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Effects of Triton X-100 and Calcium Chloride on the *Porcine Pancreas* Lipase Treatment of PET Fabrics

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폴리에스터 직물의 리파제 처리시 Triton X-100 및 염화칼슘의 영향

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Abstract

In this study, we reported the effect of *porcine pancreas* lipase treatment in the presence of a calcium chloride and Triton X-100 on moisture regain and wettability of PET fabrics. The moisture regain of PET fabrics in the presence of 0.5% surfactant showed a 1.5-fold decrease, compared to the absence of it. Triton X-100 acted as an inhibitor to *porcine pancreas* lipase hydrolytic activity. The moisture regain and wettability of *porcine pancreas* lipase treated PET fabrics improved when more than 10mM of calcium chloride was added to the treatment solution. *Porcine pancreas* lipase treatment caused voids and cracks on PET fabrics.

Key words: *Porcine pancreas* lipase, Triton X-100, Calcium chloride, PET fabric, Moisture regain; 리파제, Triton X-100, 염화칼슘, 폴리에스터, 수분특성

I. Introduction

Rapid technological developments are now stimulating the textile industry to embrace enzyme technology, a trend strengthened by concerns regarding health, energy, and environment(Beilen & Li, 2002). The textile industry is under considerable environmental pressure owing to its large energy use, high concentration of chemicals, and water consumption, and subsequent environmental pollution(Cavaco-Paulo & Gübitz, 2003; Kirk et al., 2002). Thus, the application of enzyme technology to textile wet processing is an example of more environmentally compatible processes(Cavaco-Paulo & Gübitz, 2003).

Polyethylene terephthalate(PET) is one of the most commonly used synthetic fibers. The advantages of PET include its considerable strength, stretch resistance, wrinkle resistance, and abrasion resistance. A significant disadvantage of PET, however, is its hydrophobicity.

Enzymatic hydrolysis on PET fabrics allows more environmentally sustainable finishing and the modification of their hydrophobicity(Cavaco-Paulo & Gübitz, 2003; Kim & Song, 2006). Examples of applicable enzymes for improving the hydrophilicity of PET are lipases, polyesterases, and cutinases (Chaudhary et al., 1998; Chaya & Kitano, 1999; Guebitz & Cavaco-Paulo, 2007; Hsieh & Cram, 1998; Kim & Song, 2006; Walter et al., 1995; Yoon et al.,

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2002). Among these enzymes, lipases are used for enzyme applications in most fields, such as the textile, paper, detergent, cosmetic, and pharmaceutical industries, due to their usefulness in both hydrolytic and synthetic reactions(Hasan et al., 2006). In addition, lipases have been reported as hydrolyzing ester linkages in PET, producing polar hydroxyl and carboxylic groups(Guebitz & Cavaco-Paulo, 2007; Hsieh & Cram, 1998; Kim & Song, 2006; Yoon et al., 2002). Many lipases have been explored to hydrolyze PET. Among them, *porcine pancreas* lipase is a relatively cheap and widely used commercial enzyme. It is useful, therefore, to have a detailed study of its additives from the viewpoint of broadening its application.

Several studies about the effects of activators on lipase activity have been reported(Decker, 1977; Sharma et al., 2001). Lipases need a calcium ion as a cofactor for an effective hydrolytic activity(Cavaco-Paulo & Gübitz, 2003; Decker, 1977) and retain their activity in the presence of it(Sharma et al., 2001). These studies, however, have been limited to substrates such as olive oil or tributyrin. There have been few studies that investigated the effect of activators on textiles during enzymatic processing(Kim & Song, 2006).

In addition to calcium ions, nonionic surfactants are typical auxiliaries used to enhance enzyme penetration and adsorption, and fiber swelling in enzymatic processing(Cavaco-Paulo & Gübitz, 2003). Also, it has been reported that when polyester is treated with lipases, a surfactant should be included in the treatment solution(Hsieh & Cram, 1998). It is important to discern any inhibitory action of the surfactants on the lipase hydrolytic activity.

In this study, we report the effect of the lipase treatment in the presence of an activator(calcium chloride) and a nonionic surfactant(Triton X-100) on the wettability of PET fabrics.

II. Experimental

1. Materials

100% PET fabric(test fabric from KS K 0905) was used for the experiment(Table 1). The PET fabric consisted of filament fibers and had plain weave structures.

Commercial *porcine pancreas* lipase(EC 3.1.1.3, powder, Sigma) abbreviated as PPL, was used without further purification. The activity of PPL is 30-90unit/mg. One unit is the amount of enzyme which liberates 1μmol fatty acid from a triglyceride per minute at pH 7.7, 37°C using olive oil as a substrate.

Tris(hydroxymethyl) amino methane(pKa 8.3 at 20°C, Sigma Chemical Co.) was used as a buffer. Tris buffer solution was used as the basis for all applications. The pH of the buffer solution was adjusted with 1M HCl(Duksan Pure Chemicals, Korea) and 0.1M NaOH(Junsei Chemicals, Japan). All the chemicals were used without further purification.

2. Enzymatic Treatment

Each fabric sample was cut into specific dimensions and weighed approximately 1g. PET fabrics were treated with lipase in tris buffer solution, using a liquor ratio 80:1. Triton X-100 and calcium chloride was added to the treatment solution in different concentration levels from 0.01 to 0.5%(w/v) and from 1mM to 50mM, respectively. All the lipase treatments were performed at 150 rpm using a shaking water bath(BS-21, Jeio Tech., Korea). The enzyme inactivation was performed at 80°C for 10 minutes. The PPL-treated samples were thoroughly washed with water and dried at room temperature. Then, moisture regain, wettability, and SEM micrographs of lipase-treated PET fabrics were measured.

The moisture regain was evaluated according to

Table 1. The characteristics of fabric

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

ASTM D629-99. The wettability of PPL-treated PET fabrics was evaluated via water absorbency and water contact angle. The water absorbency of the PET fabrics was evaluated according to the AATCC test method 79-1992. The water contact angle(WCA) of the PET fabrics was measured using the contact angle measurement system(KRUSS DSA100, KRÜSS, Inc., Germany). Each test was carried out 10 times.

Changes in the surface of the PPL-treated PET fabrics were analyzed with a scanning electron microscope(SEM, JSM-5410, Japan) after the samples were plated with gold.

III. Results and Discussion

1. Effect of Nonionic Surfactant on Moisture Regain and Wettability

PET fabrics were treated at pH 7.5, 40°C, 90 minutes, and 50%(owf) lipase. A nonionic surfactant (Triton X-100) was added to the treatment solution with various concentration levels, from 0.01 to 0.5% (w/v).

<Fig. 1> shows the moisture regain of the PET fabrics treated with lipase in the presence of Triton X-100. The moisture regain of the PET fabrics decreased dramatically with increasing surfactant concentration. Despite using a very small concentration(0.01, 0.03%) of surfactant, it had the effect of decreasing moisture regain. At the 0.5% concentration, the moisture regain showed a sharp decline. Compared to the absence of surfactant, the moisture regain of PET fabrics treated with PPL in the presence of 0.5% surfactant decreased almost 1.5 fold. Even though nonionic surfactants have been reported to enhance enzyme penetration and adsorption(Cavaco-Paulo & Gübitz, 2003), Trion X-100 inhibited the PPL hydrolysis reaction.

The PET fabrics were immediately covered with detergent and the PET surface could be changed to a hydrophilic surface during the treatment(Kim, 2003; Kim & Song, 2006; Walter et al., 1995). However, the lipases could attach to the sample surface efficiently when the sample had a hydrophobic surface(Blow, 1991; Walter et al., 1995). Thus, lipases did not attach to the samples due to changing the surface into a hydrophilic surface. Compared to this,

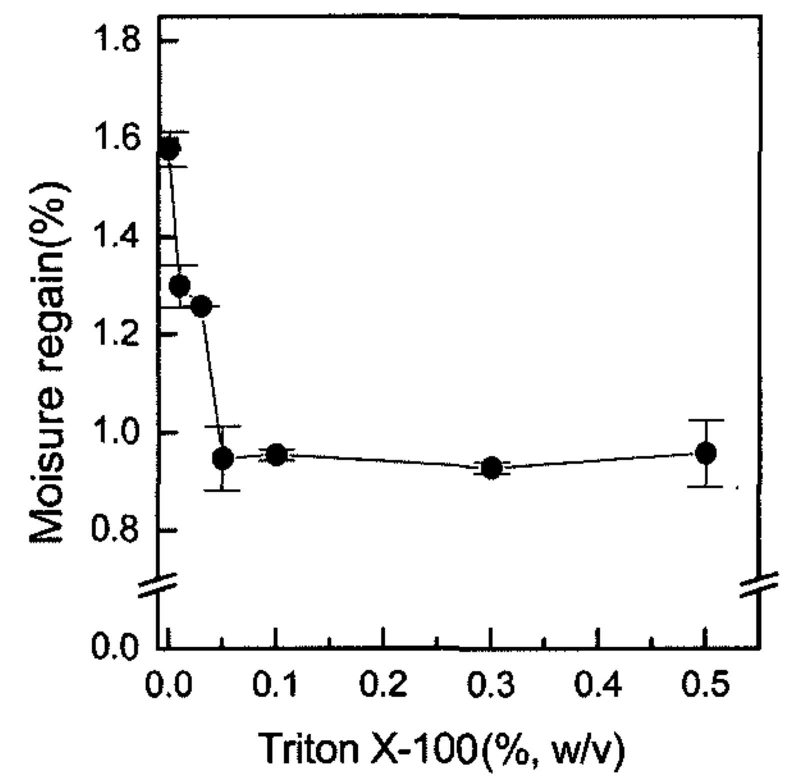


Fig. 1. Moisture regain of PPL treated PET fabrics in the presence of Triton X-100. Treatment conditions: 50%(owf) PPL; pH 7.5; temperature, 40°C; treatment time, 90 minutes.

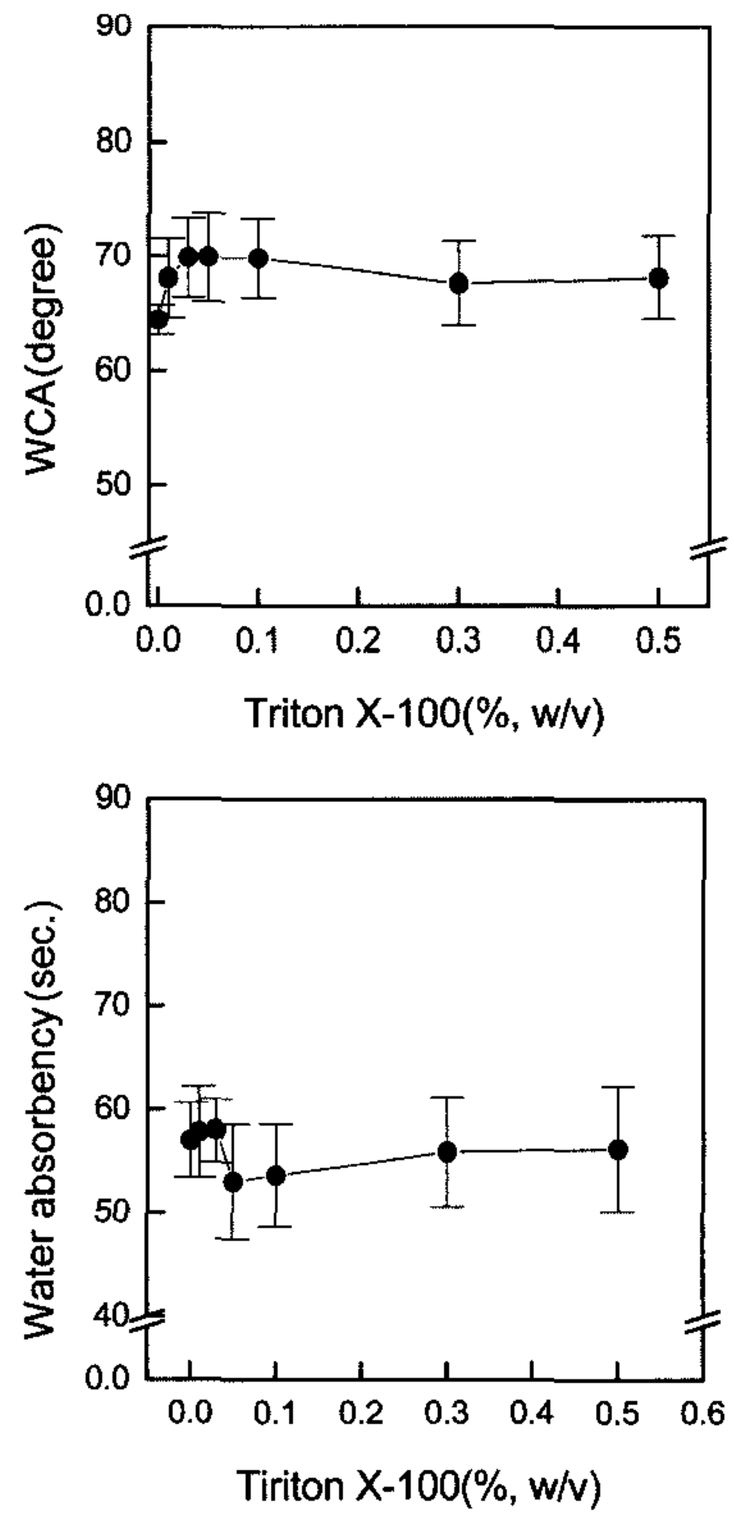


Fig. 2. Wettability of PPL treated PET fabrics in the presence of Triton X-100. Treatment conditions: 50%(owf) PPL; pH 7.5; temperature, 40°C; treatment time, 90 minutes.

adding surfactant in the lipase test(JIS K 0601), using olive oil as a substrate, provided a much larger surface through the dispersion action of the surfactant. However, in the case of a solid material with a fixed surface area, such as fabrics, the surfactant only reduced the hydrophobic character without increasing the surface area(Kim & Song 2006; Walter et al., 1995). This result could be confirmed through the water absorbency results.

<Fig. 2> shows the WCA and water absorbency of the PET fabrics treated with lipase in the presence of Triton X-100. WCA increased slightly as the surfactant was increased, while the moisture regain of the PPL treated fabrics decreased very sharply(Fig. 1). However, the time for water absorbency decreased with an increase in surfactant concentration. This confirmed that the nonionic surfactant changed the PET surface into a hydrophilic surface by covering the PET surface, thus shortening the time needed for water absorption.

It could be concluded that Triton X-100 acted as an inhibitor to PPL hydrolytic activity. Therefore, when PET fabrics were treated with PPL, Triton X-100 should not be added to the treatment solution.

2. Effect of Calcium Chloride on Moisture Regain and Wettability

Calcium chloride was added to the treatment solution in different amounts, from 1mM to 50mM. <Fig. 3 and 4> show the effect of calcium chloride on moisture regain and wettability, respectively. The moisture regain and wettability of PET fabrics decreased up to 3mM, but they improved when the amount of calcium chloride went from 10mM to 30mM.

At low concentrations, the decrease in moisture regain and wettability might be related to a change in the ionic strength of the medium, but the exact reason for the decrease at low concentrations was not proven in this study. It should be analyzed in a further study.

In general, when ionic strength(calcium chloride concentration) increased to just below the critical amount, enzyme stability improved in the medium (Cavaco-Paulo & Gübitz, 2003). As shown in <Fig. 3 and 4>, the moisture regain and wettability of the PET fabrics increased when calcium chloride was

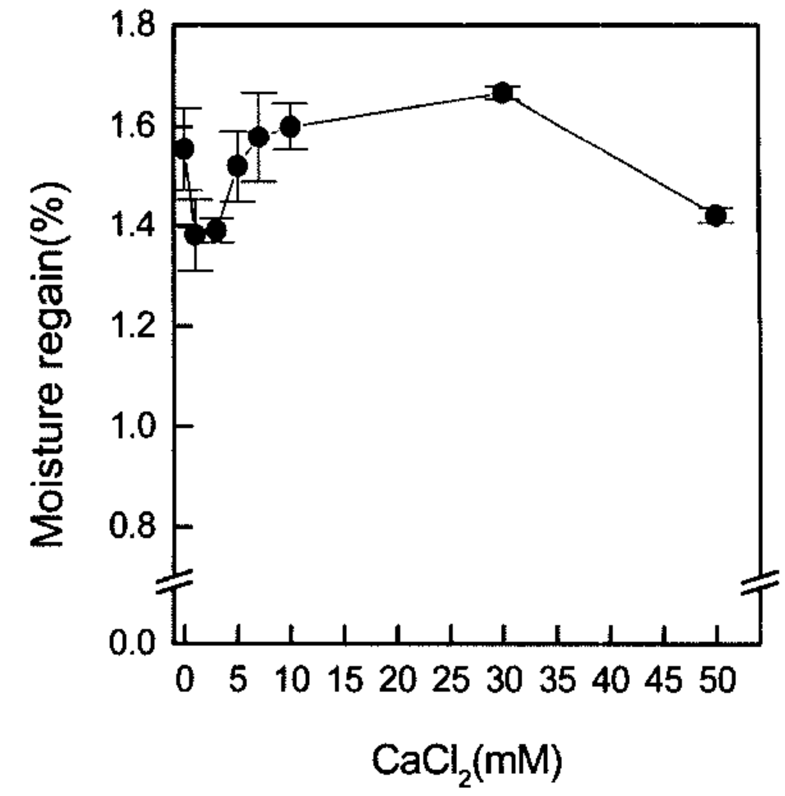


Fig. 3. Moisture regain of PPL treated PET fabrics in the presence of calcium chloride. Treatment conditions: 50%(owf) PPL; pH 7.5; temperature, 40°C; treatment time, 90 minutes.

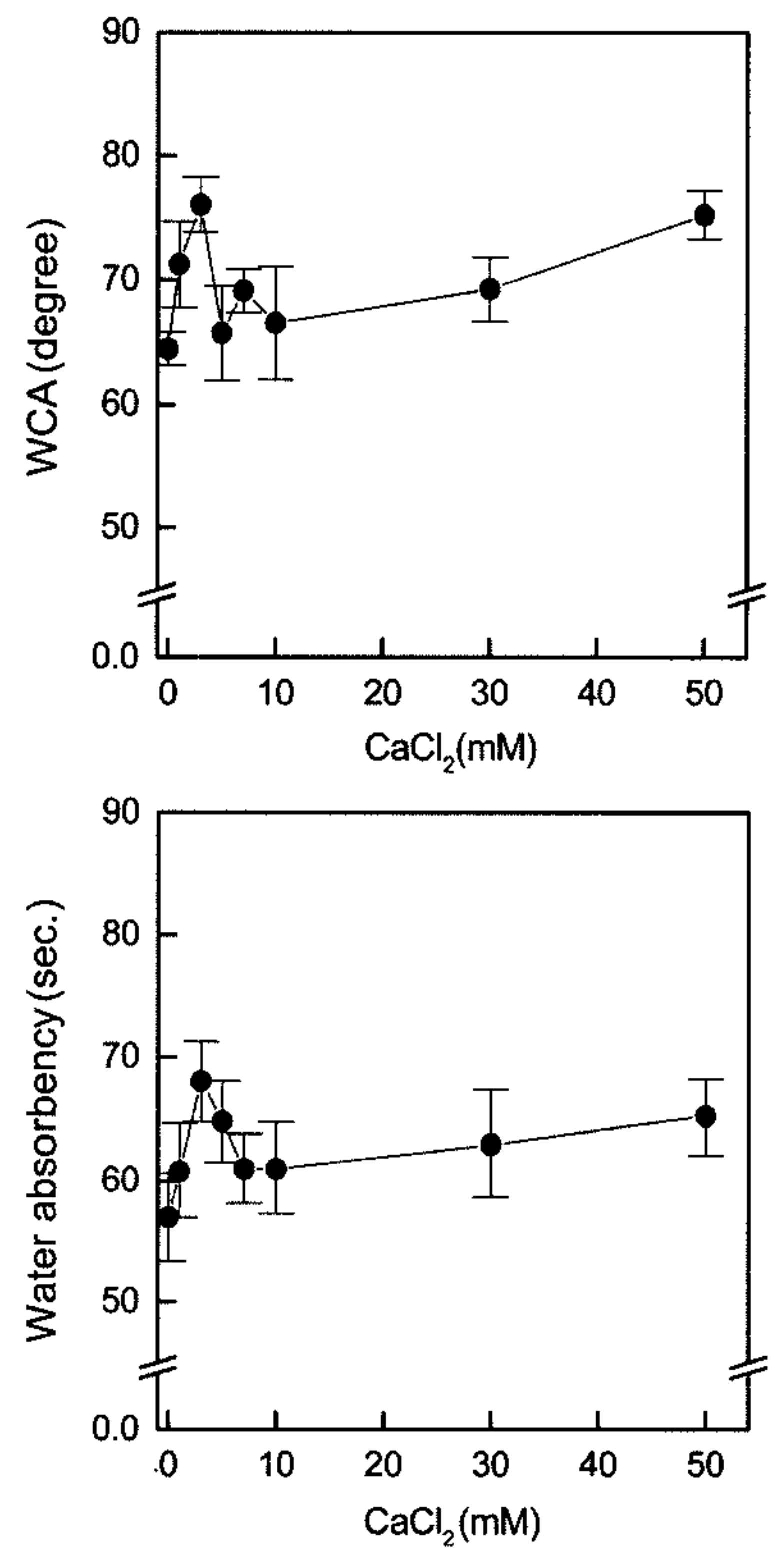


Fig. 4. Wettability of PPL treated PET fabrics in the presence of calcium chloride. Treatment conditions: 50%(owf) PPL; pH 7.5; temperature, 40°C; treatment time, 90 minutes.

added above 10mM. Thus, when more than 10mM of calcium chloride was added to the PPL treatment solution, it could assist the enzymatic hydrolysis efficiently.

3. Effect of Treatment Conditions on Wettability of Lipase Treated PET Fabrics

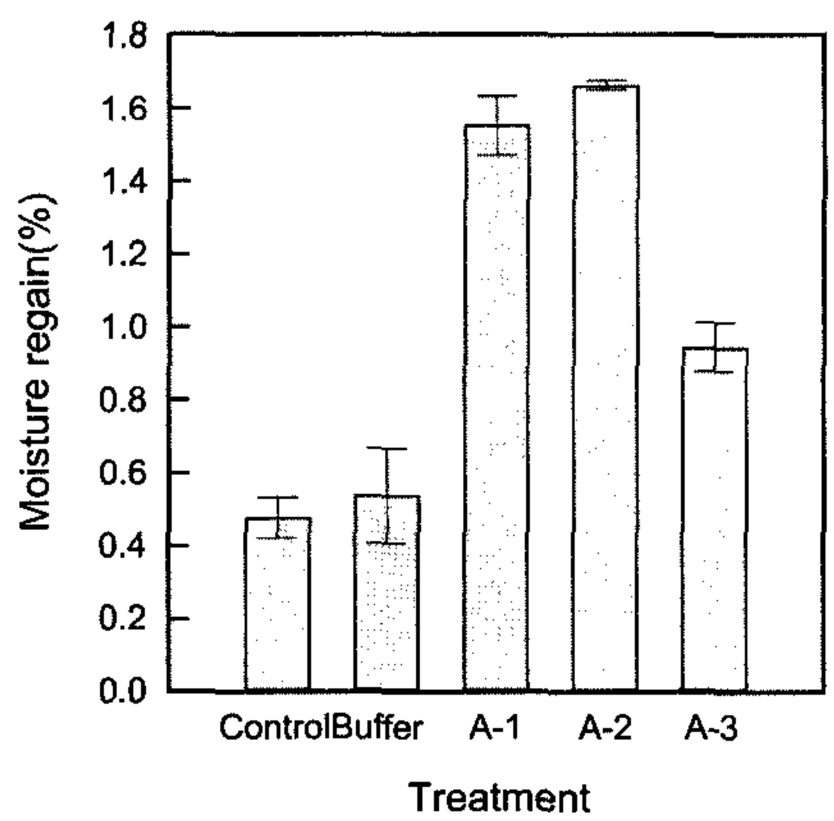
<Fig. 5> shows the effect of the treatment conditions on the moisture regain of the PET fabrics. To check the effect of buffer treatment, the PET fabric was immersed in 50mM TRIS at pH 7.5 and 40°C for 60minutes. The moisture regain of the buffer treated fabric increased very slightly in comparison with that of the untreated PET fabric. However, there were no significant differences between the untreated(0.478%±0.055) and the buffer treated PET fabric(0.539%±0.131).

The moisture regain of the PPL treated fabric(A-1) showed a 3.5-fold increase compared to that of the untreated fabric. The moisture regain of the PET treated in the presence of calcium chloride(A-2) exhibited the highest value(1.666%±0.013), while that of the PET treated in the presence of Triton X-100(A-3) decreased rapidly to 0.947%±0.067.

<Fig. 6> shows the effect of the treatment conditions on wettability. The wettability of the buffer treated fabric improved very slightly in comparison with the untreated PET fabric. However, there were no significant differences between the untreated(98.78°±0.055, 101.25sec.±2.872) and buffer treated PET fabrics(93.1°±3.35, 93.525 sec±1.546).

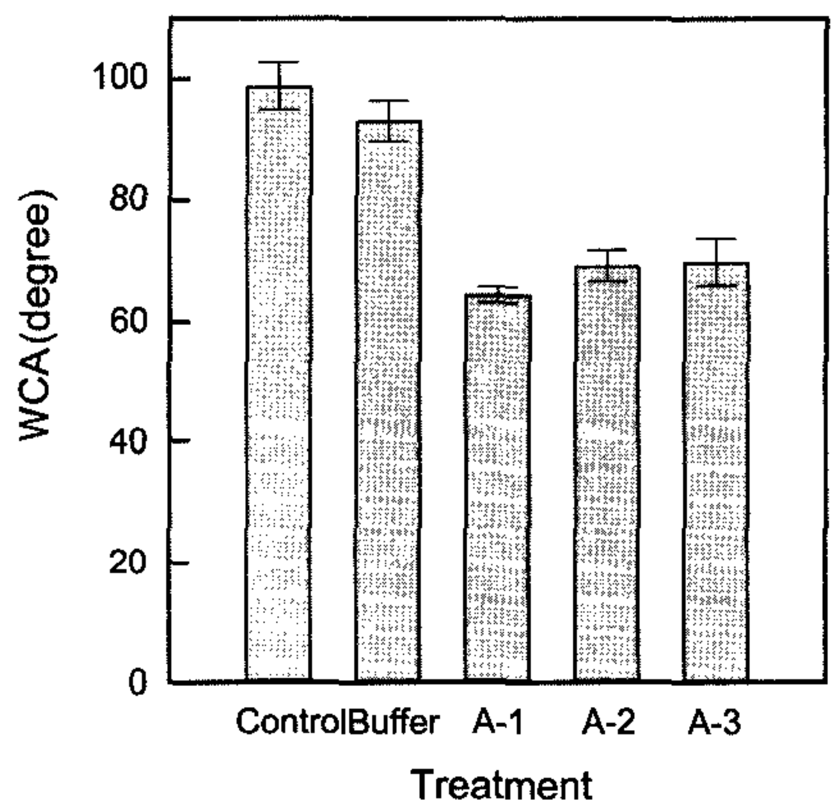
The WCA and water absorbent time of the PPL treated PET fabrics(A-1) decreased to 64.438°±1.29 and 57 sec.±3.656, respectively.

Since hydrolysis on PET fabrics is limited to the surface due to the large size of the enzyme molecules, hydrophilic groups are formed on the surface of the PET, which can improve the wettability(Hsieh

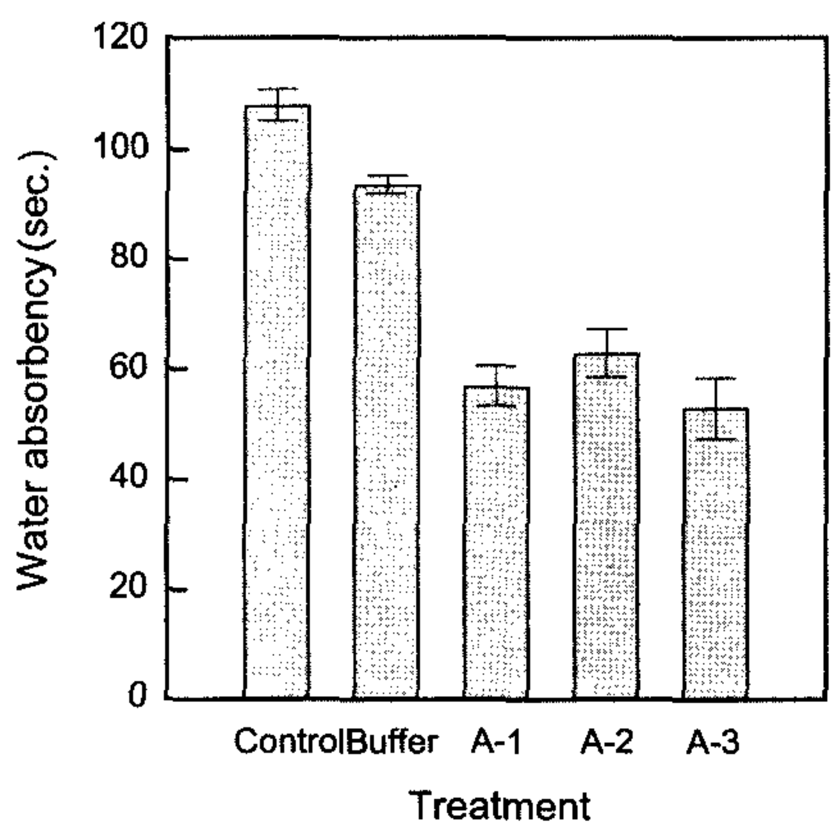


A-1: 90 minutes, 50%(owf)(optimum condition),
A-2: 30mM $CaCl_2$, 90minutes, 50%(owf),
A-3: 0.05% Triton X-100, 90 minutes, 50%(owf)

Fig. 5. Moisture regain of lipase treated PET fabrics with various treatment conditions.

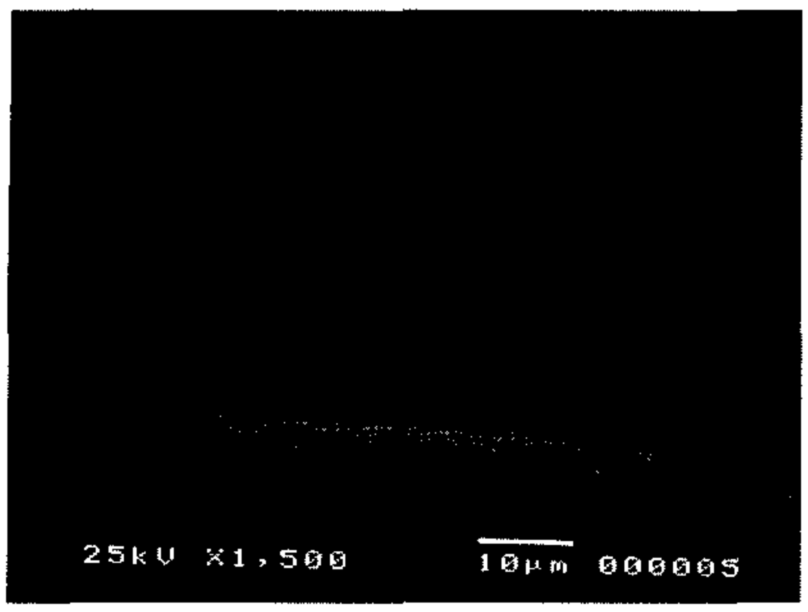


A-1: 90 minutes, 50%(owf)(optimum condition),
A-2: 30mM $CaCl_2$, 90 minutes, 50%(owf),
A-3: 0.05% Triton X-100, 90 minutes, 50%(owf)

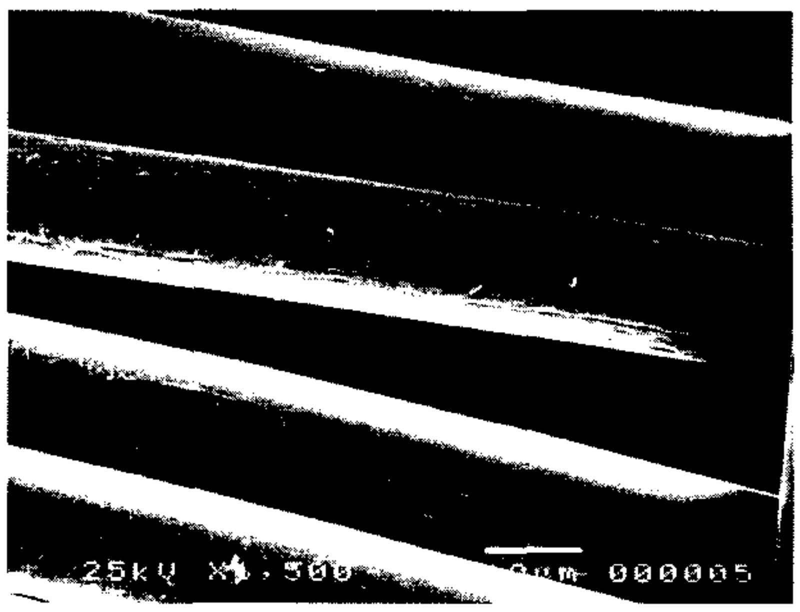


A-1: 90 minutes, 50%(owf)(optimum condition),
A-2: 30mM $CaCl_2$, 90 minutes, 50%(owf),
A-3: 0.05% Triton X-100, 90 minutes, 50%(owf)

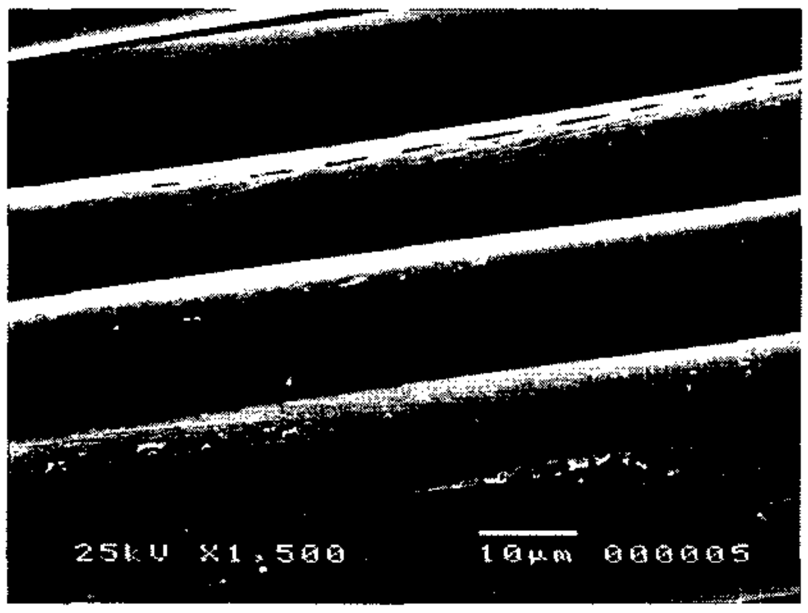
Fig. 6. Wettability of lipase treated PET fabrics with various treatment conditions.



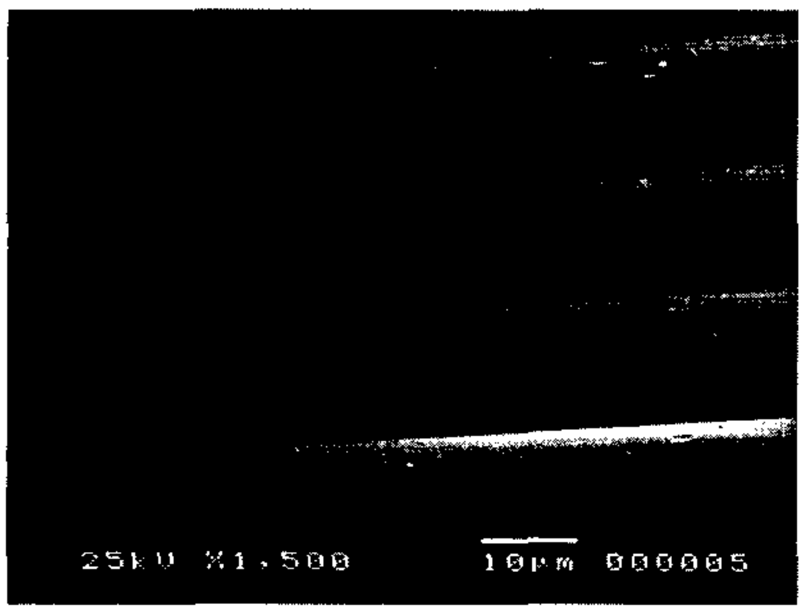
Untreated



ⓐ PPL treatment
(pH 7.5, 40°C, 50%(owf), 90 min.)



ⓑ PPL treatment in the presence of 30mM $CaCl_2$



ⓒ PPL treatment in the presence of 0.5% Triton X-100

Fig. 7. SEM micrographs of PPL treated PET fabrics.

& Cram, 1998; Kim & Song, 2006; Yoon et al., 2002). As a result, lipase treatment was an effective method to improve the wettability of PET fabrics.

4. SEM Micrographs

<Fig. 7> shows surface micrographs of PET fabrics after PPL treatment. The surface of the PET treated under optimum conditions and in the presence of calcium chloride showed numerous cracks and voids in comparison with the untreated PET fabric. The degradation pattern was very different from the typical surface pitting caused by NaOH treatment (Kim & Song, 2006). These voids and cracks might be largely responsible for increasing the moisture regain and wettability.

However, PET fabric treated with lipase in the presence of Triton X-100 PET showed only slight surface changes. From the SEM micrograph of sampleⓒ, we could conclude that the PET surface changed only slightly because the Triton X-100 inhibited lipase hydrolysis. Therefore, moisture regain sharply decreased when PET fabrics were treated with lipase in the presence of Triton X-100.

IV. Conclusions

Enzymatic hydrolysis on PET fabrics allows eco friendly finishing and the modification of their hydrophobicity. Many lipases have been explored to hydrolyze PET. Among them, PPL is a relatively cheap and widely used commercial enzyme. It is useful, therefore, to have a detailed study of its additives from the viewpoint of broadening its application. In this study, we reported the effect of PPL treatment in the presence of a calcium chloride and Triton X-100 on the wettability and moisture regain of PET fabrics.

The moisture regain of PET fabrics in the presence of 0.5% surfactant showed almost 1.5-fold decrease, compared to the absence of it. Triton X-100 inhibited the hydrolytic activity of PPL.

The moisture regain and wettability of PPL treated PET fabrics improved when more than 10mM of calcium chloride was added to the treatment solution.

Voids and cracks caused by PPL treatment were largely responsible for increasing water-related properties.

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요 약

본 연구는 폴리에스터 직물에 리파제 처리시 첨가제에 따른 수분특성 변화를 검토하였다. 활성제(염화칼슘) 및 비이온 계면활성제(Triton X-100) 첨가가 수분율, 접촉각, 흡수속도, 표면형태변화에 미치는 영향을 비교, 분석하였다. 연구결과, 리파제 처리된 폴리에스터 직물의 수분율은 비이온 계면활성제인 Triton X-100 첨가시 현저히 감소하는 것으로 나타났다. 그러나 리파제의 활성제로 알려진 염화칼슘 첨가시 폴리에스터 직물의 수분특성은 다소 증가하는 것으로 나타났다. 특히 리파제 처리시 염화칼슘이 10 mM 이상 첨가된 경우 폴리에스터 직물의 수분특성이 증가되었다. 리파제 처리된 폴리에스터 직물의 표면관찰 결과, 섬유 표면에 생성된 보이드와 크랙이 폴리에스터 직물의 수분특성 증가에 영향을 미치는 것으로 확인되었다. 이상의 결과를 통해, 폴리에스터 직물에 리파제 처리시 Triton X-100은 리파제의 활성을 저해하고, 염화칼슘은 리파제의 활성을 다소 증가시키는 것을 확인하였다.