(REFEREED RESEARCH)

A STUDY ON SURFACE CHARACTERIZATION OF ENZYME TREATED POLYETHYLENE TEREPHTHALATE FIBERS BY XPS AND AFM

ENZİMATİK İŞLEM GÖRMÜŞ POLİETİLEN TEREFTALAT LİFLERİNİN XPS VE AFM İLE YÜZEY KARAKTERİZASYONU ÜZERİNE BİR ÇALIŞMA

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ABSTRACT

Polyesters are widely used in various industrial applications and preferred for their outstanding properties such as high strength, resistance to abrasion, shrinking, wrinkling, most of the chemicals and environmental conditions. However the hydrophobic surface structure due to the lack of polar groups on the surface brings difficulties in processing and utilization of polyesters. Enzymatic reactions have been pointed out as an alternative eco-friendly method to overcome the hydrophobic surface structure of PET. The effect of enzymatic treatments on PET surface has been examined and explained by many papers in terms of improved hydrophilic characteristics. The goal of this study is to be able to enlighten the chemical background of improved hydrophilicity rather than to confirm the improvements by indirect methods. XPS (X-ray Photoelectron Spectroscopy) was utilized to monitor surface chemistry of cutinase and lipase treated PET fabrics in terms of elemental composition and chemical states of C atoms on the surface. In addition, surface morphology of enzyme treated PET fabrics was examined by AFM (Atomic Force Microscopy).

Key Words: PET fabric, Enzymatic treatment, Surface modification, XPS, AFM.

ÖZET

Çeşitli sanayi uygulamalarında geniş çaplı kullanım alanı bulan poliester lifleri; yüksek mukavemet ile aşınma, gerilme, çekme, buruşma, kimyasal madde ve çevre koşullarına yüksek dayanım gibi olağanüstü özellikleri için tercih edilmektedir. Ancak poliester lif yüzeyinin, polar grupların eksikliğine bağlı olarak hidrofob yüzey yapısına sahip olması; üretim aşamaları ve kullanım esnasında çeşitli sıkıntılar yaratmaktadır. PET liflerde hidrofob yüzey yapısının aşılmasında; doğa dostu alternatif yöntem olarak enzimatik işlemler gösterilmektedir. Enzimatik işlemlerin, PET yüzeylerde hidrofil özelliğin iyileştirilmesi açısından etkileri incelenmiş ve birçok makalede açıklanmıştır. Bu çalışmanın amacı; hidrofil özellikteki iyileşmeleri dolaylı yöntemler ile doğrulamaktan ziyade iyileşmelerin kimyasal altyapısını açıklamaya çalışmaktır. XPS (X-ray Fotoelektron Spektroskopisi) kullanılarak kütinaz ve lipaz ile işlem gören PET kumaşlarda yüzey kimyasal yapısı elemental bileşim ve C atomlarının kimyasal durumları açısından incelenmiştir. Ayrıca enzimatik işlem gören PET kumaşların yüzey morfolojisi AFM (Atomik Kuvvet Mikroskopisi) ile incelenmiştir.

Anahtar Kelimeler: PET kumaş, Enzimatik işlem, Yüzey modifikasyonu, XPS, AFM.

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1. INTRODUCTION

Among all synthetic polymers, polyethylene terephthalate (PET) based polyesters are widely used in various industrial applications especially as textile materials. They are preferred for their outstanding properties such as high strength, resistance to abrasion, shrinking, wrinkling, most of the chemicals and environmental conditions. On the other hand the hydrophobic surface structure due to the lack of polar groups on the surface brings difficulties in processing (low surface reactivity and poor wettability) and in utilization (poor moisture management, low detergency and accumulation of static electricity). The main goal in surface modification methods is to overcome the hydrophobic surface structure of PET for better efficiency in processing and wear comfort. Strong alkaline treatment at high temperature is the most utilized way to improve the hydrophilicity. However this process requires high consumption of chemicals and energy

and if not well controlled significant strength and weight losses occur due to peeling mechanism by alkaline attack (1,2).

Enzymatic reactions have been pointed out as an alternative method to alkaline process; due to possibility of processing only with their specific substrates at mild conditions preventing undesired side reactions (3). During recent years enzymes from various bacteria and fungi have been investigated in terms of their efficiency in modification of PET surfaces (4,5). It was reported that hydrolysis of ester groups by esterases, lipases or cutinases lead to an increase in free hydroxyl- and carboxylate end groups on the surface of PET. The improved hydrophilicity after enzymatic reactions was claimed to be the result of those generated polar groups on the surface (6-9). Furthermore it was signed that afterwards the enzymatic treatment probable adsorption of protein on the surface might influence the hydrophilicity depending on the polarity of the amino acids of adsorbed protein (10).

The stated polar groups, generated on the surface by enzymatic hydrolysis, were tried to be monitored by measuring the rising height of water, drop dissipation time, moisture regain and K/S values after reactive dyeing (11-15). In addition to show the hydrolysis efficiency; the release of terephthalic acid (TFA) was monitored as well. It was concluded that the increment in rising height of water, K/S values and the amount of released TFA proved the enzymatic surface hydrolysis.

The effect of enzymatic treatments on PET has been examined and explained by many papers in terms of improved hydrophilic characteristics. Even the improvements were clearly remarked by the utilized methods mentioned above; the corresponding chemical changes on the polymer surface could not be clarified. In order to quantify chemical structure, elemental composition and the modifications in bonding mechanism of C atoms; X-ray photoelectron spectroscopy (XPS) should be utilized.

There are a few research in which the elemental composition of enzyme treated PET was investigated in terms of carbon and oxygen content on the surface and the O/C ratio. It was indicated that, according to obtained improvements in rising height of water and K/S values, higher O/C ratio was expected due to created polar groups on the surface by hydrolysis of ester bonds. However on the contrary to expectations, it was found that the elemental content of oxygen was getting lower and O/C ratio was decreased after enzymatic treatment. Furthermore in XPS spectra, significant N content was observed which proves the possibility of adsorbed protein on the surface due to residual enzymes despite all washing procedures (16-18). Since the adsorbed protein changes the atomic percentages on the surface, no clear conclusion could be drawn from elemental composition data in previous studies. Therefore clarification of chemical states of carbon-oxygen bonds on the fiber surface gains much more importance.

In this study, the aim is to be able to enlighten the chemical background of improved hydrophilicity rather than to show the obtained improvement in enzyme treated PET fabrics. Thus instead of indirect methods such as capillary rising etc., chemical structure of enzyme treated PET fabrics was investigated in terms of elemental composition on near-surface and chemical state of carbon-oxygen bonds by survey scan spectra and curve fitting of the C_{1s} peaks. In addition, surface morphology was examined by atomic force microscopy (AFM), since no distinctive physical changes but roughness were reported before by utilizing scanning electron microscopy (SEM) (14,17).

2. MATERIALS AND METHODS

Polyester fabrics, approximately 130 g/m^2, knitted in 1*1 interlock structure were supplied from a local supplier. The multifilament polyester yarns are 80 denier and the diameter of single fiber is 15 µm approximately. Prior to enzymatic treatments; the fabrics were cleaned by soxhlet extraction method for 6 h with dichloromethane and dried at room temperature.

Cutinase from *Humicola Insolens* and Lipase from *Candida SP* were kindly supplied from Novozymes as enzymes solutions in these laboratory codes of NS-29061 and NS-29078 respectively since they were not commercial yet.

All other chemicals used in this work were laboratory grade reagents.

2.1. Enzymatic Treatment

Depending on the source and the genetic modification of enzymes, the optimum application parameters differ in literature. Various parameters in enzyme concentration, temperature and pH of application bath, fabric to liquor ratio and process time have been performed in our previous studies (19). Based on the previously obtained results, treatment conditions were determined as 40˚C and pH 8 for enzyme bath including 2 % w/v enzyme solution. Exhausting application method was used on a rotary shaker at 42 rpm and fabric to liquor ratio was chosen as 1:20. Enzymatic treatments were applied for 60 minutes with mechanical agitation to enhance the activity of enzymes towards PET fabric. After 60 minutes of enzymatic treatment, PET fabrics were taken from the enzyme bath. In order to deactivate the adsorbed enzymes on the fabric washing with boiling water for 3 minutes was applied prior to washing and rinsing for 10 minutes with distilled water. The samples were dried at room temperature.

2.2. Rising Height of Water

According to DIN 53924, 1 cm of vertically suspended PET fabric strips (2 cm x 30 cm) were immersed into potassium dichromate aqueous solution (1 % conc.) and rising height of water was observed for 180 sec. Based on wicking principle, occurrence of capillary rising is related with two main case; (i) wetting of fabric by the liquid due to higher surface energy of fabric than that of liquid (ii) equilibrium between capillary forces of fiber and weight of rising liquid in the fiber. Better rising height values state the more improved hydrophilicity. However this is not enough to explain the modifications in chemical structure of PET surface.

2.3. X-ray Photoelectron Spectroscopy (XPS)

PHI 5000 VersaProbe system was utilized to quantify the elemental

composition and atomic ratios on the near-surface by using monochromatic Al K_{α}- radiation with 58.7 eV of pass energy. The pressure in the analyze chamber is maintained at 10^{-9} Pa. The analyzing size is 8 mm x 8 mm and the take off angle is 45°. Besides investigating elemental composition by XPS survey spectra; chemical states of carbon-oxygen bonds were analyzed in details according to curve fitted C_{1s} peak spectra by XPSpeak 4.1 software.

2.4. Atomic Force Microscopy (AFM)

Vecoo MultiMode V Atomic Force Microscope was utilized to observe the surface of untreated and cutinase treated PET fabrics. Tapping mode was preferred as scanning method. Scanning speed at scanning range of 5 µ and 1 µ was 1.0 Hz whereas at scanning range of 500 nm it was adjusted to 2.0 Hz in order to prevent disfiguration of topographical image.

3. RESULTS AND DISCUSSIONS

3.1. Rising Height of Water

The liquid should wet the fabric prior to wick into fibers in order to form a rising height value. Surface tension of liquid should be overcome by surface free energy of the fabric to get wet. Since the surface free energy is related with the polar groups on the surface, the higher rising height values indicate the better wettability due to new generated polar groups on the surface.

Untreated and enzyme treated PET fabrics were evaluated in terms of wettability according to DIN 53924. The mean values of ten readings were given in Figure 1.

The values in Fig.1 indicated that the hydrophobic surface structure in untreated PET fabric was overcome by enzymatic treatments. While the water was not absorbed by untreated fabric, enzyme treated ones were wetted immediately. Even though the rising height values could be taken into account as a sign of improved hydrophilicity, this is not enough to clarify the changes in surface chemistry.

3.2. X-ray Photoelectron Spectroscopy

Elemental Composition

The relative atomic percentages in terms of elemental composition on the surface of PET fabrics were given in Table 1. The values were derived from XPS survey scan spectra at corresponding binding energies.

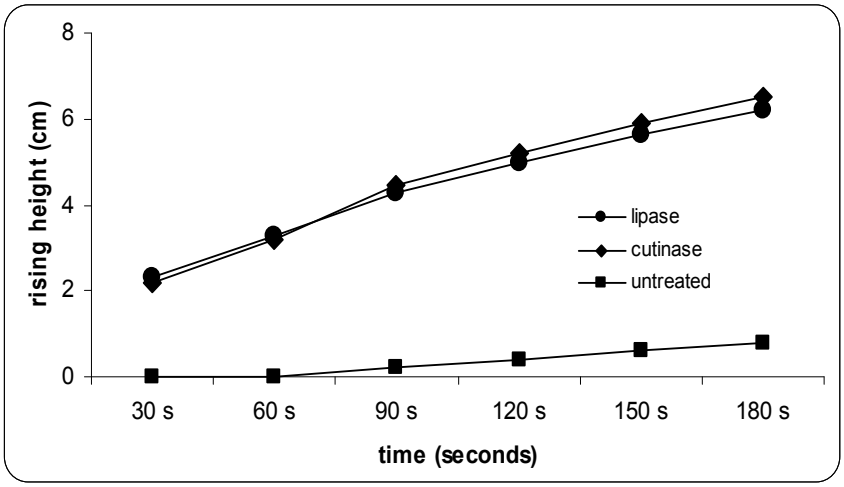

Figure 1. Rising height values

Table 1. Elemental composition on the surfaces of untreated and enzyme treated PET fabrics

	Relative Atomic Percentages			
	C (%)	**O (%)**	**N (%)**	**O/C**
Untreated	75	25	-	0,33
Cutinase	75,6	18,2	6,2	0,24
Lipase	77,8	20,2	2	0,26

Two characteristic peaks at around 285 eV and 530 eV representing C and O atoms respectively were observed in survey scan spectra of untreated and treated PET fabrics whereas in addition these two peaks a third peak at around 400 eV was also detected in enzyme treated PET fabrics. Binding energy at around 400 eV is characteristic for N atoms. Since PET based polyesters normally do not have N atoms in the polymer chain, the third peak in the survey scan spectra of enzyme treated PET fabrics is assumed to occur due to the adsorbed protein on the surface. This proves the possibility of residual enzymes on the surface even after washing processes as indicated before (16-18).

Despite the fact that enzyme treatment improved wettability performances, O/C ratios were seemed to be decreased in enzyme treated PET fabrics according to the relative atomic percentage values derived from XPS survey scan spectra. Since survey scan spectra represents total amount of elemental composition as 100 %, individual atomic percentages are

calculated as relative. Thus an increment in N content shall lead to decrease in other atom contents.

Here the expected changes in atomic percentages were appeared as an increment in C atom content whereas a decrease in O atom content. The explanation for this situation might be: the increased N content due to adsorbed protein and the increased C content due to the dominant C-C bonds in protein chemical structure lead to a mandatory decrease in O content. Thus the reason of lower O/C ratio is the adsorbed protein on the surface through enzyme application.

Observed improvements in wettability performances of enzyme treated PET fabrics bring the predictions of successfully modified surface by created new polar groups. However according to the data in Table 1, to draw a clear comment about polar groups on the surface seem to be impossible. Therefore it is necessary to examine the chemical states of C_{1s} bonding.

Chemical State

The chemical states of C_{1s} bonding were examined by curve fitting of the C_{1s} peak. XPSpeak 4.1 software was utilized for curve fitting. Binding energy of the C_{1s} core level at 284.6 eV was used for calibration of the energy scale. The C_{1s} spectrum was divided into five components in order to evaluate which oxygen-containing functional groups were formed on the surface. Curve fitting was performed at 284.6 eV for C-C bonds, at 286.1 eV for C-O-C bonds, at 286.6 eV for C-OH bonds, at 288.1 eV for C=O bonds and 290 eV for O-C=O bonds.

Curve fitting of C_{1s} peak in C spectra of untreated and enzyme treated PET fabrics were given in Figure 2.

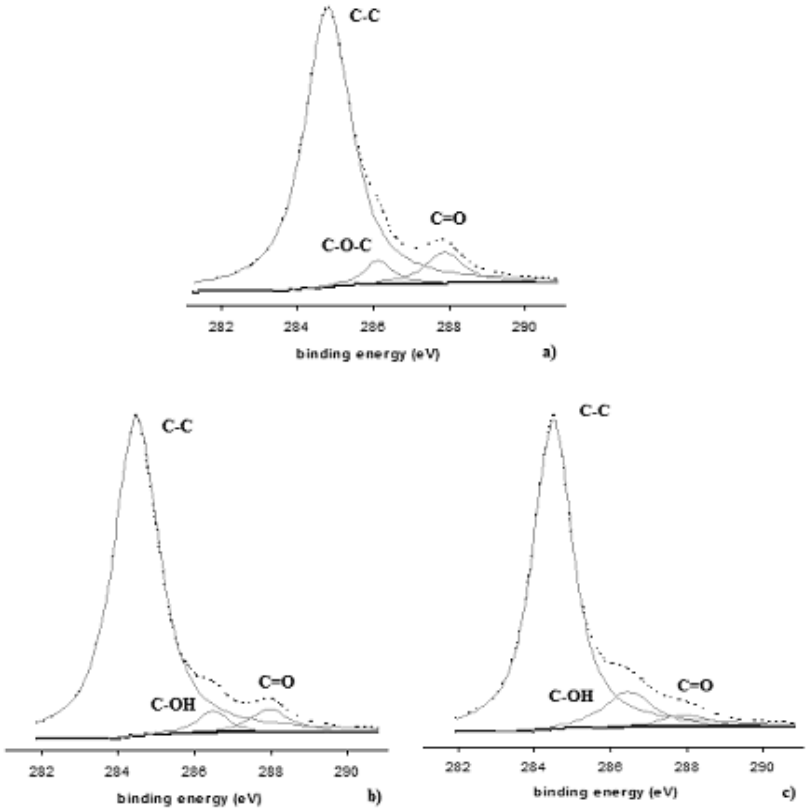

Figure 2. Curve fitting of C1s peak in C spectra of untreated and enzyme treated PET fabrics
[a) Untreated, b) Cutinase treated, c) Lipase treated]

By means of these curve fitted C spectra, the existing peaks and the represented groups by them are able to be distinguished. C-C peaks represent the CH-CH bonds in terephthalate and ethylene groups while C=O peaks represent C=O bonds in ester groups as well. C-O-C peaks point out the bonding between ester and ethylene groups. On the other hand, C-OH peaks indicate the created polar groups due to destroyed bonds on the surface by enzyme attack.

These three spectra varied both in binding energies and intensities of observed peaks. The most distinctive change in the spectra of enzyme treated PET fabrics when compared with untreated one was the shift of the peak at 286.1 eV through 286.6 eV. This shift indicates an increment in C-OH bonds that was occurred due to decreased C-O-C bonds on the surface. The other perceived feature in the spectra of enzyme treated PET fabrics was the difference in intensities of both C-OH and C=O peaks.

In order to observe the changes in intensities of the peaks, areas under the peaks were calculated by XPSpeak 4.1 software. The results were given in Table 2.

Table 2. The calculated values of areas under the peaks

Binding Energies (eV)	**C-C** (284.6)	**C-O-C** (286.1)	**C-OH** (286.6)	**C=O** (288.1)	**O=C-O** (290)
Untreated	6463,7	350,7	0,4	623,5	0,1
Cutinase	8356,2	0,6	377,6	519,3	0,1
Lipase	6962,4	0,1	890,1	285,3	0,1

Compared to values of untreated PET fabric; the amount of C-C bonds and C-OH bonds increased while C-O-C bonds and C=O bonds decreased on the surface of enzyme treated PET fabrics.

The increment of C-C bonds on the surface of enzyme treated PET fabrics could be due to the CH-CH bonds of the adsorbed protein. The higher amount of C-C bonds in cutinase treated PET fabric confirms this assumption since the atomic percentage of N atoms representing adsorbed protein was also higher in this fabric.

Moreover no decline in C-C peak remarks that no cleavages were occurred in CH-CH bonds. Thus the increment in C-OH bonds should be related with the hydrolysis of C-O-C bonds between ester and ethylene groups or C=O bonds in the ester groups.

In Figure 2, the observed shift of the peak at 286.1 eV through 286.6 eV confirmed the cleavage of the C-O-C bonds between ester and ethylene groups during enzymatic treatment. The efficiency of cutinase and lipase in hydrolyzing C-O-C bonds could be considered as similar due to having similar values for C-O-C bonds in Table 2. Despite this similar efficiency; in lipase treated PET fabric the value of C-OH bonds was higher whereas the value of C=O bonds was lower than that of cutinase. It could be considered that, the mentioned differences confirm the assumption of hydrolysis in ester groups.

The possible hydrolysis mechanisms of PET polymers on the surface of enzyme treated PET fabrics due to the organic chemistry principles of ester hydrolysis in aqueous and alkaline aqueous media (20) were shown in Figure 3.

In the first step, PET polymer was hydrolyzed through ester bonds by enzyme attack of cutinase or lipase. Introduced OH groups on the polymer afterwards the hydrolyzed ester groups were occurred due to (i) the electron withdrawal and electron attracting substituent in aqueous media and (ii) the attack of excess OH^- groups to C atom in alkaline media as shown in Figure 3.

3.3. Atomic Force Microscopy (AFM)

3-D AFM micrographs of untreated and cutinase treated PET fabrics, which were obtained at different scanning ranges such as 5μ, 1μ and 500 nm, were given respectively in Figure 4 and 5.

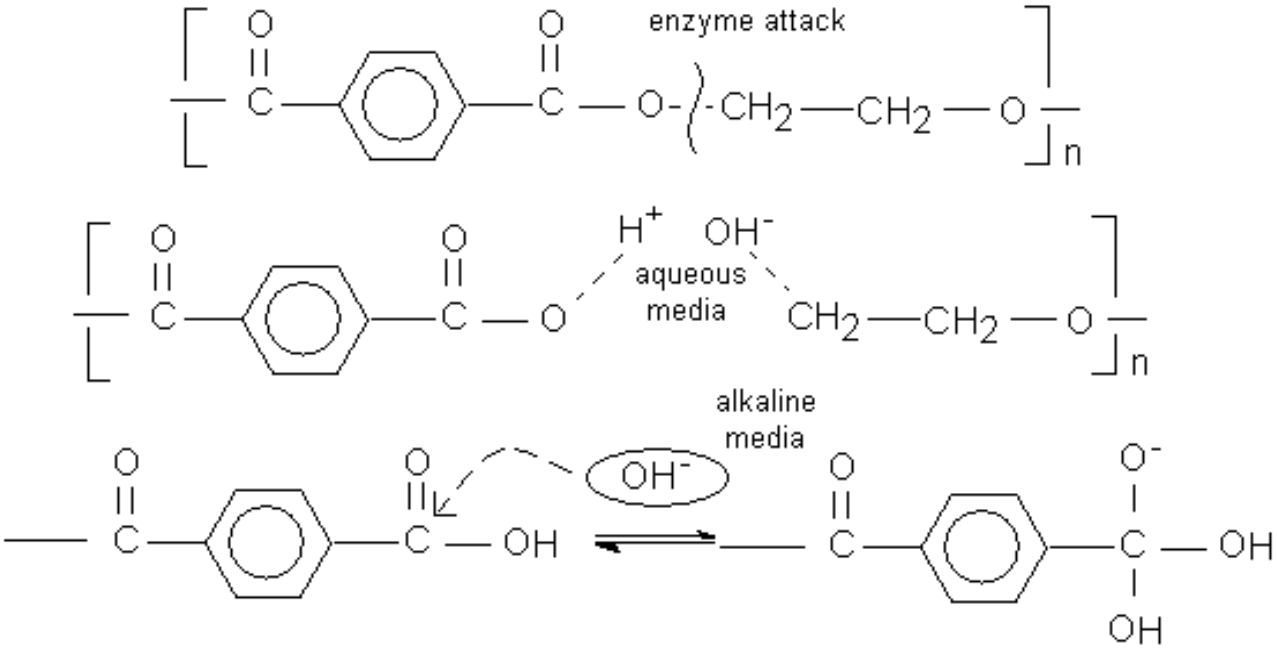

Figure 3. Possible hydrolysis mechanisms of PET polymers by enzyme attacks

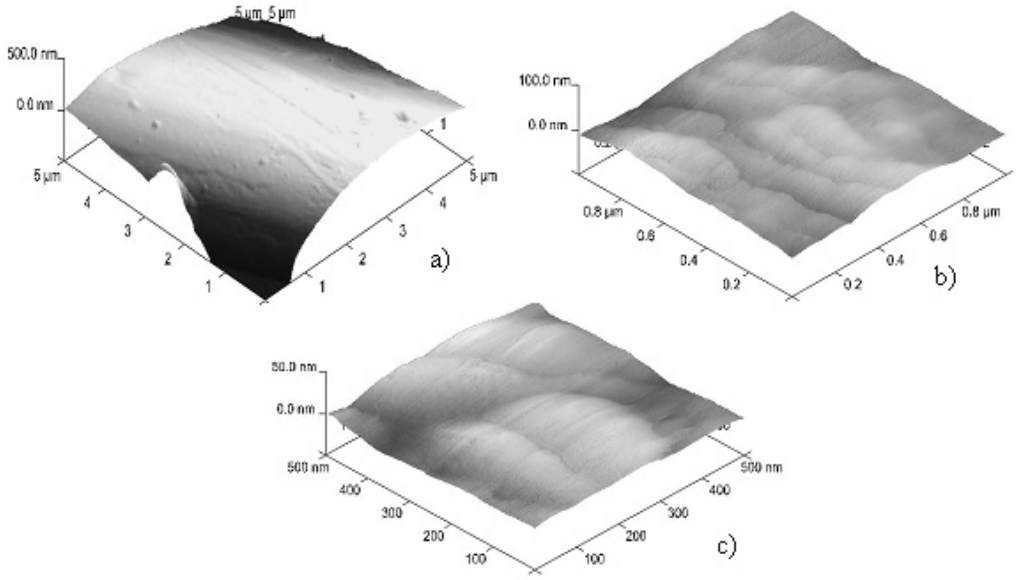

Figure 4. AFM micrographs of untreated fabric

a) 5µ X 5µ b) 1µ X 1µ c) 500nm X 500nm

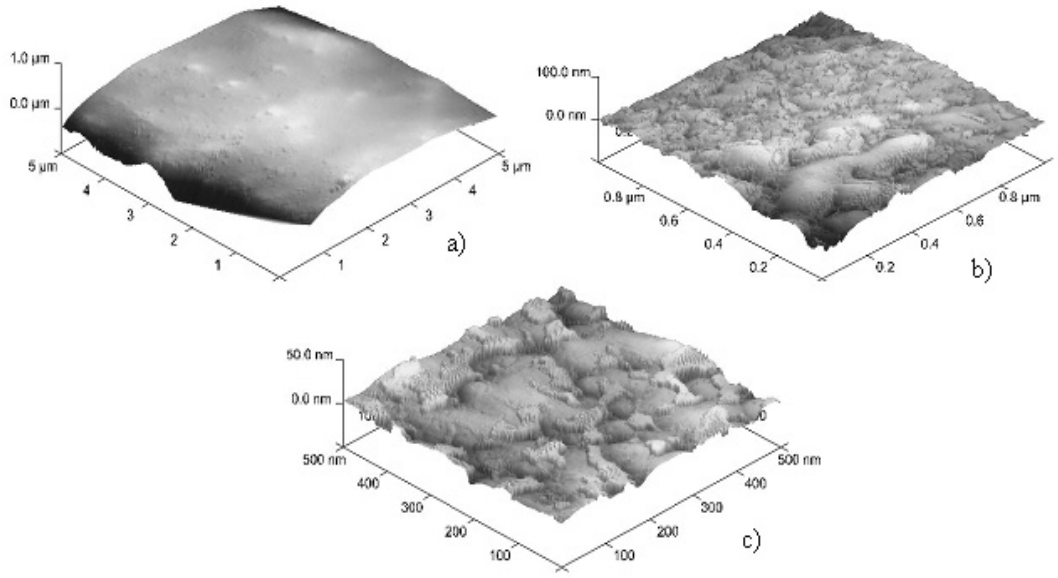

Figure 5. AFM micrographs of cutinase treated fabric

a) 5µ X 5µ b) 1µ X 1µ c) 500nm X 500nm

As shown in Figure 4 and proved by SEM micrographs in many papers before, fiber in untreated PET fabric has smooth surface structure. In AFM micrographs of cutinase treated PET fabrics at 5µ X 5µ area, the smooth surface of untreated PET fabric seems to become a little rougher. In order to examine in details, the scanned area were narrowed focusing onto the roughness. According to the AFM micrographs of cutinase treated PET fabric at 1µ X 1µ and 500nm X 500nm areas, the roughness on the surface seem to be based on not only the cracks due to the hydrolyzed ester bonds but also adsorbed protein due to the residual enzymes.

4. CONCLUSIONS

According to the curve fitting of the C_{1s} peaks and the values derived from the area under these peaks, these results were drawn: (i) the hydrolysis of C-O-C bonds in untreated PET fabric by enzyme attack lead to a shift in the peak at 286.1 eV through 286.6 eV which represents the C-OH groups, (ii) cutinase and lipase have similar effects on the cleavage of C-O-C bonds between ester and ethylene groups however lipase introduced higher amount of C-OH groups by destroying C=O groups as well, (iii) the surface chemistry of PET varies due to being treated by enzymes from different sources.

The hydrophobic surface structure of PET was overcome by introduced C-OH groups via enzymatic hydrolysis. However despite having better hydrophilic characteristics, which was proved by both the results of capillary rising height and chemical states of C_{1s} bonding, the O/C ratio on the surface of enzyme treated PET fabrics was decreased. This is due to the residual enzymes on the fiber surface which were indicated as N content detected by XPS analysis and observed roughness by AFM micrographs.

The results of XPS analysis in this study show that (i) as long as residual enzymes are present on the fiber surface, to examine the chemical modifications on the surface referring to relative atomic percentage lead to miscalculations and (ii) the conventional washing process seems to be inadequate to remove residual enzymes.

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