Enzymatic Hydrophilization of Polyester Fabrics Using a Recombinant Cutinase Cut 190 and Their Surface Characterization

Fusako Kawai*1,2, Tokozo Kawase*2, Takeshi Shiono*2, Hiroshi Urakawa*1,2, Sachiko Sukigara*2, Chendi Tu*2, and Masaki Yamamoto*1

*1 Center for Fiber and Textile Science, Kyoto Institute of Technology, Hashigami-cho 1, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan
*2 Graduate School of Science and Technology, Kyoto Institute of Technology, Hashigami-cho 1, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

Abstract: Polyester fabrics (poly(ethylene terephthalate) (PET) and Ecoface®) were treated with a recombinant cutinase, Cut 190°, from a thermophilic actinomycete (Saccharomonospora viridis AHK 190) for a bio-hydrophilization of polyester fabric surface. After incubation of amorphous PET film with Cut 190° at 50 °C, contact angles of water and formamide on the enzyme treated film decreased and polar component of surface free energy, γs, increased to show the enzyme-hydrophilization of PET surface, indicating the increase of hydrophilic groups (COOH and OH) on the film surface. Similarly, polyester fabrics were treated by Cut 190° at 65 °C, and their surfaces were characterized using scanning electron microscopy (SEM), Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), X-ray photoelectron spectroscopy (XPS) analyses. Enzyme-treated polyester fabrics did not display significant changes by SEM and ATR-FTIR analyses. However, XPS analysis showed that the enzyme-treatment induced significant changes in the region of 3-5 nm depth from the surface. Only enzyme-treated polyester fabrics showed capillary rise of water, which was explained in terms of the increase in surface hydrophilicity. Increased color density of the enzyme-treated fabrics with methylene blue also suggested the increment of COOH groups on the fabric surface. On the other hand, the enzyme treatment did not affect tensile properties, supporting that the enzymatic hydrolysis is limited to the surface of fabrics.

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1. Introduction

Poly(ethylene terephthalate) (PET) is the major synthetic fiber and the global production of PET was 43.3 million metric tons in 2012, meaning about 80% of the entire manmade fibers [1]. Because of the excellent chemical, physical, and mechanical properties, PET has been used in a great number of application areas such as films, bottles, mechanical appliances, medical supplies, apparel and clothing material, home furnishing and interior textiles, and hygiene and medical textiles. The main downstream industries based on PET are production of polyester fibers, accounting for around 65% of global consumption. However, PET suffers of some drawbacks due to the intrinsic hydrophobic nature of the polymer. That is, the hydrophobic nature of PET causes a variety of problems with regard to the surface physicochemical (e.g., wettability, adhesion, adsorption, and surface reaction), electrical (e.g., static electrification), mechanical (e.g., friction and lubrication), and biological (e.g., biocompatibility and feel) properties.

Most of disadvantages coming from the hydrophobicity of PET surface can be improved by converting the surface to hydrophilic one. In the past several decades, a large number of researches have been devoted to surface modification of PET. The methods employed for the hydrophilization of PET surface are divided broadly into two categories. One
is physical modification (dry process) such as low-temperature plasma discharge and etching [2–13] which are usually conducted at ambient pressure. Recently, Gotoh et al. reported the atmospheric pressure plasma jet (APPJ) treatment of PET substrates (film, mesh, and fabric) [14–18]. Based on scanning electron microscopy observation, X-ray photoelectron spectroscopy (XPS) analysis, contact angle measurements, and detergency experiments, they concluded that APPJ exposure increased the surface oxygen concentration, enhanced the hydrophilization of PET, and resulted in detergency improvement. Another is chemical modification (wet process) such as acid-alkaline treatment [19–24], coating [25–29], blending, and graft polymerization [30–38]. Conventional alkaline treatment has been used to increase hydrophilicity of PET textile materials, but the treatments resulted in pit-like structure and lead to reduced fiber strength [39]. With respect to the surface graft polymerization, Kawase et al. studied chemical-induced graft polymerization of acrylic acid on PET film and fabric, and characterized the PET surface using contact angle measurements, Fourier transform infrared spectroscopy (FT-IR), and XPS analysis to conclude that the COOH groups grafted on PET surface influence only the polar component χ′ of surface energy and not the dispersive one χ″ [31]. The plasma treatment can yield very hydrophilic surface but its durability may be poor, whereas the durability of surface graft polymerization is fairly good but associated with solvent waste problems.

In this decade, studies involving the use of enzymes for novel and eco-friendly processing on PET have also been reported [40–44], where the enzymatic surface hydrophilization of PET fabrics has been an attractive target for potential application of cutinases. For example, Vertommen et al. reported that the enzymatic hydrolysis of PET fabrics by cutinase from Fusarium solani pisi produced hydroxyl and carboxyl groups on the fabric surface to result in the improvement of surface hydrophilicity of the fabrics [42]. Brueckner et al. also compared the PET hydrolysis by alkaline treatment and by enzymatic hydrolysis using Thermobifida fusca cutinase and Thermomyces lanuginosus lipase [45]. They confirmed that the enzymatic hydrolysis led to an increase of hydroxyl and carboxyl groups on the PET surface resulting in an enhancement of water absorption and dyeability.

The catalytic activity of commercially available cutinases is not sufficiently high to fit the requirements of the textile industry. For industrial purposes, thermostable enzymes have been sought on the view point of the durability for repeated uses and the efficiency at higher temperatures. As a candidate of enzyme for the PET surface hydrolysis, many cutinases were cloned from thermophilic actinomycetes, compost habitants [46]. In the preceding works [47–49], we have also cloned a gene encoding a cutinase (Cut 190) from a compost actinomycete, Saccharomonospora viridis AHK 190, and expressed it as a 6xhis-tagged protein as pQE 80 L-cut 190 in Escherichia coli Rosseta-gami B (DE 3).

In this work, we investigated the chemical and structural changes induced by a novel cutinase (Cut 190)-assisted surface hydrolysis of PET fabrics to confirm the usefulness of Cut 190 for the enzymatic surface hydrophilization of polyester fabrics at low temperature. We also characterized the enzyme-treated PET surface by SEM observation, contact angle measurements, FT-IR, XPS, water absorption tests, dyeing tests, and tensile property measurements.

2. Experimental

2.1 Materials and methods

Amorphous poly(ethylene terephthalate) (polyester, PET) film (0.25 mm-thick) was purchased from Goodfellow Cambridge, Ltd. (Tokyo, Japan). Polyester plain fabric and Ecoface® plain fabric were provided by Ichimura Sangyo Co., Ltd. (Osaka, Japan). The material properties of polyester and Ecoface® used in this study are summarized in Table 1. Ecoface® is a compostable polyester fiber containing Apexa® type 4027 resin, which is an environmentally-conscious resin developed by E.I. du Pont de Nemours and Company.

Recombinant Cut 190 (S226 P/R228 S) (designated as Cut 190* hereafter) cloned from Saccharomonospora viridis AHK 190 was expressed, purified and characterized, as described previously [48]. Prior to the surface hydrolysis, polyester and Ecoface® fabrics were cut into approximately 10 × 10 cm², pretreated in MillQ water at 60°C for 30 min three times to remove water-soluble contaminants from fiber and fabric, rinsed in ethanol at room temperature for 1 h, and air-dried on filter paper. For water absorption test, fabrics were cut into approximately 5 (warp) × 1 (weft) cm² sizes. For
Table 1  Elements of polyester fabrics (PET and Ecoface®).

<table>
<thead>
<tr>
<th>Material</th>
<th>Thread for weaving</th>
<th>Density (pieces of string/inch)</th>
<th>Weight (g/m²)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>weft</td>
<td>warp</td>
<td>vertical</td>
<td>horizontal</td>
</tr>
<tr>
<td>PET</td>
<td>84dt-36f</td>
<td>84dt-36f</td>
<td>91</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>(DTY)</td>
<td>(DTY)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ecoface®</td>
<td>84dt-36f</td>
<td>84dt-36f</td>
<td>97</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>(DTY)</td>
<td>(DTY)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| dt: decitex, f: filament, DTY: draw textured yarn |

tensile strength measurement, fabrics of 10 (weft) × 10 (warp) cm² sizes were used.

2.2 Enzymatic surface hydrolysis of PET

It is known that enzymes preferentially attack the amorphous regions of polyesters [50-52], and the concept of "chain mobility" has been proposed as one of the main factors responsible for the biodegradability of polyesters [52]. In the amorphous phase the chain mobility is less restricted than in the crystalline phase, especially at temperatures close to glass transition (Tg: approximately 60-65°C in aqueous solution), thus allowing a closer contact between the polymer chains and the active site of the enzyme.

At first, the enzyme reactions on PET film surface were performed as follows: The reaction mixture consisting of 100 mM Tris-HCl buffer (pH 8.0), 25 mM CaCl₂, 24% glycerol, 3 μM purified Cut 190° and PET film (approximately 1 × 1 cm²) in a total volume of 20 mL was incubated at 50°C for 20 h. After the incubation, the film was put in an appropriate amount of MilliQ water and sonicated at 52 W for 10 s to remove the enzyme attached. The same process was repeated three times by changing MilliQ water every time. Finally, the washed sample was dried at 58°C for at least 24 h and kept in a vacuumed desiccator with silica gel pellets. As control (enzyme-untreated), PET film was incubated without enzyme under the same temperature and time.

However, because of the drawing process, PET fiber and fabric are known to have higher crystallinity than the original PET pellets and amorphous PET fabrics. Despite this, we expected that the enzyme Cut 190° would hydrolyze ester groups located near the PET surface to lead to an increase of both COOH and OH groups on the surface, resulting in hydrophilization. Fabric samples (10 × 10 cm²) were also incubated with the enzyme solution at 65°C for three days (enzyme-treated) in a total volume of 25.0 mL. Like films, fabrics were incubated without enzyme under the same temperature and time (enzyme-untreated fabric).

The obtained films and fabrics were subjected to the measurements described below.

2.3 Scanning electron microscopy (SEM)

An S-300 N scanning electron microscope (VE-7800, KEYENCE Corp., Osaka, Japan) was used for the analysis. Samples were coated with a thin layer of gold under vacuum, using an ion coater (IB-2, Eiko Engineering Co. Ltd., Tokyo, Japan) and SEM images were collected under vacuum at an accelerating voltage of 10 kV with the magnification of 500 or 1000.

2.4 Contact angle measurement

To determine the surface energies of polyester, we measured the contact angles of double-distilled water and formamide as wetting liquids on the films using a contact angle meter CA-A (Kyowa Interface Science Co. Ltd., Saitama, Japan). Polyester films before and after the enzymatic treatments were held on a metallic plate. A drop of water or formamide with a drop size of 5 μL was put on the surface of film, and after 30 s contact angles were measured. Measurements were repeated at least five different points of two sample surfaces. The standard deviations were less than 2.2. All measurements were done in a conditioned room at 25°C and 60% humidity.

2.5 Determination of surface free energies

Similar to the previous work [31], the total surface free energy, γs, is assumed to be the sum of contributions from different intermolecular forces at the surfaces, namely, the dispersion component, γd, and the polar component, γp.

\[ γ_s = γ_d + γ_p \]  
(1)

Owens and Wendt derived the following geometric mean expression for Young’s equation [53]:

\[ γ_s(1 + \cosθ) = 2(γ_dγ_p)^{1/2} + 2(γ_dγ_p)^{1/2} \]  
(2)
In this work, based on the surface tensions of water and formamide and their interface tensions with n-octane using Shimadzu surface tensiometer ST-1 at 25°C (Shimadzu, Kyoto, Japan), the values of γ, γ′, and γ″ of water and formamide were determined 72.0, 218.0, and 51.0 mN m⁻¹ for water, and 58.2, 36.0, and 22.2 mN m⁻¹ for formamide, respectively.

As shown in the previous work, Cut 190° treatment at 50°C did not change surface morphology (roughness) of PET film [47]. Therefore, the surface energies of PET films, γ, γ′, and γ″ (=-γ″ + γ′′), can be determined using Equation 2 and measured contact angles of water and formamide.

2.6 Spectrometry measurements

Spectra of attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) were recorded on a Nicolet Avatar 370 DTGS FTIR spectrometer using the diamond ATR apparatus Smart Orbit (Thermo Electric Co., USA).

X-ray photoelectron spectroscopy (XPS) measurements were done on a JPS-9010 MC/SP (JEOL, Japan) with MgKα X-ray source at the condition of 10 kV and 10 mA. The fabric samples after used for wafer absorption test were cut into 5 × 5 mm² pieces and used for XPS measurements. The XPS analyses of PET and Ecoface® fabrics were done on C₁s, and O₁s peaks. The residual pressure in the chamber was about 2 × 10⁻⁶ Pa. Surface charge buildup was corrected by considering the shift of the C₁s peak at 285.0 eV. After smoothing of the spectra, the sub-peaks were resolved using XPSPEAK 4.1 software.

2.7 Water absorption test

Referring to AATCC 197 Vertical Wicking of Textiles [54], water absorption test was devised with modifying the Washburn method using a Wilhelmy-type surface tension meter KSV Sigma 701 instrument as follows: The PET and/or Ecoface® fabrics, 5 (warp) × 1 (weft) cm² rectangular pieces, were used for the absorption test. A piece of fabric was suspended from the balance. The flexible sample holder was used to hold the fabric sample. The wetting liquid vessel was electrically raised until the fabric edge just touched the liquid surface, and then the changes of weight of fabric were recorded continuously with time. For the wicking liquids, n-decane (ρ = 0.730 g mL⁻¹ at 25°C), water (ρ = 0.997 g mL⁻¹ at 25°C) and formamide (ρ = 1.134 g mL⁻¹ at 25°C) were used. At first, the wetting dynamic of n-decane was measured at 25°C for 10 min, and the equilibrium weight of fabric was determined (Wₒ). After completely dried, absorption measurements using water and formamide were successively executed at 25°C. The volumes of absorbed liquid (Wₒ/ρ) were plotted against wetting time, and the time to reach 95% amount of equilibrium volume (Tₑₒ) and the initial absorption rate (Vₒₒ), the slope of the absorption curve at the initial period (<0.2 s) were analyzed.

2.8 Dyeing test

According to Johar [55], carboxylic acid groups in organic compounds can be detected with cationic dyes, such as eosin, mercurichrome, and methylene blue. In this work, we also examined the dyeing test to detect COOH groups on the polyester fabric surface. Dyeing test was performed using methylene blue (CI: 52015), a cationic dye. Dyeability of fabrics was determined with a reflectance spectrophotometer (KONICA MINOLTA CM-2600d). As the spectrum of dyed fabrics (PET and Ecoface®) showed the maximal peak at 440 nm, the reflectance of dyed fabric was measured at 440 nm. The color strength was assessed using the Kubelka-Munk equation: K/S = (1-R)²/2R.

2.9 Measurements of Tensile properties

Kawabata Evaluation System for Fabrics (KES-F) [56,57] was used for testing tensile properties of original, enzyme-untreated, and enzyme-treated polyester fabrics. Measurements were carried out with warp and weft directions for each fabric on a tensile and shear tester KES-FB 1 (Kato Tech Co., Ltd., Kyoto, Japan) and a surface tester KES-SE-STP (Kato Tech Co., Ltd., Kyoto, Japan).

For testing tensile properties, cyclic force extension tests were carried out at a maximum tensile load of 380 N/m at a speed of 0.2 mm/s. Loading and unloading cycles were performed. The fabric sample (10 × 10 cm²) was cut into 10 cm × 5 cm, cramped, and extended along 5 cm direction. The tensile properties in both the warp and weft directions were measured. The tensile energy (WT, Nm/m²), tensile extension at 380 N/m (EM, %), tensile resilience (RT, %) and linearity (LT) were obtained for all fabrics.

3. Results and discussion

3.1 Polyester substrates

This work aims to investigate the improvement in the hydrophilicity of polyester substrate without harming the mechanical properties of the material.
The substrates used in this work were a 100% poly (ethylene terephthalate) (PET) amorphous film, PET fabric (plain), and Ecoface® fabric (plain).

With regard to Ecoface®, it is claimed the degradation of Ecoface® has been confirmed by a degradation experiment in the compost. Hence, we employed Ecoface® fabric as a potential polyester substrate with expectation that the enzymatic hydrophilization by Cut 190° on the Ecoface® fabric surface might be facilitated than that on a 100% PET fabric.

3.2 Surface energies of polyester film

At first, to confirm the surface hydrophilization by the enzyme, we treated amorphous PET film with Cut 190° under incubation at 50 °C, which is lower than Tg, for 20 h, and the contact angles of water and formamide were measured to determine the surface free energies of PET films, $\gamma_i$, $\gamma_s^0$ and $\gamma_s (= \gamma_i + \gamma_s^0)$. Results are summarized in Table 2.

As expected, all contact angles for enzyme-treated films were smaller than those for the original and enzyme-untreated films. In addition, it is noted that enzymatic hydrolysis lead to the remarkable increase of surface energy polar component, $\gamma_s$, indicating that the increase of hydrophilic groups, such as COOH and OH, on the enzyme-treated polyester surface. These results indicated that the enzyme-treatment using Cut 190° can hydrophilize the polyester surface even at 50 °C by hydrolysis.

3.3 Surface characterization of enzyme-treated polyester fabrics using SEM

We performed SEM image analysis on polyester fabrics before and after enzyme treatment at 65 °C, expecting that the enzymatic hydrolysis at the fabric surface might cause the roughening of the surface.

As shown in Fig. 1, no distinct changes of surface morphologies on both PET and Ecoface® fabrics were observed even after enzyme treatment probably because of short time treatment and high crystallinity. This finding agreed with the report by Brueckner et al. [45], using the cutinase from Thermobifida fusca.

3.4 Surface characterization of enzyme-treated polyester fabrics using ATR-FTIR, and XPS

As often discussed, the contact angles should respond to the functional groups less than nm thick in direct contact with the liquid. On the other hand, it has been widely accepted that ATR-FTIR and XPS characterizations have different degrees of surface sensitivity in comparison with the contact angle measurements [31,58]. Then, we measured the ATR-FTIR of enzyme-untreated and enzyme-treated films and fabrics of polyester.

Donelli et al. investigated the changes induced by a lysozyme enzyme on the surface properties of PET by means of water contact angle, ATR-FTIR, and Fluorescence spectroscopy [59]. They observed the structural and conformational changes of the ethylene glycol and benzene moieties of PET, and the decrease in intensity of carbonyl stretching at 1,720 cm⁻¹ upon enzyme reaction. However, in this work, no significant difference was detected between enzyme-untreated
and treated films and fabrics of polyester, probably because our enzyme hydrolysis would proceed in remarkably shallow region from the surface.

With respect to the degree of surface sensitivity, XPS is known to detect a thinner outer layer (3–5 nm) of the interface in comparison with ATR-FTIR characterization (detectable of deeper outer layer of sub-μm depth). Therefore, the XPS analysis was performed on the surface of enzyme-treated polyester fabrics.

Fig. 2 shows the $C_{1s}$ and $O_{1s}$ spectra of the original, enzyme-untreated and enzyme-treated polyester and Ecoface® fabrics. With the aid of curve fitting technique, we could separate the $C_{1s}$ spectra of original and enzyme-untreated PET and Ecoface® fabrics into three individual components at 285.0 eV (C-H), 286.6 eV (COO, ester), and 289.0 eV (C=O). In contrast, the $C_{1s}$ spectra of enzyme-treated fabrics showed the variation (broadening) of peaks at around 286–288 eV, and could be fitted to four individual components at 285.0 eV (C-H), 286.6 eV (COO, ester), 287.8 eV, and 289.0 eV (C=O). It was quite interesting that a new peak appeared at 287.8 eV only for the enzyme-treated fabrics. At the present, we assigned this new peak of 287.8 eV to $C_{1s}$ of C=O of COOH, which would be produced by enzymatic hydrolysis. Aside from our results, Brueckner et al. reported that the new $C_{1s}$ peak appeared at 289 eV with cutinase/lipase-treated PET fabrics [45]. In addition, while the $O_{1s}$ spectra of original and enzyme-untreated fabrics consisted of two peaks at 532.2 eV and 533.6 eV, a new peak appeared at 531.2 eV in the $O_{1s}$ spectrum of enzyme-treated fabrics. We are now speculating that this peak at 531.2 eV would be attributable to the $O_{1s}$ of COOH and/or OH.

Based on the results of SEM, ATR-FTIR and XPS characterizations, it is reasonably concluded that enzymatic hydrolysis can proceed only in the thinner surface region (~10 nm depth from the surface) of polyester fabrics, but not in the region of ~μm depth level, and exert no detectable change on the polymer inside.

3.5 Water absorption test of polyester fabrics

The enzymatic hydrolysis of ester bonds at the surface of PET generates new free hydroxyl and carboxyl groups, thus leading to increased hydrophilicity of PET surface. To quantify the changes in hydrophilicity of fabrics, Brueckner employed the water dissipation test (drop test) [45]. In this work, we examined the capillary rise of liquid

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![Fig. 2](image-url)  
Fig. 2 XPS spectra of the $C_{1s}$ and $O_{1s}$ peaks of the original, enzyme-untreated and enzyme-treated polyester fabrics (PET and Ecoface®). Dashed lines indicate the deconvoluted results of the $C_{1s}$ and $O_{1s}$ peaks into the individual components: (a) original fabrics; (b) enzyme-untreated fabrics; and (c) enzyme-treated fabrics.
(absorption test) using \( n \)-decane, formamide, and water as wetting liquids to compare the changes in the wettability of the original, enzyme-untreated and enzyme-treated fabrics of PET and Ecoface®.

Fabrics may be considered as planar porous surfaces. However, for this type of wetting test, quite many factors such as porosity, capillaries (radius, contact angle etc.), fabric properties, permeability of liquids, and so on should be considered. To compare the wetting dynamics of the enzyme-untreated and treated polyester fabrics, we measured dynamics of absorption of liquid into fabrics. As an example, Fig. 3 shows the absorption curves of \( n \)-decane, formamide, and water into enzyme-treated polyester fabric, where the volumes of absorbed liquid \( (W_t/\rho_l) \) were plotted against the wetting time. As dynamic parameters of absorption, the absorption time of 95% amount of equilibrium volume \( (T_{0.95}) \) and the initial absorption rate \( (V_{init}) \) the slope of the absorption curve at the initial period (<0.2 s) were determined. Results are listed in Table 3.

As shown in Table 3, both \( n \)-decane and formamide could penetrate and rise into all fabrics, where \( T_{0.95} \) and \( V_{init} \) of \( n \)-decane were superior to those of formamide regardless of kind of polyester fabrics. In comparison with original, enzyme-untreated, and enzyme-treated fabrics, no significant changes in decane absorption were observed, but slight lowering of \( V_{init} \) of formamide absorption was observed for enzyme-untreated fabrics. This might be attributed to CaCl\(_2\) in the processing buffer, which would convert the COOH group existing on the original fabric partially to COOCa. However, as mentioned above, no such change on the surface was observed by FTIR measurement. However, water could not penetrate into original and enzyme-untreated PET and Ecoface® fabrics.

To the contrary, though the absorption velocities were rather small, it is noteworthy that water could be absorbed into only enzyme-treated fabrics regardless of polyester types, PET and Ecoface®. Therefore, it is reasonably concluded that the enzyme treatment can hydrolyze the ester bonds at the surface, hydrophilize the polyester fabric surface, and enhance the wettability against water.

Contrary to our expectation, it may be interesting that all dynamic parameters of liquid-absorption into Ecoface® fabrics were inferior to those into PET fabrics.

### 3.6 Dyeing of polyester fabrics with methylene blue

As described in Experimental details, carboxylic acid groups in organic compounds can be detected

![Fig. 3 Dynamics of capillary rise (absorption) of liquid into Cut 190° treated PET fabric at 25 °C.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_{0.95} ) (s)</th>
<th>( V_{init} ) (mL s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( n )-Decane</td>
<td>Formamide</td>
</tr>
<tr>
<td>Original PET</td>
<td>54.1</td>
<td>167.1</td>
</tr>
<tr>
<td>Enzyme-untreated PET</td>
<td>59.5</td>
<td>171.3</td>
</tr>
<tr>
<td>Enzyme-treated PET</td>
<td>51.1</td>
<td>138.3</td>
</tr>
<tr>
<td>Original Ecoface( ^\circ )</td>
<td>56.6</td>
<td>231.9</td>
</tr>
<tr>
<td>Enzyme-untreated Ecoface( ^\circ )</td>
<td>53.6</td>
<td>264.6</td>
</tr>
<tr>
<td>Enzyme-treated Ecoface( ^\circ )</td>
<td>52.9</td>
<td>228.0</td>
</tr>
</tbody>
</table>

* : No capillary rise was observed.
with cationic dyes, such as eosin, mercuriochrome, and methylene blue [55]. In this work, we also examined the dyeing test using methylene blue to detect COOH groups on the surface. Results of reflectance (R) and K/S values of dyed fabrics are shown in Table 4.

Regardless of polyester type, PET or Ecoface®, enzyme-treated fabrics showed the larger decrease of R values and the larger increase of K/S values by dyeing with methylene blue than those of enzyme-untreated fabrics. These results clearly indicate that the enzyme treatment increased the amount of carboxyl groups on fabric surface.

However, it may be surprising that the K/S values of the enzyme-untreated fabrics was rather large in both PET and Ecoface® while hydrophilization of the surface was not observed for those fabrics. It might also be due to CaCl2 in the processing buffer, but the exact reason is not explained at the present.

3.7 Characterization of polyester fabrics by tensile properties

Next, to confirm whether enzymatic hydrolysis may cause serious changes on the mechanical properties of fabrics, tensile properties were measured by means of Kawabata evaluation system (KES). In Table 5, the values of tensile energy (WT), resilience (RT), extension (EM) and linearity (LT) of enzyme-treated polyester fabrics in both directions (warp and weft) were listed, compared with those of enzyme-untreated and original fabrics. As expected, effect of the enzymatic treatment on the tensile properties was not clearly observed.

As shown in Fig. 1, the enzyme treatment did not change the surface morphology of fabrics. In addition, ATR-FTIR results showed that the structures of the polymers were considered to be stable. Those results supported that the enzymatic hydrolysis would occur up to 10 nm levels at most on the surface but not range over μm depth level from the surface.

Considering all characterization results together, it was confirmed that the enzymatic hydrolysis by the novel cutinase Cut 190* led to an increase of hydroxyl and carboxyl groups on the PET surface, resulting in an enhancement of water absorption and dyeability without serious damage of the polyester structures.

3.8 Comparison of polyester fabrics

As mentioned in 3.1, Ecoface® fabric was adopted as a potential polyester substrate with expecting the enhanced enzymatic hydrophilization by Cut 190*, but the results were at the same level of surface hydrophilization as PET fabric. This is probably because the hydrolysis reaction on the surface did not differ at the mild conditions of enzymatic treatment (temperature, time, enzyme amount) in this study. More examination is necessary to discuss further.

4. Conclusion

PET film and polyester fabrics (PET and Ecoface®) were treated with a recombinant cutinase Cut 190* from a thermophilic actinomycete (Saccharomonospora viridis AHK 190). Contact angle measurements on films and surface energy calculation suggested the hydrophilization of the PET surface. Although no visible change of surfaces of polyester fabrics was observed by SEM and no spectral change was detected by ATR-FTIR analysis, the enzymatic hydrolysis by Cut 190* was confirmed by XPS measurement, water absorption test and methylene blue dyeing of the polyester fabrics. It was clarified that the cutinase treatment produced COOH groups on their surfaces (several nm level of depth), resulting in the increase of surface hydrophilicity. Effect of the enzymatic treatment on the tensile properties was not clearly observed. These results

Table 4 Effect of enzyme treatment on dyeing of PET and Ecoface® fabrics with methylene blue.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R (%)*</th>
<th>K/S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original PET</td>
<td>92.2</td>
<td></td>
</tr>
<tr>
<td>Enzyme-untreated PET</td>
<td>70.8</td>
<td>0.0602</td>
</tr>
<tr>
<td>Enzyme-treated PET</td>
<td>68.0</td>
<td>0.0753</td>
</tr>
<tr>
<td>Original Ecoface®</td>
<td>88.5</td>
<td></td>
</tr>
<tr>
<td>Enzyme-untreated Ecoface®</td>
<td>71.8</td>
<td>0.0554</td>
</tr>
<tr>
<td>Enzyme-treated Ecoface®</td>
<td>68.8</td>
<td>0.0707</td>
</tr>
</tbody>
</table>

*: Values of reflectance at 440 nm.
Table 5  Effect of enzyme treatment on tensile characteristic values of polyester fabrics.

a. PET

<table>
<thead>
<tr>
<th></th>
<th>Original</th>
<th>Enzyme-untreated</th>
<th>Enzyme-treated</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Warp</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WT (N*m/m³)</td>
<td>186.1</td>
<td>181.9</td>
<td>188.7</td>
</tr>
<tr>
<td>EM (%)</td>
<td>1.44</td>
<td>1.34</td>
<td>1.41</td>
</tr>
<tr>
<td>RT (%)</td>
<td>69.0</td>
<td>69.6</td>
<td>70.1</td>
</tr>
<tr>
<td>LT</td>
<td>0.822</td>
<td>0.837</td>
<td>0.797</td>
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<tr>
<td><strong>Weft</strong></td>
<td></td>
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</tr>
<tr>
<td>WT (N*m/m³)</td>
<td>776.8</td>
<td>769.9</td>
<td>764.9</td>
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<tr>
<td>EM (%)</td>
<td>6.17</td>
<td>6.01</td>
<td>6.11</td>
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<tr>
<td>RT (%)</td>
<td>70.0</td>
<td>70.2</td>
<td>68.1</td>
</tr>
<tr>
<td>LT</td>
<td>0.733</td>
<td>0.725</td>
<td>0.721</td>
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</table>

b. Ecoface®

<table>
<thead>
<tr>
<th></th>
<th>Original</th>
<th>Enzyme-untreated</th>
<th>Enzyme-treated</th>
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<tbody>
<tr>
<td><strong>Warp</strong></td>
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<tr>
<td>WT (N*m/m³)</td>
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<td>275.5</td>
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<td>EM (%)</td>
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<td>2.09</td>
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<td>67.9</td>
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<td>69.4</td>
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<td>LT</td>
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<td>0.795</td>
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<tr>
<td><strong>Weft</strong></td>
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<td></td>
</tr>
<tr>
<td>WT (N*m/m³)</td>
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<td>891.5</td>
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<tr>
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<td>62.8</td>
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<tr>
<td>LT</td>
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<td>0.723</td>
<td>0.751</td>
</tr>
</tbody>
</table>

supported that the enzymatic hydrolysis would occur only in the 10 nm levels from the surface.

All the data suggested that the cutinase would be quite promising for surface hydrophilization of polyester without serious damage of the polymer structures.

References

1. Statiscal Data from Japan Chemical Fibers Association: http://www.jcfa.gr.jp/english/tdcj/2_world_production/2-2_production-syn.html
54. AATCC Test Method 197-2013. Vertical Wicking of Textiles Developed in 2011 by AATCC Committee RA 63