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Characterization and performance of ramie fabrics treated with modified cellulase

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In this study, a modification procedure for ramie fabrics was developed using modified cellulases. Cellulase was modified by covalent coupling to Eudragit S-100, which resulted in a larger molecule, to trigger its activity toward the cellulosic fiber surface. The modified fabrics were characterized by using atomic force microscope, thermogravimetric analysis, and Kawabata Evaluation System for Fabric techniques in order to determine their morphology, thermal stability, and handle. In addition, the moisture evaporation, wicking property, and air permeability of the modified ramie fabrics were investigated. Furthermore, the weight loss and copper number were determined to identify the damages in the modified ramie fibers. The results show that the modified cellulase can prevent excessive damage to ramie fabrics with the desired performance because the hydrolytic attack of the modified cellulase is restricted to the surface of the ramie fibers.

Keywords: ramie; modified cellulase; Eudragit S-100; characteristics; performance

Introduction

Cellulase treatment has been widely used in textile industry as an environmental-friendly wet-processing application for bio-washing of denims to achieve the worn look, biopolishing by removing fuzz fibers and pills, and improving the softness and brightness of cellulosic fabrics (Cavaco-Paulo, 1998; Emilia & Péter, 2004; Kalia & Sheoran, 2011; Mamma, Kalantzi, & Christakopoulos, 2004). Numerous methods, such as producing cellulases with greater stability for specific processes, high specific activity on solid substrates, and less damage to cellulosic fabrics (Bower, Clarkson, Larenas, & Ward, 1998; Lee & Lee, 1987; Zhang, Tang, An, Fu, & Ma, 2009), have been proposed to enhance the feasibility of cellulase processing in the textile industry.

Ramie, a well-known natural cellulosic fiber, has excellent characteristics such as high tensile strength, excellent thermal conductivity, high water and perspiration adsorption, and antibacterial functions (Goda, Sreekala, Gomes, Kaji, & Ohgi, 2006; Liu, Yang, Zhang, Liu, & Xiong, 2007). However, it also has some disadvantages such as rigidity and prickle sensation to human skin, which hinder its wide application. Therefore, renewed interest in natural fibers has resulted in numerous modifications to improve the properties of ramie fibers, and cellulase treatments have been an effective method. However, the cellulase modification process of ramie fibers often results in a certain loss of tensile strength along with desired properties (Ibrahim, El-Badry, Eid, & Hassan, 2011). Enlarging the cellulase molecule will focus the cellulase attack more relatively on the surface of the fiber. The diffusion velocity of the enlarged cellulase molecule will be limited toward the interior of the ramie fiber. Immobilization of the cellulase by covalent coupling to a water insoluble carrier is one of the methods to enlarge the molecular size and volume of the biocatalyst thus triggering its activity toward the fiber surface (Lenting & Warmoeskerken, 2001).

In our previous study, cellulases were modified by coupling Eudragit S-100 (a copolymer of methacrylic acid and methyl methacrylate) to carbodiimide. About 76% of the enzyme activity was recovered after the modification process. The modified cellulase retained 38% of the enzyme activity of the natural cellulase after five cycles of repeated uses, which exhibited good reuse ability. The effect of enzymatic treatments and degradation of cotton fabrics were also evaluated (Yu, Yuan, Wang, & Fan, 2013; Yu, Yuan, Wang, Fan, & Wang, 2012). In this study, the comfort and degradation of ramie fabrics treated with the modified cellulase are studied. These studies will be very useful for broadening applications of cellulases on ramie fabrics.

Materials and methods

Materials

A commercial-grade aqueous mixed enzyme preparation (Cellulase Suhong B989 N) with a CMCase activity of

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92 U/mL was supplied by Novozymes (Shanghai, China), and Eudragit S-100 was supplied by Degussa-Hüls, SA, (Shanghai, China). Carbodiimide hydrochloride and ethanolamine were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). All other chemicals used were of analytical grade. 100% ramie fabrics were obtained from Xinshen Company (Henan, China). The specifications of the ramie fabric are given in Table 1.

Modification of cellulase

Carbodiimide-coupling agent (0.2%, w/v) solution was added to Eudragit S-100 (1.5%, w/v) solution, and the mixture was stirred at 40 °C for 10 min. Thereafter, the natural cellulase (1%, v/v) solution was added into the above reactor. The mixture was stirred at 40 °C for 6 h. After modification, the pH of the mixture was adjusted with acetate buffer to be within the range of 4.0–4.5 to precipitate the Eudragit–cellulase conjugate. The precipitate was then centrifuged at room temperature for 10 min and washed by re-suspending in acetate buffer (pH 4.5). The suspension was pelleted again by centrifugation, and the supernatant was separated. The modified cellulase precipitate was then re-dissolved in acetate buffer (pH 5.0) and maintained at 4 °C (Yu et al., 2013).

Enzymatic treatment of ramie fabrics

Ramie samples were dipped in 0.5–6% (o.w.f) natural or modified cellulase solution at a material-to-liquor ratio of 1:20 and were maintained at 30–70 °C and pH of 4.5–7.0 for 120 min. After the cellulase treatment, the ramie fabrics were first rinsed with deionized water to wash away abraded fibers attached to the fabrics, and the residual cellulases on the fabrics were deactivated by incubation in deionized water at 80 °C for 20 min. The treated fabrics were then washed with water and finally air dried. In the above experiments, the fabrics were treated in parallel under identical conditions with identical quantities (activity units) of modified and natural cellulases. Each experiment was performed in triplicate, and the results were averaged.

Weight loss

The cellulase-treated fabric samples were dried at 105 °C for 2 h and then conditioned in a standard atmosphere to reach equilibrium. The weight loss was calculated by Equation (1).

$$\text{Weight loss } (\%) = (W_1 - W_2)/W_1 \times 100, \qquad (1)$$

where W_1 and W_2 denote the weights of the fabric before and after enzymatic treatment, respectively.

Table 1. Specifications of the ramie fabric.

Weave construction	Plain
Fabric thickness (mm)	0.245
Fabric weight (g/m^2)	125
Fabric density (yarns/cm)	29/24

Copper number measurement

Ramie fibers (2.0 g) were placed in 250 mL Erlenmeyer flasks containing 5 mL of copper sulfate pentahydrate solution (100 g/L) and 95 mL of sodium bicarbonate solution (50 g/L) and incubated at 100 °C for 3 h. After the reaction, the ramie fibers were washed with sodium carbonate solution (35 g/L) and distilled water. The ramie fibers were separated from the solution by filtration with a sand core funnel. The ramie fibers were then added into a reactor containing 100 g/L ammonium iron sulfate dodecahydrate and 10 mL of sulfuric acid (140 g/L). After reaction for 10 min, the solution was concentrated by filtration, and the ramie fibers were washed with 1 mol/L sulfuric acid and distilled water. The solution was then titrated with 0.02 M potassium permanganate. The copper number was calculated by Equation (2) (Wu, Shao, & Fu, 2012):

$$\text{Copper number} = V \times C_{\text{KMnO}_4} \times 0.06354/D \times 100\%, \qquad (2)$$

where D is the weight of the ramie fibers, and V and C_{KMnO4} denote the volume and concentration of the consumed potassium permanganate solution, respectively.

Atomic force microscopy

A CSPM 4000 Atomic force microscope (AFM) (Benyuan Co. Ltd, Beijing, China) was used to obtain the three-dimensional images of the ramie fibers. The samples were immobilized on magnetic stubs and imaged in air using the tapping mode with the same silicon cantilever at room temperature. The scanning frequency was set to be 2.0 Hz.

Thermogravimetric analysis (TGA) measurements

TGA test of the fibers was performed using a TGA/SDTA 851e thermogravimetric analyzer (METTLER TOLEDO, Switzerland). Approximately 5 mg of sample was used in each test. The sample was heated from ambient to 600 °C at a temperature ramp of 10 °C min^{-1} under nitrogen atmosphere.

Moisture evaporation measurement

A sample with a size of 20 cm × 20 cm was dipped in distilled water for 20 min and then weighed after padding (pickup 50%). Evaporation occurred under standard atmosphere conditions of 65% relative humidity and 20 °C. The moisture evaporation value was calculated as below.

$$\text{Moisture evaporation} = (W_1 - W_2)/20S, \quad (3)$$

where W_1 is the weight of the fabric after padding, and W_2 is the weight of the fabric placed in atmosphere for 20 min. Further, S is the area of the fabric.

Capillary rise measurement

A YG (B) 871 capillometer was utilized for capillary rise measurement. The samples were placed vertically with the lower end dipped in a thin layer of a diluted potassium chromate aqueous solution. The capillometer was placed in a closed chamber to maintain a saturated vapor atmosphere. Potassium chromate was chosen to indicate the height of capillary rise, and a ruler marked off in millimeters placed along the yarn was used for easy height measurement. Height readings were recorded 30 min after the yarns were dipped in the liquid. Each measurement was carried out five times, and the averages were regarded as the final height values (Wang, Zha, & Wang, 2008).

Air permeability

Air permeability of the fabric, defined as the volume of air measured in cubic meters passed per minute through a square meter of fabric at a constant pressure ($m^3/m^2/$min), was measured by Numerical air permeability tester according to ASTM standard D737.

Fabric handle measurement

The Kawabata Evaluation System for Fabric was used for measuring the bending properties of the fabric samples included bending rigidity and bending movement (Cavaco-Paulo & Jose Rios, 1997).

Results and discussion

Effects of enzymatic treatment parameters on ramie fabric weight loss

Cellulase treatment often results in fiber loss due to the breaking of weakened fibers. Therefore, the weight loss during enzymatic treatment can be used as a measure of the extent of enzymatic hydrolysis (Kan, Yuen, & Jiang, 2008). Different variables such as cellulase concentration, reaction temperature, and time have an impact on the weight loss of ramie fabrics. The effects of enzymatic treatment parameters on the weight loss of ramie fabrics are shown in Figures 1–3.

Figure 1 shows the effect of cellulase concentration on the weight loss of ramie fabrics treated with natural or modified cellulases. As can be seen clearly, concentration-dependent trend of the catalytic activity of the modified cellulase was the same as that of natural cellulase. The weight loss increased when the cellulase concentration increased in the range of 0.5–2%; however, a slight change in weight loss occurred when the cellulase concentration increased further above 2%. Moreover, the differences in the weight losses of ramie fabrics treated with the natural and modified cellulases were constant at ca. 0.2%. The weight losses of the ramie fabrics treated with natural and modified cellulases (6% o.w.f.) were 2.79 and 2.62%, respectively.

The variation in the weight loss of ramie fabrics treated with natural and modified cellulases at different reaction temperatures is shown in Figure 2. The results show that the weight loss of the ramie fabrics was significantly influenced in the temperature range of 30–70 °C. As can be seen, for both cellulases, the weight loss of the ramie fabrics increased with temperature and was maximum at 50 °C. Further, increase in temperature (>50 °C) resulted in a decrease in the weight loss. The maximum weight loss produced by the modified cellulase (1.82%) was less than that obtained with natural cellulase (2.28%).

The weight loss of the ramie fabrics treated with the natural and modified cellulases as a function of pH is shown in Figure 3. For both versions of the enzymes, the optimum pH value for the maximum weight loss of the ramie fabrics in the reactions catalyzed by cellulase was found to be approximately 5.0. The weight loss then decreased gradually with further increase in pH. A weight loss of 2.28% was reached when the ramie fabric was treated with the natural cellulase at pH 5.0.

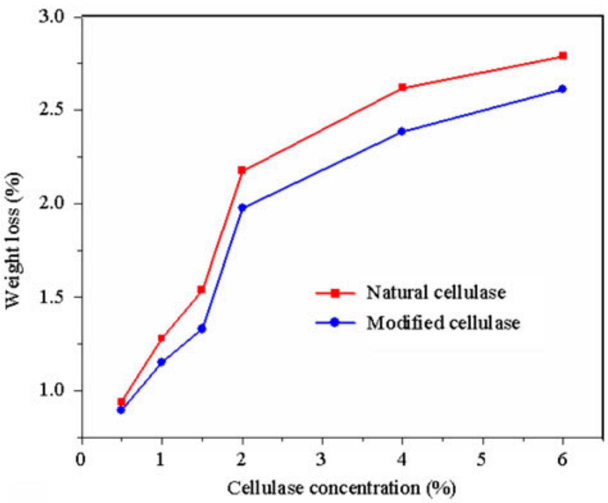

Figure 1. Effect of cellulase concentration on weight loss.

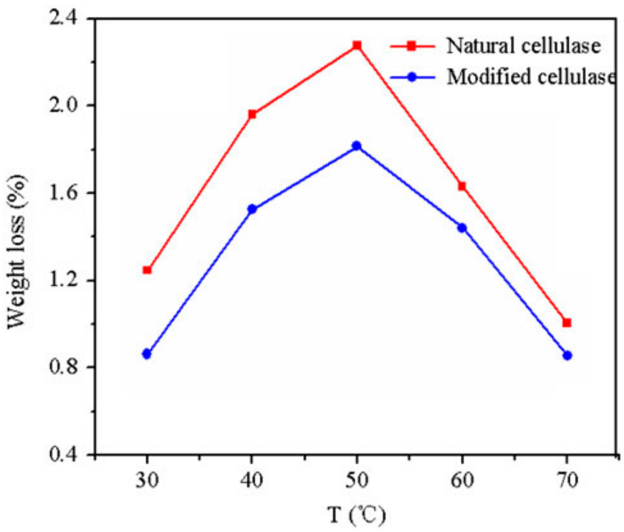

Figure 2. Effect of temperature on weight loss.

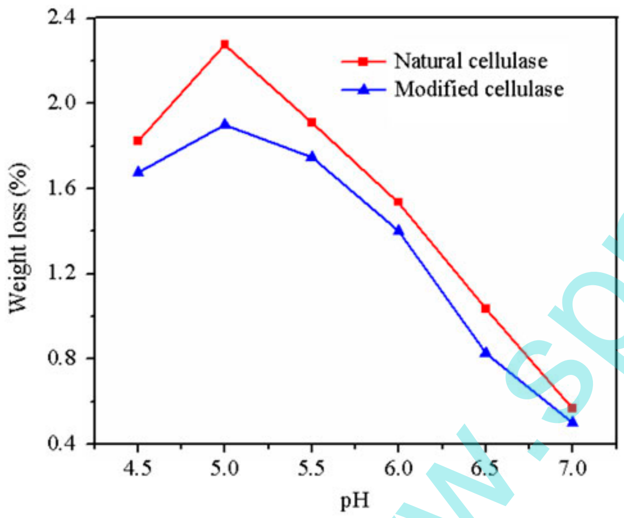

Figure 3. Effect of pH on weight loss.

However, the treatment of the ramie fabrics with modified cellulase, under the same conditions as those of natural cellulase, resulted in a lower weight loss (1.90%).

As can be seen clearly, the weight loss of the ramie fabrics treated with natural cellulase was greater than that of ramie fabrics treated with modified cellulase under the same conditions. It implied that less damage was caused by the modified cellulase because of the localization of the hydrolytic attack on the fiber surfaces. Figures 2 and 3 also show that the optimum pH value and temperature of the modified cellulase are wider than those of natural cellulase's. As several long chains of Eudragit S-100 are grafted onto the surface of the enzyme, the modified cellulase is more rigid in the solution, and it demonstrated better thermal and pH stability when compared with the natural enzyme (Yu et al., 2012).

Fiber damages of ramie fabric

The untreated ramie fibers (control) having a copper number of 0.0166 were subjected to cellulase (natural and modified) under previously mentioned conditions. The copper numbers of the ramie fibers after treatment with different concentrations of cellulases (natural and modified) are shown in Figure 4. Enzymatic treatment of ramie fiber with natural and modified cellulase results in an increase of its copper number, depending on the extent of the reaction (Kantouch, Hebeish, & El-Rafie, 1970). A copper number of 0.0201 was achieved when the ramie fiber was treated with natural cellulase (2.0%). However, the treatment of ramie fibers with modified cellulase, under the same conditions as those of natural cellulase, resulted in a lower copper number (0.0167), which was very close to the control.

Overall, both the natural and modified cellulases treatments resulted in deterioration of the ramie fibers because of ruptures in the enzymatically weakened fibers; however, the ramie fibers treated with the modified cellulase showed lower copper number than those treated with the natural cellulase. Therefore, the modified cellulase treatment caused less damage to the ramie fabrics. Because the Eudragit S-100 macromolecules (polyacrylates) were grafted onto the surface of the enzyme, the hydrolytic attack of the modified cellulase was restricted to the surface of the ramie fibers.

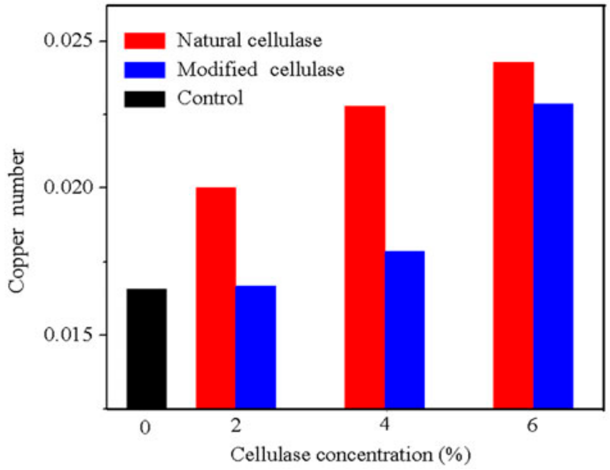

Figure 4. Effect of enzymatic treatment on the copper number of ramie fiber.

Effect of enzymatic treatment on the surface of ramie fiber

The tapping-mode of AFM was used to investigate the effects of natural and modified cellulases on the surface of the ramie fibers. As shown in Figure 5, the ramie fiber control has a rugged appearance with parallel microfibrils. After natural and modified cellulase treatments, significant structural changes were observed. When the ramie fibers were treated with natural cellulase, the disruption of the fibers was apparent. The surface structure presented high levels of peeling and cracking. However, the modified cellulase removed the loose outer portions of ramie fibers resulting in a smoothing effect without severe damage.

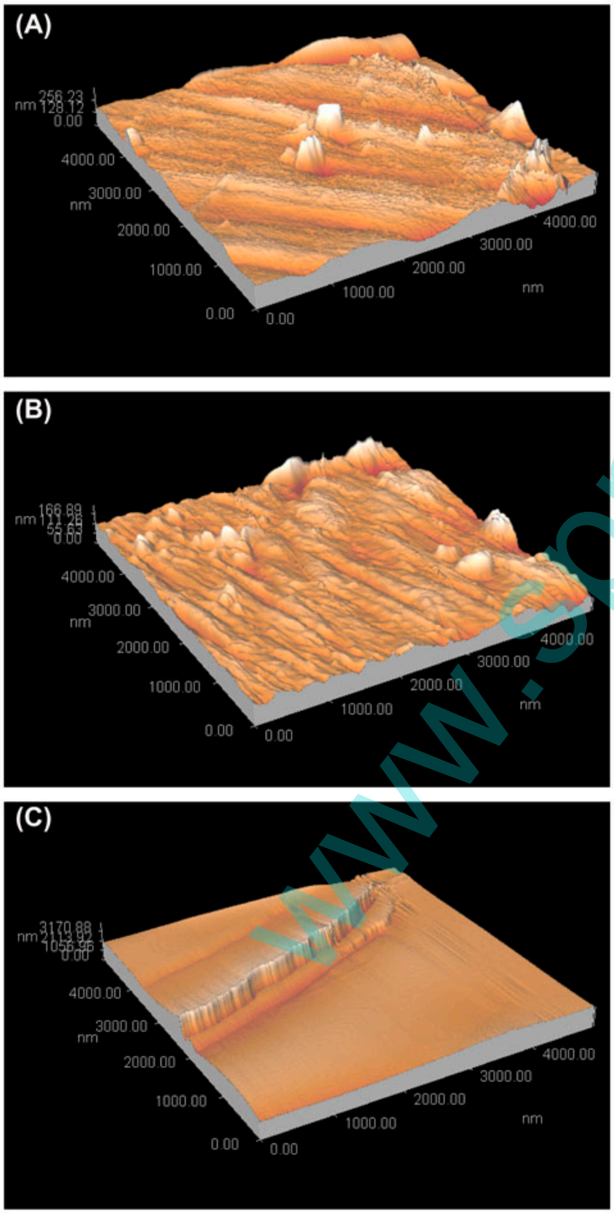

Figure 5. 3-D topographic images of ramie fibers treated with (A) buffer (control), (B) natural cellulase, and (C) modified cellulase.

Thermogravimetric analysis

TGA was used to investigate the decomposition patterns and thermal stability of the ramie fibers. The TGA graphs of the untreated and cellulase-treated ramie fibers are shown in Figure 6. Figure 6 also shows the weight loss derivative curves, which provides the rate at which the different samples decompose. In the case of the untreated ramie fiber, after initial loss of moisture and desorption of gases at approximately 100–120 °C, a major decomposition occurred from 300 to 390 °C. For the ramie fibers treated with natural and modified cellulases, the decomposition patterns were similar to that of the untreated ramie fiber. The pyrolysis of the primary components occurred at approximately 369 °C in untreated and cellulase-treated ramie fibers. It has been reported that the thermal stability of cellulose depends on its crystallinity (Yin et al., 2007). Since amorphous regions are often too narrow for the large enzyme molecules to penetrate effectively, there was hardly any change in the ratio of ordered and less-ordered regions (Buschle-Diller, Zeronian, Pan, & Yoon, 1994). Therefore, thermal stability was only slightly affected by cellulase modification.

Comfort characteristics

The effect of cellulase treatment on the comfort characteristics of ramie fabrics was also investigated (Table 2). The bending properties include the bending rigidity (B) and bending moment (2HB), which have

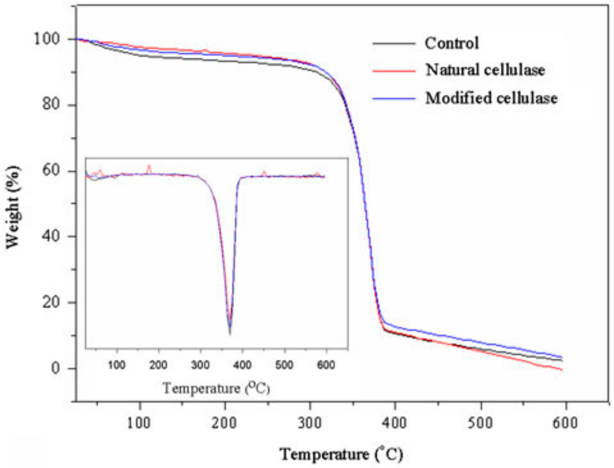

Figure 6. TGA curves of untreated ramie fiber and ramie fibers treated with natural and modified cellulases.

Table 2. Effect of cellulase treatment on comfort characteristics of ramie fabrics.

	Cellulase concentration (%)	Bending rigidity (gf cm^2/cm)	Bending moment (gf cm/cm)	Wicking in length (cm)	Moisture evaporation (g/m^2 min)	Air permeability (m^3/m^2/min)
Control	0	0.1596	0.0589	11.52	0.7000	40.13
Natural cellulase	2	0.1411	0.0562	14.38	0.7856	42.53
	4	0.1384	0.0506	14.51	0.8750	45.05
	6	0.1337	0.0507	14.68	0.8653	46.87
Modified cellulase	2	0.141	0.0576	12.45	0.8067	50.19
	4	0.1308	0.0478	13.12	0.9625	50.86
	6	0.1272	0.0428	13.79	0.8782	51.55

important effects on the handle and tailoring performance of the fabric. Bending rigidity (B) is defined as the ability of a fabric to resist the bending movement. Bending moment (2HB) reveals the recovery ability of the fabric after bending. The smaller the values of 2HB, the better the fabric bending recovery ability will be. The values of bending rigidity and bending moment of the untreated ramie fabrics (control) were higher than those of the ramie fabrics' treated with natural and modified cellulases. The results indicated that cellulase treatment can enhance the flexibility and elastic recovery of ramie fabrics (Kan, Yuen, & Lam, 2009).

The wicking and moisture evaporation properties of the ramie fabric primarily depend on the characteristics of the fiber and the structure of the component yarns and fabrics (Khanum & Shivaprakash, 2013). As can be seen in Table 2, the cellulase-treated ramie fabrics have higher wicking and moisture evaporation values when compared with those of the untreated fabric. The air permeability of the ramie fabric was also improved by cellulase treatment. This can be attributed to the fact that cellulases can hydrolyze accessible intramolecular β-1,4-glucosidic bonds of cellulose chains randomly (Percival Zhang, Himmel, & Mielenz, 2006). Therefore, enzymatic treatment removed the fuzz fibers and pills of the fabric surfaces and increased the distance between yarns, thus enhancing the flow of water droplets and vapor through the loose structural matrix of the yarns. Meanwhile, more spaces were available in fabrics for the passage of air.

Conclusions

Concentration of cellulases (natural or modified), reaction temperature, and pH can significantly influence the properties of cellulase-treated fabrics. The optimum conditions were 2% (o.w.f.), pH 5.0, and 50 °C for both the cellulases. The ramie fabrics treated with the modified cellulase exhibited lower weight loss and copper number when compared with those treated with natural cellulase. Both the natural and modified cellulases improved the appearance, softness, moisture evaporation, wicking property, and air permeability of the fabric when compared with the control. After cellulase treatments, the thermal stability of the fiber was almost the same as that of the control. The experimental results showed that the modified cellulase treatment can improve the comfort of the ramie fabrics without excessive damage to the fibers. Hence, ramie apparel can be used for daily fashion wear; specialized medical applications; different types of athletic gear; and protective ensembles for military, industrial, and special personnel.

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References

Bower, B. S., Clarkson, K. A., Larenas, E. A., & Ward, M. (1998). *Enlarged cellulase compositions for use in the treatment of textiles*. Patent Application WO 9828411. Geneva, World Intellectual Property Organization.

Buschle-Diller, G., Zeronian, S. H., Pan, N., & Yoon, M. Y. (1994). Enzymatic hydrolysis of cotton, linen, ramie, and viscose rayon fabrics. *Textile Research Journal, 64*, 270–279.

Cavaco-Paulo, A. (1998). Mechanism of cellulase action in textile processes. *Carbohydrate Polymers, 37*, 273–277.

Cavaco-Paulo, A., & Jose Rios, M. (1997). Mechanical properties of cellulase-treated fabrics analyzed. *American Dyestuff Reporter, 86*, 20–28.

Emilia, C., & Péter, S. (2004). Improving softness and hand of linen and linen-containing fabrics with finishing. *AATCC Review, 4*, 17–21.

Goda, K., Sreekala, M. S., Gomes, A., Kaji, T., & Ohgi, J. (2006). Improvement of plant based natural fibers of toughening green composites – Effect of load application during mercerization of ramie fibers. *Composites Part A: Applied Science and Manufacturing, 37*, 2213–2220.

Ibrahim, N. A., El-Badry, K., Eid, B. M., & Hassan, T. M. (2011). A new approach for biofinishing of cellulose-containing fabrics using acid cellulases. *Carbohydrate Polymers, 83*, 116–121.

Kalia, S., & Sheoran, R. (2011). Modification of ramie fibers using microwave-assisted grafting and cellulase enzyme-assisted biopolishing: A comparative study of morphology, thermal stability, and Crystallinity. *International Journal of Polymer Analysis and Characterization, 16*, 307–318.

Kan, C., Yuen, C., & Jiang, S. (2008). Enzymatic treatment of linen. *The Journal of The Textile Institute, 99*, 363–368.

Kan, C., Yuen, C., & Lam, Y. (2009). Effect of enzyme treatment and dyeing on the mechanical properties of linen. *Coloration Technology, 125*, 269–276.

Kantouch, A., Hebeish, A., & EI-Rafie, M. H. (1970). Action of sodium chlorite on cellulose and cellulose derivatives. *Textile Research Journal, 40*, 178–184.

Khanum, H., & Shivaprakash, A. V. (2013). Product Development of Blended Milk Casein Knitted Garment (Part-I). *Man-Made Textiles in India, 41*, 50–56.

Lee, L. L., & Lee., J. C. (1987). Thermal stability of proteins in the presence of poly(ethylene glycols). *Biochemistry, 26*, 7813–7819.

Lenting, H. B. M., & Warmoeskerken, M. (2001). Guidelines to come to minimized tensile strength loss upon cellulase application. *Journal of Biotechnology, 89*, 227–232.

Liu, Z. T., Yang, Y., Zhang, L., Liu, Z. W., & Xiong, H. (2007). Study on the cationic modification and dyeing of ramie fiber. *Cellulose, 14*, 337–345.

Mamma, D., Kalantzi, S., & Christakopoulos, P. (2004). Effect of adsorption characteristics of a modified cellulase on indigo backstaining. *Journal of Chemical Technology and Biotechnology, 79*, 639–644.

Percival Zhang, Y. H., Himmel, M. E., & Mielenz, J. R. (2006). Outlook for cellulase improvement: Screening and selection strategies. *Biotechnology Advances, 24*, 452–481.

Wang, N., Zha, A., & Wang, J. (2008). Study on the wicking property of polyester filament yarns. *Fibers and Polymers, 9*, 97–100.

Wu, Y., Shao, J., & Fu, G. (2012). The study on the mechanism of improving of P/C fabric soil release property by cellulase washing. *Journal of Zhejiang Sci-Tech University, 29*, 40–43.

Yin, C. Y., Li, J. B., Xu, Q., Peng, Q., & liu, Y. B., & Shen, X. Y. (2007). Chemical modification of cotton cellulose in supercritical carbon dioxide: Synthesis and characterization of cellulose carbamate. *Carbohydrate Polymers, 67*, 147–154.

Yu, Y., Yuan, J., Wang, Q., & Fan, X. (2013). Immobilization of cellulases on the reversibly soluble polymer Eudragit S-100 for cotton treatment. *Engineering in Life Sciences, 13*, 194–200.

Yu, Y., Yuan, J., Wang, Q., Fan, X., & Wang, P. (2012). Covalent immobilization of cellulases onto a water-soluble–insoluble reversible polymer. *Applied Biochemistry Biotechnology, 166*, 1433–1441.

Zhang, Y., Tang, L., An, X., Fu, E., & Ma, C. (2009). Modification of cellulase and its application to extraction of diosgenin from Dioscorea zingiberensis C.H. Wright. *Biochemical Engineering Journal, 47*, 80–86.