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Lipase Treatment of Polyester Fabrics

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Abstract: The aim of this paper is to improve moisture regain of PET fabrics using a lipase treatment. Effects of nine lipase sources, lipase activator and nonionic surfactant on moisture regain of PET fabrics are examined. Moisture regains of lipase-treated samples improve by two times in average compared with untreated and buffer-treated samples. Alkaline treatment creates larger pitting by more aggressive attack into fiber which is proved by SEM and water contact angle measurement. Moisture regain by alkaline treatment (0.568 % ± 0.08) does not improve. However, lipase-treatment (L2 treatment) improves moisture regain up to 2.4 times (1.272 % ± 0.05). Although lipase treatment is more moderate than alkaline treatment, lipase hydrolysis on PET fabrics improves moisture regain, efficiently. K/S values improved confirm that carboxyl and hydroxyl groups are produced on the surface of PET fabrics by lipase hydrolysis. Moisture regain and dyeability improve by lipase hydrolysis on PET fabrics.

Keywords: Polyethylene terephthalate (PET) fabric, Lipase, Enzyme treatment, Alkaline treatment, Moisture regain, Non-ionic surfactant, Activator

Introduction

Polyethylene terephthalate (PET) is one of the most commonly used synthetic fibers. Major advantages of PET are high strength, stretch resistance, washability, wrinkle resistance and abrasion resistance. However, PET has undesirable properties such as pilling, static and lack of dyeability associated with its hydrophobic nature. PET fiber has a low moisture regain about 0.4 %. The most conventional and industrially way to modify polyester fabrics is an alkaline treatment, but alkaline treatment affects on strength of polyester fabrics. Furthermore, the high amount of sodium hydroxide and high operating temperature are large disadvantages [1,2]. More environmentally process is desirable. A recent alternative is a use of enzymes in surface modification.

Studies about enzymatic treatment of polyester have been focused on biodegradation of aliphatic polyester using a lipase [3-5], and biological synthesis of polymer with enzymes [6]. Only a few studies [7-10] have been reported regarding enzymatic modification of PET fabric. Improvement hydrophilicity of polyesters by hydrolysis of ester bonds has been reported [7-10]. These studies focus that the applicable enzymes are lipases and polyesterases.

Lipase is known to hydrolyze water-insoluble esters or triglycerides composed of long chain fatty acids [3,11,12]. Thus, the application and studies about lipases in textile processing have been focused on detergent [13].

Several studies about effects of activators on lipase activity have been reported [11,12,14]. Typically, lipases need calcium as a cofactor for an effective catalytic activity [13] and retain its activity in the presence of Ca^{2+} and Mg^{2+} [11]. Also, Ca^{2+} is reported that it is apparently essential for lipase activity [14]. However, these studies have been limited substrates to olive oil or tributyrin. There has been no study that investigates the effect of activators on textiles during enzymatic process.

Hypothesis of this study is as follows. If enzymes can hydrolyze ester linkage in PET fabrics, polar hydroxyl (-OH) and carboxyl (-COOH) groups will be formed on the surface of PET fabrics. As a result, moisture regain and wettability will improve due to the forming of hydrophilic groups on PET fabrics [7]. Carboxyl and hydroxyl groups on PET fabrics can be evaluated through dyeability of basic dyes and reactive dyes, respectively [8,15].

Effects of varying lipase sources on the moisture regain of PET fabrics are examined. In particular, nine commercial lipases are used with activator (calcium chloride) and nonionic surfactant (Triton X-100). To find out the wettability of samples, water contact angle (WCA) of PET fabrics is measured. Nitrogen content is examined whether enzyme protein absorbs on PET fabrics or not.

Experimental

100 % polyester fabric (Table 1) has been used. The PET fabric consists of filament fiber and has plain weave structures. All fabric samples are rinsed with water at 60 °C for 10 minutes and dried at room temperature.

Nine commercial lipases obtained from Fluka (Table 2) are used. All enzymes used are powder. Tris (hydroxymethyl) amino methane (Ka 8.3 at 20 °C, Sigma Chemical Co., TRIS) is used as a buffer. To keep ionic properties of treatment

Table 1. Characteristics of the fabric

Fiber	Yarn count (denier)	Fabric count (yarns/inch^2)	Fabric weight (g/m^2)	Thickness (mm)
Polyester 100 %	70	113 × 95	70 ± 5	0.094 ±0.02

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Table 2. Lipases and their properties

Sample number	Source	Cat.-No (Fluka)	Activity (unit/mg)	Description of unit/ (Optimum pH & temp.)
L1	*Aspergillus*	84205	0.5	1 μmol acetic acid from triacetin pH 7.4, 40 °C
L2	*Candida antarctica*	62299	3	1 μmol oleic acid from triolein* pH 8.0, 40 °C * : One unit is the amount of ezyme which liberates 1 mol oleic acid per minutes using triolein as substrate.
L3	*Candida cylindracea*	62316	2	
L4	*Mucor miehei*	62298	1	
L5	*Pseudomonas cepacia*	62309	50	
L6	*Pseudomonas fluorescens*	95608	40	
L7	*Rhizopus arrhizus*	62305	10	1 μmol butyric acid from tributyrin pH 8.0, 40 °C
L8	*Phizopus niveus*	62310	1.5	1 μmol fatty acid from olive oil pH 7.7, 37 °C
L9	*Hog pancreas*	62300	15-35	1 μmol fatty from olive oil pH 8.0, 37 °C

solution constantly, TRIS buffer solution is used as the basis for all applications. The pH is adjusted to each pH by using 1N HCl or 0.1 N NaOH. The amount of lipases is 1 g/*l*. All treatments are performed at 150 rpm with a shaking water bath for 30 minutes, using a liquor ratio 80:1. Temperature and pH are controlled according to the optimal condition from manufacturers (Table 2). The enzyme is inactivated at 80 °C for 10 minutes. Fabrics are rinsed with water and dried at room temperature.

To check effects of activator (calcium chloride) and non-ionic surfactant (Triton X-100), lipase treatment is performed in the presence of calcium chloride or Triton X-100. Calcium chloride is obtained from Kanto Chemicals and Triton X-100 is obtained from Sigma. Calcium chloride and Triton X-100 add to the buffer solution 7.5 mM and 1 g/*l*, respectively.

Moisture regain of lipase-treated PET samples is measured according to ASTM D629-99. The water contact angle (WCA) of PET fabrics is measured using a contact angle measurement system (KRUSS DSA, KRUSS Inc., German). Both moisture ragin and WCA are performed ten times. Nitrogen content of enzyme treated PET is performed using Eurovector elemental analyzer (Euro EA, Italy). To check the carboxyl and hydroxyl groups on the surface of PET samples, each sample is dyed with methylene blue (0.1 mM, 90 rpm for 20 minutes at 40 °C) and reactive dye (C.I. Reactive Yellow 160 A, 2 %(owf), 90 rpm for 30 minutes at 60 °C), respectively. K/S values are measured using computer color matching system (CCM, JX 777, Japan).

Surface modification of enzyme treated PET samples is analyzed using scanning electron microscope (SEM, Jeol JSM-5410, Japan).

Results and Discussion

Results are presented as follows: buffer treatment, lipase source, activator, nonionic surfactant, WCA, nitrogen content, K/S values, and SEM micrographs.

First, a buffer-effect on PET fabrics is examined before lipase treatment. PET fabrics are immersed in the 50 mM TRIS buffer at 40 °C for 30 minutes. The moisture regain of buffer-treated samples is as high as 0.539 % (±0.041). Compared to untreated samples (0.478 %± 0.134), moisture regain of buffer-treated samples increases slightly. Therefore, only buffer treatment cannot improve the moisture regain. For all examinations, TRIS buffer solution is used as the basis.

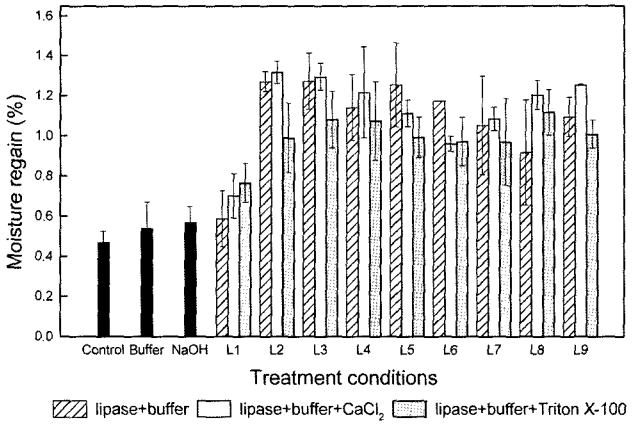


Figure 1. Moisture regains of lipase-treated PET fabrics in various conditions.

Second, the effect of lipase source on moisture regain is investigated. Figure 1 shows that the hydrolytic activity of lipase improves the moisture regain of PET samples. The moisture regain of lipase-treated samples, except L1 and L8 treatment, improves by almost 2 times in average compared to buffer-treated samples. Especially, L1 treatment does not affect on moisture regain of PET fabrics. It is important that L2 and L3 treatment is very effective lipase to improve moisture regain of PET fabrics by 2.4 times. Thus, moisture regain of PET fabrics by lipase treatment can depend on lipase sources [7]. Moisture regain is dependent on lipase sources because of the covalent differences in or on the surface of the protein [13]. To find out specific reason, the study about evaluation an active site of protein is necessary, but that is out of scope of this paper.

Different lipase activities from a manufacturer (Table 2)

do not affect on moisture regains of PET fabrics, significantly [7]. The reason may be due to huge overdose of enzymes (1 g/l) in every treatment. In addition, hydrolytic activity of enzyme is affected by substrate strongly, but lipase activities from a manufacturer are examined using triacetin, triolein, tributylrin, and olive oil as substrates. When PET fabrics are used as substrate, these activities from a manufacturer can be changed. Therefore, in textile enzyme process, hydrolytic activity is evaluated using the weight loss of textile after treatment. However, the weight loss of PET samples by lipase treatment is only 0.165±0.07 %. Since weight loss of PET samples does not show any significant differences depending on lipase sources, evaluation of hydrolytic activity by weight loss is not considered in this paper. Therefore, this article has focused on moisture regain and wettability of PET samples because improvements of these moisture-related properties could support the forming of carboxyl and hydroxyl groups by lipase hydrolysis.

Alkaline treatment of PET fabrics is performed to compare with lipase treatment. PET fabrics are treated with 5 %(owf) NaOH at 90°C for 60 minutes. The weight loss of alkaline treated samples is 18.5 %. Moisture regain by alkaline treatment (0.568 %±0.08) does not show any significant improvement. However, lipase-treatment (L2 treatment) improves moisture regain up to 2.4 times (1.272%±0.05). Although lipase treatment is more moderate than alkaline treatment, lipase hydrolysis on PET fabrics improves moisture regain, efficiently.

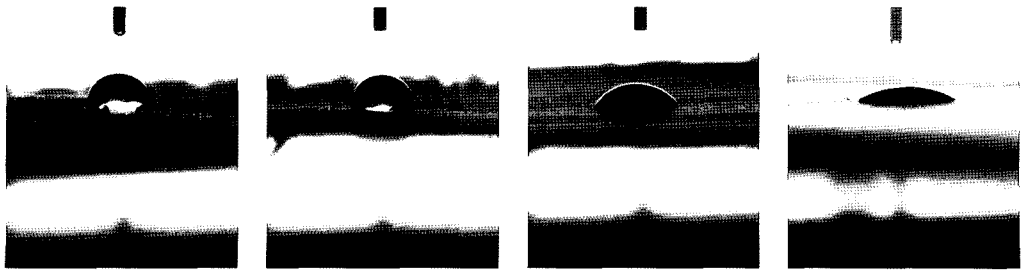
In the case of activator, the effect of calcium chloride on the moisture regain of lipase-treated PET fabrics is investigated (Figure 1). Although calcium chloride has reported to assist lipase hydrolysis efficiently [11,14], the effect of calcium chloride is dependent on lipase sources. Particularly, moisture regains of samples treated with L8 and L9 with activator improve compared to treatment without activator by 1.3 times and 1.1 times, respectively. However, moisture regains of L5 and L6 treatments with activator are by almost 1.2 times lower than treatments without it. For other lipases, moisture regains of samples improve slightly in the presence of activator.

Nonionic surfactant is typical auxiliaries in lipase test [13,16]. In textile process, nonionic surfactants can enhance enzyme penetration and adsorption [13]. Figure 1 shows the effect of nonionic surfactant on moisture regain of samples. Compared to samples in the absence of nonionic surfactant, moisture regain of samples in the presence of Triton X-100 is reduced by about 1.2 times except L1 and L8. It confirms that Triton X-100 can inhibit the lipase hydrolysis reaction. Since PET fabrics are immediately covered by non-ionic surfactant, PET surface can be changed hydrophilic surface during treatment [4,17]. Lipases cannot attach to PET samples with hydrophilic surface because lipases can attach to sample surface efficiently when sample has hydrophobic surface [4,18]. Typically, surfactant in lipase test [16] using olive oil as substrate provides much larger surface through the dispersion action of the surfactant. However, in the case of a solid material with a fixed surface area, the surfactant only reduces the hydrophobic character without increasing the surface area [4]. As a result, it can be concluded that Triton X-100 acts as inhibitors to lipase hydrolysis in PET fabrics.

Figure 2 shows WCA of untreated, alkaline treated and lipase-treated samples. WCA of lipase-treated sample (57.083 ° ±3.323) decreases compared to untreated sample and buffer-treated sample (96.4 °±3.016, 91.1 °±2.579). Hydrolysis of PET fabrics limits to the surface of sample due to large size of the enzyme molecules. As a result, hydrophilic groups are forming on the surface of PET fabrics, and the wettability can improve [7,8,13,19]. In addition, wettability improved by lipase hydrolysis is caused by degradation of PET surface (Figure 4). WCA value of lipase treatment (57.083 °±3.323) is higher than that of alkaline treatment(34.1 °±2.25). Because of the surface pitting on PET fabrics by alkaline treatment, WCA can decrease a lot. However, lipase treatment can improve wettability with milder treatment condition, such as a low temperature and a short operating time, than alkaline treatment.

Nitrogen content of lipase-treated samples is examined whether enzyme protein adsorbs or not. Nitrogen contents of samples are 0.034 %±0.05. This shows that protein adsorption by lipase treatment can be negligible [7]. It is concluded that the enzyme protein molecule dose not adsorb on PET surface. Therefore, improvement in moisture regain is associated with forming hydrophilic groups on samples by lipase hydrolysis rather than protein adsorption.

Hydrolysis reaction of lipase is limited to surface of PET



(a) Untreated (b) Buffer treatment (c) Lipase treatment (d) Alkaline treatment

Figure 2. Water contact angles of PET fabrics treated differently.

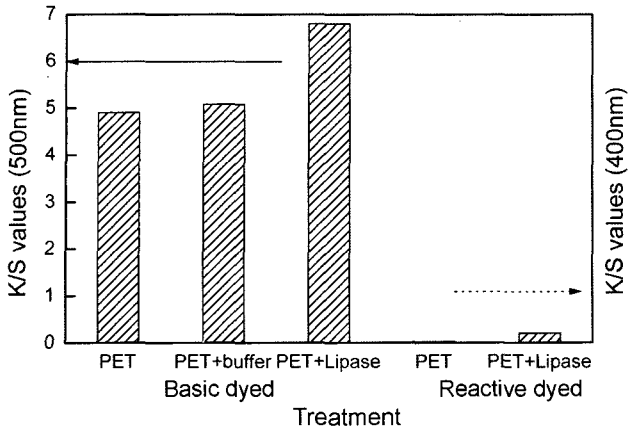


Figure 3. K/S values of basic dyed and reactive dyed PET fabrics.

fabrics. Since amorphous regions are too narrow for the large size enzyme molecules to penetrate into it, polar hydroxyl and carboxylic groups are produced on the surface of PET fabrics [7,8,13]. Figure 3 shows K/S values of basic dyed and reactive dyed samples. In the case of basic dye, the dyeability of lipase-treated samples improves by 1.3 times compared with untreated and buffer-treated samples. This result supports that the binding capacity of basic dye improves because lipase hydrolysis increases carboxyl end groups on surface of PET fabrics [7,8]. The dyeability of reactive dye shows that lipase-treated samples improve by 4.3 times compared with untreated samples. Although untreated samples are not dyed at all, lipase-treated samples are dyed slightly. In the case of lipase-treated samples, improving dyeability of reactive dye can support that the forming of hydroxyl group on the surface of PET fabrics due to lipase hydrolysis [15]. That is, it is highly supported that carboxyl and hydroxyl groups on the surface of PET fabrics increase by enzymatic treatment. As a result, improved moisture regains of samples are associated with hydrolysis of lipase because lipase treatment is forming carboxyl and hydroxyl groups on the surface of PET fabrics.

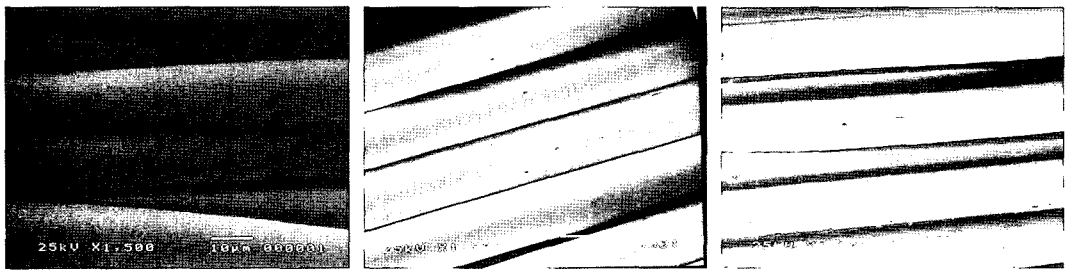
Figure 4 shows surface micrographs of samples. The surface of lipase-treated sample (b) shows a great deal of cracks and voids by lipase hydrolysis in comparison with the untreated sample (a). The degradation pattern is very different from the typical surface pitting caused by alkaline treatment (c). The amount of degradation between lipase-treatment and alkaline treatment differs because lipase-treated samples and alkaline treated samples show obvious differences in weight loss, 0.165 % and 18.5 %, respectively. Furthermore, degradation of PET surface can be highly responsible for improvement of wettability.

Conclusion

This study provides a mild and eco-friendly method to improve moisture regain of PET fabrics. Effects of lipase on moisture regain of PET fabrics are investigated. In particular, it is examined the effect of lipase sources, calcium chloride and Triton X-100 on moisture regain of PET fabrics. The moisture regain of lipase-treated samples, except L1 treatment, improves by about two times compared with buffer-treated samples. However, alkaline treatment does not show any improvement in moisture regain. Although lipase treatment is milder than alkaline treatment, more -OH and -COOH groups are revealed by enzyme treatment. Increasing hydroxyl and carboxyl groups is conformed by improvement of moisture regain, wettability, and dyeability.

For the effect of activator, moisture regain of sample with L8 treatment in the presence of calcium chloride improves by 1.3 times compared with sample in the absence of calcium chloride. For other lipases, the presence of activator has no influence on moisture regain. In the case of nonionic surfactant, although nonionic surfactant is a typical auxiliary in lipase test, the nonionic surfactant inhibits hydrolytic activity of lipase in the case of PET fabrics.

Nitrogen contents of samples do not increase by lipase treatment. K/S values improved support that the forming of carboxyl and hydroxyl groups on the surface of PET fabrics by lipase hydrolysis. As a result, the improved moisture regains of samples are associated with hydrolytic action of lipase because lipase hydrolysis forms carboxyl and hydroxyl groups on the surface of PET fabrics. The surface of lipase-treated sample shows a great deal of cracks and voids in



(a) Untreated sample (b) Lipase treatment (c) Alkaline treatment

Figure 4. SEM micrographs of PET fabrics.

comparison with the untreated sample.

The weight loss by lipase treatment is not significant, so it is necessary to study evaluation system about hydrolytic activity of lipase on PET fabrics as a substitute for weight loss, in the further study.

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