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STRUCTURAL CHARACTERISTICS OF MERCERIZED ENZYME SCOURED COTTON – INFLUENCE OF THE TREATMENT SEQUENCE

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The surface, structure, and accessibility of scoured-mercerized and mercerized-scoured cotton yarns using acid and alkaline pectinases have been studied through surface free energy, dyeing with appropriate dyes for non-cellulosic components, X-ray diffraction and infrared spectroscopy. The accessibility was also examined in terms of monolayer capacity, moisture regain, and water retention values. It was observed that scoured-mercerized cotton yarns had higher quantity of removed non-cellulosic components, higher values of polar and total surface free energy components, lower crystallinity, higher monolayer capacity, higher moisture regains, as well as higher water retention values, compared to the mercerized-scoured ones. Mercerized acid pectinase scoured cotton had small pores the size of water molecules. The sequence of the treatment steps (scouring-mercerization or mercerization-scouring) had a significant influence on integral crystallinity, monolayer capacity, and moisture regains.

Keywords: cotton, accessibility, mercerization, pectinases, scouring, treatment sequence

INTRODUCTION

The treatment of cotton yarns includes singeing to remove protruding fibers; mercerization to give better dimensional stability, increased luster, increased dye and chemical finish uptake; scouring to remove non-cellulosic impurities; oxidative bleaching to destroy natural coloring matter, as well as dyeing.[1]

Mercerization also changes the fine structure and morphology of cotton. In general, crystallinity and crystallite size are decreased, while the orientation of the cellulose chains with respect to the fiber axis is improved. The cellulose I crystal lattice is more or less entirely converted to the cellulose II form during mercerization. It depends on the treatment temperature and concentration of sodium hydroxide as well as on the tension applied.[2] If tension is applied during the process of mercerization, conversion to cellulose II is incomplete.[3]

Mercerization of yarn is usually done on dry raw or wet scoured yarns.[1]

The common industrial process for removing non-cellulosic impurities, located mainly in the cuticle and primary layer, is carried out by treating the cotton with boiling sodium hydroxide solution in the presence of chelating agents and surfactants.[4] Scoured cotton has improved wettability, while its cuticle and non-cellulosic components are almost completely removed.

Several works have been carried out to replace conventional alkaline scouring with milder enzymatic scouring processes using different enzymes, such as cellulases, pectinases, lipases, proteases, and their mixtures. Pectinases appear to be the most suitable for this purpose.[5-14]

Although there is a considerable interest in the enzymatic scouring on cotton, little attention has been paid to how enzymatic scouring, both before and after mercerization, influences the structure of cotton fiber. In this work, an attempt has been made to examine the effects of mercerization, type of scouring and treatment sequence (scouring-mercerization or mercerization-scouring), on the structure and accessibility of cotton fiber.

EXPERIMENTAL

Materials

Plied ring-worsted cotton yarn with a linear density of 30×2 tex and spun with 330 twists/m was used.

BioPrep 3000L (Novozymes), an alkaline pectinase (EC 4.2.2.2) produced by the submerged fermentation of a genetically modified bacillus microorganism with

3000 APSU/g cotton and pectate lyase activity, as well as NS 29048 (Novozymes), an acidic polygalacturonase pectinase, were used for enzymatic scouring.

Methods

Scouring-mercerization treatment of cotton yarns

Hanks of raw cotton yarns were scoured with sodium hydroxide or with alkaline or acid pectinase in an Ahiba Turbomat TM-6 apparatus for laboratory dyeing. A part of the cotton yarn hanks was subjected to alkaline or enzymatic scouring, and then was centrifuged and wet mercerized. After mercerization, the yarns were neutralized, rinsed and dried at 80 °C.

Mercerization-scouring treatment of cotton yarns

The other part of the raw cotton yarns was dry mercerized, neutralized, rinsed, dried at 80 °C, differently scoured, rinsed and dried again at 80 °C.

Mercerization was done on Jäegli hank mercerization equipment by rolling the hanks in 23.5% NaOH solution and 1 g/dm^3 Subitol MEZ-N (CHT-Germany) wetting agent at 18 °C. The hanks were then extended to the original length by applying tension, rinsed with hot (80 °C) and cold (18 °C) water for 1 min under tension, neutralized and rinsed again.

Alkaline and acid pectinase scouring was done by procedures previously developed and described in several papers.[10,11]

Alkaline pectinase scouring was done with 0.666 g BioPrep 3000L per kg material, 0.15 g/dm^3 Na_3PO_4 (pH 9), 1 g/dm^3 nonionic surfactant Kemonecer NI (Kemo-Croatia) as wetting agent at 55 °C for 30 min at a liquor ratio (LR) of 50:1. After that, 0.4 g/dm^3 EDTA was added to the scouring bath and the temperature was raised to 90 °C for 15 min to stop the enzyme activity. Yarns were rinsed at 90 °C for 10 min, at 70 °C for 10 min and once with cold water.[10]

Acid pectinase scouring was done with 0.625 g NS 29048 per kg material, in acetate buffer containing 0.5 g/dm^3 CH_3COOH and 0.5 g/dm^3 CH_3COONa (pH 4), 1 g/dm^3 Kemonecer NI at 45 °C for 30 min at LR 50:1. After that, 0.8 g/dm^3 EDTA was added and the temperature was raised to 90 °C for 15 min to stop the enzyme activity. Yarns were rinsed at 90 °C for 10 min, at 70 °C for 10 min and once with cold water.[11]

Conventional alkaline scouring was done by the procedure described previously.[10,11]

The sample codes of the obtained yarns are given in Table 1.

Testing and analysis

The CIE degree of whiteness was measured on a Datacolor Spectraflesh SF 600+ reflection spectrophotometer (D65 light source, 10° observer) according to AATCC Evaluation Procedure 6.[15]

Yarn wettability was determined by thin-layer wicking experiments. The rate of liquid penetration (wicking) into a porous solid can be described by the general form of the Washburn equation[16]:

$$x^2 = \frac{R\gamma_L \cos\theta}{2\eta} t \qquad (1)$$

where x is the distance of liquid penetration, R is the apparent (effective) capillary radius of the porous solid, t is the penetration time for the distance x, γ_L is the surface tension of the liquid, θ is the dynamic contact angle of the liquid that appears at the penetration front, and η is the liquid viscosity (Table 2).

Table 1
Yarn sample codes

Codes	Samples
R	Raw
SA	Scoured with NaOH
SB	Scoured with BioPrep 3000L
SN	Scoured with NS 29048
SAM	Scoured with NaOH, mercerized
SBM	Scoured with BioPrep 3000L, mercerized
SNM	Scoured with NS 29048, mercerized
RM	Raw, mercerized
MSA	Mercerized, scoured with NaOH
MSB	Mercerized, scoured with BioPrep 3000L
MSN	Mercerized, scoured with NS 29048

Table 2
Surface tension, including components and viscosities of the liquids studied at 20 °C

Liquid	Liquid abbreviation	γ_L (mJm^{-2})	γ_L^d (mJm^{-2})	γ_L^p (mJm^{-2})	η (mPas)
n-heptane	C7	20.4	20.4	0	0.41
Diiodomethane	DIM	50.8	50.8	0	2.80
Water	W	72.8	21.8	51.0	1.00
Formamide	FA	58.0	39.0	19.0	4.55

The dispersion, polar, and total surface energy components of the yarns were measured and determined as it was previously described.[17]

To detect the wax quantities of cotton, dyeing in 0.4% Oil Red (C.I. 26125) was performed, as described by Akin *et al.*[18,19]

To detect pectin and protein, cationic and acid dyes were used, respectively.[20] Lightness values of dyed mercerized-scoured yarns were measured on a Datacolor Spectraflesh SF 600+ reflection spectrophotometer.

Wide-angle X-ray scattering (WAXS) data were collected in the range 8–30° 2θ on a Philips PW 1710 diffractometer equipped with a curved graphite monochromator (working conditions: $U = 40$ kV, $I = 30$ mA), using Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å) and the step-scan mode. Scan time and step length were 5 s and 0.05° 2θ, respectively. Before data collection, the fibres ($m = 0.2$ g) were cut in 1-2 mm long pieces and slightly pressed (2 MPa) in about 2 mm thick pellets of 20 mm diameter.

Integral crystallinity was determined[21] after a full WAXS profile fitting in the 8-28° 2θ region. The patterns were modeled as a series of Voigt peaks located close to the expected diffraction maxima plus a very wide peak representing the amorphous background. The fraction of an amorphous phase was estimated as the ratio of the amorphous integrated diffraction intensity (I_{am}) to the total integrated diffraction intensity (I_{tot}), as shown below:

$$\text{Integral crystallinity} = 100\times(1 - I_{\mathrm{am}}/I_{\mathrm{tot}}) \qquad (2)$$

Structural changes in the treated cotton yarns were measured by an FTIR-ATR apparatus Spectrum GX 69876 (Perkin Elmer) in the scanning range from 4000 cm^{-1} to 500 and with a resolution of 4 cm^{-1}. All specimens were scanned three times, and 16 scans were collected from each run. The infrared crystallinity (lateral order index) and conversion of cellulose I to cellulose II were calculated according to the following ratios: a1420/a895, a895/a1420, a895/a1156 and a895/a1025.[22-25]

Monolayer capacity (MLC)[26] was determined by dyeing cotton yarns for 24 h at 80 °C at a liquor-to-material ratio of 125:1 and various dye concentrations (ranging from 0.1 to 0.9 g/dm^3) of Congo Red (Direct Red 28; C.I. 22120) with a molar mass of 696.67 g/mol and 2 g/dm^3 sodium chloride. The dye bath liquor was allowed to cool to 21°C and was diluted for spectrophotometer readings. The amount (in mmol dye/kg fiber) of the dye adsorbed by the fibre was determined according to the differences of concentration of the dye solution before and after dyeing. The Langmuir equation was used to calculate MLC of the cotton fibre. For all adsorption isotherms of Congo Red, the plot of dye concentration in the bath at equilibrium and the ratio of equilibrium concentration in the bath and in the fibre was found to be a straight line. MLC was calculated from the reciprocal value of the tangent of the angle and is given in mmol/kg fibre.

Moisture regain (MR) was determined keeping the cotton yarns in an atmosphere of 65% RH at 21 °C to constant weight. After that, the samples were dried for 4 h at 105°C and reweighed. MR content was calculated using the following relationship:

$$MR(\%) = \frac{m_1 - m_2}{m_1}\cdot 100 \qquad (3)$$

where m_1 is the weight of yarns conditioned in the atmosphere of 65% RH and 21°C; and m_2, the weight of dried yarns.

Water retention values (WRV) were determined on dry processed samples, which were allowed to swell in water for 2 h at room temperature before centrifugation for 20 min at 3000 rpm. After centrifugation, the samples were transferred into tarred weighing bottles, weighed before drying in an air oven for 4 h at 105 °C and reweighed. Water retention value was calculated using the following equation:

$$WRV(\%) = \frac{m_2 - m_1}{m_1}\cdot 100 \qquad (4)$$

where m_2 is the weight of centrifuged wet yarns; and m_1, the weight of dried yarns.

All investigated parameters were analyzed by main effects analysis of variance (ANOVA), considering the type of scouring (variable A) and the temperature of drying after mercerizing (variable B), using STATISTICA 6. ANOVA gives information about the influence of variables on the response of the investigated parameters,[27] and is based on the Fisher (F) test. Evaluated F values must be higher than the tabulated ones. The tabulated F test value for a significance level of $\alpha = 0.05$, for degrees of freedom $\nu_1=2$ and $\nu_2=2$, and type of scouring (variable A) is F_A (2, 2) = 19.00. The value for different temperatures of drying after mercerizing (variable B) and for degrees of freedom $\nu_1=1$ and $\nu_2=2$ is F_B (1, 2) = 18.51. The coefficients of correlation between the investigated parameters were also calculated.[27]

RESULTS AND DISCUSION

CIE whiteness degree and lightness of cuticle non-cellulosic components stained with appropriate dyes

Different types of scouring and the treatment sequence, such as scouring-mercerization or mercerization-scouring, altered the quantities of the non-cellulosic components remaining on the treated cotton samples, thus giving different whiteness degrees (Table 3). The analysis of the whiteness degree of the scoured, scoured-mercerized and mercerized-scoured yarns revealed that the treatment sequence had a major influence on the elimination of non-cellulosic components, the trend of elimination following the order: scouring, mercerization-scouring and scouring-mercerization. The type of scouring also influenced the whiteness degree. The highest CIE whiteness was noticed on alkaline scoured, followed by alkaline pectinase and acid pectinase scoured cotton yarns. This trend was observed for different treatment sequences. During milder enzymatic scouring, part of the non-cellulosic and colored amino components remained on the cotton surface. It explains why SB and SN had lower whiteness than SA.[5] In addition, SAM, SBM and SNM had 8.78%, 5.17% and 4.85%, respectively, higher CIE whiteness, while MSA, MSB and MSN had 2.71%, 2.26% and 3.73%, respectively, higher CIE whiteness, compared to their counterpart only scoured yarns.

The type of scouring had a significant influence on CIE whiteness, while the treatment sequence did not appear to have a notable effect on it (Table 4).

After the treatments, different quantities of non-cellulosic residues gave different color on the treated cotton samples, when they were stained with appropriate dyes.[18] So, using this technique, the changes in the cuticle can be detected visually. Himmelsbach S. D. *et al.* demonstrated that this method is also suitable for determining the structure and composition of seed coat fragments.[19] Canal J. M. *et al.* studied the efficiency of enzymatic scouring by dyeing scoured cotton with dyes for non-cellulosic components of cotton surface.[20]

Differently treated yarns were dyed with Oil Red (OR) to determine the waxes, with methylene blue (MB) for pectins, and with bemacid blue (BB) for proteins. The lightness results measured on the dyed yarns are given in Table 3. Comparing L^*_{OR} values of scoured, scoured-mercerized and mercerized-scoured cotton, it is evident that the alkaline scoured cotton achieved the highest value, followed by alkaline pectinase and acid pectinase scoured cotton. Scoured-mercerized cotton yarns had the highest L* values after being stained with Oil Red, methylene blue as well as bemacid blue, indicating the highest removal of non-cellulosic components. The L^*_{OR}, L^*_{MB} and L^*_{BB} values confirmed previously reported results for whiteness and provided high positive coefficients of correlation (above 0.6) among them and with CIE whiteness.

Wettability and surface free energy

The results presented in Table 5 indicate that all scouring processes increased the wettability of cotton yarns, compared with the raw sample. The latter was highly hydrophobic, which prevented DIM, W, and FA from penetrating into its porous structure. Mercerization of the raw cotton yarn (sample RM) did not change its wettability significantly. Although non-cellulosic components were partly removed from the cotton surface during the mercerization (80% higher degree of whiteness on mercerized cotton, compared to raw cotton), this process alone did not improve the wettability of cotton. For this reason, scouring of cotton should be carried out. The results presented in Table 6 also reveal that the sequence of the treatment process has an influence on the surface free energy of the cotton fibers. As expected, the value of the polar component, χ_s^p, was additionally affected by the liquid combination.[17] The results of Table 6 indicate that the polar component of the differently treated yarns depended on the type of scouring applied and on the scouring/mercerization sequence, but the influence was not significant (Table 4). The type of scouring and treatment sequence increased the χ_s^{tot} values in the following order: MSN, SN, SB, SBM, SNM, MSB, SA, MSA and SAM.

Table 3

CIE whiteness and L* values of raw, scoured, scoured-mercerized and mercerized-scoured yarns dyed with Oil Red (L^*_{OR}), methylene blue (L^*_{MB}) and bemacid blue (L^*_{BB})

Samples	CIE whiteness	L^*_{OR}	L^*_{MB}	L^*_{BB}
R	12.10	44.26	50.36	75.54
SA	47.80	56.47	66.51	77.22
SB	30.90	52.24	60.58	74.40
SN	26.80	51.83	58.19	74.41
SAM	52.00	64.99	68.55	77.62
SBM	32.50	60.27	66.12	75.73
SNM	28.10	56.53	62.62	75.69
RM	21.80	54.36	55.09	75.93
MSA	49.10	61.28	67.22	78.74
MSB	31.60	55.21	60.40	74.15
MSN	27.80	50.23	57.17	74.74

Table 4

Fisher (F) test values and p-values for significance of the type of scouring (Variable A, F_A) and of the scouring/mercerization sequence (Variable B, F_B) for all investigated properties

Factors	CIE whiteness	Θ (^{O})	γ_s^d	γ_s^p	γ_s^{tot}	L^*_{OR}	L^*_{MB}	L^*_{BB}	IC	895/1420	895/1156	895/1025	MLC	MR	WRV	WRV/MLC
F_A	**312.9**[a]	**52.1**	2.8	10.6	10.3	**56.9**	10.6	6.4	1.83	6.76	10.21	1.53	**132.0**	**35.2**	0.86	1.47
p_A	**0.003**	**0.02**	0.3	0.08	0.09	**0.02**	0.08	0.13	0.35	0.13	0.09	0.39	**0.007**	**0.027**	0.54	0.40
F_B	3.0	3.42	3.1	3.2	2.2	**45.1**	8.6	0.33	**92.9**	**23.0**	7.53	0.5	**1887.2**	**313.8**	0.45	0.70
p_B	0.224	0.21	0.2	0.2	0.27	**0.02**	0.09	0.62	**0.01**	**0.04**	0.11	0.55	**0.0005**	**0.003**	0.57	0.49

[a] F values and p-values set in bold indicate significant influence of factors A and B on the measured properties

Table 5
Liquid penetration rate (x^2/t), capillary radius, R, and contact angles of different liquids on raw, scoured, scoured-mercerized and mercerized-scoured yarns

Sample	x^2/t (cm^{2}s^{-1})				R	θ (^{o})		
	C7	DIM	W	FA	(μm)	DIM	W	FA
R	1.730	/[a]	/	/	6.96	-[b]	-	-
SA	2.307	0.056	0.279	0.354	9.27	86.2	85.26	53.2
SB	2.107	0.037	0.092	0.232	8.47	87.2	88.28	64.5
SN	2.027	0.019	0.077	0.208	8.15	88.6	88.52	66.4
SAM	1.622	0.029	0.383	0.369	6.52	87.18	80.71	27.38
SBM	1.913	0.021	0.099	0.246	7.69	88.27	87.96	59.87
SNM	1.818	0.0214	0.110	0.248	7.31	88.15	87.63	57.84
RM	1.875	/	/	/	7.54	-	-	-
MSA	1.883	0.063	0.449	0.374	7.57	84.7	80.61	39.2
MSB	1.914	0.043	0.102	0.264	7.69	86.4	87.90	57.3
MSN	1.935	0.021	0.025	0.032	7.78	88.3	89.49	86.3

[a] Liquid depression; [b] Calculation could not be made

These results correlate with the hydrophilicity of the yarns, (coefficient of correlation γ_s^{tot} - θ is -0.94). While the dispersive components, γ_s^d (which fell in the range from 13.33 to 15.15) seemed to be slightly affected, the polar components were more affected by the treatment processes (Table 6). This is reasonable, since the removal of non-cellulosic components during the scouring processes results in an increase of the polar hydroxyl groups on the cotton surface.

Supramolecular structure and accessibility of differently treated cotton

Mercerization has an influence on the fine structure, degree of crystallinity, conversion of cellulose I to cellulose II, as well as on the accessibility of cotton.

The IC calculated for R cotton yarns is 70% (Table 7). The IC values of scoured-mercerized yarns are between 60.8 and 62.8%, depending on the type of scouring, while those of the mercerized-scoured ones range between 66.4 and 66.7%. The results from Table 4 show that the order in which the scouring step is applied has a significant influence on the IC, while the type of scouring does not. SAM has 8.4%, SBM 7.1% and SNM 5.8% lower IC than the corresponding mercerized-scoured yarns. The differences of IC within the group of scoured-mercerized yarns are in the range of 2%, while in the group of mercerized-scoured ones within 0.3%. After scouring, cuticle is almost completely removed. Mercerization of the scoured cotton yarns allowed easier penetration of the strong alkali solution and therefore led to higher conversion of cellulose I to cellulose II, resulting in cotton with lower IC. Rigorous conditions during alkaline scouring and additional mercerization produced cotton with lower IC, compared to those of SBM and SNM. The differences of IC on mercerized-scoured yarns are negligible because mercerizing is the process that changes the IC, so additional scouring after mercerizing did not introduce any significant changes.

Infrared spectroscopy was used to characterize the fine structure, degree of crystallinity, conversion of cellulose I to cellulose II, as well as the degree of mercerization of the samples. O'Connor *et al.* defined the index of crystallinity as the a1372cm^{-1}/a2900cm^{-1} ratio.[22] Hurtubise and Krassig designated as the lateral order index (LOI) what was earlier defined as index of crystallinity by O'Connor.[23] Some other ratios that determine the conversion of cellulose I to cellulose II are a895cm^{-1}/a1156cm^{-1}, a895cm^{-1}/a1025cm^{-1} and a895cm^{-1}/a1420cm^{-1} (index of mercerization, MI).[24,25] In our research, we used several ratios for determining the structural changes of cotton, the conversion of cellulose I to cellulose II, as well as the degree of mercerization. The results are given in Table 7. Higher values of the infrared ratios for the scoured-mercerized yarns indicated a higher degree of mercerization, which confirmed the previously presented discussion regarding the IC values determined by x-ray diffraction. All infrared ratios have high positive correlations among them (above 0.96), and could be used to determine the degree of mercerization.

Mercerized cotton has a decreased IC and an altered porous and void system. The porous and void system of the fiber can be determined by nitrogen sorption and mercury porosimetry, usually performed on dry, non-swollen materials.[26] Cellulosic fibers are typically processed in a wet state, resulting in a swollen pore structure, which is far more accessible to reagents and, in general, differs considerably from that of the dry state. Hence, the characterization of the void system of water-swollen substrates is far more relevant. Many researchers have focused on solute exclusion techniques developed to assess the cellulose pore size distribution.[28,29] Surface area determinations are based on sorption data using water as a sensor or larger molecules, such as direct dyes, which also physically adsorb, but do not chemically react with the substrate.

Table 6
Values of surface free energy, γ_s^{tot}, its dispersion, γ_s^d, and polar, γ_s^p, components on raw, scoured, scoured-mercerized and mercerized-scoured yarns

Sample	Liquid combination	γ_s^d (mJm^{-2})	γ_s^d (average) (mJm^{-2})	γ_s^p (mJm^{-2})	γ_s^p (average) (mJm^{-2})	γ_s^{tot} (mJm^{-2})	γ_s^{tot} (average) (mJm^{-2})
SA	DIM, W	14.44	14.44	9.18	18.08	23.62	32.52
	DIM, FA	14.44		26.98		41.42	
SB	DIM, W	13.97	13.97	7.87	12.59	21.84	26.56
	DIM, FA	13.97		17.32		31.29	
SN	DIM, W	13.33	13.33	8.09	12.39	21.41	25.72
	DIM, FA	13.33		16.70		30.02	
SAM	DIM, W	13.98	13.98	12.08	31.98	26.06	45.96
	DIM, FA	13.98		51.89		65.87	
SBM	DIM, W	13.48	13.48	8.28	15.33	21.76	28.8
	DIM, FA	13.48		22.39		35.87	
SNM	DIM, W	13.53	13.53	8.43	16.34	21.96	29.87
	DIM, FA	13.53		24.25		37.78	
MSA	DIM, W	15.15	15.15	11.45	25.14	26.61	40.30
	DIM, FA	15.15		38.83		53.99	
MSB	DIM, W	14.34	14.34	7.88	15.56	22.23	29.91
	DIM, FA	14.34		23.24		37.59	
MSN	DIM, W	13.46	13.46	7.52	5.42	20.99	18.89
	DIM, FA	13.46		3.33		16.80	

Table 7
Integral crystallinity, FTIR/ATR absorbance ratios, monolayer capacity, moisture regain, water retention values and WRV/MLC ratio of raw, scoured, scoured-mercerized and mercerized-soured yarns

Samples	IC (%)	MI a895/a1420	a895/ a1156	a895/ a1025	MLC (mmol dye/kg fiber)	MR (%)	WRV (%)	WRV/MLC
R	70.00	0.66	0.6	0.146	-	-	-	-
SA	-	-	-	-	43.60	5.77	32.60	0.75
SB	-	-	-	-	40.59	5.43	27.63	0.68
SN	-	-	-	-	42.18	5.41	23.28	0.55
SAM	60.80	2.96	0.982	0.205	53.96	7.17	36.82	0.68
SBM	61.80	3.07	1.000	0.219	55.68	7.02	33.51	0.60
SNM	62.80	2.56	0.964	0.209	56.04	6.94	32.48	0.58
RM	66.40	-	-	-	-	-	-	-
MSA	66.40	2.55	0.977	0.210	48.68	6.74	33.26	0.68
MSB	66.50	2.48	0.974	0.211	50.47	6.52	29.36	0.59
MSN	66.70	2.27	0.941	0.203	51.22	6.42	35.54	0.69

The Langmuir isotherm has been used to calculate the internally available surface area for the respective sensor molecules.[2,26,30]

In the present study, MLC was calculated from the adsorption isotherms of Congo Red on differently treated cotton and the results are given in Table 7. The type of scouring and the sequence of the treatment have a significant influence on the MLC (Table 4). An increase of the MLC is more evident on the scoured-mercerized yarns than on the mercerized-scoured ones. This can be explained by the lower IC of the scoured-mercerized cotton yarns, compared to the mercerized-scoured ones, and by the higher degree of mercerization confirmed earlier in this study by FTIR-ATR spectroscopy. SAM, SBM and SNM had 24%, 37% and 34%, respectively, higher MLC than those of the corresponding scoured yarns. On the other hand, MSA, MSB and MSN had 12%, 24% and 21%, respectively, higher MLC than those of the scoured samples. Part of the amorphous cellulose was destroyed during alkaline scouring on mercerized yarns under alkaline conditions (pH12), decreasing the internal specific surface of the fiber. Alkaline pectinase digested only pectin, removing part of the cuticle layer without reacting with cellulose. So, the porous system and the internal specific surface of the fiber were not altered. Acid pectinase (pH 4) also removed part of the cuticle layer, but as the digestion was done in an acid medium (pH 4), part of the cellulose on the crystallite surface was hydrolyzed, leaving more space for the absorption of direct dyes, and thus increasing the MLC. Therefore, SBM had 3.1% and SNM 3.8% higher MLC than that of SAM. Similar results were obtained on mercerized-scoured yarns. MSB had 3.7% and MSN 5.2% higher MLC than that of MSA.

Water vapor is absorbed into the primary and secondary cellulosic layers. The cotton yarns free from non-cellulosic components have a higher MR than the cotton with non-cellulosic components. The MR is the highest on the alkaline scoured cotton, due to the completely removed non-cellulosic components, decreasing for the alkaline pectinase and acid pectinase scoured yarns. This tendency is the same for scoured-mercerized and mercerized-scoured yarns. The type of scouring and the treatment sequence have a significant influence on the MR (Table 4). The scoured-mercerized yarns have higher MR than mercerized-scoured ones, due to the more completely removed cuticle and lower IC. SAM , SBM and SNM have 24%, 29% and 28%, respectively, higher MR than the corresponding scoured yarns, while the MR of MSA, MSB and MSN are higher by 17%, 20% and 19%, respectively. Comparing enzymatic scoured with alkaline scoured yarns, the MR of SBM is by 2.1% and that of SNM by 3.2% lower than that of SAM. Similar results with bigger differences were received for mercerized-scoured yarns. MSB has a 3.3% and MSN a 4.7% lower MR than that of MSA.

WRV represents the saturation point defined as the total amount of water present within the cell walls, expressed as the ratio of water to solid.[26] It provides information about the total amount of water that is contained in the non-crystalline regions of fibers, including voids and capillaries. Therefore, the saturation point is the point of the retention of all the water in the cotton amorphous region, including voids, pores and capillaries, and could be used for measuring non-crystalline cellulose before and after mercerization.

The highest WRV value for scoured-mercerized cotton was remarked for SAM, followed by SBM and SNM. On the other hand, the highest WRV for mercerized-scoured cotton was noted for MSN, followed by MSA and MSB (Table 7). It is evident that scoured-mercerized yarns have higher WRV than mercerized-scoured yarns, with the exception of SNM, compared to the MSN sample. Acid pectinase scoured and mercerized cotton yarn (scouring in acid medium) has more pores, which can absorb water molecules. MSN has 6.8% higher WRV than MSA, and a 21.0% higher value than MSB.

Inglesby K. M. and Zeronian H. S. explored the specific internal surface of differently treated cotton with water and dye molecules as sensors.[26] The specific internal surface ratio of water to dye could be informative about the size of the pores. If the water/dye specific internal surface ratio is smaller, there are more pores of the dye molecule size.[26] The WRV/MLC can be also a measure to determine the quantity of larger or smaller pores in the fiber. Higher WRV/MLC ratio means that cotton contains smaller pores, of the water molecule size, and lower WRV/MLC stands for larger pores, the size of Congo Red molecule.

The results from Table 7 indicate that SAM, SBM, MSA and MSB have lower WRV/MLC values than the corresponding scoured cotton yarns. It implies that these cotton samples have more pores of the dye molecule size. On the other hand, SNM and MSN have higher WRV/MLC values than the corresponding scoured cotton. It means that acid pectinase-mercerized and mercerized-acid pectinase scoured cotton specimens have more pores the size of water molecules. In comparison with SNM, MSN has more small pores the size of water molecules.

CONCLUSION

The modification of the cotton structure by different types of scouring and the impact of the cotton wet processing sequence were examined in this study. The modification of cotton was examined through surface characteristics, structural and sorption properties. The influence of the type of scouring and of the sequence of wet processing, scouring-mercerization or mercerization-scouring, on the measured properties was also explored. From the results obtained, the following conclusions can be drawn:

- Scoured-mercerized cotton has higher CIE whiteness, higher values of polar and total surface free energy components, higher wettability and a lower amount of non-cellulosic components on the cotton fiber surface.
- Scoured-mercerized cotton yarns have lower IC and higher degree of mercerization (calculated from FTIR-ATR spectra) than mercerized-scoured cotton.
- Scoured-mercerized cotton yarns have higher MLC, MR and WRV than mercerized-scoured. The exception is MSN, which has pores of water dimensions and higher WRV than SNM.
- The scouring/mercerization sequence has a significant influence on IC, MLC and MR.

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