Effect of Enzymatic Treatment on Dyeing and Finishing of Cellulosic Fibers: A Study of the Basic Mechanisms and Optimization of the Process

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Goal Statement

The major goals of this project were to study the mechanism of enzymatic hydrolysis reactions of cellulosic fibers with whole cellulase systems and to evaluate the effect of dyes and finishing agents as well as dyeing auxiliaries and agitation in their influence on the enzymatic action. The understanding of the fundamentals of this important process ultimately leads to its optimum use to improve the properties of cellulosic fabrics.

Abstract

The finishing process of cellulosic textile materials with cellulases has reached enormous industrial importance over the past decade. Nontoxic and environmentally benign, these biocatalysts are capable of improving hand and appearance properties of cellulosic goods at very low concentrations. For this project commercially available whole cellulase enzyme systems were used. The treatments were carried out on 100% cotton fabric, cotton/polyester blends and on cellulosics other than cotton. Prior or subsequent to the enzymatic treatment, dyeing with four different dye classes and two types of finishing processes – an easy-care finish with formaldehyde-free crosslinking agents and a soil-release finish - were performed and the properties of the treated materials studied. Color yield improved for most dyes used in this study and less finishing agents were necessary if the fabrics were enzymatically pretreated. Hand properties were studied using the Kawabata system and considerable improvements in softness and comfort were documented. Conclusions on the underlying mechanisms of these reactions could be drawn.

Background

In whole cellulase enzyme systems three major groups of high-molecular weight proteins work synergistically on the hydrolysis of the substrate. Accessible cellulose chains in amorphous areas and on crystallite surfaces are split at the ß-glucosidic bond by endo-type cellulases at random and by exo-type cellulases from the chain end. The generated smaller fragments are then further hydrolyzed by the same mechanism. Cellobiose units and very short fragments are finally decomposed to glucose by ß-glucosidases. The overall reaction rate is controlled by the hydrolysis products which have an inhibiting effect on the activity of each of these enzymes.

Cellulases are of very large molecular size. The reaction is therefore initially concentrated on fiber surfaces and proceeds only slowly towards the interior of the fiber. Peeling on the fiber surfaces – usually referred to as biopolishing – is observed and small fibrils are loosened and removed, especially when the treatment is performed with agitation. In industrial operations usually jets or tumblers are used for the enzymatic treatment. Mechanical action during the treatment also helps enzyme adsorption and desorption processes. The observed weight loss during the initial stages of the treatment does not yet indicate any fiber damage. With prolonged treatment duration, however, the degradation process also occurs in the accessible amorphous areas of larger pores and at crystallite surfaces. This process can eventually lead to significant fiber deterioration, indicated by cracks in fibrillar direction and associated high strength loss. The effect is additionally intensified by mechanical abrasion during the treatment.

As biocatalysts, cellulases are substrate-specific in their action. Any change in the structure or accessibility of the substrate can have a considerable influence on the course of the hydrolysis reaction. Any dyeing or finishing process performed in conjunction with the enzymatic treatment can therefore be of significant impact on the properties of the end-product. Especially dyes and finishing compounds that form covalent bonds with the cellulose strongly affect the substrate recognition of the enzymes. On the other hand, in case of a cellulase pretreatment, dye- or finishing-binding sites on fiber surfaces and in amorphous areas might be altered by the action of the enzymes. Valuable information can thus be obtained on the mechanistic aspects of this reaction through the use of carefully selected dyes.

Vital practical aspects of this process are possible cost savings of dyes and finishing compounds due to the modified fiber surface and structure of the textile material. Polishing, for example, leads to smoother surfaces and less light scattering, hence to more brilliant colors. Equivalent performance properties, such as color strength, might be achievable with less dyes and chemicals.

Treatment Conditions

Cellulases are catalysts and small quantities are sufficient for the achievement of the desired effects. In fact, increasing the concentration above a certain amount does not yield better results or improve the reaction rate. Agitation during the treatment, on the other hand, drastically reduces the necessary treatment duration. For example, under otherwise identical conditions, application of cellulases in a tumbler as opposed to an incubator with circular shaking motion reduces the treatment time by a factor of 10 for comparable weight losses of the treated cotton fabric.

Catalysts in general are not consumed during the reaction and have to be deactivated once the desired performance level has been reached. Since they are most active within a certain temperature and pH range, the denaturation of the cellulases can easily be incorporated in a subsequent dyeing or finishing step by simply rinsing with hot water. Increasing the pH value or washing the fabric with diluted aqueous carbonate solutions are also often recommended deactivation processes.

Surface active substances are frequently used as auxiliaries for improvement of dyeing and finishing. If they entail the enhancement of fabric wettability, they could be expected to also improve the efficiency of the process. Three types of surfactants, cationic, anionic and nonionic, were used in this project to see whether they would in fact accelerate the enzymatic hydrolysis. However, only cationic surfactants supported the reaction to a certain point, while nonionic surfactants had basically no measurable effect and anionic agents even slowed down the reaction. It is possible that enzyme and surfactant interact to a certain extent and form complexes. This would lower the effectiveness of the cellulase. Another possibility could be competitive adsorption and/or incomplete desorption of enzyme and surfactant at the cellulosic surface.

Enzymatic Treatment and Dyeing

Reactive Dyes

Fiber-reactive dyes are the only dye class that form covalent bonds with the hydroxyl groups of the cellulose substrate. Cellulase enzymes cause changes in dye-site availability and accessibility which will be most clearly visible with this dye class. Reactive dyes carry different types of reactive groups and can be mono- or bifunctional. It seems though that the type of the reactive group only plays a minor role while its position within the dye molecule is decisive (see Figure 1). Bifunctional dyes with the reactive groups far enough apart from each other can cause crosslinking of the cellulose structure to a certain extent. These dyes may form bridges along one cellulose chain or between two separate chains. If dyed prior to the enzymatic treatment, substrate penetration and recognition are obstructed for the enzyme.

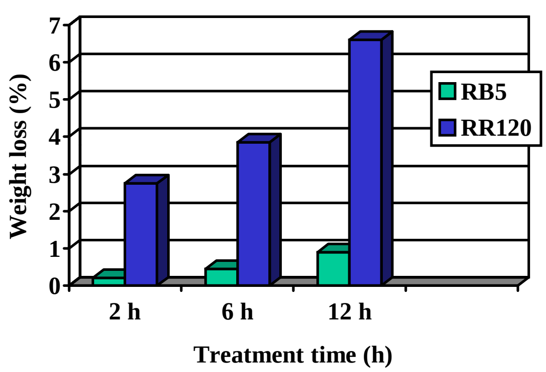

Figure 1. Weight loss versus treatment time for enzymatically treated fabric dyed with different bifunctional reactive dyes (RB5: C.I. Reactive Black 5; RR120: C.I. Reactive Red 120) .

Figure 1 clearly illustrates the impact of bifunctional dyes on the course of the enzymatic treatment. In RB5 the functional groups are at either end of the dye molecule, while in RR120 the two functional groups are adjacent to each other. RB5 causes considerable crosslinking within the cellulose structure and obstructs the access for the enzyme. RR120, on the other hand, shows the behavior found for mono-functional dyes.

If the fabric is enzymatically treated prior to dyeing, independent of number and position of functional groups higher color strength was observed. Very short treatment times were sufficient for excellent results, especially if the cellulase treatment was performed in the tumbler. For example, for RB5 the K/S value increased by 16% for a 5-min enzyme treatment as compared to the K/S value of the untreated. A 10-min treatment further increased the K/S to 19% and prolonged treatments did not yield higher K/S values. In the case of the mono-functional Reactive Yellow 3 dye, the highest color strength (32% higher than the control sample) was also achieved after a 10-min enzymatic pretreatment and could not be further increased.

Direct Dyes

When fabric was dyed with various direct dyes prior to a cellulase treatment, the molecular size of the dye molecule seems to be the most important factor. Direct dyes are held in the fiber by secondary forces only and the larger the dye molecule, the better the alignment along the cellulose chains and the stronger the interaction. Some results are presented in Figure 2 for a relatively small red direct dye and a very large green direct dye. Clearly lower weight losses were obtained for the more voluminous dyes which seem to block the enzymatic access to a certain extent. However, the interpretation of these results is not quite as simple. Factors, such as changes in fiber porosity (found with other analytical means) also play a role for dyeing, as well as the poor washfastness properties of direct dyes due to their weak bonding.

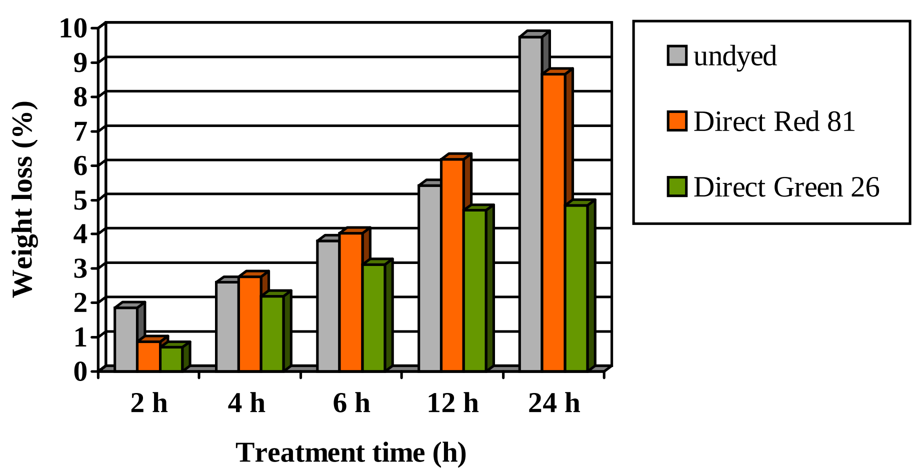

Figure 2. Enzymatic treatment after dyeing with direct dyes: weight loss (%) as a function of treatment time (h); shaking incubator treatment.

Aftertreatments of direct dyed fabric to improve the washfastness were not performed as the agents used for these aftertreatment could interfere with the effect of the cellulases. Enzymatic pretreatment somewhat helped to reduce the problem of neps. Neps consist of immature fibers of lower cellulose content which do not pick up the same amount of dye if any at all. Most likely enzymatic treatment with agitation aids with the break-off of these fiber entanglements.

Vat Dyes
All the studied dyes were different in molecular weight and shape, ranging from relatively small to bulky which for this dye class seemed to be the major factor. Generally, vat dyes are held inside the fiber in water-insoluble, more or less aggregated form by a pigment-type bond. The enzymatic pretreatment in this case caused a more or less high increase in color yield for most, but not all of the dyes under investigation (Table 1). Relatively mild treatment conditions were sufficient to achieve noticeable increases in color strength. This makes the pretreatment even more attractive as fiber damage is low to negligible at this point. However, it is not yet understood why some of the dyes improved the color strength to a higher extent than others.

Table 1. Increase in color strength of selected vat-dyed samples after an enzymatic pretreatment (shaking incubator treatment).

Treatment Time [h]	Weight loss [%]	Percent color strength based on untreated sample Vat Green 1	Indigo
2	0.58	150.9	208.9
4	1.39	152.3	220.2
6	2.05	147.7	209.3
12	3.56	156.3	209.2

Sulphur Dyes
Sulphur dyes form large water-insoluble molecules networked over disulfide bonds. The details of their chemical structures are usually not known. Several different commercial sulfur dyes were applied to enzymatically pretreated fabric. The data in Table 2 clearly show that in case of these sulfur dyes the same color strength can be achieved at lower dye pick-up.

Table 2. Color strength of enzymatically pretreated cotton fabric dyed with sulfur dyes.

Treatment Time [h]	Weight loss [%]	Rel. dye pick-up	K/S
C.I. Sulfur Green 2			
Untreated	0	1.00	9.25
0.5	2.25	0.68	9.13
1.0	3.20	0.45	9.03
2.0	4.60	0.35	9.14
C.I. Sulfur Blue 13			
Untreated	0	1.00	20.50
0.5	2.27	0.91	20.41

1.0	3.13	0.81	20.17
2.0	4.69	0.58	19.54

Table 2. continued.

C.I. Sulfur Blue 20			
Untreated	0	1.00	19.92
0.5	2.02	0.68	19.43
1.0	3.09	0.84	19.61
2.0	4.40	0.42	19.90

Obviously, with the cellulase pretreatment the amount of dye pick-up can be reduced by half on the average which translates in considerable cost savings.

Formaldehyde-Free Crosslinking in Conjunction with Enzymatic Treatment

Commercial easy-care finishes for cotton and cotton blends are usually performed with formaldehyde-based crosslinking agents, the most common being DMDHEU. With these agents wrinkle recovery is generally good, the textile products however often exhibit a stiff uncomfortable hand and lower tensile strength. Free or bound formaldehyde might be released from fabrics that were finished with these compounds. This problem has led to more stringent environmental and safety regulations.

For this research, formaldehyde-free crosslinking agents, such as BTCA (1,2,3,4-butane tetracarboxylic acid) and commercial products based on maleic acid, were applied to enzymatically pretreated fabrics with the goal to combine the benefits of environmentally friendly easy care with the softening effect of the enzyme treatment. Water retention values (WRV) were determined to estimate the degree of crosslinking. As the dyeing experiments had shown (see previous sections), less dyestuff for comparable color strength was sufficient when the textile material was treated with cellulases, it was expected that less finishing compounds might also be sufficient after an enzymatic pretreatment.

Compared to the untreated control the WRV decreased slightly after crosslinking of the enzymatically pretreated fabric, irrespective of treatment duration and weight loss. The wet pick-up of crosslinking agent was lower in all cases, however, simultaneously the wrinkle recovery angles were 20-50% higher depending on the type of compound used. The tensile strength loss was tolerable for short cellulase pretreatments followed by crosslinking with any of the reagents used for this study, but relatively high for longer pretreatments. In this case, the type of crosslinking agent played a much more significant role. Nevertheless, carefully controlling both pretreatment and crosslinking conditions can translate into considerable cost savings where less crosslinking compounds are necessary for excellent wrinkle recovery.

Wrinkle recovery angles decreased slightly when previously crosslinked fabric was treated with cellulases. The softness of these fabrics improved somewhat, most likely due to a surface polishing effect. As expected, the enzymes were unable to penetrate the crosslinked fabric to a larger extent as the observed low weight losses and still relatively low WRV documented. In this case, the benefits of the enzymatic hydrolysis are limited.

Water-Repellent and Soil-Release Finishing of Enzymatically Pretreated Cotton Fabric

A commercially available water-repellent formulation was applied to enzymatically pretreated fabric in concentrations of 0.25% to 3.0% (ows). The fabric had been treated with cellulases for up to 2 h in the tumbler. To evaluate the efficiency of the finish the AATCC Spray Test 22-1989 was performed. For good water-repellent properties a finish concentration of 3% was necessary in the case of the untreated fabric, while for enzymatically pretreated fabric to show the same level of performance a concentration of only 0.375% was sufficient. Clearly, considerable quantities of finishing agents could be saved.

The quality of the finishing was further evaluated by assessing comfort parameters, such as fabric stiffness and moisture pick-up. Fabric stiffness decreased with less finishing pick-up which, of course, is expected. Flexural rigidity decreased by 10-15% on the average when the cellulase pretreatment had been performed. However, treatment duration did not play any significant role. Samples treated for only 30 min and samples treated for 2 h exhibited comparable fabric softness. The difference in moisture regain between all the samples was negligible.

Kawabata Hand Evaluation of Enzymatically Treated Cotton and Cotton/Polyester Fabric

We looked at the overall changes in the tactile properties of knit fabrics arising from enzyme treatment. We made an attempt to define the treatment conditions for knit fabrics made of different types of staple yarns (ring yarns, OE yarns, etc.). Our goal here is to understand and define the structural changes occurring in knit fabrics made from the new generation yarns so that enzyme treatment can be adopted as a tool for improving their tactile qualities. We also tried to establish optimum treatment conditions for knit fabrics of a range of base weights and loop geometries (plain, rib, interlock, etc.). Our primary goal here is to establish some basic guidelines for treating a range of knit fabrics.

Our work on woven fabrics again focused on understanding the interactive effects of yarn and fabric structures and the treatment conditions on the tactile properties of the treated fabrics. We believe this work is beneficial in setting broad guidelines for the treatment of woven fabrics.

KES Work on Spun Yarns

Our work on woven and knitted fabrics revealed that there is a need to go back and look at what happens at the yarn level before we can satisfactorily explain and account for the property changes seen in the treated fabrics. Accordingly we looked at the structural and property changes of the treated yarns made from ring, rotor, airjet and friction spinning systems. We included in our study both cotton and cotton/ polyester yarns and also yarns corresponding to random blending and core-sheath fiber arrangement. Our results showed that there is a good agreement between the property changes seen in the treated yarns and the corresponding treated fabrics. Results also revealed that the treatment conditions required to achieve a perceptible improvement in the hand related mechanical properties are widely different for different yarns. Significant improvement in softness was noticed in all the treated yarns but the strength loss was widely different (2-15%) for different yarns. Yarn structure as reflected by the spinning system and the blend composition of the yarn were found to influence the strength loss.

Cellulase Treatment of Cellulosics Other than Cotton

Cellulases are effective on cellulosic substrates other than cotton, such as linen, hemp, jute and viscose rayon. Hemp and linen are generally very similar in their properties and also react alike during the enzymatic hydrolysis process. Mild, short-term treatments lead to surface polishing and a very soft product. Both linen and hemp however break down faster than cotton upon more severe treatment conditions, especially if agitation is involved. Jute contains the highest amount of noncellulosic by-products, e.g., lignin and hemicellulose and the enzymatic hydrolysis with cellulases was slower than with the other natural cellulosics under investigation. A slight bleaching effect could be achieved which unfortunately did not prove to be permanent. Regenerated cellulosic fibers did not show any significant effect for relatively long incubation time. However, under more drastic conditions the fiber deterioration was more severe than in the case of any of the natural fibers.

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Industry Interactions: 25
Contacts with Academic (non-NTC): 5
Other non-NTC Interactions: 10