

Iwona Kardas,
*Barbara Lipp-Symonowicz,
*Sławomir Sztajnowski

Institute of Biopolymers and Chemical Fibres,
Member of EPNOE,
European Polysaccharide Network of Excellence,
www.epnoe.eu
ul. Skłodowskiej-Curie 19/27,
90-570 Łódź, Poland
E-mail: ikardas@poczta.fm

*Fibre Physics and Textile Metrology Department,
Center of Advanced Technology Pro Humano Tex,
Technical University of Lodz,
ul. Żeromskiego 116, 90-234 Łódź, Poland

Comparison of the Effect of PET Fibres' Surface Modification Using Enzymes and Chemical Substances with Respect to Changes in Mechanical Properties

Abstract

This paper presents a comparison of the chemical modification effectiveness, as the traditional and the most used possibility of PET fibres surface modification and the biochemical modification, as the new method, being the alternative to the traditional one in aspect of their influence on the fibres mechanical properties. The object of the investigations were PET fibres, differentiated in their orientation and crystallinity degree, as a result of technological draw ratio differences in the range of characteristic values for typical fibre assortments designated for cloth and technical fabrics. Our previous investigations enabled to determine that the change in the general surface characteristics of PET fibres (micro-topography and hydrophilicity) leads to changes in both their volumetric (dyeability) and surface properties (wettability, pilling, oil-soil removal, electric properties), PET fibre modification more advantageous for as well as to identify that enzymatic processing is. In this paper, the effects of modification were analysed from the point of view of changes in the mechanical properties. In the case of enzymatically treated fibres, the influence of enzyme preparations on changes in the fibre's mechanical properties is evidently dependent on the kind of enzymes, especially for fibres with lower draw ratios. Changes in the fibre's elongation at break are generally bigger for fibres treated with chemical substances. The decrease in tenacity and elongation is clearly smaller when fibres with higher draw ratios are treated with Lipozyme and Esterase.

Key words: polyester fibres, surface modification, mechanical properties.

Introduction

Polyester fibres are characterised by a low surface energy and limited reactivity. To use them as components of composites or to impart to them specific surface properties required in various applications, one has to modify their surface by appropriate methods. The incorporation of new functional groups as a result of a reaction with a proper chemical substance is one of the possible changes in the physical and chemical character of the fibre surface. In order to restrict any change in the polymer to the fibre surface layer only, leaving the internal part unchanged, it is required to select appropriate chemicals and experimental conditions.

The conventional methods of chemically modifying PET fibres most frequently used in the industry are those that use chemical reactions to split the macromolecular chain of the fibre-forming polymer, which improves some unfavourable fibre properties. An aqueous sodium hydroxide solution is most frequently used to modify PET fibres. Its action improves the electrical properties, sorption and wettability of fibres but also brings about fibre weight loss, thickness reduction and a decreased breaking force approximately proportional to the treatment time [1 - 4], and consequently a loss of tensile strength [1 - 3, 5 - 10]. These ef-

fects reduce the range of its application, especially in technical areas.

Another type of compound frequently used for chemical modification are amines with various functionalities. The modification of fibres with both mono-functional and bi-functional amine aqueous solutions causes a gradual change in their strength properties [5, 11 - 15, 17], where the extent of changes depends on the initial fibre structure [11]. The increase in amine functionality brings about a slight decrease in fibre strength only when the modification time is prolonged [16 - 18].

Nowadays the uses of enzymes in textile industries are being developed because of their harmless effluents and high effectiveness. [19 - 22] A relatively new and interesting alternative to the previous methods of modifying polyester fibre surfaces consists in using enzymes. Investigations hitherto carried out involving PET fibre surface modification using different kinds of enzymes have brought about the improvement of a number of selected fibres and fabric properties without any distinct loss of fibre tensile strength. [23 - 29] The investigations presented in most of the papers have a fragmentary character, comprising no defined fibres in respect of their structure. The choice of enzyme preparation is often quite casual.

In a previous paper the authors compared the effectiveness of chemical modification, as the traditional and most used approach to PET fibre surface modification and biochemical modification, as the new method, being the alternative to the traditional one in aspect of their changes of micro-topography, molecular and supermolecular structure of the fibre surface layers. Selected fibre surface and volumetric properties has been assessed [30, 31].

In the study [30], the effect of changes in the surface structure of PET fibres on their selected volumetric and surface properties was assessed in terms of its micro-topography, molecular and supermolecular structures.

The tests performed by the authors of the present paper concerning the physical and chemical characteristics of a PET fibre surface indicate that the most effective method of modification from the point of view of physical and physico-chemical characteristics, both the micro-topography and micro-structure of the fibre surface layer, is modification with *Esterase* preparation. As a result, a uniform and homogeneous relief-type texture of the fibre surface and the highest increase in the crystallinity degree χ_{IR} were obtained, which seems to be a result of the selective and effective action of this enzyme i.e. 'etching' the non-crystalline

Table 1. Characteristics of PET fibres used.

Draw ratio R	Thickness of fibre, μm	Total orientation factor f_o	Fibre crystallinity index X_{IR} , %
3.0 ×	32.2	0.6246	60.3
3.5 ×	28.4	0.7430	66.7
4.0 ×	27.2	0.8584	71.1
5.2 ×	24.7	0.9993	77.2

Table 2. Parameters of the chemical treatment.

Concentration aqueous, %	Treatment time, min	Treatment temperature, °C
12% solution of NaOH	120	60
20% solution of NaOH	60	60
	120	
70% aqueous solution ethylamine	120	22
97% aqueous solution ethylenediamine	20	22
	80	
	120	

portion of the polymer from the fibre surface due to the hydrolytic decomposition of its macromolecular chains.

Analysing the physical and chemical structure of a fibre surface, one can observe that the change in the surface character towards hydrophilicity results from the decomposition (shortening) of PET chains in the surface layer of fibres. The increased extent of the hydrophilicity of the fibre surface due to the modification is confirmed by the fact that the value of the polar component of enzyme-modified fibres is increased by more than ten times in comparison with that of unmodified fibres.

From the analysis of the above-mentioned changes in terms of the effectiveness of particular modification methods, it follows that the most effective fibre modification methods intended to change the physico-chemical characteristics of fibers, especially to increase their hydrophilicity, are those that use enzymatic preparations, in particular *Lipozyme* and *Esterase*.

In [31], the effect of changes in the surface structure of PET fibres on their selected volumetric and surface properties was assessed in terms of its micro-topography, molecular and supermolecular structures.

The change in the general surface characteristics of the fibres under investigation (micro-topography and hydrophilicity) results in very beneficial changes in both volumetric and surface properties.

The change in the surface of PET fibres from hydrophobic to hydrophilic after modification with enzymes also resulted

in an improvement in the resistance to soiling and oil-soil release as well as in the dyeability with disperse dyes. The chemically-modified fibres show a high susceptibility to combining oily impurities and a low oil-soil-release capability

The consequence of the increased water absorption by the fabric obtained was a durable improvement in antistatic properties resulting from the reduced surface resistance for all types of modification.

Another aim of the modification of PET fibres with commercially available enzymatic preparations was to totally reduce their susceptibility to pilling. The chemically-modified fibres are characterised by an increased susceptibility to fabric pilling.

Considering the advantages obtained by PET fibre modification, their influence on the mechanical properties especially tenacity and elongation at break, of the fibres processed should be investigated and taken into account our investigations was concerned with the consequences of changes in the mechanical properties of the PET fibres, differing in their initial structure after enzymatic and chemical treatment.

■ Experimental

Materials and methods

Glossy, continuous polyester fibres of poly(ethylene terephthalate) differently (drawn ratios: $R = 3.0 \times$; $R = 3.5 \times$; $R = 4.0 \times$; $R = 5.2 \times$) were used for the investigations. The test fibres, being different with respect to the physical microstructure formed by drawing, allowed to assess the influence of the initial fibre

structure on the effects of surface modification. Such an approach has been used in a few studies, carried out in a fragmentary way. The characteristics of the fibres are given in **Table 1**.

Chemical modification

Chemical modification of the fibre surface was performed with the use of three chemical substances:

- sodium hydroxide, Chempur;
- 70% aqueous solution of ethylamine, Fluka;
- 97% aqueous solution of ethylenediamine (EDA), POCH – Gliwice.

The parameters of chemical modification with the use of sodium hydroxide are given in **Table 2**. Considering the literature data concerning the conditions and effectiveness of the treatment, variable concentrations of NaOH solutions and treatment times were used.

The parameters of modification with the use of amines also are specified in **Table 2**, assuming the modification time, cited in the literature and clearly dependent on the type of amine, as a decisive factor for amine action effectiveness. To provide a system allowing to compare the modifying action effectiveness of individual chemicals under the thermal condition used, the same treatment time of 120 min was used in all the cases.

After modification, the fibre samples were thoroughly rinsed with distilled water to obtain neutral pH followed by drying at room temperature for 24 h.

Biochemical modification

Modification of the fibre surface by the biochemical method was carried out with the use of four selected enzymatic preparations, active in relation to the fibre-forming polymer and diversified with respect to their origin, biochemical characteristics and application conditions. Characteristics of the enzymes used are given in **Table 3**.

The PET fibres were incubated with enzyme preparation in a sodium phosphate buffer, in autoclave Ahiba–Polymat Oryginal Hanau. The parameters of enzymatic modification are given in **Table 3**. All samples were treated for 30 and 120 min.

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

Table 3. Characteristics of the enzymatic preparations used in biochemical modification and their treatment conditions.

Enzyme preparation	Source	Supplier or manufacturer	Concentration enzyme preparation	Optimum temperature °C	Optimum pH	Activity
Amano Lipase A	<i>Aspergillus niger</i>	Aldrich	2 g/l	45	6.0	≥ 12,000 U/g
Amano Lipase AK	<i>Pseudomonas fluorescens</i>	Aldrich	2 g/l	55	8.0	≥ 20,000 U/g
Lipozyme®	<i>Mucor miehei</i>	Fluka	2 g/l	70	8.0	> 100 U/g
Esterase	<i>Bacillus starothermophilus</i>	Fluka	2%	65	7.0	~ 0.4 U/mg

Table 4. Values of the weight loss, % of chemically modified fibres with different draw ratios.

Draw ratio R	Treated 12% solution NaOH 120 min	Treated 20% solution NaOH 60 min	Treated 20% solution NaOH 120 min	Treated solution of ethylamine 120 min	Treated EDA 120 min		
					20	80	120
3.0×	6.50	7.22	14.72	12.62	7.32	16.52	19.68
3.5×	4.11	7.30	12.16	6.08	6.24	8.92	11.54
4.0×	4.40	5.72	9.68	0.96	0.96	1.82	3.44
5.2×	3.36	5.36	8.66	0.36	0.68	1.36	2.18

Table 5. The values of the weight loss, % of bio-chemically modified fibres with different draw ratios.

Draw ratio R	Treatment time, min	Enzyme preparation			
		Amano Lipase A	Amano Lipase AK	Lipozyme®	Esterase
3,0×	30	0.64	0.71	0.55	15.36
	120	0.68	0.72	0.65	17.82
3,5×	30	0.76	0.69	0.66	23.43
	120	0.79	0.70	0.68	26.06
4,0×	30	0.57	0.56	0.49	11.44
	120	0.60	0.62	0.53	13.07
5,2×	30	0.42	0.45	0.19	7.46
	120	0.51	0.50	0.25	9.52

with distilled water at 70 °C (6 times). All samples were air dried at room temperature for 24 hours.

Testing the weight loss of fibre after the modification process

The weight loss of fibre after the modification process was determined using the gravimetric method. 5 measurements were performed for each variant. All fibre samples were dried at room temperature for 24 hours, then they were weighed and the loss of weight was calculated from the formula:

$$x = [(m_n - m_m)/m_n] \cdot 100\%$$

where:

x – fibre weight loss in %

m_n – unmodified fibre weight in g

m_m – modified fibre weight in g

Testing mechanical properties

Stress-strain curves with the action of an axial tensile force constituted the basis for the assessment of changes in the tensile strength of the fibres modified. The fibres to be tested were air conditioned for 24 h in a standard atmosphere according to PN-EN 20139:1993 [32]. The linear density of single fibres was determined

by the gravimetric method according to PN-ISO 1973:1997 [33]. Tests were carried out with the use of an Instron tensile tester, model 4204, equipped with pneumatic sample holders. Single filaments, previously stuck on paperboard frames, were placed in the tester holder with an initial tension of 1 cN/tex. The travel rate of the traverse was 20 mm/min. The initial filament length was 20 mm. 50 measurements were performed for each variant. At the moment of break, the following values were recorded: the maximal force, breaking force, tenacity and elongation at break. The tests were carried out according to PN-EN ISO 5079:1999 [34].

Results and discussion

Values of the weight loss of chemically and bio-chemically modified fibres are listed in **Tables 4 & 5**.

Values of the tenacity of chemically and bio-chemically modified fibres are illustrated in **Figure 1**.

The mechanical parameters of the variants of fibres examined assume clearly different values depending on the initial structure specified by the fibre draw ratio.

Weight loss

For fibres modified with sodium hydroxide solutions, a notable weight loss was observed, being especially large for the highest concentration of NaOH solution and the longest treatment time. According to the increase in the draw ratio of the fibres, the weight loss decreases proportionally. The weight loss is in the range of 15% to 8.5%.

In the case of fibres modified with EDA, the weight loss shows a leapt character – high and close for fibers with a draw ratio of 3.0× and 3.5× (20% and 11.5%), and relatively low for fibres with a draw ratio of 4.0× and 5.2× (3.5% and 2%).

In the case of fibres enzymatically treated, the weight loss is considerable depending on the kind of enzymatic preparation. The highest weight loss is noticed during *Esterase* treatment. The application of remaining enzymatic preparations causes an almost comparable effect, which is relatively small – less than 1%.

During the application of *Esterase*, the fibre's weight loss is clearly dependent on the fibre's draw ratio R. For fibre drawn at 4.0× and 5.2×, the weight loss is con-

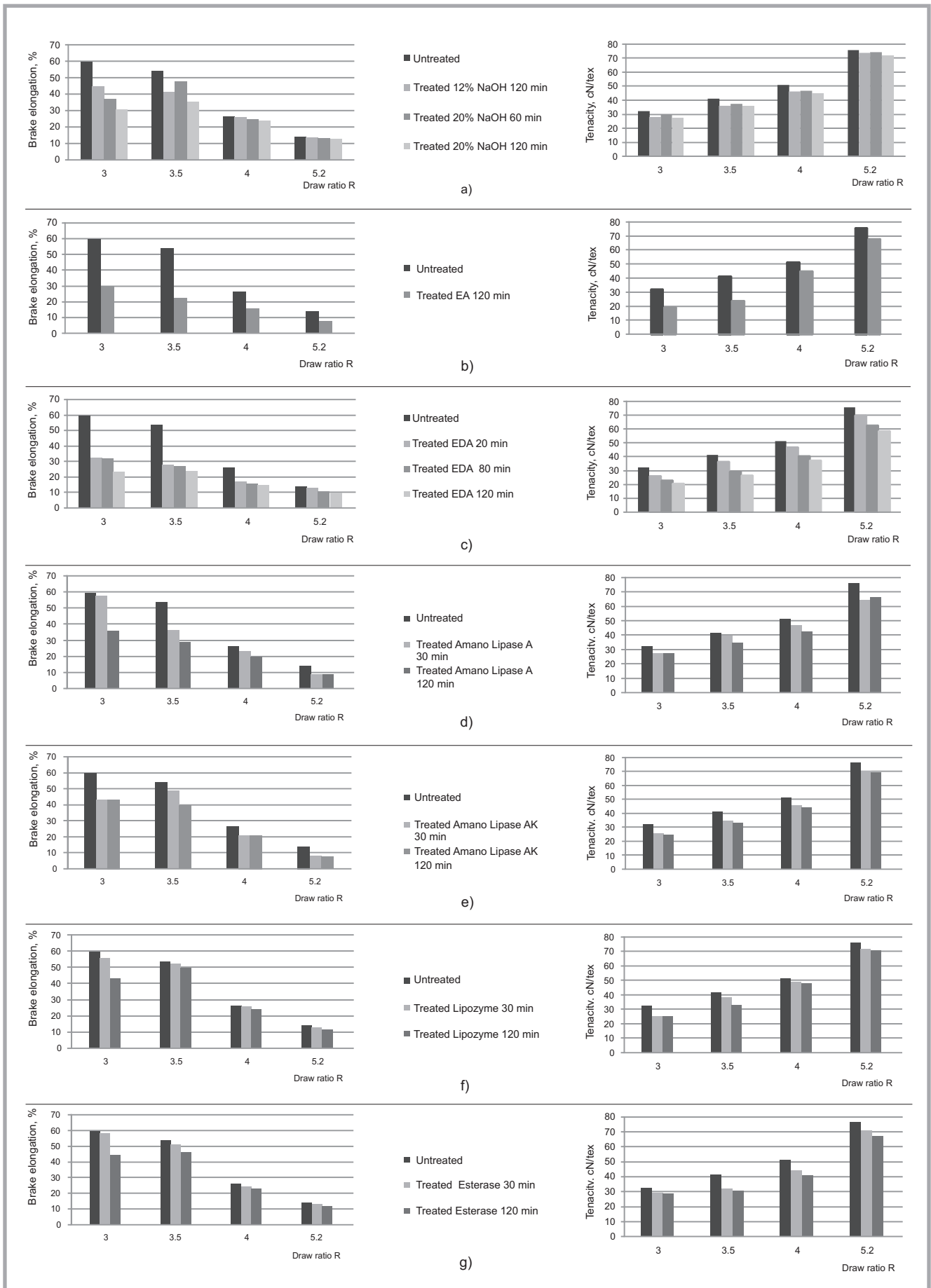


Figure 1. Changes in the brake elongation and tenacity of fibres with different draw ratios – unmodified and chemically modified with a solution of: a) NaOH, b) ethylamine, c) EDA, d) Amano Lipase A, e) Amano Lipase AK, f) Lipozyme, g) Esterase.

tained in the range of 11.5% to 7.5%, and for fibres with a draw ratio of 3.0× and 3.5×, it is 18% and 26%, respectively.

Tensile strength

The fibres modified with sodium hydroxide solutions show a clear decrease in tensile strength, especially high (15.5% and 12.5%) in the case of fibres with draw ratios of 3.0× and 3.5×. For fibres with a draw ratio of 4.0× and 5.2×, the tenacity decrease is relatively small – 7% and 5%, respectively. A clearly disadvantageous effect on strain can be seen in fibres with draw ratios of 3.0× and 3.5× (decrease of 49% and 36%), while the elongation at break of fibres with draw ratios of 4.0× and 5.2× is practically unchanged.

Fibres modified with ethylamine show a step-wise drop in tenacity depending on the fibre draw ratio. The tenacity of fibres with draw ratios of 3.0× and 3.5× is decreased by about 40%, while that of fibres with draw ratios of 4.0× and 5.2×, it is 12% and 10.5%, respectively. Very severe decreases in fibre elongation at break (from 60% to 40%) are observed for all variants of the draw ratio.

Fibres with various draw ratios modified with EDA show relatively slight differences in tensile strength changes, but a considerable drop in fibre strength is observed when the treatment time is prolonged to 120 min (from 36.5% to 23%). The fibre elongation at break is severely decreased for all variants of the draw ratio (60% - 28%).

The values of tenacity and elongation at break of the enzyme-treated fibres depend on the type of enzyme preparation. The fibres treated with *Amano Lipase A* and *Amano Lipase AK* show a considerable decrease in both tenacity and elongation in practically all the modification cases. The decrease in tenacity and elongation is clearly smaller when fibres with higher draw ratios are treated with *Lipozyme* and *Esterase*.

Conclusions

Based on the results obtained, the following conclusions can be drawn:

- Application of PET surface fibre modification with both chemical substances and enzymatic preparations cause changes in the mechanical properties of fibres expressed by changes in tenacity and elongation at break.
- The changes are the largest for fibres with the lowest draw ratios.

■ Comparison of the range of changes induced by the action of chemical substances and enzymatic preparations leads to the following statements:

- from the chemical substances applied, ethylamine has the strongest influence on changes in mechanical properties. A relatively low weight loss causes a drastically high decrease in tenacity, on the basis of which it can be deduced that the ethylamine action not only concerns the polymer layer of the fibre surface, but also the fibre volume.
- Ethylenediamine exerts a relatively small influence on the mechanical properties of fibres, which strongly depends on the treatment time prolongation.
- in the case of enzymatically treated fibres, the influence of enzyme preparation on the mechanical properties of fibre changes depends on the kind of enzymes, especially for fibres with lower draw ratios. For fibres with a higher draw ratio after enzymatic treatment for 30 minutes, the values of tenacity are practically comparable, being about 10% less than those of initial fibres.
- changes in the elongation at break of fibres are generally bigger for fibres treated with chemical substances.

In view of the test results obtained, the method of PET fibre modification with the use of enzymatic preparations can be considered as an effective, pro-ecological and energy-saving process for changing a fibre surface's structure, leading to the elimination or a significant limitation of several unbeneficial properties of PET fibres. The most effective method of fibre modification to change the physical and chemical characteristics and surface properties of fibres seems to be enzymatic preparations such as *Lipozyme* and *Esterase*.

Acknowledgment

Iwona Kardas is a grant holder of the "Mechanizm WIDDOK" programme supported by the European Social Fund and the Polish State (contract number Z/2.10/II/2.6/04/05/U/2/06).

References

1. Sanders E.M., Zeronian S.H.: *J. Appl. Polym. Sci.*, Vol. 27, 1982, 4477
2. Dave J., Kumar R., Srivastava H.C.: *J. Appl. Polym. Sci.*, Vol.33, 1987, 455
3. Collins M.J., Zeronian S.H., Semmel-meyer M.: *J. Appl. Polym. Sci.*, Vol. 42, 1991, 2149

4. East G.C, Rahman M.: *J. Appl. Polym. Sci.*, Vol. 102, 2006, 4814
5. Ellison M.S., Fisher L.D. i in.: *J. Appl. Polym. Sci.*, Vol. 27, 1982, 247
6. Collins M.J., Zeronian S.H.: *J. Appl. Polym. Sci.*, Vol. 45, 1992, 797
7. East G.C, Rahman M.: *J. Appl. Polym. Sci.*, Vol. 102, 2006, 4814
8. Zeronian S.H., Collins M.J. i in.: *Indust. Fabr.*, Vol. 3, 1984, 19
9. Namboori C.G.G., Haith M.S.: *J. Appl. Polym. Sci.*, Vol. 12, 1968, 1999
10. Filipowska B., Kubacki Z.: *Przegl. Włók.*, Vol. 39, 1985, 118
11. Haghghat Kish M., Borhani S.: *J. Appl. Polym. Sci.*, Vol. 78, 2000, 1923
12. Zeronian, S. H.; Collins, M. J. *Text Progr* 1989, 20, 14
13. Poppola A.V.: *J. Appl. Polym. Sci.*, Vol. 36, 1988, 1677
14. Holmes S. A.: *J. Appl. Polym. Sci.*, Vol. 61, 1996, 255
15. Holmes S.A.: *Text. Res. J.*, Vol. 66, 1996, 214
16. Avny Y., Rebenfeld L.: *J. Appl. Polym. Sci.*, Vol. 32, 1986, 4009
17. Fukatsu K.: *J. Appl. Polym. Sci.*, Vol. 45, 1992, 2037
18. Bide M., Zhong T. i in.: *AATCC Review*, 11, 2003, 24
19. Lipp-Symonowicz B., Tańska B., Sapieja A.: *Fibres Text. East. Eur.*, Vol.12 (2), 2004
20. Lipp-Symonowicz B., Wrzosek H., Machnowski W., Kowalska S., Kotlińska A.: *Changes in the surface structure and properties of fibres occurred during biochemical processes, Proceedings of IX International Scientific Conference, IMTEX 2007*
21. Radetic M., Jovancic P., Jovic D., Topalovic T., Puac N., Petrovic Z. L. J.: *Fibres Text. East. Eur.*, Vol. 63 (4), 2007
22. Goudarzi G., Sepehrizadeh Z., Tabatabaei Yazdi M., Jamshidiha M.: *Fibres Text. East. Eur.*, Vol. 68 (3), 2008
23. Alisch M., Feuerhack A. i in.: *Biocatalysis and Biotransformation*, Vol. 22, 2004, 347
24. Fischer-Colbrie G., Heumann S. i in.: *Biocatalysis and Biotransformation*, Vol. 22, 2004, 341
25. Andersen B.K., Borch K.: *Method of treating polyester fabrics*, US Patent No. 5,997,584, 1999, 1-23
26. Müller R.J., Kleeberg I., Deckwer W.D.: *J. Biotechnol.*, Vol. 86, 2001, 87
27. Vertommen M.A.M.E., Nierstrasz V.A. i in.: *Journal of Biotechnology*, Vol. 120, 2005, 376
28. Yoon, M.-Y., Kellis, J. and Poulouse, A.J.: *AATCC Review*, Vol. 2, 2002, 33
29. Xie J, Hsieh YL: *ACS Symp Ser.*, Vol 840, 2003, 217
30. Kardas I., Lipp-Symonowicz B., Sztajnowski S.: *The influence of enzymatic treatment on the surface modification of PET fibers*, *J. Appl. Polym. Sci.*, in press
31. Kardas I., Lipp-Symonowicz B., Sztajnowski S.: *The influence of PET fibres surface enzymatic modification on the selected properties*, *AATCC Review*, in press
32. PN-EN 20139:1993
33. PN-ISO1973:1997
34. PN-EN ISO 5079:1999

Received 27.02.2009 Reviewed 08.07.2009