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The Effects of Lipase and Cutinase Enzyme Surface Treatments on Light Reflectance and Colour Changes in Non-Circular Cross-Sectional Polyester Fibres

Vpliv površinske encimske obdelave z lipazami in kutinazami na odboj svetlobe in spremembo barve poliestrskih vlaken profiliranega prečnega prereza

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Abstract

Lipase and cutinase enzymes were applied to non-circular cross-sectional polyester fibres. Reflectance and colour changes of the fibres were investigated under specific treatment conditions. The results indicated that lipase L0777 did not affect these fibres, regardless of time of treatment or changes in pH. With cutinase, pits on the surfaces of the fibres occurred when cutinase was applied at 55°C and pH of 7.00 and 8.50, respectively, for 24 hours. This was demonstrated by reflectance and colour changes, as well as by SEM images. The wide-angled x-ray diffraction (WAXD) curves of the cutinase-treated fabrics were ambiguous in that the small changes may have been the result of heat rather than enzyme treatment. Differential scanning calorimetry (DCS) results for both untreated and cutinase-treated polyester fibres showed obvious changes. The peak at 250°C did not change but that at 265°C increased in area, indicating re-crystallisation.
Keywords: reflectance, colour, lipase, cutinase, polyester fabric

Izvleček

Poliestrska vlakna profiliranega prečnega prereza so bila encimsko obdelana z lipazami in kutinazami. Raziskan je bil vpliv specifične obdelave na odboj svetlobe in barvne spremembe vlaken. Rezultati so pokazali, da lipaze L0777 niso vplivale na odboj svetlobe s površine vlaken, ne glede na čas obdelave ali spremembo vrednosti pH. Kutinaze so povzročile luknjičavost na površju vlaken pri 24-urni obdelavi pri temperaturi 55 °C in vrednosti pH 7,00 in 8,50. Spremembe so bile spremljane z odbojem svetlobe in spremembo barve ter elektronsko mikroskopskimi posnetki površja vlaken. Krivulje širokokotnega sipanja rentgenskih žarkov (WAXD) s kutinazami obdelanih vzorcev so pokazale manjše spremembe strukture, ki pa so lahko posledica delovanja toplote in ne encimske obdelave. Rezultati diferencialne kalorimetrije (DSC) kažejo povečanje površine eksotermnega vrha pri temperaturi 265 °C, kar dokazuje rekristalizacijo vlaken pri vlaknih, encimsko obdelanih s kutinazami.
Ključne besede: odboj svetlobe, barva, lipaze, kutinaze, poliestrska tkanina

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1 Introduction

Historical applications of enzyme treatments in natural textiles are the "dew retting" of flax using enzymes secreted from micro-organisms in soils; amylases for removing starch sizing from cotton fabrics [1]; cellulases for the bio-polishing of fabrics and incorporation within detergents for removing surface fuzz, reducing the scattering of light and the "brightening" of cotton fabrics [2]; and scouring [3–5] which uses cellulases [6–9], pectinases [10–13] and pectate lyases [14–16]. Other enzymes have been used for changing the chemical and physical surface properties of common polyester, polyethylene terephthalate (PET).

Interest in modifying the surfaces of PET initially focused on alkaline treatments. Figure 1 [17] shows the hydrolysis reaction of PET with sodium hydroxide, in which the electron-deficient carbonyl of PET is attacked by hydroxyl ions in aqueous sodium hydroxide, resulting in chain scission and the formations of carboxylate and hydroxyl end groups. It is believed that this reaction is limited to the surface and it was concluded that most of the resulting PET oligomer left the fibre surface and went into the solution. It was observed that after the reactions the turbid sodium hydroxide solution gradually cleared and a white layer of sediments was found in the bottom of the solution.

The development of biotechnologies with specific applications to fibres has presented new possibilities. Lipases [18, 19, 20], with the capability of catalysing hydrolysis and the synthesis of esters formed from glycerol and long-chain fatty acids, have created applications [21, 22] that have led to possibilities in bioprocess engineering [23]. Early studies by Tokiwa and Suzuki [24, 25] demonstrated that lipases could hydrolyse certain polyesters, and that the rate of hydrolysis was strongly related to the polyester melting point, the chemical structure of the polyester, or the number of polyester molecules within the reactive mixture [26]. Figure 2 illustrates the model.

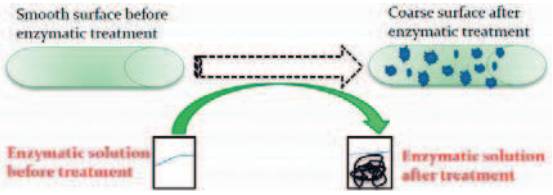


Figure 2: Process of chemical reaction between PET and enzymes

The time-dependent degradation profiles of PET were strongly influenced by the material's surfaces and by the addition of surfactants [27], producing monomeric-like materials. Cross-linked heterochain aromatic polyesters resisted microbial degradation [28]. The temperature difference between the melting point of the polymer and where polyester degradation by lipase took place turned out to be the primary controlling parameter for aliphatic polyesters [29]. Selectivity of lipases with regard to aliphatic or aromatic environments near the ester bonds did not occur, but the lengths of the aliphatic domains and the specific inter-structure were factors [30–32].

Compared to alkaline treatments, five of six lipases were more effective in improving the wetting and absorbent properties of PET fabrics [33]. Full strength was retained. This was confirmed by Chaya and Kitano [34]. Peeling and stratification were observed on surface layers of the fibres with the formations of hydroxyl and carboxylic groups and ester derivatives [35]. Increased hydrophilicity of PET fabrics lipase treatment has also been shown by Alisch-Mark et al. [36], Kim and Song [37–39] using different surfactants in the experiments [40]. Khoddami et al. [41] implied that esterase hydrolysis was limited to surfaces and more affected by any increase in surface area than changes in the internal structure from drawing. Billing et al. [42] found that an esterase showed high specificity towards short and middle chain-length fatty acyl esters of p-nitrophenol. Donelli et al. [43] indicated that crystallinity increased and amorphous content decreased but

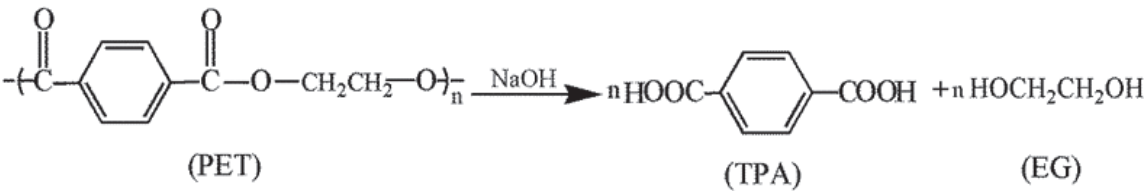


Figure 1: Schematic of chemical reaction between PET with NaOH [17]

their enzyme had higher activity on amorphous PET but minor changes in crystalline PET.

Cutin is part of the cutical, the waxy polymeric coating on all plant surfaces. Cutin consists of omega hydroxyl acids and their derivatives, which are interlinked via ester bonds, thus forming a large polyester polymer. Cutinase studies have been active. Masaki et al. [44] demonstrated that a cutinase could degrade high molecular weight polylactic acid (PLA) and other "biodegradable" plastics. Vertommen et al. [45] showed the effect of crystallinity. For Donelli et al. [46] both alkaline and enzyme treatments increased hydrolysis in amorphous and crystalline films. Crystalline PET was modified more strongly by alkali than by cutinase, whilst the opposite occurred for the amorphous film. This implied that alkali was more effective than cutinase in enhancing the hydrophilicity of PET films, with the effect stronger on amorphous than crystalline films.

A genetically modified bacterial cutinase [47] provided valuable insight as to how enzymes can be improved by molecular engineering for synthetic fibre changes. The modified cutinase [48] hydrolysed fatty acid monoesters with varied acyl chain lengths and had preference for short-chain substrates. The activity was higher than cutinases from bacteria and fungi. Cutinases from *Humilica insolens* (HiC), *Pseudomonas mendocina* (PmC) and *Fusarium solani* (FsC) on PET films [49] used films with a low-crystallinity of 7% (*lc*) and biaxially oriented (*bo*) poly(ethylene terephthalate) (PET) with a crystallinity of 35% as model substrates. The cutinases had a 10-fold higher activity for *lc*PET than for the *bo*-PET. For all three cutinases, the aqueous soluble degradation products were exclusively terephthalic acid (TPA) and ethylene glycol (EG).

Aqueous, insoluble oligoesters, particularly cyclic trimers commonly extracted from PET fibres during dyeing, are often blamed for the greying of PET fabrics. These can be removed by enzyme-catalysed hydrolysis under mild conditions, which cleans the dyeing machine and improves the lustres of fabrics [50]. Recili and Gorensek [51] the influence of treatments of PET on the quantity of extracted oligomers and their compositons. Alisch-Mark et al. [36] demonstrated that the colour in the fabrics became more intense, corresponding to an increase in hydroxyl groups on the surfaces of hydrolase-treated fibres. Wang et al. [52] stated that bis (2-hydroxyethyl) terephthalate (BHT)-induced extracellular lipase catalyses the hydrolysis of the PET model substrate diethyl p-phthalate (DP). There was an increase in K/S values of dyed PET fabrics after enzymatic treatment, as well as increased moisture regain and weight loss. The water contact angle and static half decay time decreased slightly. Eberl et al. [53] confirmed that a lipase from *Thermomyces lanuginosus* and cutinases from *Thermobifida fusca* and *Fusarium solani* hydrolyse PET.

Lipases and cutinases are both EC 3.1.1, hydrolases that could hydrolyse the ester bond in PET. Lipases specifically attack the ester bond in lipids (fats). Cutinases are specific for the hydrolysis of primary alcohol esters contained in cutin, the protective covering of plants. Given the extensive work mentioned above on the surface modification of PET with enzymes such as lipases and cutinases, it is postulated that lipases and/or cutinases could change the surfaces of PET fibres, thus creating changes in the light reflected, and the colours of the PET fabrics.

2 Materials and Experimental

2.1 Fabrics and fibres

Polyethylene terephthalate (PET) fabrics incorporating melt spun non-circular cross-sectional (NCCS) filament yarns in the filling (weft) direction

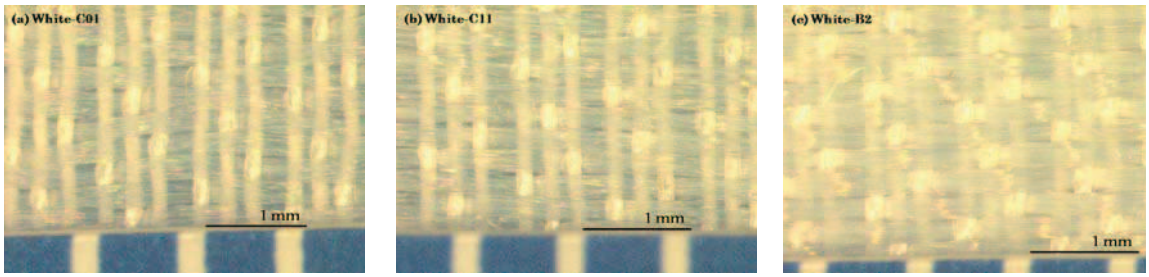


Figure 3: Optical images of fabrics

were used during all experiments. The warp direction consisted of fully drawn PET filament yarns (FDY). Figure 3 shows optical images of the fabrics. Sample C01 had round cross-sectional fibres with crystallinity of 25.60% and an orientation degree of 76.1%. Sample C11 had a crystallinity of 20.85% and an orientation degree of 79.20%. Sample B2 had a crystallinity of 21.90% and an orientation degree of 81.20%. All of these were non-circular cross-section fibres, as shown in Figure 4. In order to observe the different cross-sections clearly using the optical apparatus, the NCCS PET fibres were dyed black, and the fibres with circular cross-sections were red.

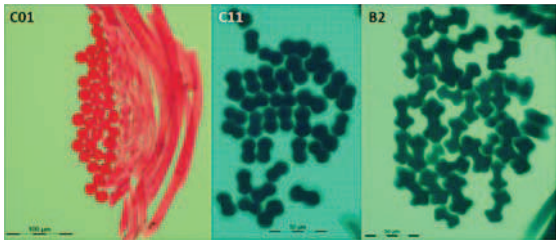


Figure 4: Cross-sectional images of fibres

The fabrics for enzymatic experiments were first scoured to remove any dust and/or oil that might have remained on the fabric after weaving. All the fabric samples were subjected to a solution of 1g/l of sodium hydroxide (NaOH) and 3g/L sodium hydrosulphite (Na_2SO_4) at a liquor to fabric ratio of 20:1 for 20 minutes at 80°C. These were then washed thoroughly in cold distilled water and then conditioned at 26°C and 65% relative humidity for 24 hours.

2.2 Hydrolysis Treatments

The fabrics were treated with sodium hydroxide (NaOH), and with lipase and cutinase enzymes in order to compare the effects of the enzymes on the known effects of strong NaOH treatment on polyester fibres.

Sodium hydroxide treatments Fabrics were treated with 2% w/v NaOH solution at 95°C for 0.5, 1, 3, 5 and 6 hours, at a liquor ratio of 50:1.

Enzyme treatments Two enzymes were used for treating the PET fabrics, a lipase and a cutinase. These are both subsets of hydrolases (EC 3.1.1) that act on carboxylic ester bonds.

Lipase treatments A tris(hydroxymethyl)aminomethane (TRIS) buffer at pH 8 was used for all treatments, with the pH value adjusted by using either 1NHCl or 0.1NNaOH. The ratio of PET fabric mass (g) to volume of TRIS buffer solution (ml) was 1:80. The treatment times were 90 minutes at 40°C in a shaking water bath at 150rpm with lipase at a concentration of 6.25ml/l in solution. The lipase used was L0777 (EC 3.1.1.3 – a triacylglycerol lipase), obtained from Sigma Aldrich. It was isolated from *Thermocmyces lanuginousus* with an activity of more than 100,000 units/g.

Cutinase treatments The lipase used in this experiment was 'Stickaway' from Novozymes at a concentration of 6.25ml/l in solution. The treatment conditions are listed in Table 1.

Table 1: Cutinase treatment conditions

No.	Temperature (°C)	Time (h)	pH	Note
1#	-	-	-	untreated
2#	40	48	7.50	treated
3#	40	48	8.50	treated
4#	55	48	8.50	treated
5#	55	96	8.50	treated

2.3 Reflectance and Colour Yield

Reflectance (R%) was measured within the visible light regions of 360 to 750nm. The CIE L*a*b*C* values were monitored using a Colour-Eye 7000A Spectrophotometer (Macbeth, USA) with specular component included (SCI) and with specular excluded (SCE).

2.4 Surface Morphology

The surfaces of the treated fabrics were examined using an FEI Quanta FEG scanning electron microscope (SEM) with accelerating voltage of 5kV.

2.5 Wide Angle X–Ray Diffraction

Wide angle X-ray diffraction (WAXD) was carried out on the untreated and enzyme treated samples in order to investigate the crystallographic structure before and after the treatments were applied. Wide-angle X-ray diffraction data were collected using a Philips Analytical X-ray Instrument, X' Pert-MPD (PWD 3020 vertical goniometer and PW 3710 control unit) employing Bragg-Brentano para- focusing optics. The WAXD patterns were recorded over step sizes of 0.05° within a 10-80° range with a scanning rate of 2°/min. Line focus Ni-filtered CuK-radiation

from an X-ray tube (operated at 40kV and 45mA) was collimated through Soller slits of 0.04 radians, a fixed divergence slit of 1° and a mask before applying the X-rays to the samples.

2.6 Differential Scanning Calorimetry

The treated fibres were changed into powder in a Wiley Mill, and 4 milligram samples weighed out. The temperature range for differential scanning calorimetry (DSC) was from 95 to 290°C, heating at 10°C/min within a flowing 40cc/min nitrogen atmosphere.

3 Results and Discussion

3.1 Lipase Treatment for Ninety Minutes

The reflectance of the specimens and the CIE L*a*b*C* values measured changed after the lipase treatments were applied to the fabrics for 90 minutes. Figure 5 shows the colour index values and reflectance of specimens before enzyme treatments.

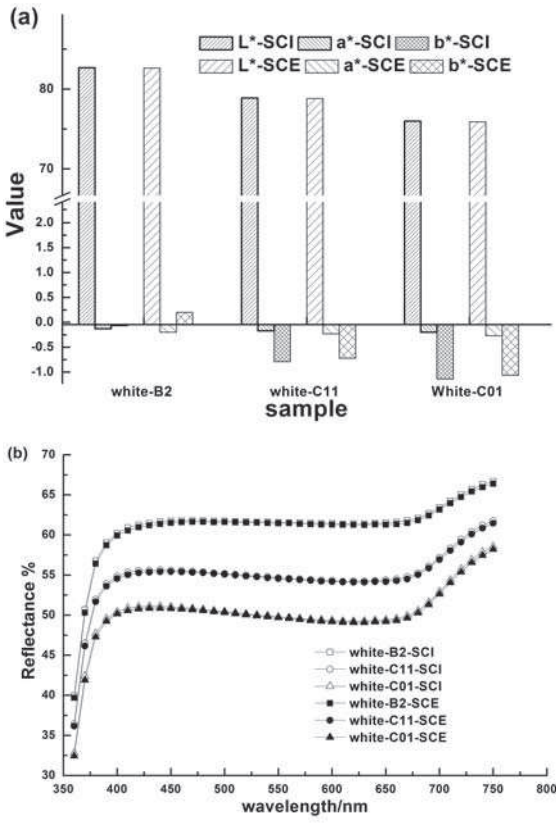


*Figure 5: CIE L*a*b* values (a) and reflectance R% (b) of samples with specular component included (SCI) and excluded (SCE) before lipase treatments*

Figure 5a shows that the inclusion (SCI) or exclusion (SCE) of the specular component made no significant difference in CIE L*, a* and b* values. Figure 5b indicated that the reflectance across the visible light range of wavelengths was essentially the same regardless of whether specular reflectance was included or not.

Figure 6a indicates that after lipase treatment with specular component included there was a significant difference in visible light reflectance for the C11 samples, less than one for the CO1 samples and virtually none for the B2 samples. This was confirmed by the CIE L* differences as shown in Figure 6b.

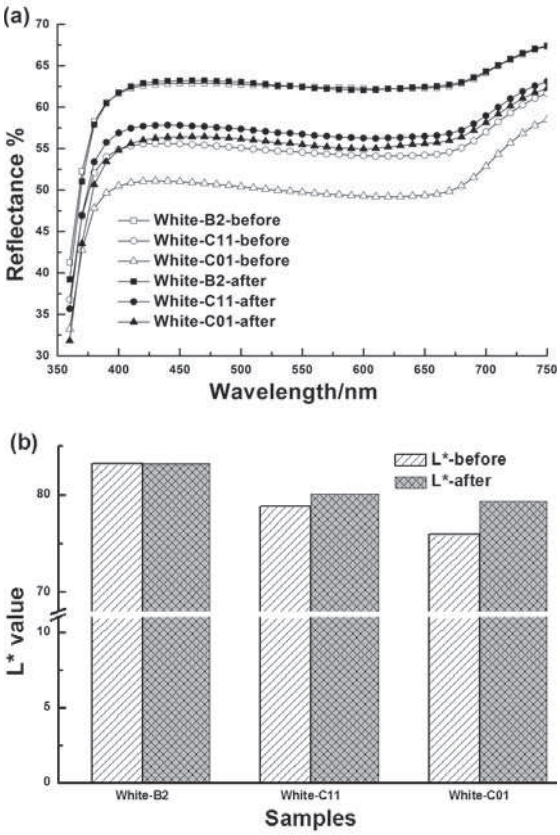


Figure 6: Reflectance R% (a) and CIE L values (b) of samples before and after lipase treatment for 90 minutes with specular component included (SCI) mode*

3.2 Treatment with Lipase for 24 hours

In order to ascertain whether longer treatment might create more change in the fibres, the white samples were treated in a TRIS buffer adjusted to pH 9.0 at 40°C for 24 hours at the same concentration of lipase. After that the reflectance and colour indexes were measured in both the SCI and SCE

modes. The comparisons between 90min and 24 hour treatments are shown in Figures 7–9. The data in these figures show that treatment by the lipase L0777 for 24 hours had little effect on the reflectance and colour index values in neither the SCE nor SCI modes.

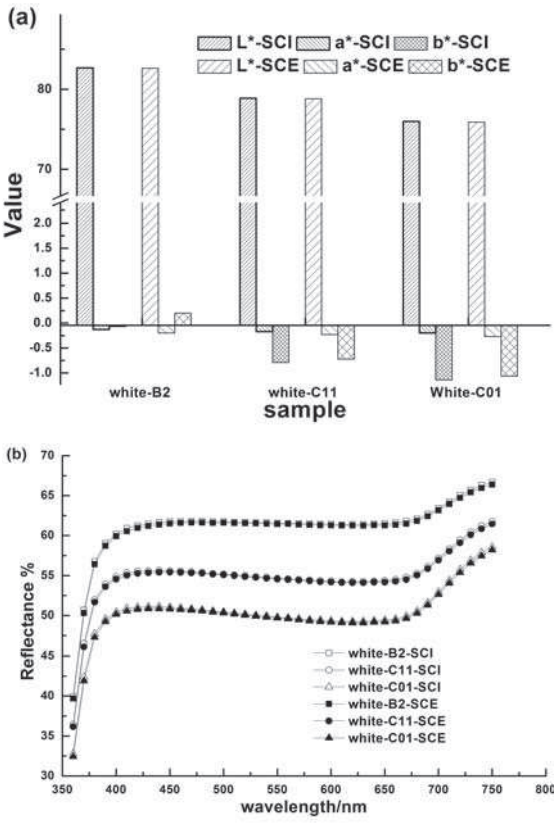


Figure 7: Reflectance R% of the samples treated with lipase for 90min (a) and 24h (b) with specular component included (SCI) and excluded (SCE)

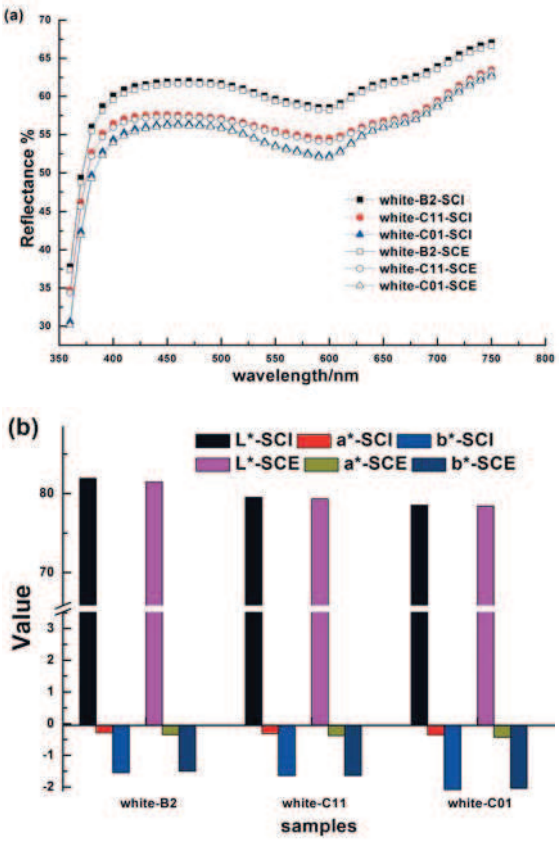


*Figure 9: Reflectance R% (a) and CIE L*a*b* values (b) of the lipase treated white samples with TRIS buffer at pH 9 for 24h under SCI and SCE modes*

3.3 SEM Images of the Fibres after Lipase Treatments

The SEM images of the samples treated with lipase for 90 minutes and 24 hours are shown in Table 2.

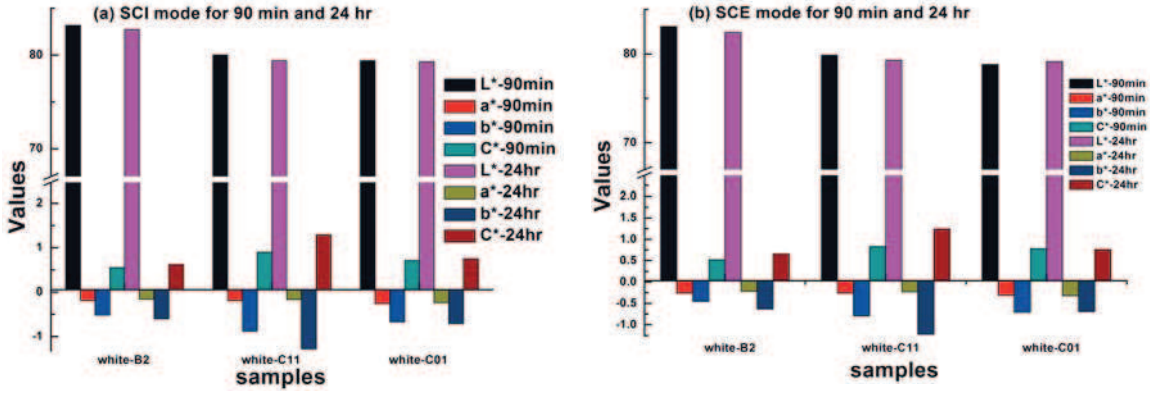
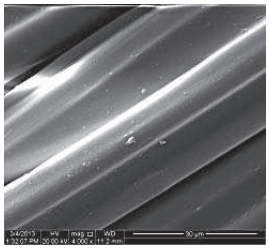
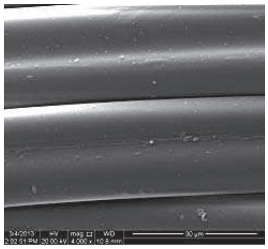
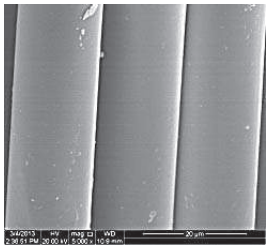
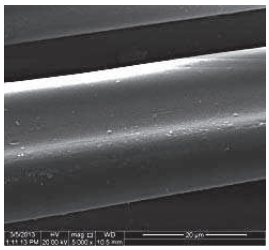
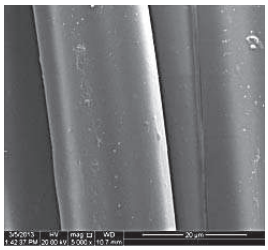
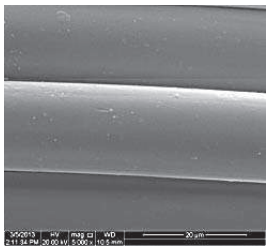


*Figure 8: CIE L*a*b* values of the lipase treated white samples for 90min (a) and 24h (b) with specular components included (SCI) and excluded (SCE)*

Table 2: SEM images (5000 ×) of PET fibres after lipase treatments

Samples	White-B2	White-C11	White-C01
L0777 lipase treated for 90 minutes			
L0777 lipase treated for 24 hours			

As can be seen from the SEM images, there were no pits or cracks induced by the lipase L0777 treatment on the surfaces of the PET fibres. This correlates with the small differences in reflectance and colour changes shown in the previous figures. The solution to this question might either be by using another more effective enzyme, or changing the treatment conditions.

3.4 Reflectance and CIE L*a*b* values before and after cutinase treatments

The differences in cutinase treatments for all the fabrics made of fibres with cross-section of C11 are listed in Table 2. The reflectance R% in the visible light region of the cutinase treated non-circular cross-section fibre fabrics was tested to explore the effects of different cutinase treatments on the fabrics. The reflectance within the visible region is shown in Figure 10(a). The primary differences within the reflectance spectra are in the 540-620nm region. The reflectances of treated sample 2# and 4#, as well that of sample 3#, were lower than that of untreated 1# and over-treated 5# within the wavelength range of 540 to 620nm. In the 510 to 640nm range, the reflectance of the over-treated sample was higher than that of the untreated sample over the entire visible light region. This means that careful attention should be paid to the enzymatic treatment conditions and any unexpected by-effects noted.

The reflectance levels for sample 2# were lower than those of sample 1# across the entire wavelength region, which means that the cutinase would be effective during the surface modification of non-circular cross-section polyester fabric under the relatively modest conditions shown in Table 3. This trend was further confirmed by the reflectances of sample #3, which was incubated at pH 8.50. The reflectance of #3 within the wavelength region from 510 to 640nm was the lowest for all the samples, indicating that the variance in pH values had a significant effect. When the treatment temperature was increased, sample 4# had almost the same reflectance values as those of sample 2#. This suggests that temperature might have less significance. However, the reflectance values of sample 5# were the highest for all samples, even than that of the untreated sample #1. There might be two reasons for this. Firstly, either the higher temperature or the longer treatment time might have created a rough surface of fibre, even more than in the solution at pH 8.50. Secondly, the longer treatment time may have had a synergistic effect with both the higher temperature and pH value. The *CIE L*a*b* values* of the cutinase treated NCCS PET fabrics were also measured to determine whether the colours of these samples changed after applying the treatments. These results are shown in Figure 10b. The CIE L* value represents the whiteness or brightness of the samples, and ΔL^* implies the difference between the treated samples and the

standard/untreated one. The results shown in the figure demonstrate that the ΔL* values of all the treated samples had decreased, which means that the treated samples became less bright when compared to the untreated sample. The exception was sample #5, which sharply increased in CIE L* value after the cutinase treatment. This was contrary to what was expected.

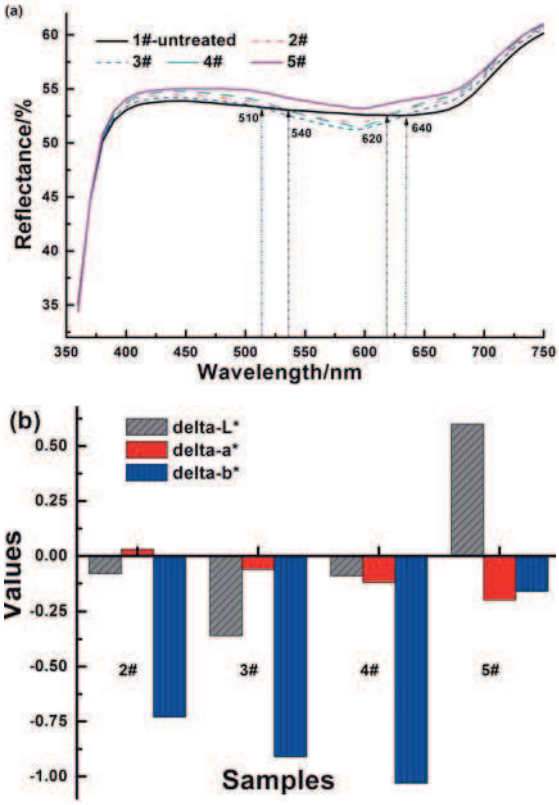


*Figure 10: Reflectance (a) and CIE L*a*b* values (b) of the untreated and treated samples in the visible region*

3.5 SEM Images of Fabrics after Cutinase Treatments

The SEM images of the cutinase treated samples are shown in Figure 11. Some pits on the surface of the treated PET fibres can be seen in Figure 11. A number of cracks appeared as the pH values of the TRIS buffer increased up to 8.50 with the presence of cutinase. These data matched well with those of Kim et al. [37, 39], although there was some difference in the details of the cutinase used and conditions applied. It appears that the pH value of the TRIS buffer has a significant effect on cutinase activities, especially on its hydrolysis of PET fibres.

Figure 12 shows the surface of the treated fibres as the treatment temperature increased to 55°C with TRIS buffer pH at 8.50. As can be seen in Figure 12, the surface of the PET fibres seems to have been uniformly degraded, thus not forming individual pits on the surface.

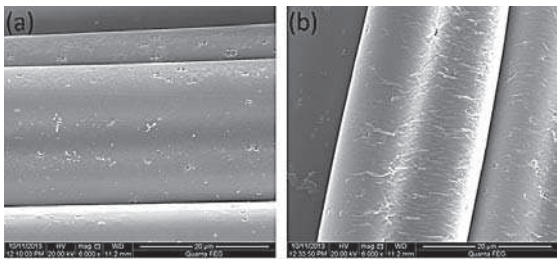


Figure 11: SEM Images (6000 ×) of cutinase treated PET fibre C11 in TRIS buffer for 24 hours: (a) at pH=7.00 and at (b) pH=8.50

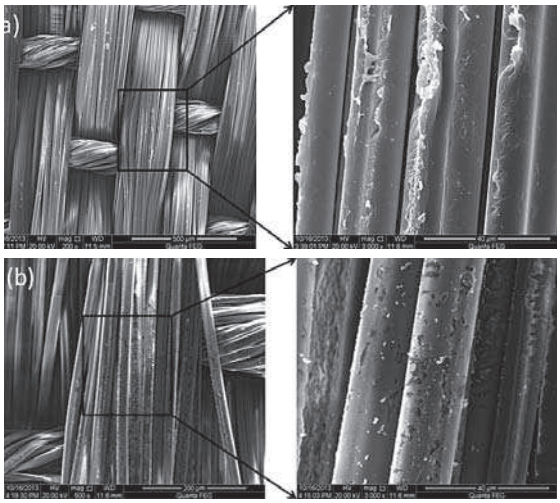


Figure 12: SEM images (3000 ×) of lipase treated PET fabrics with fibre C11 – (a) 48 hours; (b) 96 hours

3.6 SEM images of NaOH- treated fabrics

Sodium hydroxide attacks the surface of the PET fibres. The SEM images shown in Figure 13 indicate that pits occurred on the surface of the PET fibres after 0.5 hours, which matched the results in literature [52]. The numbers and area covered by the pits increased as the treatment time increased.

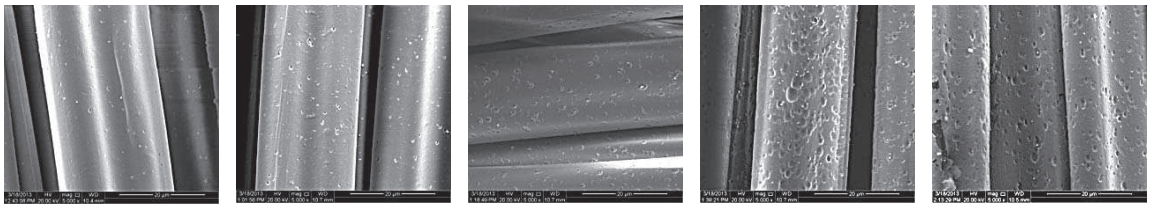


Figure 13: SEM Images of NaOH-treated PET fabrics with fibre C11 (5000×)

3.7 Wide Angle X–Ray Diffraction

The results from wide angle X-Ray diffraction (WAXD) of the untreated and cutinase treated samples are shown in Figure 14. There is a major peak with high intensity (110) and minor peaks (010 and 100) for the untreated sample. The 110 peak disappears during the cutinase treatment although it is unclear as to whether the crystallinity changes between the untreated and cutinase treated samples resulted from the cutinase only, or the water heat-treatment.

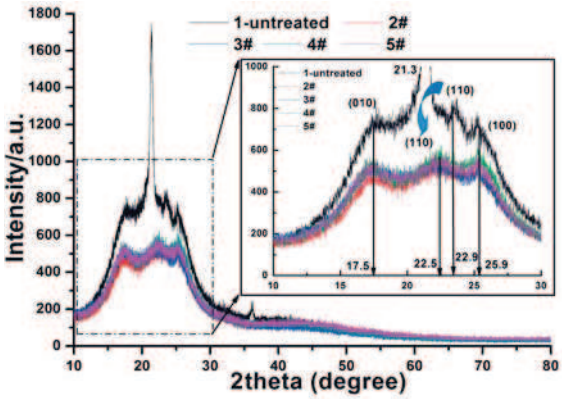
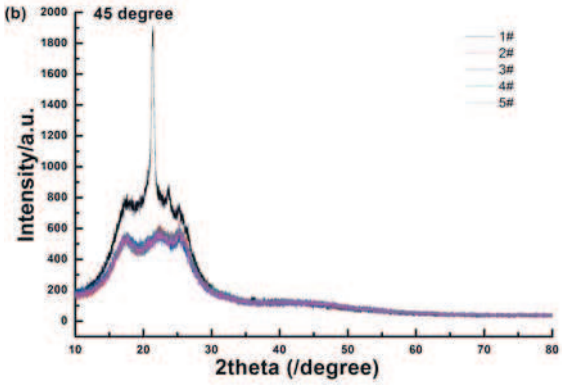
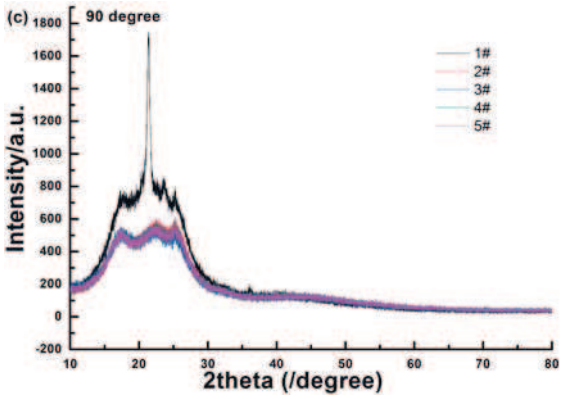
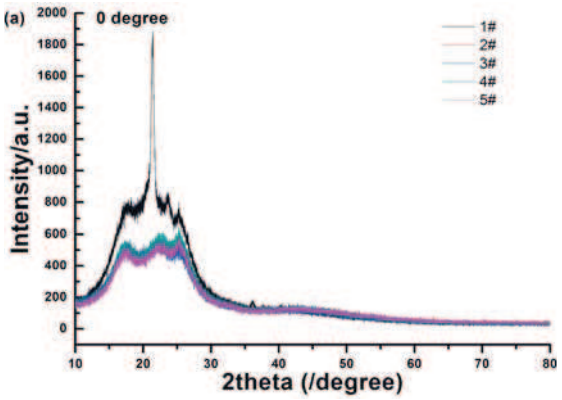


Figure 14: WAXD Results of untreated and cutinase treated samples







(d) testng scheme

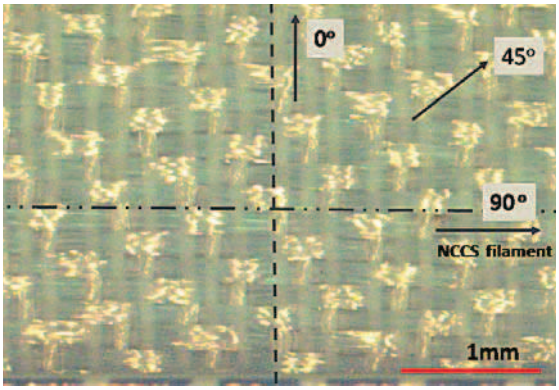


Figure 15: WAXD results from differing orientations of untreated and cutinase treated samples (a, b, c, d)

Table 3: Gaussian Fit Analysis of WAXD curves

Samples		Peak (2θ) (°)	Area	Width	Height
1#	P1*	21.27	10810.09	10.67	807.94
	P2*	21.36	411.99	0.39	832.17
2#	P1	17.34	1412.37	4.38	357.20
	P2	23.65	2754.70	5.97	367.70
3#	P1	17.57	1809.91	4.84	297.93
	P2	23.77	2323.41	5.55	333.83
4#	P1	17.27	1640.28	4.28	305.52
	P2	23.82	3038.63	5.85	414.44
5#	P1	17.24	1614.36	4.38	295.09
	P2	23.67	2865.35	5.94	384.59

*Note: P1- peak 1, P2-peak 2 derived by using Gaussian double-peak fitting

The inserted image in Figure 14 suggests that the peak at 2θ = 21.3° disappeared and that the peak at 2θ = 22.9° (110) decreased in intensity. There were also intensity decreases in peaks for 010 and 100 reflection planes. The Gaussian double peaks-fitting was used to analyse the WAXD curves in Figures 14 and 15. The results are shown in Table 3 and Figure 16.

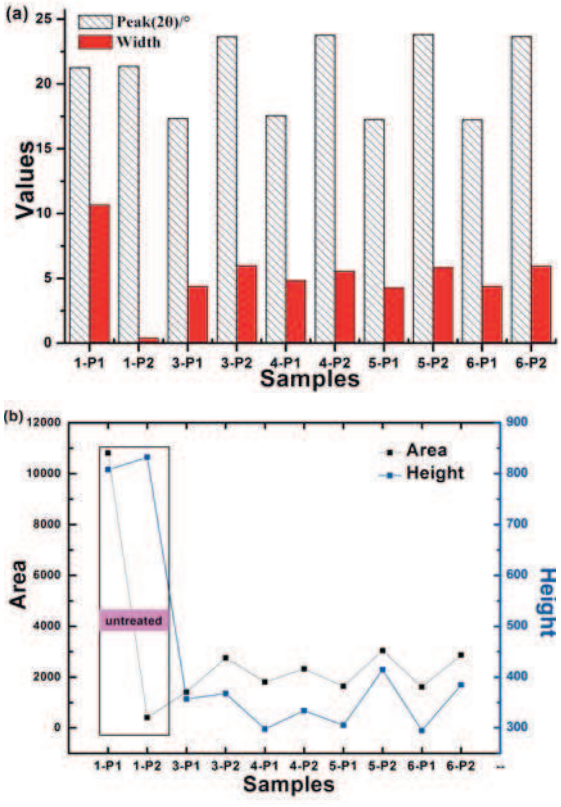


Figure 16: Analysis of WAXD curves of cutinase treated PET fabrics: (a) peak position & width; (b) areas & height

Table 3 indicates that there were sharp decreases in the intensity, area and width of the main peak (P1) between samples 1# and 2#. The intensity decreased whilst the area increased as the pH increased when comparing sample 2# with 3#. The inverse trend occurred as the treatment temperature increased, when comparing samples 3# and 4#.

3.8 Differential Scanning Calorimetry Results

The differential scanning calorimetry (DSC) curves are shown in Figure 17. These show that the crystallinities of the treated samples decreased as cutinase treatments were applied; there are two peaks in the DCS curves of both untreated and treated PET fibres. The obvious change is that the peak at 250°C did not change but the peak at 265°C increased in area. The trend follows the changes in pH, temperature and time of treatment. The two peaks at 250 and 265°C in the DSC curves might be ascribed to the core-shell crystallisation characteristics of melt spun PET filaments with circulated ambient air cooling; 250°C would represent the core part and 265°C the shell. Similarly to the reaction of PET with sodium hydroxide [52], lipase and cutinase also attacked the surfaces of the substrates used [33-38, 40], especially within the amorphous region [41, 44, 45, 48]. This caused the crystallinity percentage of the outer layer surface to increase [48], leading to the corresponding increase in melting

energy, reflected by the increase in the area under the peak at 265°C within the DSC profile.

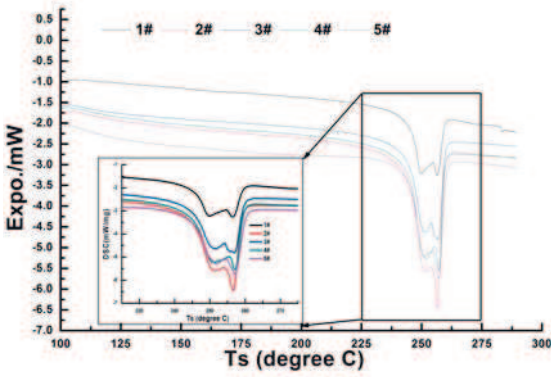


Figure 17: DSC results for untreated and cutinase treated samples

4 Conclusions

The purpose of this study was to determine whether treatment by lipase and cutinase enzymes, known to attack polyethylene terephthalate (PET) fibres, could alter the light reflectance and colour properties of non-circular cross-sectional (NCCS) PET fibres and the fabrics they comprise. NCCS fibres have increased surface areas compared to conventional circular cross-section fibres, presenting additional opportunity for lipase or cutinase actions. The application of 2 % w/v NaOH creates surface pits on PET fibres. The use of lipase L0777, however, was ineffective during surface modification to those fabrics under specific treatment conditions. There were no minor improvements after long hours of treatment and changes in pH values. Whether or not the specular factor was included (SCI) or excluded (SCE) in reflectance measurements it had insignificant effects on the reflectance spectrum and colour changes of the untreated and lipase treated white NCCS PET fabrics. However, surface pits on the fibres resulted when cutinase treatments were applied at a temperature of 55°C and pH values of 7.00 and 8.50, respectively, for 24 hours. These results were confirmed by the reflectance and colour changes as well as in the SEM images. These results were comparable to those obtained in NaOH treated fibres. The internal structural differences between the untreated and cutinase treated PET fabrics were confirmed by wide-angle x-ray diffraction (WAXD) and differential scanning calorimetry (DSC) analysis. WAXD patterns showed that the most prominent peak at $2\theta = 21.3^{o}$ disappeared after cutinase treatment, as well as a small peak shift from $2\theta = 22.9^{o}$ to $2\theta = 22.5^{o}$ (110). These changes in WAXD were not dependent on the X-ray incident angles (0^{o}, 45^{o} and 90^{o}). These internal changes are undoubtedly the result of the heat treatment involved rather than the enzymes themselves. The results from cutinase suggest the need for extensive investigation into this class of enzymes for application when modifying PET surfaces, both for changes in reflectance properties but also for creating more reactive surfaces for further functional changes.

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