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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Principal Investigators

Gisela Buschle-Diller (Auburn), William K. Walsh (Auburn), P. Radhakrishnaiah (Georgia Tech)

Goals

The major goal of this project is to study the basic mechanisms of enzymatic hydrolysis reactions of cellulosic fibers with whole cellulase systems in conjunction with dyeing and finishing. Dyes and finishing agents, auxiliaries and agitation can dramatically affect the enzymatic action and thus can be used to investigate the underlying mechanisms. It is further essential to understand all influencing factors to develop the most efficient treatment process.

Abstract

Cellulase enzymes are nontoxic and environmentally friendly biocatalysts. They are capable of significantly improving the hand and appearance properties of cellulosic materials. As biotechnology makes rapid progress concerning the availability of these enzymes and their application conditions, this finishing process has reached enormous industrial importance over the past few years. Cellulases perform best at a specific pH range and a temperature around 40-55°C, and both tolerable temperature and pH have become much more flexible. As biocatalysts, very small amounts are sufficient to accelerate a specific reaction. The enzymes are not consumed during this reaction. Their deactivation is performed by a simple shift in temperature or pH. For this project commercially available whole cellulase enzyme systems were used. The treatments were carried out on 100% cotton fabric, cotton in blends with polyester, or on cellulosics other than cotton. Prior or subsequent to the enzymatic treatment, dyeing with four different dye classes and easy-care finishing with formaldehyde-free crosslinking agents 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. Yarn type and fabric structure (e.g., weaving or knitting style) were found to be of significant influence.

Enzymatic Hydrolysis of Cellulosic Substrates

Cellulase enzyme complexes usually consist of 3 major types of high-molecular weight proteins that synergistically catalyze the break-down of a cellulosic substrate at the ß-glucosidic bond. Exo-type cellulases cause chain scission from the non-reducing chain end and endo-type cellulases attack at random, both producing smaller chain fragments. ß-Glucosidases break down cellobiose and very short fragments to the final product glucose. The hydrolysis products of each reaction step have a controlling (inhibiting) effect on the activity of the respective enzymes:

CELLULOSE

↓ SYNERGISTIC REACTION OF
EXO- AND ENDOGLUCANASES

SHORTER CHAIN FRAGMENTS + CELLOBIOSE
INHIBITION

↓ FURTHER BREAK-DOWN WITH
EXO-, ENDOGLUCANASES AND
ß-GLUCOSIDASES

GLUCOSE
INHIBITION

In the initial stages of the hydrolysis, cellulases primarily act on fiber surfaces due to their large size. Simultaneously considerable mechanical action is usually involved in industrial applications by the use of jets or tumblers for the enzymatic treatment. Mechanical action during the treatment in the initial stages helps enzyme adsorption and desorption processes as well as aids the removal of enzymatically loosened material from fiber surfaces, leaving the fibers very smooth. Due to this polishing effect some weight loss is observed, which however does not yet indicate any fiber damage. Only with prolonged treatment duration degradation also occurs in the accessible amorphous areas of large pores and at crystallite surfaces. This process can eventually lead to significant fiber deterioration, indicated by a high weight and strength loss. Cracks in fibrillar direction as well as extensive surface peeling occur as indicators of this effect which is additionally overlaid by the effect of pure mechanical abrasion during the treatment.

Cellulases are strictly 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. Since the enzymatic treatment is often performed prior or subsequent to dyeing and finishing, it is very important to study the interaction of enzymes with compounds used for these processes. Dyes form physical and/or chemical bonds with cellulose depending on the respective dye class and thus influence substrate recognition for the enzymes in the case of a hydrolysis treatment after dyeing. On the other hand, in case of an enzymatic pretreatment, the dye binding situation in the amorphous areas and at fiber surfaces might be different. Therefore, with either process sequence, valuable information can be obtained on the mechanistic aspects of this reaction through the use of carefully selected dyes. Similar observations can be made with finishing agents that react by forming crosslinks externally on the fiber surface and internally between cellulose chains. Besides acquiring important knowledge on the mechanism of enzymatic hydrolysis, vital practical information becomes available on how to best benefit from this process.

Adjusting the Treatment Conditions

As mentioned above, enzymes are biocatalysts and as such do not require large amounts for the achievement of the desired effects. In fact, increasing the concentration does not yield better results. Agitation during the treatment drastically reduces the necessary treatment duration. For example, under otherwise identical conditions, we found that the application of cellulases in a tumbler as opposed to a shaking incubator reduced the treatment time by a factor of 10 to result in comparable weight losses of the treated cotton fabric.

Auxiliaries, as used for the application of dyeing and finishing compounds, could be expected to enhance the efficiency of the process, especially if they improve the wettability of the textile substrate. We used three types of surfactants in this project to see whether we could 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 even slowed the reaction down. The observed effects can be understood when the enzyme/surfactant interaction is taken into account, however, more experiments are necessary at this stage.

Dyeing of Enzymatically Pretreated Cotton Fabric

Direct Dyes
Enzymatically pretreated fabric was dyed with various direct dyes, selected by molecular size. Direct dyes are held in the fiber by secondary forces only. The larger the dye molecule, the better the alignment along the cellulose chain and the stronger the dye/fiber interaction. The washfastness of these dyes is generally poor and aftertreatments are often necessary for better fixation. Cellulases not only change the fiber surface, but also reduce the amount of existing amorphous areas as well as creating new dyeable regions as the treatment proceeds. A change in the porosity of the substrate can also be expected. In this study it was found that the color yield (K/S values) did not significantly change for samples exhibiting very small or very large weight losses, independent of the direct dye used. A small increase in K/S was observed for medium weight losses. An effect similar to this degradation pattern was also perceived with other methods (SEM, moisture sorption, crystallinity and porosity measurements) and possibly reflects a temporary state where easily accessible areas are being enzymatically removed while simultaneously new dye-sites become available. With careful process control, advantage of this temporary stage can be taken which could lead to considerable cost savings in regard to this dye class.

Vat Dyes
Vat dyes are held inside the fiber in water-insoluble form by a pigment-type bond. All the dyes we chose for this study were different in molecular weight and shape, ranging from relatively small to bulky, flat to spherical. The enzymatic pretreatment in this case caused a more or less high increase in color yield for most of these dyes. Table I shows some typical results for four vat dyes. It is obvious that the enzymatic pretreatment created better structural conditions for the accommodation of this type of dyes. Relatively short treatment times 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 the color strength of some of these dyes was improved to a higher extent than in the case of others.

Table I. Increase in color strength of selected vat-dyed samples after an enzymatic pretreatment.

Treatment Time [h]	Percent color strength based on untreated sample			
	Vat Green 1	Indigo	Vat Red 10	Vat Red 32
2	150.9	208.9	322.1	80.5
4	152.3	220.2	333.9	83.0
6	147.7	209.3	339.2	80.1
12	156.3	209.2	330.9	77.7
24	122.3	188.8	298.0	70.8

Reactive Dyes

To study the effect of a cellulase treatment with regard to reactive dyeing is probably most interesting and conclusive as reactive dyes form covalent bonds with the hydroxyl groups of cellulose. Changes in dye-site availability could be expected to become clearly visible with this dye class. We selected a number of reactive dyes that differed in the type of reactive group(s) and their position(s) within the dye molecule. Table II shows some results of reactive-dyed fabric that had been enzymatically pretreated in a Laundrometer with mechanical action. Reactive Black 5 is a bifunctional, Reactive Yellow 3 a monofunctional reactive dye. As found with vat dyes, reactive dyes also exhibited improved color yield when the fabric was enzymatically pretreated. Higher color strength was observed independent of the number, type and position of the functional groups (Table II) and, as in the case of vat dyes, short treatment times were best for overall good results. Generally, it seems that less dye is sufficient after a pretreatment with cellulase to achieve the same level of color depth compared to the untreated control. This would imply considerable cost savings irrespective of the dye class.

Table II. Color strength of reactive-dyed fabric after enzymatic pretreatment.

Treatment time (Laundrometer)	K/S C.I. Reactive Black 5	C.I. Reactive Yellow 3
no pretreatment	19.26	11.81
5 min	22.38	13.10
10 min	22.93	15.57
15 min	22.60	13.39

Sulphur Dyes

Sulphur dyes are similar in application to vat dyes. They form large water-insoluble molecules networked over disulfide bonds. Experiments using with these dyes are currently in progress.

Enzymatic Treatment of Dyed Fabric

Weight losses of dyed fabric upon enzymatic treatment were generally equal or slightly lower compared to undyed control samples, irrespective of the dye class. Major exceptions were bifunctional reactive dyes, especially when the reactive groups were positioned in a way that both groups could form covalent bonds with the hydroxyl groups of cellulose. An example of such a dye is Reactive Black 5. In this case weight losses were very low which indicates crosslinking to a certain extent by the dye. The crosslinking can occur between two cellulose chains or along one chain. With all other dyes, monofunctional reactive and vat dyes, the enzymatic substrate recognition did not seem to be significantly affected. These dyes were washfast under the selected treatment conditions and the enzymatically separated surface fuzz was deeply colored.

Direct dyes generally have poor washfastness and some dye was carried into the treatment bath. Aftertreatments for better dye fixation were not practical as they might interfere with the cellulases. Weight losses after the hydrolysis treatment were higher for some of the direct dyes and lower for others. As a rule, it appeared that fabric dyed with smaller-sized dyes lost more weight during the treatment than fabric dyed with dyes of larger molecular weight. It is possible that the smaller dyes presented less an obstacle to the cellulases. However, it is also possible that these dyes desorbed easier from the fabric as their dye/fiber interactions are weaker.

Formaldehyde-Free Crosslinking in Conjunction with Enzymatic Treatment

Easy-care finishing is usually achieved with formaldehyde-based crosslinking agents. Although crease recovery is generally good, the textile products often exhibit a stiff uncomfortable hand and lower tensile strength. Additionally, the liberation of free and/or bound formaldehyde from fabrics that were finished with these compounds have led to more stringent environmental and safety regulations.

For our research, formaldehyde-free crosslinking agents, such as BTCA (1,2,3,4-butane tetracarboxylic acid) and other commercial products, were chosen to be applied to enzymatically pretreated fabrics with the goal of combining 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.

It was found that compared to the untreated control the WRV decreased slightly after crosslinking of enzymatically pretreated fabric, irrespective of treatment duration and weight loss, indicating a more closed structure. The wet pick-up of crosslinking agent was lower in all cases, however, 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 we used in this study, but relatively high for longer pretreatments. This is expected as the strength losses caused by the enzyme treatments and by the formation of crosslinks add up. In this case, the type of crosslinking agent played a much more significant role. Nevertheless, carefully controlling both pretreatment and finishing 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.

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. The fabrics were obtained from the textile industry in a large array of different styles. We made an attempt to define the treatment conditions for these fabrics made of different types of staple yarns (ring-spun yarns, open-end yarns, etc.). Our goal here was to understand and define the structural changes occurring in knit fabrics made from the new generation yarns so that the 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 large 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. Tensile, bending, compression, shearing and other surface related properties are currently studied using the Kawabata system and correlated to enzyme treatment conditions. We believe this work is beneficial in setting broad guidelines for the treatment of woven fabrics.

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 proceeded much 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 times. However, under more drastic conditions (for example, more aggressive cellulases) the fiber deterioration was more severe than in the case of any of the natural fibers.

Publications and Presentations

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[*Other Contributors* (TE, Auburn and Davis, CA): *Graduate Students*: Moussa Traore, Xianghong Shi, Maria Inglesby; *Visiting Scholars* (GA Tech): X. Meng, G. Huang, Y. Wang; *Undergraduate Students*: Abby Whittington]
Industry Interactions: 19
Contacts with Academic (non-NTC): 2
Other non-NTC Interactions: 6