The Influence of Enzymatic Treatment on the Surface Modification of PET Fibers

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ABSTRACT: The paper deals with the assessment of the surface modification of glossy continuous poly(ethylene terephthalate) fibers from the point of view of changes in their surface structure in terms of its micro-topography and the molecular and supermolecular structure of the filament surface layers. The performed SEM and AFM investigations have shown differences in the fiber surface carving before and after modification (smoothing or increased roughness), depending on the type of applied enzymatic preparation. Measurements with the use of the ATR-IR method have shown changes in the physicochemical character of the investigated fiber surface. The cleavage of the ester bonds in PET macromolecular chains, resulting from the modifications used, leads to the formation of reactive —OH and —COOH groups. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3117–3126, 2011

Key words: enzymes; fibers; modification; polyesters; surfaces

INTRODUCTION

The growing demand for polyester fiber fabrics and the constantly extending range of their use in technical and special goods justify the need for the improvement in some of their properties that lower the quality of goods made from them, limit the range of their use, and make finishing processes difficult.

Some of their disadvantageous properties result from the specific structure of fiber surface, i.e., from their unfavorable physical and physicochemical characteristics that should be changed by various types of modifications if some properties are to be improved.

The possibilities of modifying the microtopography and physicochemical properties of polyester fibers are considerably limited, which results, first from the strongly crystallized, highly oriented fiber surface layer being formed under specified spinning conditions and second from the chemical passivity of the fiber-forming polymer.

Among the hitherto known surface modification methods, one can mention the low-temperature plasma treatment[1–8] and the selective-controlled chemical treatment. These methods, however, are not free from drawbacks that depend on technical, economical, and ecological factors.

A relatively new, interesting alternative to the previous methods of modifying polyester fiber surface consists in using enzymes. The isolation of new enzymes at the end of the 20th century made it possible to functionalize fiber surface.[9–13] It has denied the previous views that aromatic polyesters are not susceptible to the action of hydrolytic enzymes.[14–16]

Currently, lipases and esterases are most frequently used to modify the poly(ethylene terephthalate) (PET) fiber surface by the hydrolysis of ester bond. Recent literature reports on the modification of PET fiber surface concern the treatments with an enzymatic preparation isolated from thermophilous bacteria such as *Fusarium solani pisi* and fungus *Thermobifida fusca* (TfH). These enzymes, often called cutinases, show an effective catalytic and hydrolytic action—intermediate between the actions of lipase and esterase.[17,18] These cutinases can modify both fibers[10,19] and films of PET.[18–24]

According to Marek and Martinkova,[25,26] the action of enzymes on PET macromolecule brings about ester bond splitting resulting in the formation of reactive groups such as —OH and —COOH in accordance with the following mechanism:

$$\text{R–COOR}' \xrightarrow{\text{enzyme}} \text{R–COOH} + \text{R}'\text{–OH}$$

From the analysis of literature data, it follows that PET fibers modified with lipases, esterases, or cutinases show the presence of hydroxyl and carboxyl

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TABLE I
The Characteristics of the Enzymatic Preparations Used in Biochemical Modification

Enzyme preparation	Supplier or manufacturer	Source	Optimum temperature (°C)	Optimum pH	Activity
Amano Lipase A	Aldrich	*Aspergillus niger*	45	6.0	≥12,000 u/g
Amano Lipase AK	Aldrich	*Pseudomonas fluorescens*	55	8.0	≥20,000 u/g
Lipozyme®	Fluka	*Mucor miehei*	70	8.0	>100U/g[a]
Esterase	Fluka	*Bacillus starothermophilus*	65	7.0	~ 0.4 u/mg[b]

[a] 1 U corresponds to the amount of enzyme which sets free 1 μmol stearic acid per minute at pH 8.0 and 70°C (tristearin, Fluka No. 69498 as substrate).
[b] 1 u corresponds to the amount of enzyme which releases 1 μmol 4-nitrophenol per minute at pH 7.0 and 65°C (4-nitrophenyl-*n*-caproate as substrate).

groups on their surface[10,14,19,25–33] as confirmed by test dyeing these fibers with reactive and basic dyes.[25,26,32] The appearance of hydrophilic groups (—OH, —COOH) on the PET fiber surface has changed the surface character from hydrophobic to hydrophilic, which should provide an opportunity to improve many unfavorable properties of PET fibers and fabrics to obtain improved wettability,[10,11,17,25,27,28,34–39] durable improvement in electric conduction resulting from decreased surface resistance,[25,26,33,34] improved resistance to soiling and improved oil removability,[25,37] improved fiber dyeability with disperse dyes,[10,11,37,38] and reduced susceptibility to pilling,[11,12,17,20,25] leading to an improved fabric handle and reduced gloss.[12]

Relatively few publications concern studies on the change in the surface topography of the biochemically modified PET fibers, and its effect on the earlier mentioned properties.[20,22,23]

The research material presented in this article in the form of complex investigations constitutes an essential extension of the knowledge within this scope.

EXPERIMENTAL

Materials

Fibers

Glossy, continuous polyester fibers with PET were used for the investigations:

- draw ratio $R = 4.0$x;
- thickness of fiber, 27.2 μm;
- total orientation factor $f_o = 0.8584$; and
- fiber crystallinity index $x_{IR} = 71.1\%$.

Enzymes

The modification of fiber surface by the biochemical method was carried out with the use of four selected enzymatic preparations, active in relation to the fiber-forming polymer and diversified with respect to their origin, biochemical characteristics, and application conditions. The characteristics of the enzymes used are given in Table I.

Treatment procedure

The PET fiber was incubated with enzyme preparation in the sodium phosphate buffer, in autoclave Ahiba-Polymat Oryginal Hanau. Conditions of treatment are shown in Table II.

After enzymatic treatment, all samples were washed first with hot water for 10 min, then with sodium carbonate solution for 10 min at 70°C (to remove the remaining protein), and finally rinsed with distilled water at 70°C (six times). All samples were air dried at room temperature for 24 h.

Measurement methods

The assessment of PET fiber surface structure was considered in terms of physical and physicochemical characteristics.

The physical characteristics of fiber surface were evaluated from the point of view of:

- fiber surface microtopography using the scanning electron microscopy (SEM) and atomic force microscopy (AFM),
- physical microstructure of the fiber surface layer using the method of infrared absorption spectroscopy—the reflection technique ATR-IR.

TABLE II
Parameters of Biochemical Modification

Enzyme preparation	Concentration enzyme preparation	Treatment temperature (°C)	pH	Treatment time (min)
Amano Lipase A	2 g/L	45	6.0	30 120
Amano Lipase AK	2 g/L	55	8.0	30 120
Lipozyme®	2 g/L	70	8.0	30 120
Esterase	2%	65	7.0	30 120

In the physicochemical characteristics of fiber surface, the following parameters were tested:

- molecular structure of fiber surface layer using the ATR-IR method,
- electrokinetic charge,
- the presence of —OH groups in the fiber surface layer by test dyeing with reactive dyes,
- adhesiveness of polar and nonpolar liquids by the method of contact angle.

Scanning electron microscopy

The microtopography of PET fiber surface before and after biochemical modification was assessed with the use of a JSH 5200 LV microscope from JEOL. Image magnifications were: 1000× and 5000×. The fiber surface images were digitally recorded with the use of SEMAFORE program ver. 3.0 PRO.

Atomic force microscopy

The topography of PET fiber surface before and after biochemical modification was tested by means of an AFM microscope using the contact mode. The obtained images were analyzed with the use of computer program Modular Analyze System ver. 2.0.02.

IR absorption spectroscopy—ATR technique

Considering the mechanism of enzyme action on fibers, the crystallinity degree of fibers was accepted as the essential parameter from the point of view of fiber surface modification. It was determined with the use of the ATR-IR technique.

The measurement was carried out with the use of an FTIR-8101M spectrophotometer equipped with ATR attachment, type 300, from SPECTRATECH, with variable incidence angle from 30° to 60°, that made it possible to perform measurements for various depths. The spectrophotometer was coupled with a control unit DR-8001M from Shimadzu.

The measurement conditions:

- range of IR radiation: 2000–400 cm^{-1},
- thirty two scanning procedures of each sample by IR radiation were carried out to obtain absorption spectra.

The absorption spectra of the fiber preparations under investigation were plotted in the system: $A = f(1/\lambda)$ as a basis for the interpretation of changes in the supermolecular structure of the fiber surface layer. Selected "crystalline" bands were corrected in relation to the internal standard band and then their absorbance was determined.

TABLE III
The Dependence of the Band Position on the Type of Absorbing Chemical Group of PET Fibers[41]

Band position (cm^{-1})	Absorbing chemical group
793	C=O + CCO
1406	Terminal group

The crystallinity index was determined from the formula proposed by Krimm[40]:

$$X_{IR} = A_{845}/A_{870}$$

where x_{IR} is the crystallinity index of the tested fiber, A_{845} is the corrected absorbance of the crystalline band at a wave number of 845 cm^{-1}, and A_{870} is the absorbance of the internal standard band at a wave number of 870 cm^{-1}.

The determination of band absorbance was carried out with the use of the program ACD Labs ver. 4.60.

Physicochemical characteristics of fiber surface

IR absorption spectroscopy—ATR technique

The absorption spectra of the fiber preparations under investigation were plotted in the system: $A = f(1/\lambda)$ as a basis for the interpretation of changes in the molecular structure of the fiber surface layer. ATR-IR spectra were used to determine the absorbance values for selected bands, correlated with the groups of ester bond and terminal groups of PET macromolecule. The dependence of the band position on the type of absorbing chemical group of PET fibers is presented in Table III.

Electrokinetic charge measurements

For monitoring the changes in the electrokinetic potential, the Particle Charge Detector (PPCD 03), a product of Mütek, Germany, was used. This equipment enables very fast measurement of electrokinetic charge, proportional to electrokinetic potential. Fiber samples with a weight of 0.2 g, previously disintegrated by means of a microtome, were immersed in 100 mL of distilled water and stirred. The dispersion prepared in this way was poured into a vessel containing an electrode. The values of electrokinetic charge were read in mV.

Testing the presence of —OH groups in the fiber surface layer by dyeing with reactive dyes

The formation of reactive —OH groups on the PET fiber surface was confirmed by dyeing the fibers with a reactive, dichlorotriazine dye: Helactin Red F-2B in the form of commercial product. Unmodified and chemically and biochemically modified fibers were

TABLE IV
The Values of Surface Tension and Its Components for Liquids Used, mJ/m^2 [43]

Liquid	γ^C	γ^C_D	γ^C_P
Glycerol	64.0	34.0	30.0
α-bromonaphthalene	44.4	44.4	0

impregnated with an aqueous bath containing 25 g/L of the dye, followed by a thermal treatment at a temperature of 50°C for 60 min. The dyed samples were rinsed with distilled water and dried at room temperature. The dyeing effects were assessed visually.

Testing the adhesiveness of polar and nonpolar liquids by the method of contact angle

The surface tension of fibers was determined on the basis of the measured, under equilibrium conditions of the fiber–liquid system, value of contact angle, Θ, with a liquid with a known surface tension. The method of this determination was based on Owens's procedure.[42] The basis for the calculation of the dispersive and polar components of the fiber surface tension is constituted by Dupre's converted equations of adhesion work.

$$\gamma^{C1}(1+\cos\Theta_1) = 2\sqrt{\gamma_P^W\gamma_P^{C1}} + 2\sqrt{\gamma_D^W\gamma_D^{C1}}$$
$$\gamma^{C2}(1+\cos\Theta_2) = 2\sqrt{\gamma_P^W\gamma_P^{C2}} + 2\sqrt{\gamma_D^W\gamma_D^{C2}}$$

Two liquids were used and their characteristics are given in Table IV.

The fiber–liquid contact angle was measured by the numeric method. The basis of algorithm was Laplace's equation converted to a differential form by Yamaki and Katayama[43] that takes into account the linearly symmetric shape of the drop profile and the cylindrical shape of fiber. The tests of wetting process and fiber observations were carried out under a Biolar PI microscope equipped with a computer image analyzer.

The values of contact angle were determined as averages from measurements of 20 liquid drops formed on the fiber.

RESULTS

The physical characteristics of fiber surface

Results of testing the microtopography of fiber surface by SEM

The changes in the surface of unmodified and biochemically modified PET fibers are illustrated in Figures 1–4.

Results of testing the physical microstructure of the fiber surface layer by IR absorption spectroscopy—ATR technique

The values of crystallinity degree of the PET fiber surface layer calculated from the formula proposed by Krimm[40] are listed in Table V.

Physicochemical characteristics of fiber surface

Results of testing the molecular structure of the PET fiber surface layer by IR absorption spectroscopy—ATR technique

The results of absorbance for the selected absorption bands correlated with the characteristic groups of the fiber-forming polymer of unmodified and biochemically modified fibers are listed in Table VI.

Results of measuring the electrokinetic charge

The results of measuring the electrokinetic potential of unmodified fiber and selected variants of the biochemically modified fiber are listed in Table VII.

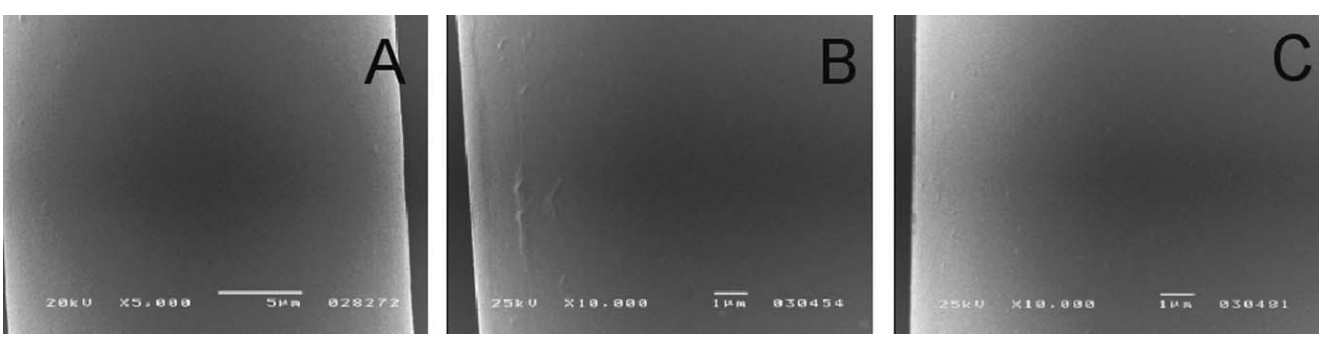

Figure 1 SEM micrographs of surface polyester fibers treated enzyme preparation Lipase A: (A) untreated fiber, (B) fiber treated 30 min, and (C) fiber treated 120 min.

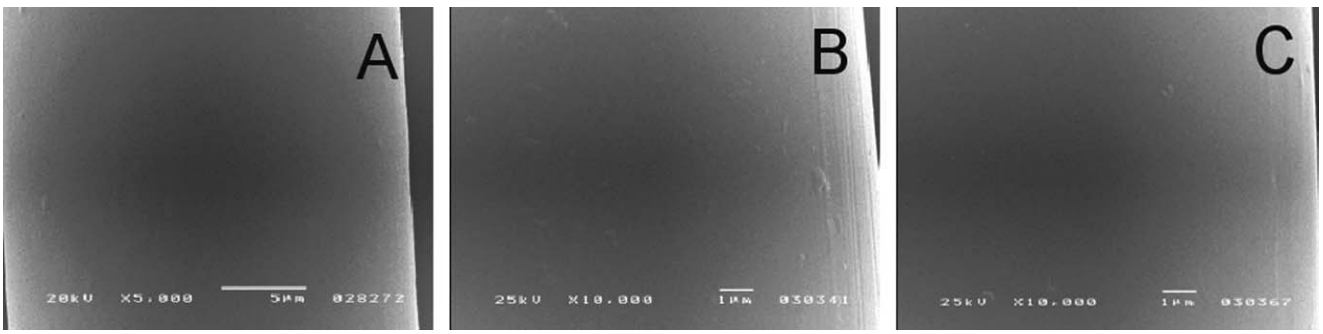

Figure 2 SEM micrographs of surface polyester fibers treated enzyme preparation Lipase AK: (A) untreated fiber, (B) fiber treated 30 min, and (C) fiber treated 120 min.

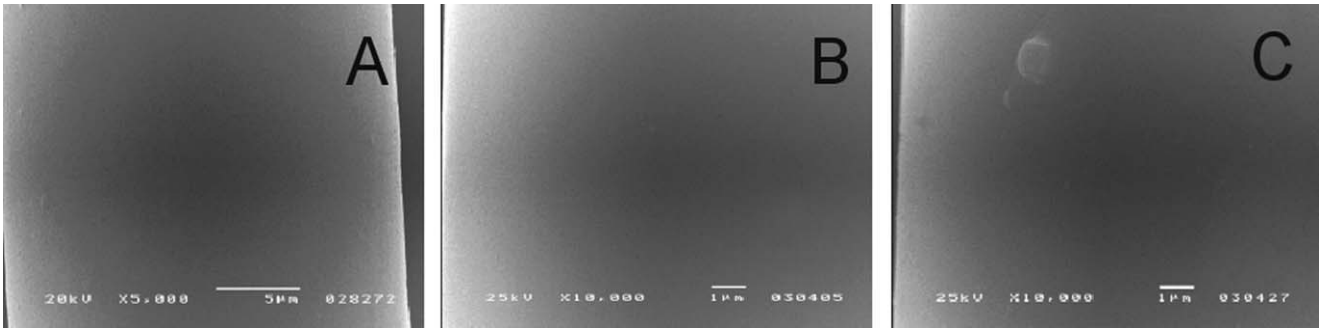

Figure 3 SEM micrographs of surface polyester fibers treated enzyme preparation Lipozyme: (A) untreated fiber, (B) fiber treated 30 min, and (C) fiber treated 120 min.

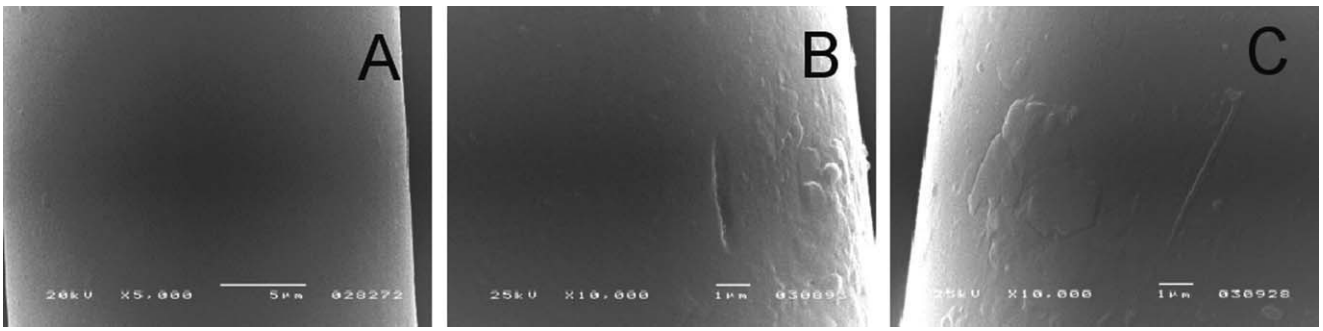

Figure 4 SEM micrographs of surface polyester fibers treated enzyme preparation Esterase: (A) untreated fiber, (B) fiber treated 30 min, and (C) fiber treated 120 min.

TABLE V
The Values of Crystallinity Degree of the PET Fiber Surface Layer

Type of fiber modification	x_{IR} (%)
Untreated	69.8
Treated enzyme preparation: lipase A 30 min	71.6
Treated enzyme preparation: lipase A 120 min	72.9
Treated enzyme preparation: lipase AK 30 min	70.8
Treated enzyme preparation: lipase AK 120 min	72.8
Treated enzyme preparation: lipozyme 30 min	72.8
Treated enzyme preparation: lipozyme 120 min	77.8
Treated enzyme preparation: esterase 30 min	74.9
Treated enzyme preparation: esterase 120 min	76.7

Results of testing the presence of —OH groups in the fiber surface layer

The presence of —OH groups in the fiber surface layer was examined by dyeing the fibers with a reactive dye. The fiber dyeing effects are illustrated in Figure 10.

Results of testing the adhesiveness of polar and nonpolar liquids by the contact angle method

The values of the polar and nonpolar components of surface tension of unmodified and biochemically modified fibers are listed in Table VIII.

TABLE VI
The Values of Absorbance Selected Absorption Bands Correlated with the Characteristic Groups of the Fiber-Forming Polymer of Unmodified and Biochemically Modified Fibers

Type of fiber modification	Band position, cm^{-1}	
	793	1406
Untreated	0 0367	0 0732
Treated enzyme preparation: lipase A 30 min	0 0351	0 0767
Treated enzyme preparation: lipase A 120 min	0 0357	0 0950
Treated enzyme preparation: lipase AK 30 min	0 0349	0 0728
Treated enzyme preparation: lipase AK 120 min	0 0315	0 0974
Treated enzyme preparation: lipozyme 30 min	0 0261	0 0801
Treated enzyme preparation: lipozyme 120 min	0 0211	0 0866
Treated enzyme preparation: esterase 30 min	0 0311	0 0827
Treated enzyme preparation: esterase 120 min	0 0281	0 0942

TABLE VII
The Results of the Electrokinetic Charge of Unmodified Fiber and Biochemically Modified Fiber

Type of fiber modification	Electrokinetic charge (mV)
Untreated	−64
Treated enzyme preparation: lipase A 30 min	−103
Treated enzyme preparation: lipase A 120 min	−169
Treated enzyme preparation: esterase 30 min	−233
Treated enzyme preparation: esterase 120 min	−167

DISCUSSION AND INTERPRETATION OF RESULTS

Discussion of the results of testing the fiber surface microtopography

The SEM images of fiber surfaces treated with enzymatic preparations such as lipase are similar and do not show any clear surface carving, whereas in the case of the fiber modified with esterase, the carving effect is clearly visible.

The difficulty of interpreting the effects of individual modifiers on the fiber surface microtopography based on the assessment of images obtained by SEM has been overcome by testing the surface of modified fibers by the AFM method (Figs. 5–9).

From the fiber surface images and diagrams, one can unmistakably conclude on the range and character of changes in the fiber surface microtopography. From them, it follows that the most effective method of modification in terms of the surface carving uniformity is the treatment with esterase and lipase AK. One should especially underline the effects obtained with esterase (uniformity of the fiber surface carving).

Discussion of the results of testing the physical microstructure of fiber surface layer after modification

The values of crystallinity index, x_{IR}, given in Table V, indicate their clear increase after fiber modification. The increase in crystallinity is the highest in the case of the modification with esterase. One may assume that it results from the selective and effective action of this enzyme to "etch" the noncrystalline

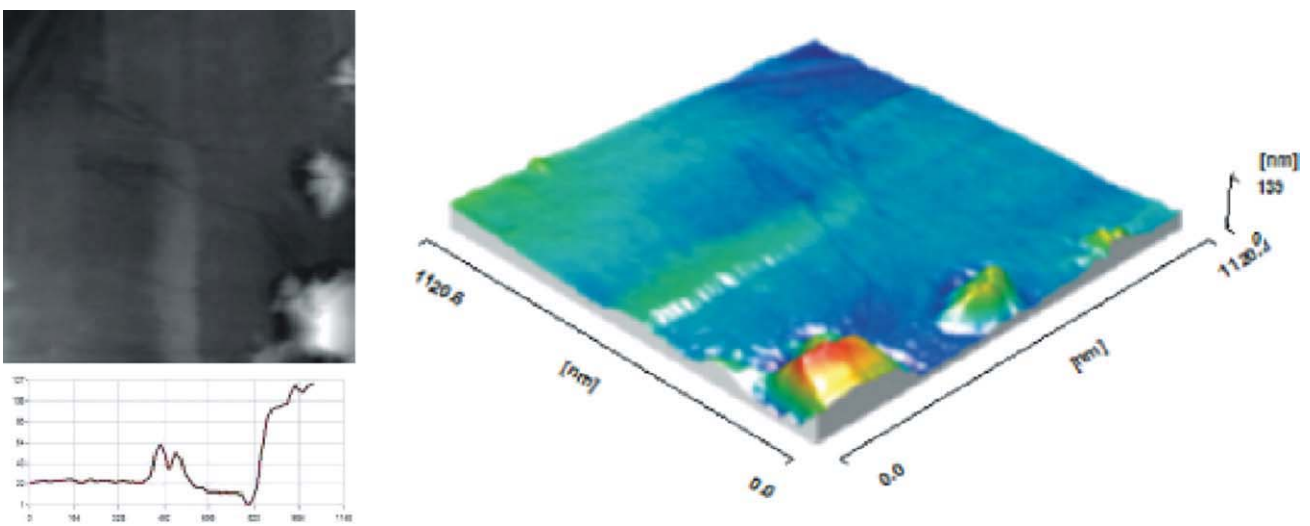

Figure 5 AFM micrographs of untreated surface polyester fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

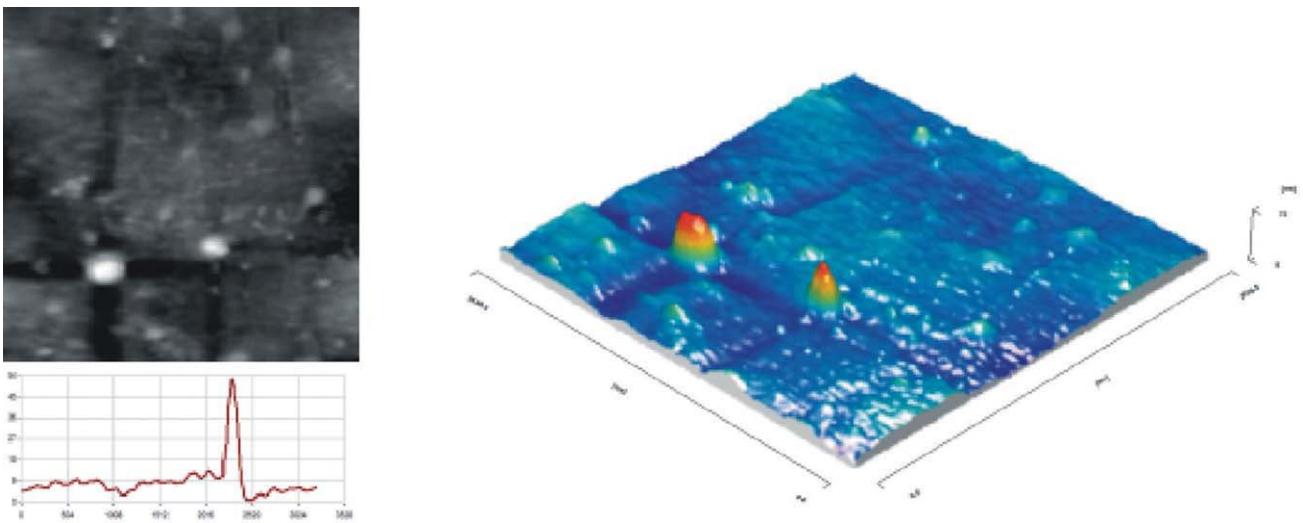

Figure 6 AFM micrographs of surface polyester fibers treated 120 min enzyme preparation Lipase A. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

matter from the fiber surface as a result of hydrolytic decomposition of polymeric chains.

Physicochemical characteristics of the fiber surface

The analysis of the intensity of absorption bands correlated with the ester group and terminal —OH group, expressed in the form of absorbance corrected in respect of the internal standard band (Table VI), indicates that under the influence of the modifiers used, the intensity of the band correlated with the ester group decreases, whereas the intensity of the band correlated with terminal —OH group increases. Such an arrangement of the absorbance results indicates the change in the fiber surface character toward "hydrophilicity" as a result of the decomposition (shortening) of PET chains in the fiber surface layer. The increased hydrophilic character of the modified fiber is confirmed by the results of fiber dyeing with reactive dyes shown in Figure 10 and by the results of wettability with a polar liquid given in Table VIII. These results show that the polar component of the enzyme-modified fibers has been increased more than ten times as compared with the polar component of unmodified fibers.

From the analysis of the earlier mentioned changes in terms of the effectiveness of particular modification methods it follows that:

- the most effective fiber-modification methods intended to change the physicochemical characteristics of fibers, especially to increase their

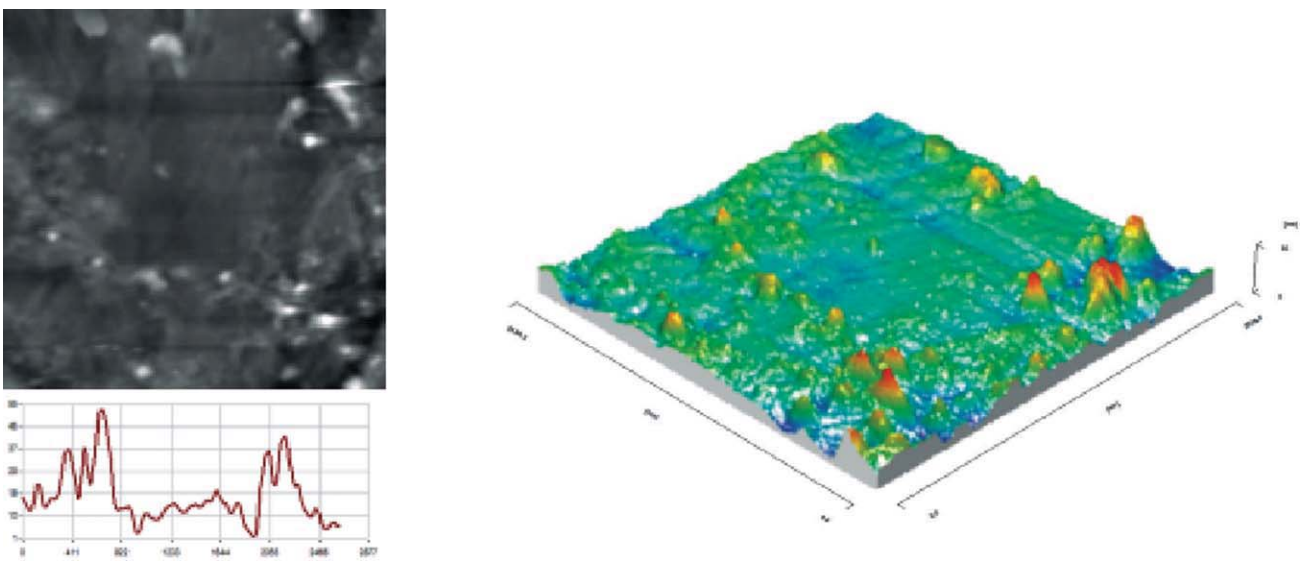

Figure 7 AFM micrographs of surface polyester fibers treated 120 min enzyme preparation Lipase AK. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

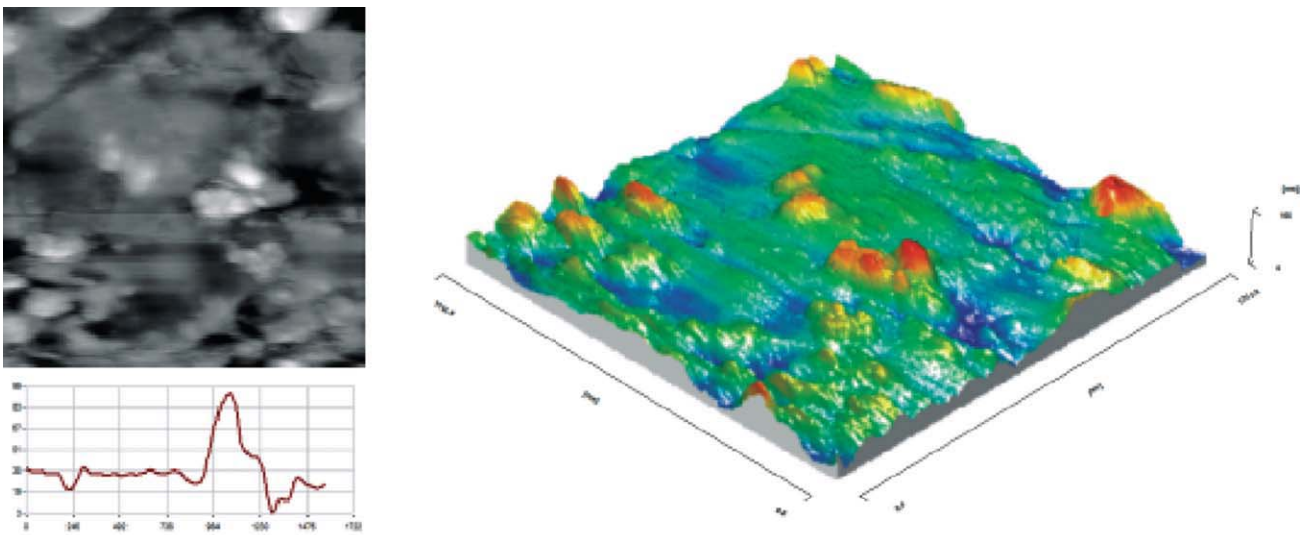

Figure 8 AFM micrographs of surface polyester fibers treated 120 min enzyme preparation Lipozyme. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrophilicity, are those that use enzymatic preparations, in particular Lipozyme and Esterase."

A special discussion is required in the case of the results of testing the fiber electrokinetic charge after fiber modification. The observed resultant increase in the electronegativeness of surface in relation to that of the surface of unmodified fibers seems to be due to its "development" after modification, whose extent is different for various modifiers.

The results of fiber electrokinetic charge in the case of enzymatic preparations clearly correspond with those obtained with the use of AFM. The fiber modified with Amano Lipase A, with the least developed surface, shows the lowest increase in the negative value of electrokinetic charge, whereas that modified with esterase, with the most developed surface, is characterized by the highest value of this potential. One should believe that the observed changes in electrokinetic charge can find their essential reflection in the changes in the adhesive properties of fibers in composite systems (to be used in technical fabrics such as transmission belts coated with plastics or rubber) as well as in the bonding stability of various substances (e.g., metals) applied on the surface of fibers or fabrics.

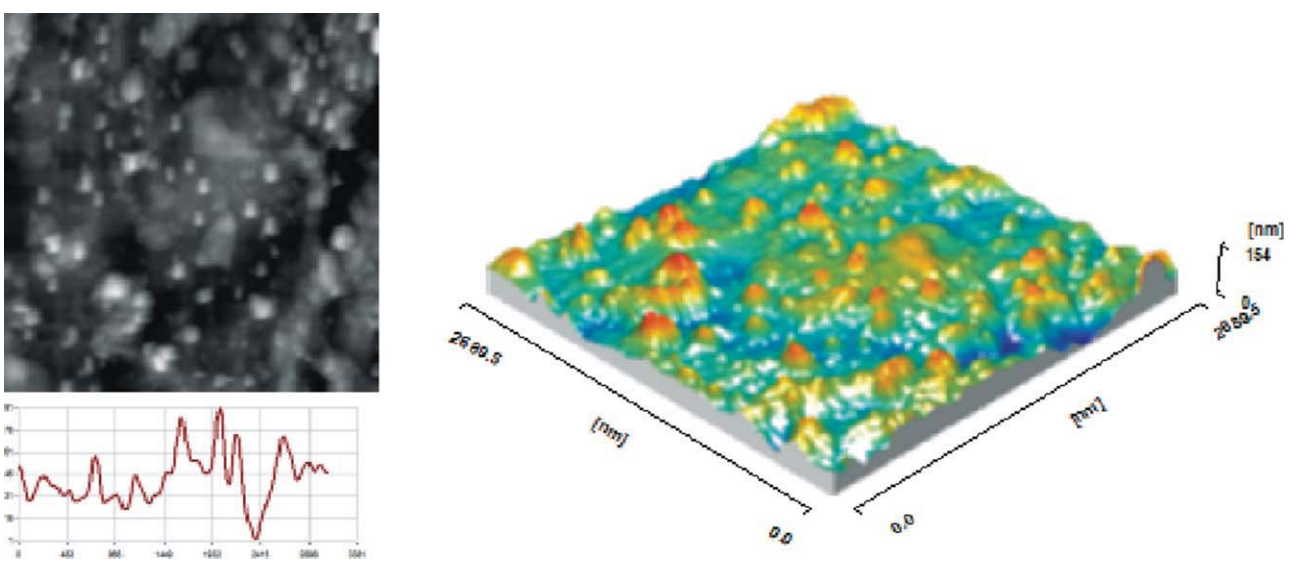

Figure 9 AFM micrographs of surface polyester fibers treated 120 min enzyme preparation Esterase. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

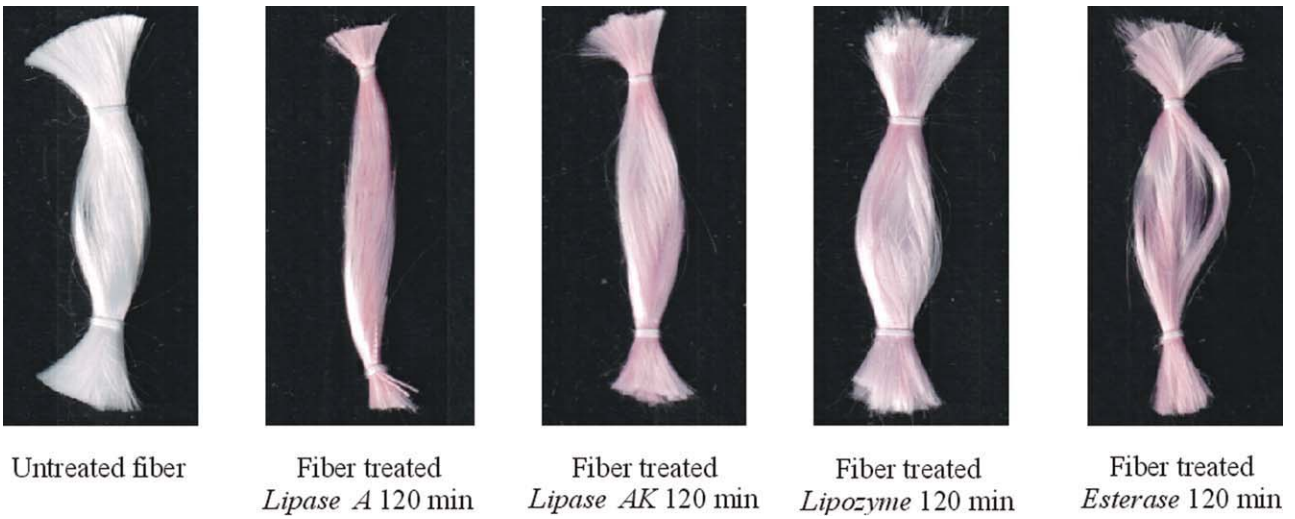

Figure 10 The fiber dyeing effects of unmodified fiber and biochemically modified fiber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com].

CONCLUSIONS

In particular, the conclusions concerning the enzymatic modification of PET fibers can be presented as follows:

1. The effect of enzymatic modification is clearly dependent on the type of enzymatic preparation.
2. The enzymatic modification of fiber surface changes both its physical and physicochemical characteristics.
3. The change in the physical characteristics manifests itself in a fine and uniform carving effect of fiber surface as well as in increased crystallinity of the fiber surface layer.
4. The change in the physicochemical characteristics consists in increasing the fiber surface hydrophilicity.
5. The influence of the change in fibers' physical characteristics has been confirmed by Kardas[44] in the improvement of PET textiles resistance to pilling effect.
6. The change in the physicochemical characteristics of fibers investigated leads to substantial improvement of PET textiles wettability in polar liquids, what is important in all PET fibers finishing processes, as dyeing, bleaching, scouring.

TABLE VIII
Values of Fiber Surface Tension Investigations—Untreated and Biochemically Modified

Type of fiber modification	Interfacial tension of fiber γ^W (mN/m)		
	γ_P^W	γ_D^W	$\gamma^W = \gamma_P^W + \gamma_D^W$
Untreated	1.2	39.7	40.9
Treated enzyme preparation: lipase A 30 min	5.9	39.4	45.3
Treated enzyme preparation: lipase A 120 min	11.0	39.5	50.5
Treated enzyme preparation: lipase AK 30 min	7.3	39.9	47.2
Treated enzyme preparation: lipase AK 120 min	11.2	40.1	51.3
Treated enzyme preparation: lipozyme 30 min	6.0	39.6	45.6
Treated enzyme preparation: lipozyme 120 min	11.8	39.8	51.6
Treated enzyme preparation: esterase 30 min	8.5	40.0	48.5
Treated enzyme preparation: esterase 120 min	13.7	40.2	53.9

In the light of the research results obtained the method of PET fibers modification with the use of enzymatic preparations should be accepted as an effective, proecological, and energy-saving approach to changing the fiber surface structure leading to the elimination or essential reduction of several unfavorable fiber properties.

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