CHARACTERIZATION BY SELECTED TECHNIQUES, INCLUDING DIRECT DYES, OF COTTON MODIFIED BY SWELLING AND ENZYME TREATMENTS

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Abstract

Wet processing and swelling treatments of cotton influence its reactivity and accessibility. Thus, pore structure, molecular order and crystallinity are structural parameters of prime importance. For this research scouring, slack mercerization and enzymatic hydrolysis with cellulases were performed on cotton yarn to create samples of varying crystal structure and internal surface. Various techniques including water retention, moisture regain and dye adsorption at equilibrium conditions were employed to elucidate the accessibility of these substrates. The overall integrity of the samples was determined by measuring tensile strength and microscopically.

Introduction

The accessibility of cellulosic substrates to moisture as well as to water-based compounds plays an important role for dyeing and finishing processes as well as for comfort related issues. The determining parameters are pore structure, degree of crystallinity and the structure of the low order or amorphous regions of the cellulosic fiber. A variety of techniques have been developed to estimate accessibility in both wet and dry state of the cellulose substrate. The method developed by Stone and Scallan (1968) uses dextrans of different size as probes to estimate pore dimensions in the wet state. Rowland and Bertoniere (1985) employed inverse gel permeation with cotton substrates as the stationary phase and various sized sugar and dextran solutions as probes. This method has been further developed by Bredereck and Buschle-Diller (1985). For the assessment of the pore structure in the dry state nitrogen sorption [Buschle-Diller et al., 1995] or mercury porosimetry [Gregg and Sing, 1982] are useful techniques.

Pore dimensions are easily modified by wetting and drying procedures, and more strongly, by intracrystalline swelling treatments. Aqueous sodium hydroxide solutions of concentrations exceeding 7 to 10% [Zeronian, 1985] are capable of penetrating not only the amorphous but the crystalline regions as well, causing considerable swelling and reorganization of the crystalline structure.

The objective of this study is to compare the pore structure and accessibility of cellulosic substrates which have been altered by various chemical treatments. Intracrystalline swelling of cellulose in 5M aqueous sodium hydroxide has been employed to create the cellulose II crystal modification. Enzymatic hydrolysis with cellulases has been performed on both scoured and slack mercerized samples for various treatment durations. Cellulases are expected to primarily influence the surface of the substrate. However, changing the porosity by swelling treatments might affect the accessibility to these large molecules. Moisture sorption and water retention measurements as well as Langmuir dyeing isotherms, assuming monomolecular dye adsorption, have been employed to assess the accessibility of the samples. To evaluate the overall integrity of the samples after the enzymatic hydrolysis treatments, scanning electron microscopy and tensile strength tests were performed.

Experimental Procedures

100% cotton yarn, ring spun with a knitting twist (N_e 26), was obtained from Southern Regional Laboratory USDA, New Orleans, LA. It was scoured in 4% aqueous sodium hydroxide solution in the manner described before [Inglesby and Zeronian, 1996]. Mercerization was carried out at 0 °C in 20% aqueous sodium hydroxide solution for 60 min under slack conditions. The yarns were neutralized in 10% acetic acid, washed in water and air-dried. Enzyme treatments were performed on the scoured and scoured/mercerized samples using 10% owf Cellusoft L (Novo Nordisk, Franklinton, NC) in 0.05M sodium acetate buffer (pH 4.8) at 50 °C in a shaking water-bath. Incubation times were 3 and 24 h in the case of the scoured starting material, and 3 h in case of the mercerized samples. The enzymes were deactivated in 100% acetone and the samples washed in water and air-dried. Weight losses were determined based on the conditioned weight.

The accessibility of the samples was determined by measuring moisture regain, water sorption and dyeing isotherms according to [Inglesby and Zeronian, 1996]. As direct dyes C.I. Direct Blue 1 (mol. wt. 992.82) and C.I. Direct Red 80 (mol. wt. 1373.09) were employed (see chemical structures below) at concentration ranges of 1-6% owf to all five substrates under investigation.

C.I. Direct Red 80 was purified with ethanol:water (95:5) by soxhlet extraction. The purification of C.I. Direct Blue 1 as well as the method of moisture regain determination has been described previously [Inglesby and Zeronian, 1996]. Water retention values were determined on cut samples soaked in distilled water for 24 h followed by centrifugation at 900 g for 30 min. Surface changes caused by the treatment with cellulases were observed with a Zeiss DSM 940 scanning electron microscope (SEM). Yarn

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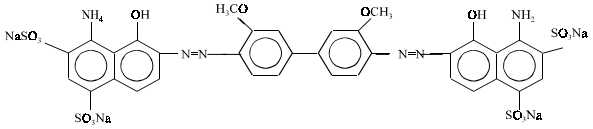
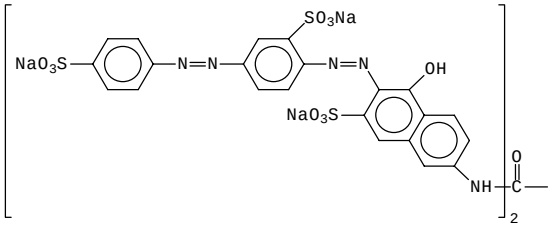
tensile strength and extensibility were measured using an Instron Tensile Tester 1100 on 7.64 cm length samples at a cross-head speed of 20 mm/min. 20 tests per sample were performed.



Chemical structure of C. I. Direct Blue 1.



Chemical structure of C.I. Direct Red 80.

Results and Discussion

Effects of Chemical Treatments on Surface Properties and Yarn Tensile Strength

From Table 1 it can be seen that the tensile strength of the yarn increased on slack mercerization. This effect is commonly observed and has been reported previously [Buschle-Diller and Zeronian, 1994]. The samples that were scoured and enzymatically treated for 3 h did not suffer significant damage as documented by the residual tensile strength data and the examination by scannning electron microscopy (SEM). However, when the incubation was extended to long treatment duration (24 h) the fibers became brittle showing cracks in the fibrillar direction and considerable surface peeling. The breaking strength of these yarns was reduced by 58%.

Table 1. Tensile strength retention of chemically modified cotton yarns (standard deviation in brackets).

Samples	Breaking load (g)	Strength retention (%)
Scoured control	272.85(24.7)	100
Scoured, 3h enzyme treatment	241.39(25.3)	88
Scoured, 24h enzyme treatment	115.86(43.2)	42
Mercerized	308.58(37.2)	100
Mercerized, 3h enzyme treatment	109.37(22.7)	35

When observed under the SEM, the mercerized fibers appeared to have almost round cross-sections and the rugosity of the surface had changed. After enzymatic treatment of only 3h duration the yarn strength was reduced by 65% although no cracks or any seriously damaged fiber areas were visible under the SEM. Surface peeling seemed to have taken place to a lesser extent than without the slack mercerization treatment.

Assessment of Accessibility

Changes in the ratio of amorphous and crystalline regions in cotton fibers following swelling and enzymatic treatments can be estimated by moisture regain. Preferred degradation of amorphous regions would yield reduced moisture regain values. However, cellulase enzymes are of large molecular size and the access to as well as the degradation of amorphous regions is limited.

Moisture regain measurements did not show any significant changes upon enzymatic treatment. As expected, the moisture sorption values for sodium hydroxide treated cotton (Table 2) were higher than for scoured samples. The higher accessibility to water vapor did not simultaneously lead to better access to the cellulase as the change in moisture regain was negligible after enzymatic hydrolysis.

Table 2. Moisture regain values of modified cotton yarns (standard deviation in brackets).

Sample	Moisture regain (%)
Scoured control	7.06(0.1)
Scoured, 3h enzyme treatment	7.22 (0.2)
Scoured, 24h enzyme treatment	7.29 (0.1)
Mercerized	10.93(0.2)
Mercerized, 3h enzyme treatment	10.70(0.1)

A similar trend was observed when water retention values of the modified samples were measured (Table 3). Water retention values indicate the saturation point for the total amount of water a fiber can hold at exterior and internal surfaces. The scoured samples were found to have a slight decrease in water retention after 3 hours of incubation, which might be interpreted as the result of the surface polishing effect of the cellulases at shorter treatment times. The water retention increased again for longer treatment durations as the overall fiber damage dominated under these conditions, forming new water absorbent regions in the fractured fibers.

Sodium hydroxide-treated samples generally have higher water retentions than nonmercerized samples (Table 3). However, the values did not change significantly upon enzymatic hydrolysis.

Table 3. Water retention of modified cotton samples (standard deviation in brackets).

Sample	Water retention values (%)
Scoured control	48.73 (0.4)
Scoured, 3h enzyme treatment	44.46 (0.3)
Scoured, 24h enzyme treatment	46.65 (0.6)
Mercerized	67.40 (0.2)
Mercerized, 3h enzyme treatment	66.18 (0.9)

Dyeing processes of cotton with direct dyes generally follow a Freundlich type of dyeing isotherm when the dyes are applied in concentrations typical for commercial applications [Burdett, 1989]. However when very dilute dye solutions are used, Langmuir behavior is observed. For this concentration range monomolecular dye adsorption can be

assumed and a saturation value calculated at equilibrium dye adsorption.

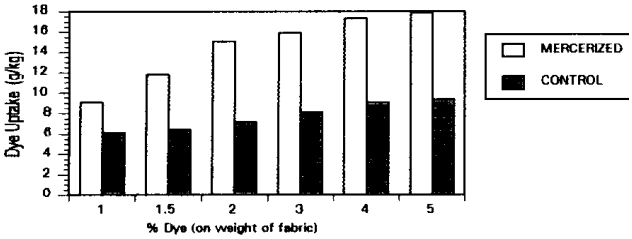


Figure 1. Dye adsorption per kg substrate versus initial dyebath concentration of control and slack mercerized cotton (C.I. Direct Blue 1).

In Figure 1 a graph is presented of the dye uptake of scoured and mercerized samples at increasing dye concentrations of C.I. Direct Blue 1, a relatively small dye. The accessible internal surface area for water was found to be considerably increased upon mercerization as is also documented in higher water retention and moisture regain values (Tables 2 and 3). Since the data fit a Langmuir isotherm, saturation values at equilibrium conditions could be calculated.

Table 4. Saturation values of C. I. Direct Blue 1 and C. I. Direct Red 80 at equilibrium adsorption

Sample	C. I. Direct Blue 1 mmol/kg)	C. I. Direct Red 80 mmol/kg)
Scoured control	12.53	11.89
Scoured, 3h enzyme treatment	12.02	12.29
Scoured, 24h enzyme treatment	9.07	11.75
Mercerized	26.09	33.81
Merc., 3h enzyme treatment	21.51	28.60

In Table 4 the results of preliminary studies for two different sized direct dyes, Direct Red 80 and Direct Blue 1, are summarized for the samples under investigation. The calculated saturation values show that the shorter 3 h enzyme treatment affected mostly the fiber surface without influencing the pore structure to any measurable extent. More severe enzymatic hydrolysis decreased the available internal surface area in the scoured samples as indicated by the Direct Blue 1 results. This dye molecule is linear with a relatively low molecular weight. In contrast, Direct Red 80 is non-linear and has a higher molecular weight. In this case the data does not have such a clear trend. In the case of the mercerized samples, a marked drop in surface area is found when either dye is used. It can be speculated that over time the enzymes degraded walls between smaller pores thus causing larger voids with decreased surface area. Using dyes of different molecular size and shape it should be possible to further explore pore size distribution. Experiments employing this approach are in progress.

Conclusions

Various techniques were applied to characterize the accessibility of scoured, slack mercerized and enzymatically treated cotton samples. Moisture regain values increased upon mercerization as expected but did not change significantly upon enzymatic hydrolysis. Water retention values on the other hand decreased to some extent after the cellulase treatment in the case of both scoured and mercerized samples, most likely as a result of fiber surface modification. Equilibrium dye adsorption of Direct Blue 1 revealed differences in accessible surface area especially between the extensively degraded scoured and mercerized samples. Saturation values for the scoured control and scoured 3 h enzymatically treated samples did not decrease significantly. In contrast, the saturation values for the 24h-treated scoured sample and the mercerized 3h-treated sample decreased by 25% and 18%, respectively. Similar trends were observed for the Direct Red 80; however, these trends were not as distinct, possibly because of its non-linear molecular shape.

References

Bredereck, K. and Buschle-Diller, G., *Melliand Text. Ber*. **70** 116-125 (1989).

Burdett, B.C., in: "The Theory of Coloration of Textiles" (ed.: A. Johnson),
Society of Dyers and Colourists, Bradford, England, 49-60 (1989).

Buschle-Diller, G., Fanter, C. and Loth, F., *Cellulose* **2,** 179-197 (1996).

Buschle-Diller, G. and Zeronian, S.H., *Text. Chem. Color*. **26**, 17-24 (1994).

Gregg, S.J. and Sing, K.S.W., "Adsorption, Surface Area and Porosity", 2nd
ed., Academic Press, London (1982).

Inglesby, M.K. and Zeronian, S.H., *Cellulose* **3,** 165-181 (1996).

Rowland, S.P. and Bertoniere, N.R., in: "Cellulose Chemistry and its Applications" (eds.: T.P.Nevell and S.H. Zeronian), Ellis Horwood Ltd., Chichester, England, Chapt. 4 (1985).

Stone, J.E. and Scallan, A.M., *Cellulose Chem. Tech*. **2,** 343-358 (1968).

Zeronian, S.H., in: "Cellulose Chemistry and its Applications" (eds.: T.P. Nevell and S.H. Zeronian), Ellis Horwood Ltd., Chichester, England, Chapts. 5 and 6 (1985).