly procedure where cellulose is dissolved in the organic solvent N-methyl morpholine-N- oxide, without formation of derivatives to give the special properties like high strength and low elongation compared to other regenerated cellulosic fibers [2]. Different production process and production conditions for conventional viscose, modal and new lyocell fibers cause differences in the structure of the fibers in spite of the same chemical compositions [3, 18]. One of the latest developments in new fiber research is the use of bamboo fiber in various textile products. The swelling behavior of regenerated cellulosic yarns with various chemical reagents had been the subject of research for several years. The quasi-crystallite disassociation and recrystallization in the quasi-crystalline phase, during the process of alkali treatment, led to changes of crystallinity and orientation index of Lyocell fibers [4]. The weight loss and the fibril number of the cellulosic fibers pre-treated with alkali increased with increasing the alkali concentrations [5]. The alkali pre-treatment of viscose fabrics followed by cellulose hydrolysis led to weight loss of 80% within 4 hours of treatment [19]. Fourier transform infrared spectroscopy is a successful analyzing technique used to characterize the structure of cellulose based polymers that basically consists of crystalline and amorphous cellulose. The total crystallinity index (TCI) and lateral order index (LOI) values obtained from the absorbance ratios 1420/893 and 1375/2900 cm^{1} were used in this study [6-7]. The elastic modulus of viscose and lyocell types of regenerated cellulose fiber increased with increasing plastic strain. With an increase in the elastic modulus of 47%, the strain hardening effect was more pronounced in lyocell, which shows higher crystallinity and higher orientation of cellulose chains than viscose, where an increase by 24% was observed[8]. The sodium hydroxide treatment led to a decrease in density, orientation and crystallinity of lyocell fiber with increase in sodium hydroxide concentration, a corresponding decrease in tensile strength was also observed [9-10]. The lyocell fibers consist of longer molecules, a greater degree of crystallinity. The most important factors influencing the mechanical properties of cellulosic fibers are the molecular mass (i.e., the length of the fiber-forming linear macromolecules), the degree of lateral order or crystallinity and the alignment of the macromolecules (i.e., their orientation with respect to the fiber axis) [11]. It was found that the usage of caustic-soda in pretreatment of viscose fabrics ensured considerable advantages in terms of color efficiency in dyeing with the use of lower dyestuff [20]. The highest *K/S* values were obtained for the fabrics pre-treated with 2.0–2.5 mol dm^{-3} NaOH. Cross-sectional analysis shows that below this optimum concentration the core fibers in the yarn were not dyed; at optimum concentration all fibers in yarn cross - section were homogeneously dyed [12, 13, 17]. The mechanical properties of the yarns made from stretch mercerized rovings were compared with those of yarns made of untreated fibers and slack mercerized fibers. A study on effect of various chemical treatments and strain hardening on inter fiber cohesion property of cotton yarns have been carried out and reported [14-15].A great deal of research was carried out on swelling and stretching of yarns in various media, the main objective of this study is to analyze the impact of alkali treatment followed by subsequent stretching on the regenerated cellulosic yarn characteristics and structural changes.

EXPERIMENTAL

Materials

30 Ne count, regenerated cellulosic yarns such as Viscose, Bamboo, Lyocell and Modal were used for this study. Laboratory grade Sodium hydroxide pellets, for preparing a mercerizing solution of 1 molar concentration (4%) was used. A suitable stretching device was designed with a capability of stretching 4 leas simultaneously an extent of 105 % level of stretch.

Stretching device

The stretching device depicted in *FIGURE 1* consists of two square metallic plates, containing four pairs of hooks for fixing the leas. The base plate is fixed and the movable plate slides up and down over a threaded central rod with a round handle at the top. The threaded rod is mounted in a bearing fixed at the center of the base plate. A metallic graduated scale mounted on fixed frame in between the two plates is used to apply predetermined stretch level to the leas.

The specifications of the instrument are:

Total height of instrument	100 cm
Maximum gauge length	90 cm
Top and bottom plate dimensions	20cm x18cm
Threaded rod diameter	2.54 cm.
Bush diameter	6 cm.

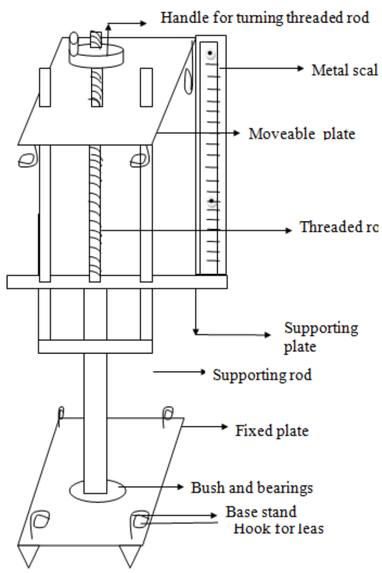

FIGURE 1. Schematic Diagram of the Stretching Device

Methods

The yarn samples (Bamboo, Viscose, Modal and Lyocell) in lea form with the standard lea loop length of 68 cm were immersed in aqueous alkali solution of 1 molar (4%) concentration with a liquor ratio of 1:20 for 5 minutes at room temperature. The swelling treatment resulted 17-18%shrinkage of yarns The shrunk yarns were subsequently stretched for 24 hours to various levels like 100%, 102%, 103% and 104% (i.e., equal and above the original lea length of 68 cm). This stretching action plays a vital role in altering the yarn properties due to phenomena called "Strain Hardening". The various stretch levels given to the regenerated cellulosic yarns are given in the Table I.

TABLE I. Levels of Stretch

Controlled Lea length in cm	Length of lea after alkali treatment cm	shrinkage after alkali treatment in %	Length of lea after stretching in cm	Length of lea after stretching in %
68	55 to 56	17 -18	68	100
68	55 to 56	17 -18	69	102
68	55 to 56	17 -18	70	103
68	55 to 56	17 -18	71	104

Tensile Testing

The alkali treated and strain hardened regenerated cellulosic yarns were tested for tenacity, elongation using Instron tester. Test conditions for Instron are gauge length: 250 mm, Strain rate: 40 mm/min, temperature: 27 degree, RH: 65%.

Minimum Twist of Cohesion measurement

An analysis of cohesion phenomena in yarns merits serious consideration as it has a direct effect on the yarn properties, particularly yarn strength. The inter-fiber cohesion in yarns was measured in terms of the minimum twist of cohesion (MTC). This is the difference between the number of turns present in a given length of yarn and the number of turns removed under a given load till it reaches the breaking point. The lesser the difference, the better is the cohesion, and vice versa [15]. Minimum Twist of Cohesion (MTC) was measured using MTC device. The device was provided with a jaw to hold the yarn and a rotating handle to remove the turns and a counter to read the number of rotations. A minimum weight (0.1gm / Tex of the sample) was hung at the bottom of the yarn to keep in taut condition. The MTC values of control, alkali treated and alkali treated cum stretched yarns were determined using this simple instrument.

Bending Rigidity (ASTM .D1388 - 08)

Bending rigidity is the resistance offered by the yarn to any bending force. Bending rigidity was determined by the loop test based on Carlene's method [16]. The mean of five tests was taken. In this method, the yarn was made in the form of a loop, and it was distorted by adding a rider. Flexural rigidity is calculated using the following formula:

Flexural Rigidity(in $g.cm^2$) = $kWL^2 \times \cos\theta / \tan\theta$

Where,

K is a constant the value of which is around 0.0047, ***W*** is weight of the rider, in gram.

L is deflection length, in cm.

θ is angle of deflection in degree.

FTIR Analysis

The structural changes were measured with a Nicolet AVATAR 320 FTIR spectrometer with CsI optics. Finely divided samples (1mg) were ground and dispersed in a KBr matrix (100mg) and a pellet was then formed by compressing the sample at 167MPa. Then each pellet was thermally treated at 40^0C for 24hr in an oven to remove the moisture. Finally, the pellets were introduced and stored in a drying device until the FTIR measurement. The spectra were measured with an average of 50 scans and a resolution of $4cm^{-1}$.

Dyeing

The control, alkali treated and alkali treated cum strain hardened regenerated cellulosic yarns were dyed using hot brand reactive dyes following usual dyeing procedure. Dyeing was carried out at 3 levels of depth of shade i.e., 0.5%, 1%, and 2%.The Dying Recipe is furnished in the *TABLE II.*

TABLE II. Dyeing Recipe

0.5% shade	**1.0% shade**	**2% shade**
M:L=1:20	M:L=1:20	M:L=1:20
NaCl=30gpl	NaCl=50gpl	NaCl=60gpl
Soda=10gpl	Soda=15gpl	Soda=20gpl
Glabber salt	Glabber salt	Glabber salt

RESULTS AND DISCUSSIONS

Minimum Twist of Cohesion Analysis

It is clearly seen from the TABLE III and FIGURE 2 that the minimum twist of cohesion (in percentage), decreased in modal, lyocell, viscose and bamboo yarns on treatment with alkali and subsequent stretching. The decrease in the minimum twist of cohesion value indicates increase in inter fiber cohesion in yarns. Inter fiber cohesion property increased in the case of all the alkali treated stretched yarns when compared to corresponding controls and 61%, 59%, 27%, and 10% respectively for Lyocell, Modal, Bamboo and Viscose. Among the four regenerated yarns, the improvement in inter fiber cohesion property is highest in the case of Modal and is sequentially followed by Lyocell, Bamboo and Viscose. The trend is shown in FIGURE 2.

TABLE III. Minimum Twist of Cohesion analysis of regenerated cellulosic yarns

Type of yarn	MTC in %			
	Bam boo	Lyocell	Viscose	Modal
Raw	47.3	52.3	32	49.5
Treated with 4% NaOH	25.2	28.1	19	30.5
Treated & Stretched at 100%	24.4	25.6	34	18.6
Treated &	25.8	29.9	38	17.6

Stretched at 102%)				
Treated & Stretched at 103%	22.9	17.3	31	17.8
Treated & Stretched at 104%	34.5	19.1	29	19.3

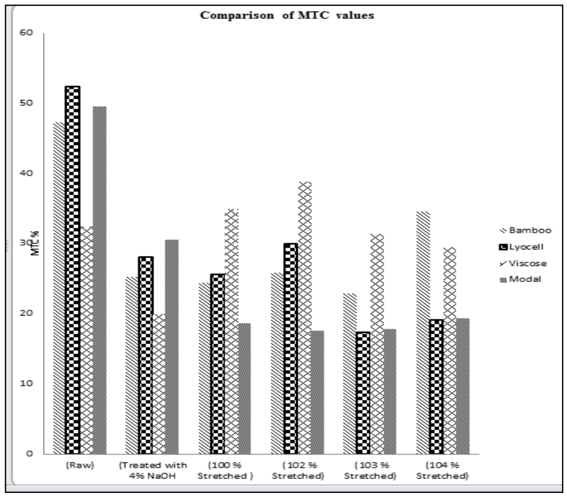

FIGURE 2. Minimum Twist of Cohesion analysis

Bending Rigidity Analysis

It is interesting to note the results from the TABLE IV and FIGURE 3 that the bending rigidity of swollen and stretched regenerated yarns became stiff as bending rigidity values were increased. Significant changes in bending property were observed in the case of the regenerated yarns like lyocell (63% rise) and viscose (77% rise). There was no impact of treatment on bamboo and modal yarns.

TABLE IV. Bending Rigidity analysis of Regenerate cellulosic yarns

Type of yarn	Bending Rigidity in g.cm^2 Bamboo	Lyocell	Viscose	Modal
Raw	1.71	1.71	1.32	1.7
Treated with 4% NaOH	1.71	2.7	1.37	1.54
Treated Stretched at 100%	1.54	1.89	1.41	1.54
Treated Stretched at 102%	1.54	2.4	1.3	1.37
Treated Stretched at 103%	1.54	1.71	1.54	1.71
Treated Stretched at 104%	1.71	2.91	1.71	1.54

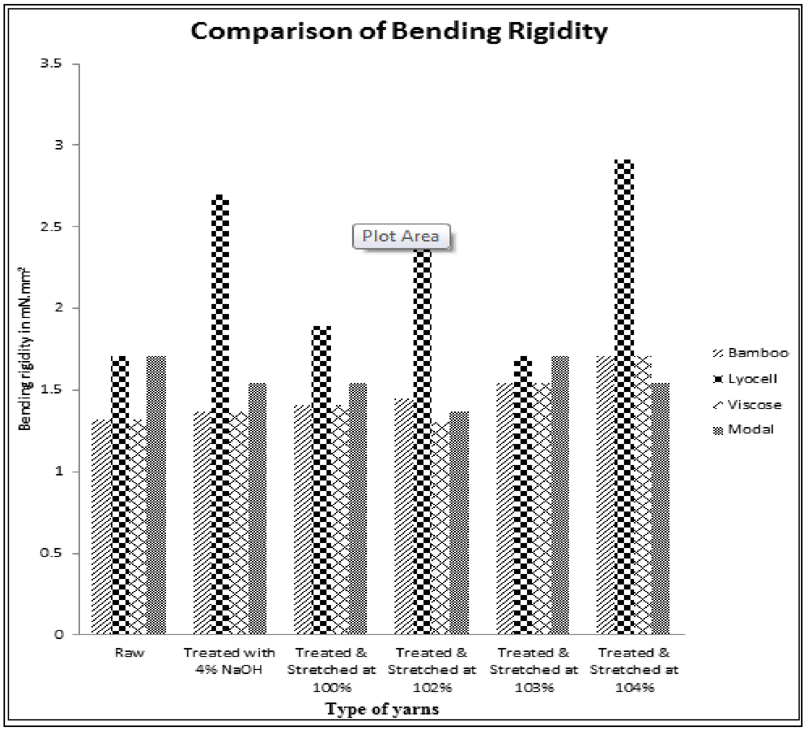

FIGURE 3. Bending Rigidity analysis of Regenerate Cellulosic yarns

Impact on Tensile strength

The tensile strengths of four regenerated cellulosic yarns before and after treatments were determined using Instron and the values are given in *TABLE V*. Among the four regenerated cellulosic yarns analyzed, the lyocell yarns exhibited highest tenacity before treatments due to structural characteristics like degree of crystallinity, molecular orientation and high molecular mass. These findings corroborated the established facts [11].

Alkali treatment on these yarns resulted in shrinkage of 17 – 18% due to lateral swelling and shrinkage of this magnitude is a good indicator of better elongation property. The alkali treatment also decreased the strength of bamboo, lyocell, viscose and modal yarns by 18%, 12%, 34% and 19%respectively, which may be due to weakened polymer chains. This corroborates the earlier findings. The alkali treated swollen yarns were neutralized and immediately subjected to stretching at various levels as described in the TABLE V using the stretching device. The strain hardening phenomenon resulted in overall increase in tensile strength of all the four regenerated yarns.

It is interesting to note that the strain hardening process has increased the strength of bamboo and modal yarns by 25% and 5% more that of controls i.e., untreated yarns' strength. Whereas in the case of lyocell and viscose, the strain hardening resulted in regain of 98% and 85% strength of control yarns respectively.

The improvement in tenacity is due to realignment of the crystalline structure during stretching. The trend followed in the improvement of strength of regenerated cellulosic yarns on stretching was Bamboo (125), modal (105%) lyocell (98%) and viscose (85%).

Among the four regenerated yarns, the improvement in tenacity is highest in the case of Lyocell and is sequentially followed by Bamboo, Modal, and Viscose. The trend is shown in FIGURE 4.

TABLE V. Mechanical properties of Regenerated cellulosic yarns

Type of yarn	Bamboo Yarns			Lyocell Yarns			Viscose Yarns			Modal Yarns		
	CT Ne	EL %	TY gm/tex	CT Ne	EL %	TY gm/tex	CT Ne	EL %	TY gm/tex	CT Ne	EL %	TY gm/tex
Raw	30	14	14.02	30	7.8	21.3	30	12	15.5	30	8.7	17.8
Treated with % NaOH	29	10	11.67	29	6.4	18.6	29	10.	10.2	28	9.5	14.28
Treated stretched at 100%	28	9	14.87	28	6.1	19.88	27	5.7	11.74	29	7.1	16.5
Treated stretched at 102%	27	8.1	14.2	27	4.0	17.6	29	8.8	11.43	27	4.6	18.2
Treated stretched at 103%	26	7.3	14.8	26	3.9	18.44	28	8.9	12.33	29	4.4	18
Treated stretched at 104%	29	7	18.8	29	5.0	19.1	26	9.1	12.5	28	4.6	18.8

CT-Count,EL-Elongation,TY-Tenacity.

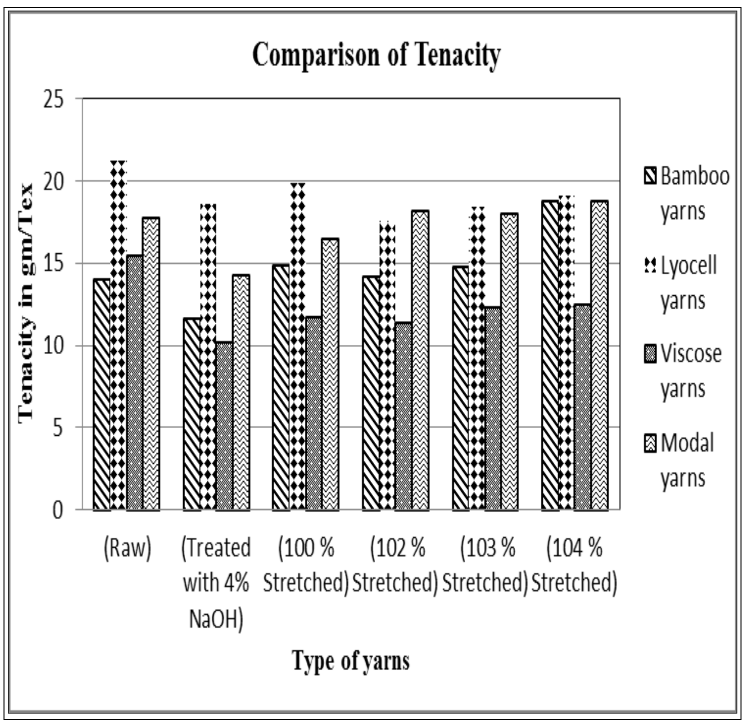

FIGURE 4. Tenacity analysis of Regenerated cellulosic yarn

Colorimetric Analysis

The dye uptake property of control, alkali treated and alkali treated cum stretched was measured using Xrite color matching software. Using Kubelka Munk function K/S, the color strength of each samples were determined and the values are shown in TABLE VI The results elucidated that there was tremendous improvement in dye uptake properties of all the regenerated cellulosic yarns subjected to alkali treated and stretching treatments. The trends in dye uptake properties of the yarns illustrated in the FIGURE 5 as highest in case of Viscose (201% of control), and sequentially followed by Modal (166% of control), Bamboo (150

% of control) and Lyocell (125% of control). Hence the alkali treatment and alkali treatment cum stretching had a strong impact on yarns' absorption property.

TABLE VI. Dye uptake properties of Regenerated cellulosic yarns

Type of yarn	K/s Values at 0.5%, 1% and 2% Depth of shades											
	Bamboo Yarns			Lyocell Yarns			Viscose Yarns			Modal Yarns		
	0.5%	**1%**	**2%**	**0.5%**	**1%**	**2%**	**0.5%**	**1%**	**2 %**	**0.5%**	**1%**	**2%**
Raw	4.01	10.2	20	7.1	13.5	25	4	11.9	18	2.6	5.8	10.3
Treated with % NaOH	6.05	14.5	24	8.6	14.3	25	6	15.2	24	5.0	10.	19.5
Treated stretched at 100%	7.24	13.7	25	9.5	15.0	21	5	12	25	3.3	8.5	16.6
Treated stretched at 102%	4.28	11.7	21	8.4	12.5	23	5	13.5	25	4.7	9.5	21.3
Treated stretched at 103%	6.53	10.0	24	6.5	13.9	24	7	14.2	30	3.4	9.7	21.1
Treated stretched at 104%	6.89	14.1	24	7.7	12.3	29	4	12.9	30	3.6	9.9	20.1

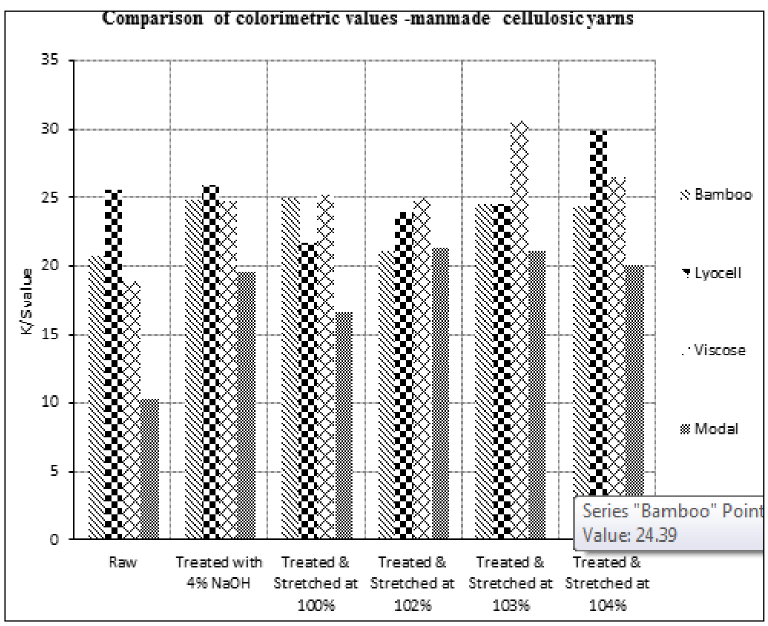

FIGURE 5. Colorimetric analysis of Regenerated cellulosic yarns

Crystallinity analysis

The crystallinity analysis by FTIR is based on the crystallinity indices proposed by Nelson and O' connor [20], which is applied to cellulose, based polymers composed of either cellulose I or II or of mixture of both components. The crystallinity study focused on determining the spectral ratios 1420/893cm^{-1} (Lateral order index, LOI) and 1375/2902cm^{-1} (Total crystallinity index, TCI). LOI increase with the decrease in degree of crystallinity, TCI is proportional to the degree of crystallinity of the cellulose samples. The results obtained shown in TABLE VII indicated that lyocell fibers exhibit present a higher crystallinity than the other regenerated cellulosic fibers. Also the swelling and stretching treatment given to the regenerated cellulosic fibers had decreased the degree of crystallinity.

Spectral behavior of regenerated cellulosic fibers

The infrared spectra characteristics of control regenerated yarns (bamboo, lyocell, viscose and modal), alkali treated, alkali treated and subsequently stretched are shown in FIGURE (6, 7, 8 and 9) respectively. Straining a material beyond its elastic limit causes weakening of the bonds between the atoms in crystal lattice this leads to realignment / dislocations of atoms in crystalline structure and thus an isomorph is created. The spectra shown in FIGURE 6 (Bamboo) FIGURE 7 (Lyocell) FIGURE 8 (Viscose) and FIGURE 9 (Modal) depict the main infrared spectral differences.

TABLE VII. Lateral order index and Total crystallinity index

Substrate	TCI 1375/2900 cm^{-1}	LOI 1420/893 cm-1
Controlled Bamboo yarn	0.45	0.428
Bamboo -Treated with 4% NaOH	0.12	0.95
Bamboo -Treated & Stretched at 104%	0.66	0.28
Controlled Lyocell	0.75	0.233
Lyocell-Treated with 4% NaOH	0.71	0.218
Lyocell-Treated & Stretched at 104%	0.67	0.25
Controlled Viscose	0.84	0.23
Viscose-Treated with 4% NaOH	0.56	0.26
Viscose-Treated & Stretched at 104%	0.7	0.24
M1 - controlled Modal	0.58	0.33
Modal -Treated with 4% NaOH	0.75	0.25
Modal -Treated & Stretched at 104%	0.72	0.23

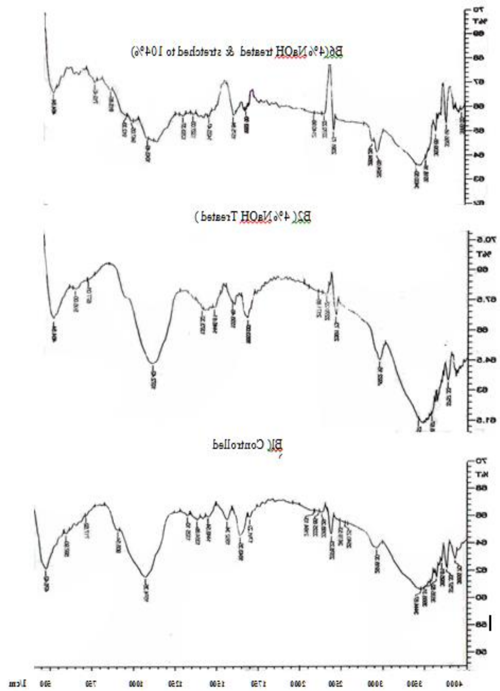

FIGURE 6. FTIR analysis of Bamboo yarns

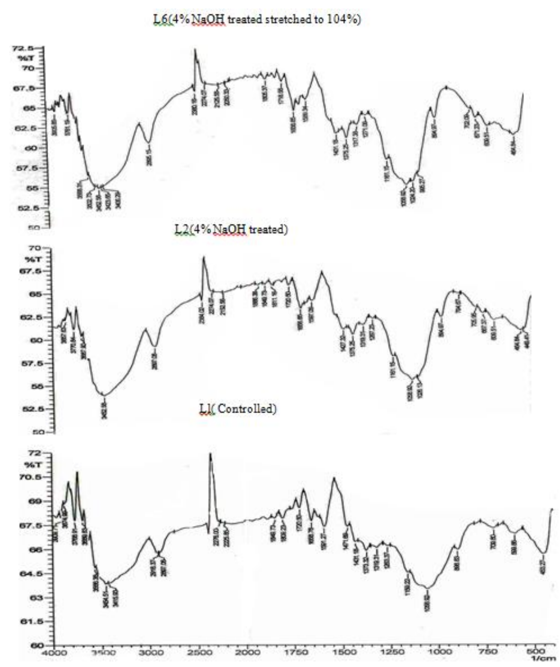

FIGURE 7. FTIR analysis of Lyocell yarns

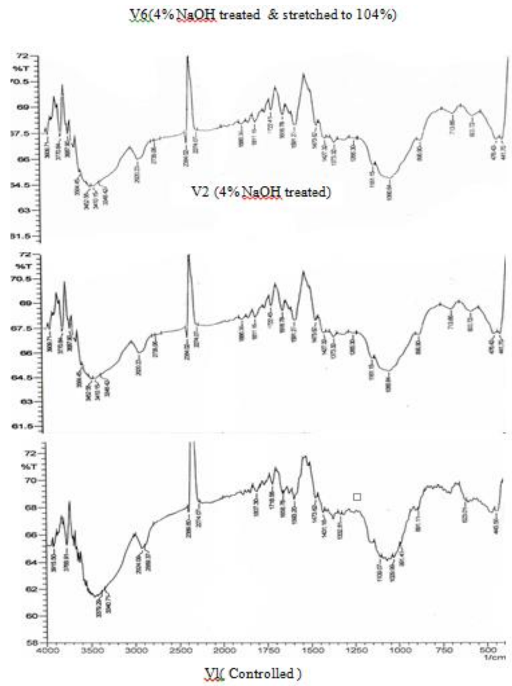

FIGURE 8. FTIR analysis of Viscose yarns

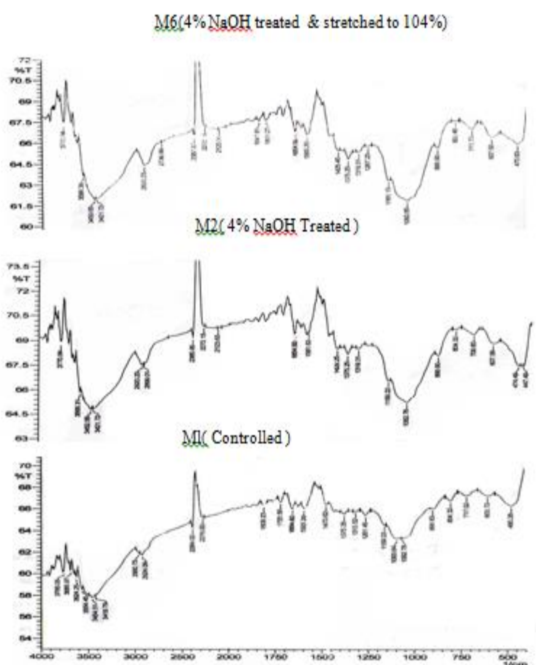

FIGURE 9. FTIR analysis of Modal yarns

CONCLUSIONS

A comparative study was made on the properties of alkali treated and stretched regenerated cellulosic (viscose, modal, lyocell and bamboo) yarns. After the alkali treatment the shrinkage percentage of the yarns were found to be the 17 to 18%. There was an improvement in inter fiber cohesion property on swelling and stretching of regenerated cellulosic yarns like lyocell, modal, viscose and bamboo. The tenacity was decreased for all the yarns following the treatment with alkali. The tenacity was improved further on stretching. It is elucidated from K/S values, the dye uptake shows a significant improvement in all the cases following treatment with alkali and stretching. The swelling and stretching treatment significantly improved mechanical and dye uptake properties of regenerated cellulosic yarns.

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