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Effectiveness of Enzymatic Hydrolysis on Polyamide Fabric

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Abstract

We compared the effectiveness of amidase (amano acylase, AA) and an endopeptidase, (trypsin, TR) in modifying the hydrophobicity of polyamide fabric. We evaluated the number of amino groups released into the reaction mixture in order to optimize the treatment conditions. We found that a large number of amino groups were released into the reaction mixture due to the cleavage of amide bonds by AA hydrolysis; however, the TR hydrolysis exhibited a relatively lower activity compared to AA hydrolysis. In AA and TR hydrolysis, significant differences were observed in the K/S values and moisture regain. Amide bonds in polyamide fabric were hydrolyzed by AA hydrolysis effectively. Compared to TR, AA formed more hydrolysis product (amino groups) on the fabric surface. Thus, the hydrophobicity of polyamide fabric was modified using AA hydrolysis (as verified by the wettability test) without any deterioration of fiber strength.

Key words: Acylase, Trypsin, Polyamide, Hydrophilicity, Hydrophobicity

I. Introduction

Surface modification using enzymes has been considered a valuable tool for modifying synthetic fibers (Silva et al., 2010). Polyamide (PA) fibers offer advantages such as lightweight, good strength, and excellent abrasion resistance. However, the hydrophobicity of PA causes discomfort when worn (Gübitz & Cavaco-Paulo, 2008; Song et al., 2012). Enzymatic modification of PA fabric for improving its hydrophilicity has been investigated using proteases (Almansa et al., 2008; Parvinzadeh et al., 2009; Silva et al., 2005; Song et al., 2012) because the synthetic amide bonds in PA fibers are similar to those in proteins. However, the amide bonds in PA fibers are non-biodegradable as they are resistant to microbial and enzymatic hydrolysis (Klun et al., 2003). Thus, in protease hydrolysis, a key feature is the balance between exo (terminal cleaving) and endo (internal cleaving) enzymes. Several biotechnological applications, particularly paper and pulp, human food, detergent, and textile sectors use endo-acting proteases (Proctor et al., 2005).

In enzymology, amidases (EC 3.5.1.4) such as acylamidase, acylase, amidohydrolase, fatty acylamidase, and N-acetylaminohydrolase are enzymes that hydrolyze amides. They belong to the enzyme class of hydrolases, similar to proteases. In PA hydrolysis, a few studies have been reported using amidases such as aryl acylamidases, aminohydrolases, and acylases (Heumann et al., 2009; Kim & Seo, 2013; Liljeblad et al., 2000; Youshko et al., 2004). Among these, only acylases are commercially available.

In order to broaden the use of biocatalytic methods involving enzymes on PA fabric, it is necessary to find effective enzymes for the hydrolysis of PA using commercially available enzymes. Therefore, the present study aims to find more effective enzymes for hydrolysis of PA fabric to modify its hydrophobicity. This was done by comparing two types of enzymes, endoproteases and acylases. Among endoproteases, trypsin

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(TR, E.C. 3.4.21.4) is known to effectively hydrolyze amide bonds in proteins. Moreover, amano acylase (AA, E.C. 3.5.1.14) is suitable for carrying out highly stable resolutions of all batches (Gadamasetti & Braish, 2007; Liljeblad & Kanerva, 2006; Youshko et al., 2004). However, the ability of these enzymes to hydrolyze amide bonds in PA fabric has not been determined. The relative hydrolytic activity of AA and TR was evaluated based on the quantity of hydrolysis product (amino groups) released into the reaction mixture owing to the reaction between amino groups and 2,4,5-trinitrobenzenesulfonic acid (TNBS) (Heumann et al., 2006; Silva & Cavaco-Paulo, 2004; Silva et al., 2005). The TNBS method is well suited for quantifying the degree of hydrolysis, regardless of the activity of the enzyme used (Spellman et al., 2003). Thus, the relative activity of AA and TR was compared at different pH, temperature, and reaction time using the TNBS method. The effect of hydrolysis of each enzyme was compared using moisture regain and K/S values of α-bromoacrylamide reactive dye, which reacted with the primary amino groups (Choudhury, 2006; Silva & Cavaco-Paulo, 2004).

II. Experimental

1. Materials

All experiments were conducted using 100% commercial PA 6 fabric (Table 1). All fabric samples were washed with 2g/L Triton-X at 50°C for 30 min, and then rinsed with water at 50°C for 30 min to desize them before enzymatic treatment. Commercially available AA (E.C. 3.5.1.14, 30,000U/g at pH 8.0 and 50°C; Sigma Chemicals Co., USA) and TR (E.C. 3. 4. 21. 4, 1,500U/mg at pH 7.6 and 25°C ; Sigma Chemicals Co., USA) were used without further purification. Sodium phosphate monobasic ($NaH_2PO_4 \cdot 2H_2O$, Sigma Chemical Co., USA) and sodium phosphate dibasic ($Na_2HPO_4 \cdot 12H_2O$, Sigma Chemical Co., USA) were used for the buffer of the enzyme. The following chemicals were used without further purification: Triton X-100 (non-ionic surfactant; Sigma Chemicals Co.), sodium carbonate (Duksan Pure Chemicals), TNBS (Sigma Chemicals Co., USA), α-bromoacrylamide reactive dye (Lunasol Blue 3G, C. I. Reactive Blue 69; Huntsman Chemicals Co., USA).

2. Enzymatic Hydrolysis

The PA fabric was treated with AA in buffer at a liquor ratio of 50:1 (buffer solution:fabric) at various pH values (7.5, 8.0, 8.5, 9.0), temperatures (40, 50, 60°C), and treatment times (10, 30, 60, 120, 180 min).

The PA fabric was treated with TR in buffer at a liquor ratio of 50:1 (buffer solution:fabric) at various pH values (7.5, 8.0, 8.5, 9.0), temperatures (20, 30, 40, 45°C), and treatment times (10, 30, 60, 180 min).

All enzymatic treatments were performed in a shaking water bath (BS-21; Jeio Tech, Korea) at 120 rpm. The enzyme was subsequently inactivated at 90°C for 10 min. The samples were washed with 2g/L sodium carbonate at 50°C for 60 min, and then with 2g/L Triton-X at 50°C for 60 min. The samples were then rinsed thoroughly and dried at room temperature.

3. Determination of Relative Activity by the Amount of Amino Groups in the Treatment Liquid

The relative activity of AA and TR on PA fabric was evaluated by quantitating the amino groups released into the treatment liquid using the TNBS method. The reaction of an amine-TNBS complex was monitored spectrophotometrically at 340nm (Garćia-Castiñeiras & Miranda-Rivera, 1983; Sashidhar et al., 1994). The TNBS method was implemented in the following steps (Adler-Nissen, 1979; Garćia-Castiñeiras & Miranda-Rivera, 1983): After enzymatic treatment, 0.25mL of the treatment liquid was mixed with 2mL of phosphate buffer and 2mL of TNBS. This mixture was incubated at 50°C for 60 min at 80rpm. After incuba-

Table 1. Fabric characteristics

Fiber (%)	Weave	Fabric count (yarns/inch)	Weight (g/m^2)	Thickness (mm)
Polyamide 100	Plain	112 × 84	57.3 (±0.5)	0.11

tion, 4mL of 0.1 N HCl was added, and the mixture was cooled to room temperature for 30 min. The formation of the amine-TNBS complex was monitored via the absorbance (ABS) at 340nm using an ultraviolet-visible spectrophotometer (S-3100; Scinco Co., Korea).

A control that consisted of AA or TR but without PA fabric subjected to the same TNBS test for the experimental samples was prepared. The relative activity was calculated using the following <Eq. 1>:

$$\text{Relative Activity (\%)} = \frac{\text{ABS (E+PA)} - \text{ABS (E)}}{\text{ABS (E)}} \times 100 \quad \cdots\cdots \text{Eq. 1.}$$

where ABS (E+PA) is the absorbance of the treatment liquid of enzyme (AA or TR) and PA fabrics at 340nm, and ABS (E) is the absorbance of the treatment liquid of only enzyme (AA or TR) at 340nm.

4. Quantification of the Ionic Groups Formed on the Fabric Surface

To detect amino groups on the fabric surface, the PA fabric was dyed using α-bromoacrylamide reactive dyes. PA fabric was dyed with 1% o.w.f. reactive dye at a liquor ratio of 50:1 at 80°C for 90 min. After dyeing, the samples were washed with Triton X-100 (2% o.w.f.) at 50°C, and then with tap water (Silva et al., 2005).

The reflectance and corresponding L*, a*, b* values and color data for the dyed samples were determined using a computational color-matching system (JX-777, Japan) and illuminant D_{65} with a 10° standard observer. The K/S value was calculated from the reflectance values through the Kubelka-Munk <Eq. 2>:

$$K/S = (1-R)^2/2R \quad \cdots\cdots \text{Eq. 2.}$$

where R is the reflectance, K is the absorption coefficient, and S is the light-scattering coefficient. All measurements were performed at least 10 times.

Moisture regain was evaluated according to ASTM D 629-08 by measuring the dry weight and moisture-conditioned weight of untreated and enzymatic treated PA fabric samples. The moisture regain of the PA fabrics was calculated using the following <Eq. 3>:

$$\text{Moisture regain (\%)} = \frac{W_m - W_d}{W_d} \times 100 \quad \cdots\cdots \text{Eq. 3.}$$

where W_m is the weight of the fabric in moisture equilibrium at 20°C and 65% relative humidity, and W_d is the weight of the fabric dried at 105°C for 1 h.

For the statistical analysis, the SPSS 20 software package was utilized. Statistically significant factors of the K/S values and moisture regain were determined by analysis of variance (one-way ANOVA). Multiple comparison tests using the Duncan test were conducted as post hoc tests. The factors were considered as significant at p values of less than 0.05.

5. Properties of PA Fabrics

The wettability of the PA fabric was evaluated by its water absorbency and WCA. The water absorbency was determined according to AATCC 79-1992. The WCA value was determined using a contact-angle measurement system (KRÜSS DSA 100; KRÜSS Inc., Germany). 3μL water was dosed on the fabric and data were obtained from the first value after dosing. Each test was conducted 10 times.

The air permeability of the PA fabric was determined in accordance with ISO 9237 using an air permeability tester under a pressure of 100 Pa. Changes in the surface of the PA fabrics were analyzed by scanning election microscopy (SEM, S-3500N, Hitachi, Japan) after plating the samples with gold.

The weight loss of the fabric was evaluated from the dry weight of the fabric before and after enzymatic treatment. Drying was done at 105°C for 1 h in a drying oven. Samples were weighed after cooling in an auto-desiccator. All samples were weighed in a closed weighing bottle. The weight loss was calculated by the following <Eq. 4>:

$$\text{Weight loss (\%)} = \frac{w_1 - w_2}{w_1} \times 100 \quad \cdots\cdots \text{Eq. 4.}$$

where w_1 is the dry weight of the fabric before treatment and w_2 is the dry weight of the fabric after treatment. The tensile strength of the PA fabric was

determined by the strip method, in accordance with KS K 0521: 2006.

III. Results and Discussion

1. Comparison of the Relative Activity of AA and TR under Different Conditions

<Fig. 1> shows the relative activity of AA and TR on the PA fabric based on the number of amino groups released into the reaction mixture, as determined by the TNBS method. In AA treatment <Fig. 1(a)>, the PA fabric was treated with 10% AA o.w.f. for 60 min at pH values ranging from 7.5 to 9.0 and temperatures ranging from 40°C to 60°C. In TR treatment <Fig. 1(b)>, the PA fabric was treated with 10% TR o.w.f. for 60 min at pH values ranging from 7.5 to 9.0 and temperatures ranging from 20°C to 45°C.

The number of amino groups released in AA and TR treatments increased until pH 8.5 at 50°C and pH 8.5 at 40°C, respectively; a plot of the number of amino groups against pH yielded a parabolic curve. When the pH of the reaction mixture was increased to > pH 9.0, the relative activity of both AA and TR decreased. Moreover, the relative activity of AA above 60°C and that of TR above 45°C decreased rapidly. Thus, pH and temperature were found to be important parameters for AA and TR hydrolyses on the PA substrate.

The relative activity of AA and TR was observed using the TNBS method, which was based on the reaction between primary amines and TNBS. When the number of amino groups increased in the reaction mixture after enzymatic hydrolysis, the relative activity of enzymes improved. This increase in the relative activity of enzymes confirmed that they hydrolyzed amide bonds in the PA fabric; a large number of amino groups were released into the reaction mixture because of the cleavage of amide bonds.

The relative activity of TR exhibited lower values compared to that of AA. AA could hydrolyze natural and synthetic amide bonds with high enantioselectivity (Banks & O'Hagan, 2000; Youshko et al., 2004) but the TR had insufficient hydrolytic activity on synthetic amides in the PA fabric. Since the amide bonds in PA fibers are non-biodegradable, they are resistant to microbial and enzymatic hydrolysis (Klun et al., 2003). Moreover, the lower relative activity of TR influenced K/S values of α-bromoacrylamide dyed

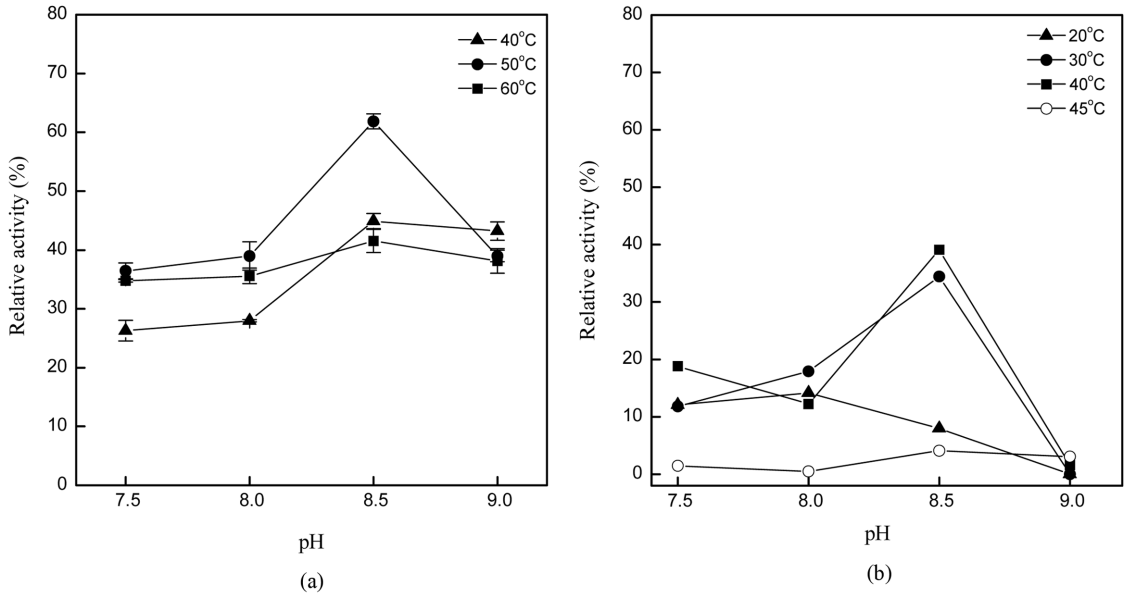


Fig. 1. Effects of pH and temperature on relative activity of AA (a) and TR (b) treatments of PA fabric. Treatment conditions: AA (a) - 10% (o.w.f.) AA, 60 min; TR (b) - 10% (o.w.f.) TR, 60 min.

PA fabric.

The optimum conditions for hydrolysis of AA and TR, as prescribed by manufacturers, were pH 8.0, 50°C and pH 7.6, 25°C, respectively. However, the relative activity under these conditions showed extremely low values compared to the others (Fig. 1). The activity of enzymes was affected by substrate form and construction (Cavaco-Paulo & Gübitz, 2003). Thus, when PA fabric was used as a substrate for AA and TR hydrolyses, the treatment conditions were optimized by evaluating the quantity of hydrolysis products.

<Fig. 2> shows K/S values of α-bromoacrylamide-dyed PA fabric at different pH and temperatures used in AA hydrolysis. This was used to detect the formation of amino groups on the surface of the fabric. K/S values of AA-treated PA fabric were similar to the behavior of relative activity of AA shown in <Fig. 1(a)>. A plot of K/S values against temperatures yielded parabolic curves; an increase with pH up to 8.5 was found. The highest K/S value was observed at 50°C and pH 8.5.

The K/S values of PA fabric are proportional to the number of amino groups present because the α-bromoacrylamide dye reacts with the primary amino groups (Choudhury, 2006; U.S. Patent No. 0289120 A1, 2008; Silva & Cavaco-Paulo, 2004). Thus, an increase in the K/S values of α-bromoacrylamide-dyed PA fabric after AA hydrolysis confirmed the formation of new amino groups on the surface of the PA fabric (U.S. Patent No. 0289120 A1, 2008; Silva & Cavaco-Paulo, 2004).

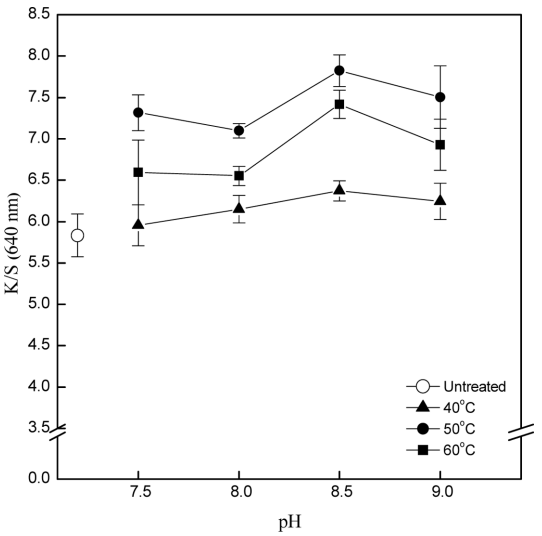


Fig. 2. Effects of pH and temperature on K/S values of AA-treated PA fabric. Treatment conditions: 10% (o.w.f.) AA, 60 min.

However, the K/S values of the dyed PA fabric did not improve after TR hydrolysis as shown in <Fig. 5>. Even though TR hydrolyzed amide bonds in the PA fabric, as shown in <Fig. 1(b)>, new amino groups were not formed on the surface of the fabric due to the low relative activity. The detailed comparison of K/S values obtained in AA and TR hydrolyses is discussed in <Fig. 5>.

<Fig. 3> shows the effect of treatment time on the relative activity of AA and TR. In AA hydrolysis <Fig. 3(a)>, the PA fabric was treated for 10-180 min with 10% AA o.w.f. at pH 8.5 and 50°C. In TR hydrolysis <Fig. 3(b)>, the PA fabric was treated for 10-180 min with 10% TR o.w.f. at pH 8.5 and 40°C.

The highest number of amino groups released into the reaction mixture was obtained at 60 min, which was attributable to the effective hydrolysis of the PA fabric by AA and TR. The relative activity decreased rapidly beyond 60 min.

The K/S values of AA-treated PA fabric improved as the treatment time increased (Fig. 4). The highest K/S value was obtained for the treatment time of 60 min but the K/S values did not improve any further because AA hydrolysis ended after 60 min. Thus, even with longer treatment times, the number of amino groups released did not increase.

Therefore, the optimal conditions for treatments with AA and TR were determined to be pH 8.5, 50°C, 60 min and pH 8.5, 40°C, 60 min, respectively.

2. Comparison of Number of Ionic Groups Formed on Fabric Surface during AA and TR Hydrolysis

<Fig. 5> shows the K/S values of untreated, AA-treated, and TR-treated PA fabric. The K/S values for AA-treated samples improved but the values for TR-treated samples did not differ from those of the untreated samples. The analysis of variance (ANOVA)

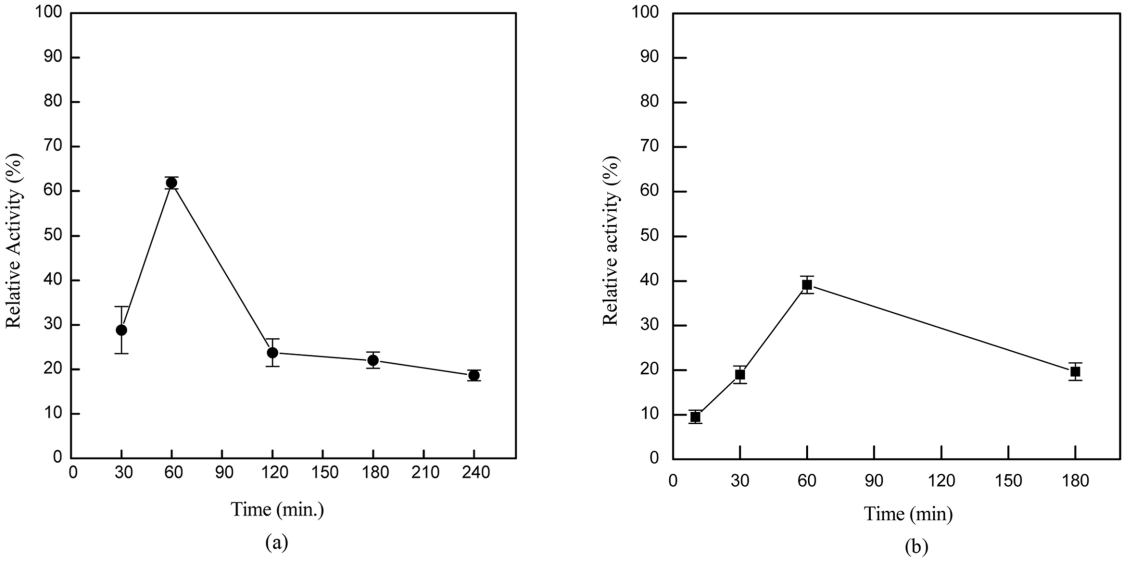


Fig. 3. Effects of treatment time on relative activity of AA (a) and TR (b) hydrolyses of PA fabrics. Treatment conditions: AA (a) - pH 8.5, 50°C, 10% (o.w.f.) AA; TR (b) - pH 8.5, 40°C, 10% (o.w.f.).

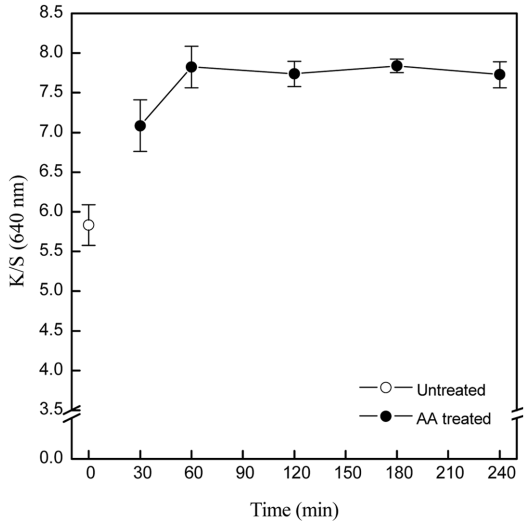


Fig. 4. Effect of treatment time on K/S values of AA-treated PA fabric. Treatment conditions: pH 8.5, 50°C, 10% (o.w.f.) AA.

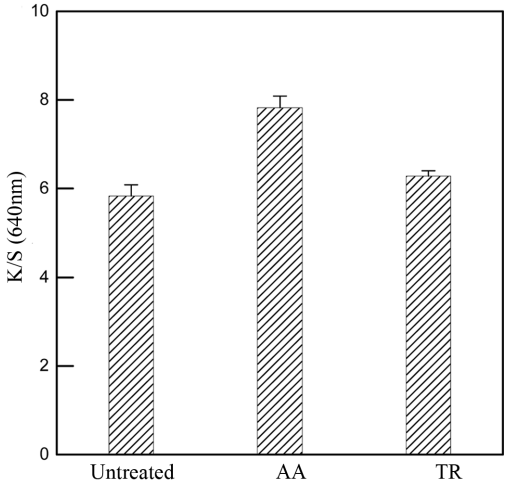


Fig. 5. K/S values of dyed PA fabric subjected to different conditions. AA: amano acylase treatment at pH 8.5, 50°C, 60 min, 10% (o.w.f.) acylase. TR: trypsin treatment at pH 8.5, 40°C, 60 min, 10% (o.w.f.) trypsin.

of the K/S values confirmed the significance levels; in particular, F=59.310 and p=.000 at 95%. The Duncan analysis indicated that the fabric could be divided into two groups based on the K/S values: i) untreated and TR-treated samples and ii) AA-treated samples. Thus, ANOVA and Duncan analysis demonstrated that the AA treatment significantly increased the K/S values of the dyed PA fabric. However, the TR-treatment did not influence the K/S values of the PA fabric. In order to improve the hydrophilicity of the PA fabric, hydrophilic ionic groups need to form on the fabric

surface after enzymatic hydrolysis. Thus, we assumed that an adequate number of ionic groups were not generated on the PA fabric by TR hydrolysis, and therefore, the K/S values did not change.

To determine whether the improvement in K/S values of α-bromoacrylamide-dyed PA fabric was influenced by the formation of hydrophilic ionic groups, the moisture regain of AA- and TR-treated PA fabric was compared (Fig. 6).

<Fig. 6> shows the moisture regain of AA- and TR-treated PA fabric. The moisture regain values of TR-treated samples were similar to those of the untreated samples. The moisture regain values of the PA fabric slightly improved with AA hydrolysis. In order to determine whether an improvement in the moisture regain by AA hydrolysis had statistically significant differences or not, one-way ANOVA and multiple comparison tests using Duncan analysis were conducted as post hoc tests.

According to the Duncan analysis, the moisture regain values were divided into two groups; i) untreated and TR-treated samples, and ii) AA-treated samples. The ANOVA of moisture regain was confirmed by the significance levels; in particular, F=32.355 and p=.001 at 95%. The factors were considered as significant at p values of less than 0.05. Thus, ANOVA demonstrated that AA hydrolysis had a statistically significant influence on an increase in the moisture regain of PA fabric. Moreover, there was no significant difference between untreated and TR-treated PA fabric. Even though TR hydrolyzed amide bonds in the PA fabric, as shown through relative activity in <Fig. 1(b)> and <Fig. 3(b)>, TR hydrolysis did not improve the hydrophilicity of PA fabric. This was because hydrophilic ionic groups (hydrolysis product) did not form on the surface of the fabric. Therefore, it was evident that TR hydrolysis was not effective in the modification of hydrophobicity of the PA fabric.

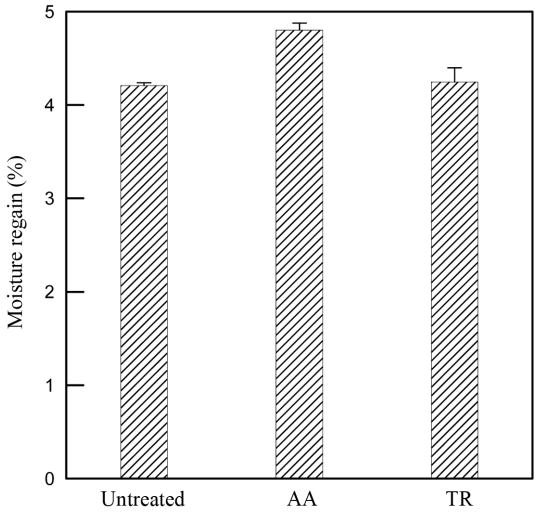


Fig. 6. Moisture regain of PA fabrics subjected to different conditions. AA: amano acylase treatment at pH 8.5, 50°C, 60 min, 10% (o.w.f.) acylase. TR: trypsin treatment at pH 8.5, 40°C, 60 min, 10% (o.w.f.) trypsin.

Thus, the wettability, air permeability, tensile strength, and scanning electron microscopy (SEM) micrographs of the PA fabric have been discussed only for the case of AA hydrolysis.

3. Properties of PA Fabric after AA-hydrolysis

<Fig. 7> shows the wettability values (water contact angle (WCA) and water absorption) for various treatment conditions. The WCAs of the untreated and buffer treated samples were 108.2°±0.562° and 107.9°±0.704°, respectively. When the PA fabric was treated with AA, the WCA of PA fabric decreased to 81.4°±0.398°. After AA treatment, the water absorption time of PA fabric was 87s±4.559s, which was shorter compared with those of the untreated (108s±0.96s) and buffer-treated fabric (101.1s±1.7s). Since the hydrophilic ionic groups were formed on the PA fabric through AA hydrolysis, the wettability of the fabric improved. The number of newly formed ionic groups increased on the surface of the fabric. The hydrolysis of enzymes was limited on the surface of the PA fabric because of the presence of amorphous regions in the synthetic fibers, which contained relatively smaller pores through which the large enzyme molecules could not pass through (Cavaco-Paulo & Gübitz, 2003; Kim & Seo, 2013; Kim & Song, 2006).

The improvement in the wettability was influenced either by the newly formed hydrophilic ionic groups or void spaces (pores) in the fabric and the roughness of the fiber surface (Kim & Song, 2006; Perin et al.,

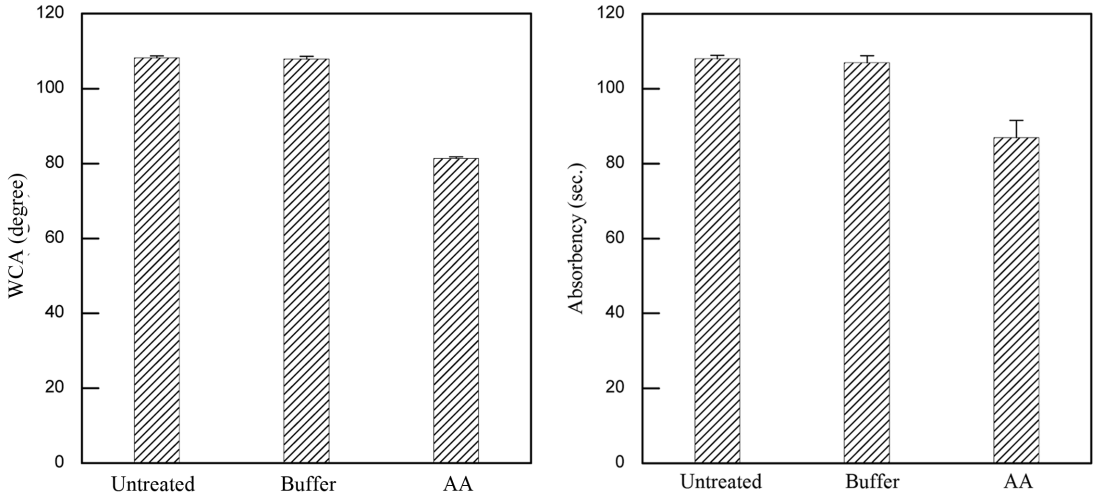


Fig. 7. Wettability of PA fabric subjected to different treatments. Buffer: pH 8.5, 50°C, 60 min. AA: pH 8.5, 50°C, 60 min, 10% (o.w.f.) AA.

2004; Simile, 2004). Changes in the pores of the woven fabric were evaluated through air permeability. When the pores in the woven fabric were big, the air permeability increased (Kaynak & Babaarslan, 2012; Kim & Seo, 2013; Ogulata, 2006). As shown in <Fig. 8>, the changes in air permeability of AA-treated PA fabric were negligible, showing minor changes within the range of acceptable error. Therefore, an improvement in the wettability was affected rather by the concentration of hydrophilic ionic groups formed than the changes in the pores of the fabric, as demonstrated by the K/S values.

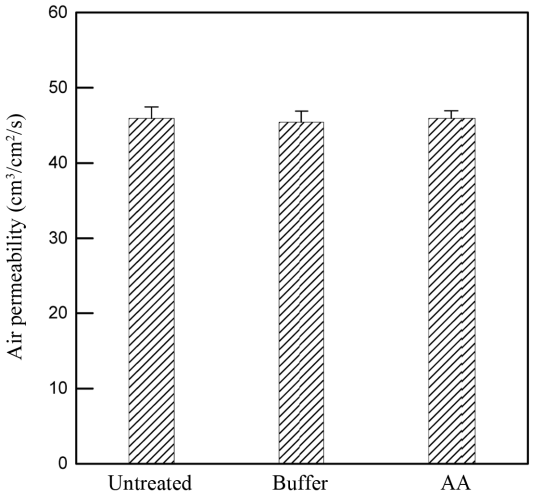


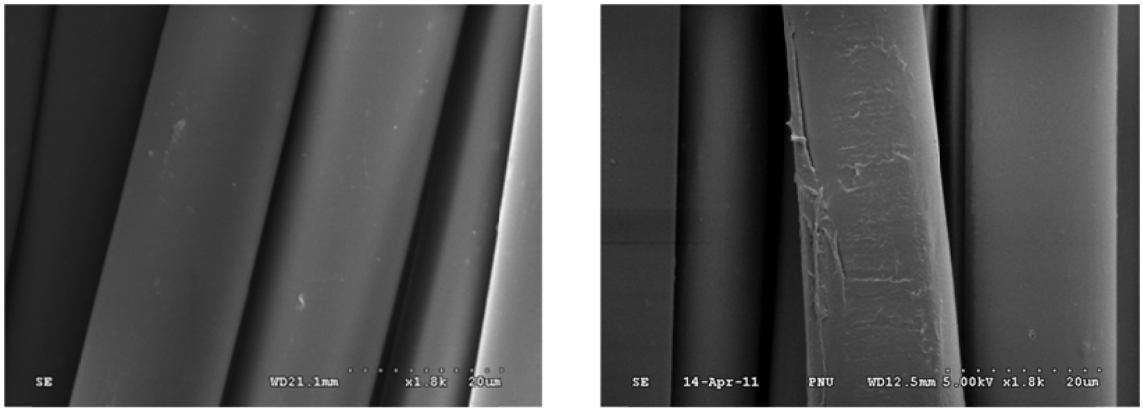
Fig. 8. Air permeability of PA fabric subjected to different treatments. Buffer: pH 8.5, 50°C for 60 min. AA: pH 8.5, 50°C for 60 min, 10% (o.w.f.) acylase.

<Fig. 9> shows SEM micrographs obtained through surface observations of untreated and AA-treated PA fabric. When the PA fabric was treated with AA, the surfaces became irregular partly owing to AA hydrolysis; however, the surface change was limited. Given that the weight loss after treatment with AA was negligible (0.144%±0.33%), it could be inferred that the fiber surface had not changed after AA hydrolysis. Moreover, the tensile strength of the PA fabric was intact after AA hydrolysis (Fig. 10).

AA hydrolysis was limited to the fabric surface and caused an increase in the amount of hydrophilic ionic groups on the PA fabric surface without changing the mechanical properties of the fabric.

IV. Conclusions

This study was conducted to assess the effectiveness of commercial AA and TR in hydrolyzing the amide bonds of the PA fabric, and thereby modifying its hydrophobicity. In order to optimize the treatment conditions, the number of amino groups released into the reaction mixture was determined. As AA and TR



(a) Untreated (b) AA-treated

Fig. 9. SEM micrographs of untreated (a) and AA-treated (b) PA fabric. Treatment conditions: pH 8.5, 50°C, 60 min, 10% (o.w.f.) acylase.

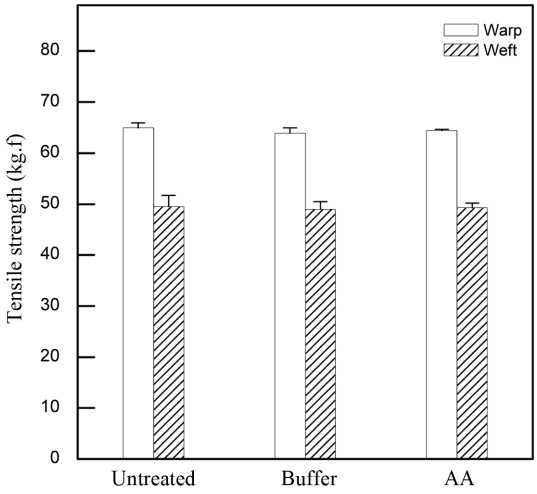


Fig. 10. Tensile strength of PA fabric subjected to various treatments. Buffer: pH 8.5, 50°C for 60 min. AA: pH 8.5, 50°C for 60 min, 10% (o.w.f.) acylase.

hydrolyzed the amide bonds in the PA fabric, the number of amino groups released into the reaction mixture increased. However, TR hydrolysis showed relatively lower activity than AA hydrolysis. The K/S values of the dyed PA fabric representing the number of amino groups formed on the fabric improved through AA hydrolysis significantly. However, TR hydrolysis did not modify the hydrophobicity of the PA fabric as suggested by the K/S values and moisture regain. The hydrophobicity of the PA fabric was modified through AA hydrolysis, and as a result, the wettability of AA-treated PA fabric improved effectively. Moreover, modification of the PA fabric using AA was an environment-friendly process that did not lower the fiber strength.

References

Adler-Nissen, J. (1979). Determination of the degree of hydrolysis of food protein hydrolysates by trinitrobenzenesulfonic acid. *Journal of Agricultural and Food Chemistry, 27*(6), 1256 –1262.

Almansa, E., Heumann, S., Eberl, A., Kaufmann, F., Cavaco-Paulo, A., & Gübitz, G. M. (2008). Surface hydrolysis of polyamide with a new polyamidase from beauveria brongniartii. *Biocatalysis and Biotransformation, 26*(5), 371–377.

Banks, J. W., & O'Hagan, D. (2000). The enzymatic resolution of an α-fluoroamide by an acylase. *Journal of Flourine Chemistry, 102*(1-2), 235–238.

Cavaco-Paulo, A., & Gübitz, M. (2003). *Textile processing with enzymes*. New York: Textile institute.

Choudhury, A. K. R. (2006). *Textile preparation and dyeing.* New Hampshire: Science publishers.

Gadamasetti, K., & Braish, T. (Eds.). (2007). *Process chemistry in the pharmaceutical industry, Volume 2: Challenges in as ever changing climate.* New York: CRC Press.

Garćia-Castiñeiras, S., & Miranda-Rivera, M. N. (1983). Loss of free amino groups in the water-insoluble fraction of nuclear senile cataracts. *Investigative Ophthalmology & Visual Science*, *24*(9), 1181–1187.

Gübitz, G. M., & Cavaco-Paulo, A. (2008). Enzymes go big:

Surface hydrolysis and functionalisation of synthetic polymers. *Trends in Biotechnology, 26*(1), 32–38.

Heumann, S., Eberl, A., Fischer-Colbrie, G., Pobeheim, H., Kaufmann, F., Ribitsch, D., Cavaco-Paulo, A., & Guebtiz, G. M. (2009). A novel aryl acylamidase from nocardia farcinica hydrolyses polyamide. *Biotechnology and Bioengineering, 102*(4), 1003–1011.

Heumann, S., Eberl, A., Pobeheim, H., Liebminger, S., Fischer-Colbrie, G., Almansa, E., Cavaco-Paulo, A., & Gübitz, G. M. (2006). New model substrates for enzymes hydrolyzing polyethyleneterephthalate and polyamide fibres. *Journal of Biochemical and Biophysical Methods, 69*(1-2), 89–99.

Kaynak, H. K., & Babaarslan, O. (2012). Polyester microfilament woven fabrics. In H. Y. Jeon (Ed.), *Woven fabrics* (pp. 155–178). Croatia: InTech.

Kim, H. R., & Seo, H. Y. (2013). Enzymatic hydrolysis of polyamide fabrics by using acylse. *Textile Research Journal, 83*(11), 1181–1189.

Kim, H. R., & Song, W. S. (2006). Lipase treatment polyester fabrics. *Fibers and Polymers, 7*(4), 339–343.

Klun, U., Friedrich, J., & Kržan, A. (2003). Polyamide-6 fibre degradation by a lignolytic fungus. *Polymer Degradation and. Stability, 79*(1), 99–104.

Liljeblad, A., & Kanerva, L. T. (2006). Biocatalysis as a profound tool in the preparation of highly enantiopure β-amino acids. *Tetrahedron, 62*(25), 5831–5854.

Liljeblad, A., Lindborg, J., & Kanerva, L. T. (2000). Acylase I in the alcoholysis of α-substituted dicarboxylic acid esters and derivatives: Enantio- and regioselectivity. *Tetrahedron-Ashymmetry, 11*(19), 3957–3966.

Miettinen-Oinonen, A., Puolakka, A., & Buchert, J. (2008). Method for modifying polyamide, *U.S. Patent No. 028-9120 A1.* Washington, DC: U.S. Patent and trademark Office.

Ogulata, R. T. (2006). Air permeability of woven fabrics. *Journal of Textile and apparel, Technology and management, 5*(2), 1–10.

Parvinzadeh, M., Assefipour, R., & Kiumarsi, A. (2009). Biohydrolysis of nylon 6,6 fiber with different proteolytic enzymes. *Polymer Degradation and Stability*, *94*(8), 1197–1205.

Perin, Z., Stana-Kleinschek, K., Sfiligoj-Smole, M., Kre, T., & Ribitsch, V. (2004). Determining the surface free energy of cellulose materials with the powder contact angle method. *Textile Research Journal, 74*(1), 55–62.

Proctor, M. R., Taylor, E. J., Nurizzo, D., Turkenburg, J. P., Lloyd, R. M., Vardakou, M., Davies, G. J., & Gilbert, H. J. (2005). Tailored catalysts for plant cell-wall degradation: redesigning the exo/endo preference of Cellvibrio japonicus arabinanase 43A. *Proceedings of the National Academy of Sciences, 102*(8), 2697–2702.

Sashidhar, R. B., Capoor, A. K., & Ramana, D. (1994). Quantitation of α-amino group using amino acids as reference standards by trinitrobenzene sulfonic acid: A simple spectrophotometric method for the estimation of hapten to carrier protein ratio. *Journal of Immunological Methods, 167*(1-2), 121–127.

Silva, C., & Cavaco-Paulo, A. (2004) Monitoring biotransformations in polyamide fibres. *Biocatalysis and Biotransformation, 22*(5-6), 357–360.

Silva, C., Cavaco-Paulo, A., & Nierstrasz, V. A. (2010). Enzymatic hydrolysis and modification of core polymer fibres for textile and other applications. In N. A. Nierstrasz & A. Cavaco-Paulo (Eds.), *Woodhead publishing series in textiles: Number 107. Advances in textile biotechnology* (pp. 77–97). Cambridge: The Textile Institute.

Silva, C. M., Carneiro, F., O'neill, A., Fonseca, L. P., Cabral, J. S. M., Guebitz, G., & Cavaco-Paulo, A. (2005). Cutinase-A new tool for biomodification of synthetic fibers. *Journal of Polymer Science Part A: Polymer Chemistry, 43*(11), 2448–2450.

Simile, C. B. (2004). *Critical evaluation of wicking in performance fabrics*. Unpublished master's thesis, Georgia Institute of Technology, Atlanta.

Song, A. R., Kim, H. R., & Song, W. S. (2012). Optimization of enzymatic treatment of polyamide fabrics by bromelain. *Fibers and Polymers, 13*(3), 282–288.

Spellman, D., McEvoy, E., O'Cuinn, G., & FitzGerald, R. J. (2003). Proteinase and exopeptidase hydrolysis of whey protein: Comparison of the TNBS, OPA and pH stat methods for quantification of degree of hydrolysis. *International Dairy Journal 13*(6), 447–453.

Youshko, M. I., Langen, L. M., Sheldon, R. A., & Švedas, V. K. (2004). Application of aminoacylase I to the enantioselective resolution of α-amino acid esters and amides. *Tetrahedron-Ashymmetry, 15*(12), 1933–1936.