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SCIENTIFIC PAPER

678.744.002.2:577.115:577.15

POLYESTER FABRIC MODIFICATION BY SOME LIPASES

In this paper, we investigated the enzymatic treatment of polyester fabric. The results show that enzymatic treatment with different lipases causes adequate effects, especially, referring to water penetration, absorption and the mechanical parameters of the processed fabric (strength, elongation, wear resistance). The results of scanning electron microscopy contributed to the structural and morphological understanding of the polyester fiber surface in the treated regime. After enzyme treatment, some changes on the fiber surface were noticed. These results confirmed that the enzymes influenced the surface of the polyester fibers. The process probably did not cause major damage of the fiber surface or major reorganization of the surface layers of the polyester fibers, so therefore their mechanical characteristics were satisfactory.

Key words: Polyester fiber, Fabric, Lipase, SEM, Strength, Elongation, Wear resistance, Water penetration, Water absorption.

Traditionally, plastic materials have shown to be very resistant to environmental impact such as humidity or microbial attack. This is especially the case for polymers such as polyethylene, polypropylene or polystyrene. However, other polymers with a heteroatom in the main chain are potentially susceptible to hydrolytic cleavage of the, e.g. ester bonds or amide bonds. Initiated by the increasing problems of plastics waste during the last decade, polymers have been developed, which can undergo a controlled biological degradation [1].

Polyesters are manufactured synthetic compositions comprising any long chain synthetic polymer composed of at least 85% by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to substituted terephthalic units and parasubstituted hydroxybenzoate units. The polyester may take the form of a fiber, yarn, fabric, film, etc. Many chemical derivatives have been developed, for example, poly(ethylene terephthalate) (PET), poly(trimethylene terephthalate) (PTT), poly(butylene terephthalate) (PBT) or poly(ethylene naphthalate) (PEN). However, PET is the most common linear polymer produced and accounts for the majority of polyester applied in industry today [2–4].

In the textile industry, polyester has certain key advantages including high strength, soft hand, stretch resistance, stain resistance, machine washability, wrinkle resistance and abrasion resistance. However, polyester is not so optimal in terms of its hydrophobicity, pilling, static, dyeability, inactive surface as a medium for adhering, i.e., softening or wettability enhancing compounds. Another problem with polyester relates to the difficulty of removing oily and/or hydrophobic stains.

These stains often adhere strongly to the fabric or fiber and cause a permanent stain.

Thus, methods for improving the surface characteristics of polyester have been developed in an attempt to improve the dyeing, stain resistance and other properties associated with the strongly hydrophobic nature of the polyester. Nonetheless, these processes often have inherent deficiencies such as cost of chemicals, energy and capital equipment, and negative effects on the strength of the material and other aesthetic properties of the fabric [5].

Pure aromatic polyesters like PET or PBT are quite insensitive to any hydrolytic degradation. No significant direct microbial or enzymatic attack of pure aromatic polyesters (e.g. PET, PBT or poly(ethylene naphthalate)) could be observed up to now [6,7]. However, recently, a laid open specification of a German patent was published [8], where a procedure is claimed to disintegrate aromatic polyesters with microbial strains of *Trichosporum* and *Arthrobacter* in a time scale of weeks. Because no blank values are included in the examples, it is still questionable if the degradation can be correlated with the action of the microorganisms. Kawai reported about the microbial degradation of polyesters from terephthalate, phthalate or isophthalate polycondensed with poly(ethylene glycol) [9]. Polyester films, i.e. PET, with ethylene glycol as the aliphatic component, can be biodegraded using lipases from *Rhizopus delemar* in phosphate buffer at 373°C [10].

The biodegradation of polyesters and ester containing copolymers and blends by lipases has been reported [11–13]. These studies have focused on how the chemical compositions of the polymers affect lipase-assisted degradation. No one has used lipases to modify polyester surfaces. Hydrolysis of the ester linkage in polyesters should produce polar hydroxyl and carboxylic groups. The insoluble nature of polyester fibers in an aqueous medium would limit enzymatic hydrolysis to the surface. We tested the effects of three

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Paper received: July 26, 2005
Paper accepted: October 31, 2005

lipases, i.e. hydrolyzing enzymes, on the surface of PET fabric, and PET fibers.

Lipases (acylglycerol acylhydrolases, EC 3.1.1.3), a large series of enzymes that catalyze the hydrolysis of various fatty esters, are widely distributed in animals, plants and microorganisms. Microbial lipases have been receiving particular attention because of their actual and potential applications in the detergent, oil and fat, dairy and pharmaceutical industries [14–15].

Lipases are used in the textile industry to assist in the removal of size lubricants, in order to provide a fabric with greater absorbency for improved levelness in dyeing. Its use also reduces the frequency of streaks and cracks in the denim abrasion systems. Commercial preparations used for the desizing of denim and other cotton fabrics, contains both alpha amylase and lipase enzymes. Lipases are also used in detergent formulations together with proteases and amylases [16].

EXPERIMENTAL

We used a polyester (PET) fabric – homopolymer poly(ethylene terephthalate) and lipases in this study.

The characteristic parameters of the 100% pure PET fabric, used in all the experiments, were:

- Weave, twill cloche, left-hand,
- Area weight (g/m^2), 200,
- Warp and weft yarn count (tex) per 16x2,
- Warp setting (cm^{-1}) 30,
- Weft setting (cm^{-1}) 22.

We used three lipases (Table 1), which are commercial products obtained from Biocatalysts. The treatments, i.e. interactions of enzymes and the PET fabric were performed in aqueous buffer solutions. On the basis of preliminary research, we selected an inorganic phosphate buffer and used it throughout this study. This buffer gave the best conditions for the enzyme treatment of polyester fabric.

We investigated the effects of hydrolysis on the fabric by varying the time of treatment. The process, i.e. biomodification and/or biodegradation of PET fabric, lasted 30, 60 and 120 min at 33°C, at a bath ratio of 1:150 (1 g textile per 150 cm^3 solution) at pH=7.2 (phosphate buffer). The concentrations of enzymes were 1 gdm^{-3} in all the treatments (the concentration was chosen based on preliminary results). After each process, denaturation of the enzymes was performed by increasing the temperature of the bath to 60°C for 15 min. The fabric was then rinsed with cool water and dried. Before any investigations, the PET fabric was conditioned at 65% relative humidity and at 21°C. Methods based on JUS F.S2.041 and JUS F.S2.042, respectively, were used to determine the water absorption and penetration. The breaking strength and elongation were determined using a dynamometer according to JUS ISO 5081. The wear resistance was determined according to JUS F.S2.023, using a JEOL

Table 1. Lipases and their properties

Sign	Commercial name	Source	Form	Activity
E1	Lipomod 338P	<i>Penicillium roqueforti</i>	Powder	4500 U/g
E2	Lipomod 224P	Porcine Pancreas		21000 U/g
E3	Lipomod 29P	Porcine Pancreas/ <i>Candida cylindracea</i>		22500 U/g

JSM–5300 scanning electron microscope (a gold coating of thickness 10 μm was deposited on the samples in vacuum for 6 min). The polyester fiber surface (from the fabric) was observed at a magnification of a few thousand. The process was performed in laboratory equipment, a vitreous vessel on a thermostatic shaker. Before enzymatic treatment, the PET fabric was washed with pure distilled water at 40°C for 30 min, and processed in methanol at 30°C for 15 min, after drying. Control samples of PET fabric were processed in the same way as the treatments with enzymes (120 min), but in the absence of enzymes.

RESULTS AND DISCUSSION

Enzymatic reactions of water-soluble substrates proceed rapidly because enzyme molecules can easily be exposed to the substrates. On the other hand, solid substrates such as PET are thought to have extremely inefficient contact with the enzyme molecules. In order to overcome this problem, enzymes that degrade solid substrates are considered to possess some characteristics that enable them to be adsorbed onto the surfaces of the solid substrates [17].

In the case of PET fibers, the primary biological attack is the enzymatically catalysed hydrolysis of the ester bond in the polymer. Investigations [17] have indicated that this enzyme degrades PET in a two-step reaction: hydrophobic adsorption onto the PET surface followed by hydrolysis of the PET ester bonds. Practically, this first step is a surface erosion process (enzymes cannot penetrate into the polymer bulk) [18].

Lipases (acylglycerol acylhydrolases, EC. 3.1.1.3) catalyse the hydrolysis of ester bonds at lipid/water interfaces. Lipases possess the unique feature of acting at an interface between the aqueous and non-aqueous phase. The concept of lipase interfacial activation arises from the fact that their catalytic activity generally depends on the aggregation state of the substrates. It is believed that activation involves the unmasking and structuring of the enzyme's active site through conformational changes requiring the presence of PET fibers in water [19].

The results of sorption characteristics, i.e. water absorption and penetration, for different treatments of the PET fabric are shown in Figure 1 and Table 2. These characteristics of the treated PET fabric samples have

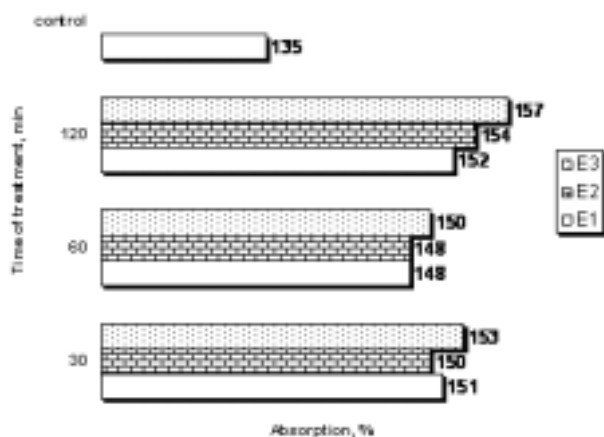


Figure 1. Water absorption of PET fabric treated by enzymes

Table 2. Water penetration of PET fabric treated by enzymes

Enzyme	Time of treatment, min	Penetration, mm	
		Warp	Weft
control	120	0	0
E1	30	10	2
	60	12	4
	120	18	8
E2	30	5	3
	60	5	3
	120	10	4
E3	30	11	2
	60	13	3
	120	19	9

Table 3. Effect of enzyme treatment on the strength and elongation of PET fabric

Enzyme	Time of treatment, min	Breaking strength, daN		Elongation of break, %	
		Warp	Weft	Warp	Weft
control	120	152	120	51	35
E1	30	150	119	52	34
	60	149	118	51	34
	120	149	118	52	35
E2	30	151	119	52	35
	60	150	119	52	36
	120	150	119	53	35
E3	30	149	119	51	33
	60	149	118	52	35
	120	148	117	53	36

larger values than the raw samples of the same fabric. These results confirmed the fact that the enzymes influence the surface of PET fibers. Under the same reaction conditions, lipases E1–E3 significantly improve the water absorption and penetration properties (best results: enzyme E3, 120 min, absorption 157%, control

sample 135%; enzyme E3, 120 min, penetration 19 mm – warp direction, control sample 0 mm), while not imposing adverse effects on the strength of the PET fabric (Table 3). The water absorption and water penetration increase in comparison with the control samples. Surface modification, i.e. degradation, is the main reason for these results. Water penetration in the warp direction is larger than in that weft direction, due to setting and capillarity. Longer treatment times gave better results.

The liquid wetting properties of fibrous materials are fundamentally important to their chemical processing and functional performance. Water sorption, i.e. the wettability of fiber surfaces can be modified by changing the chemistry of the constituent polymer or by applying topical finishes. The chemistry is based on an attack along the PET main chain, causing scissions at the ester linkages and producing carboxyl and hydroxyl polar groups. Aqueous hydrolysis is a surface reaction and the increased surface polarity enables polar interaction or hydrogen bonding with water molecules, thus increasing the water wettability and other sorption characteristics of the fibers [18].

The surface nature of enzyme hydrolysis can to make it ideal for achieving various levels of improved surface wettability and other sorption properties of PET fabrics. Different degrees of hydrolysis can be achieved by varying the kind of enzymes and/or the length of reaction in aqueous enzyme solutions. The control and understanding of the effects of hydrolysis on the quality of the fabric pore structure are crucial. The pore structure properties, such as size, size distribution and connectivity, can be limiting factors in improving liquid retention, absorption, and penetration in hydrolyzed PET fabric. Any improvement in surface wetting following the enzyme reaction would have to be due to the hydrolyzing action of the lipases.

The polyester fabrics that reacted with lipase in the sodium phosphate buffer show clearly improved water sorption. Due to the large size of the enzyme molecules, PET hydrolysis by lipases were considered as a surface phenomenon. The question of whether and how much adsorption of the enzyme proteins occurs on PET is very important. Some level of affinity is necessary for the enzyme to take action on the fiber surface. On the other hand, significant adsorption can complicate the determination of improved surface permeability. Besides, the effects of exposure to denatured lipase on surface wetting are very important. It is known that the effect of exposure to the denatured protein on the wetting and sorption characteristics is adverse in inorganic buffer [20]. Therefore, the adsorption of denatured protein, if it occurs after a reaction, for instance, would only impede and not enhance the hydrolyzing effects of the lipases.

The results of breaking strength tests of the treated PET fabric samples were not as good as those of the

control fabric (a decrease of the breaking strength was visible). Moreover, a relatively long treatment time and the temperature probably resulted in structural reorganisation of the surface layers causing poorer results. The breaking strength and elongation of break of the enzyme-treated PET fabric (Table 3) were 148 daN (Lipase E3, time 120 min, warp direction) in the worst case and 151 daN (Lipase E2, 30 min, warp direction) in the best case (control sample 152 daN). Similar results were obtained in the weft direction of PET fabric. In general, changes in the fiber surface determined the behaviour of PET yarns and fabric during the investigation. The elongation of break slightly changed varying about the mean value.

The enzyme treatment causes perceptible changes of the fiber surface. These changes can be positive (sorption properties) and partly negative (mechanical properties) and they can influence the features of the fabric to a major or minor extent. It is well known that the mechanical properties of PET fibers, yarns and fabrics are very significant and their decrease can influence the behaviour of textile materials. The polyester fabric that reacted with lipase E3 in sodium phosphate buffer showed poorer mechanical properties, but better sorption properties. Lipase E3 improves water penetration and absorption more than the other lipases. The loss of tensile strength in this study must be caused

by microbial activity and not by chemical hydrolysis of the buffer solution [21].

After treatment, the wear resistance of the PET fabric decreased more than that of the control sample (Figure 2). All treatments caused an increase of the weight loss reducing the wear resistance of PET fabric and partly decreased the quality of the final goods. The deterioration in wear resistance properties was somewhat higher for 120 min than for 30 min. Prolonging the reaction time did not significantly lead to further improvement. Increasing reaction time appears to cause slight increases in the weight loss, and changes of other properties, but these changes were very small.

The surface of the polyester fibers was analyzed by scanning electron microscopy (SEM). The SEM photographs of the fiber surface are shown in Figure 3. The fiber surface was analyzed in order to follow the surface changes and physical properties of the fibers, i.e. fabric, during the course of the enzyme reaction.

We interpreted the effects of the enzyme treatments by comparing the micrographs of polyester fibers from different treatments and the micrographs of reference specimens (control polyester).

In our analysis, the control sample had a relatively smooth microscopic appearance with characteristic discrete prominence and less roughness. Figure 3-a shows a typical SEM micrograph of the control polyester fibers.

The micrograph of fibers from treatments in enzyme solutions had specific characteristics. The surface of enzyme-treated samples (Figs. 3-b and 3-c), indicated the appearance of peelings, differentiation and stratification of the surface layers of the fibers. Figures 3-b and 3-c showed certain damage of the polyester fiber surface. Active agent processing caused perceptible changes of the surface of the polyester fiber, which, ultimately, could derive from enzymes and/or their denatured parts.

Many researchers have studied the surface changes of polyester polymers after enzyme treatments. Some authors [20] measured the nitrogen contents of lipase-treated PET fabrics and determined that the protein adsorption following enzymatic hydrolysis is

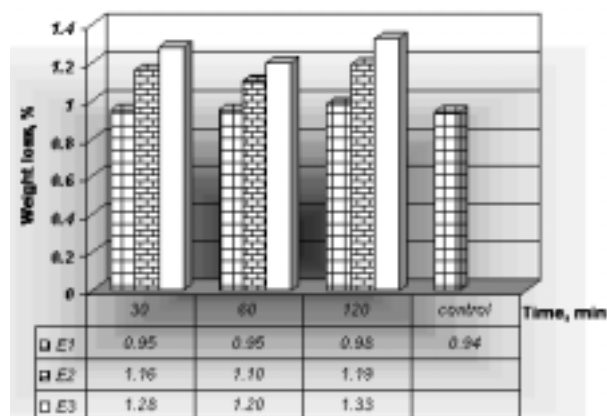


Figure 2. Effects of lipases on the wear resistance of PET fabric

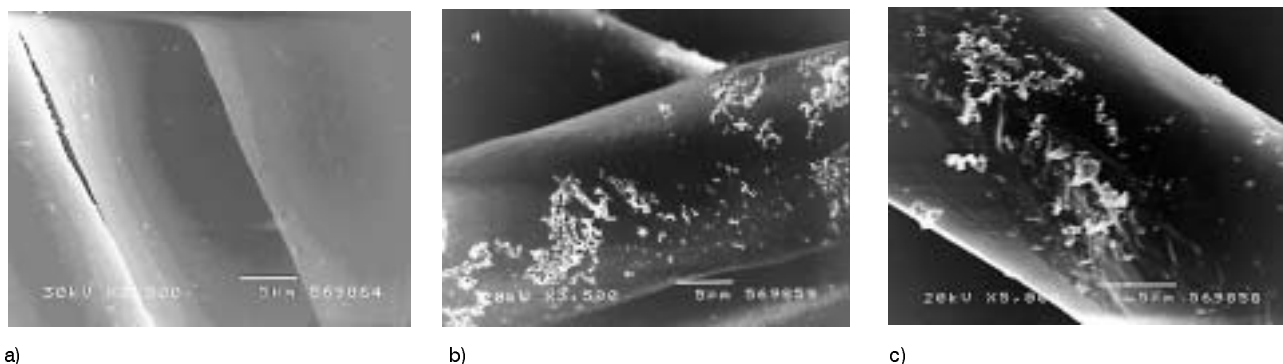


Figure 3. Micrograph of PET fibres: a) control sample; b) lipase E2-treated sample; c) lipase E3-treated sample

minimal or nil. Therefore, they concluded that the enzyme protein molecules from lipases did not adsorb onto the PET surface following hydrolysis. The improved surface wettability of the lipase-treated PET surfaces was associated with hydrolytic actions rather than protein adsorption. The hydrolytic action of lipases on esters and PET fibers should lead to the formation of hydroxyl and carboxylic groups or ester derivatives. Because of the sheer size of the enzyme molecules, the hydrolysis on polyester fibers is limited to the surface. Hydrolytic chain scissions can occur along the polyester chain and possibly the end unit. Only hydrolysis of the end unit may lead to a release of acid into the reaction solution [20].

Likewise, similar surface changes can be found in the SEM analysis of degraded polyhydroxyalkanoates, one of the largest groups of thermoplastic polyesters [22] which revealed the presence of hemispherical holes on the film surface due to colonization of the surface by microorganisms (enzymes). The formation of hemispherical holes on the film was attributed to the enzymatic actions of the cells attached to the film, indicating that degradation tended to occur in the colonization of the polyester surface by microorganisms [22].

Moreover, SEM investigations [21] showed that the damage after biodegradation (fungi and bacteria) was apparent as cracks in the surface of the polyester polyurethane. Many very small, short, cracks 2.5–20 μm long and approx. 1 μm wide had formed parallel to one another, together with fewer, larger, sometimes branching cracks 2.5 μm wide and >100 μm long. Multiple, parallel, narrow and short cracks appeared as did fewer, longer and wider cracks in many directions.

CONCLUSIONS

Lipases are an excellent alternative to classical organic techniques in the selective transformation of complex molecules. They possess many features that favour their use as an excellent biocatalyst. They impart specificity to a reaction in which a chemical process is typically more non-specific. In addition, the use of enzyme can decrease side reactions and simplify post-reaction separation problems. Lipase-catalysed processes also offer cost-effectiveness, in comparison with traditional downstream processing in which energy consumption and toxic by-products might often present a problem [19].

The results of the investigation presented in this paper have shown that enzymatic treatment with different lipases causes adequate effects, especially on the sorption properties and the mechanical parameters of the processed fabrics (strength, elongation, wear resistance). The process probably does not cause major damage of the fiber surface or major reorganisation of the surface layers of the PET fibers, so therefore their mechanical characteristics are satisfactory. The lipases

significantly improve water penetration and the absorbent properties of regular polyester fabric.

The surface of polyester fibers modified by enzyme treatment had unique characteristics as shown by SEM. These appearances reflect different degrees of enzymatic modification of the control polyester surface corresponding to different treatment conditions.

In our further investigation into enzyme applications, we intend to continue the evaluation of the effects of the applied type of enzyme (esterase, cutinase) in the process, by changing the concentration, temperature, bath ratio, buffer solution, pH, treatment time and application of surfactants. At present, enzyme application is a relative novelty in the textile industry, especially for synthetic materials, although further investigations should give more insight into the most appropriate process conditions and the specific character of the structure changes.

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IZVOD

MODIFIKACIJA POLIESTARSKE TKANINE NEKIM LIPAZAMA

(Naučni rad)

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U radu je istraživana mogućnost enzimске obrade poliestarske tkanine. Dobijeni rezultati pokazuju da obrade različitim lipazama daju odgovarajuće efekte, posebno kada se radi o penetraciji (kapilarnost) i adsorpciji vode kao i mehaničkim osobinama (jačina, izduženje, otpornost na habanje). Skening elektronska mikroskopija je iskorišćena za strukturno i morfološko razumevanje promena na površini poliestarskih vlakana u režimu obrade, koje su evidentne posle obrade enzimima. Rezultati potvrđuju da primenjeni enzimi imaju uticaja na površinu poliestarskih vlakana, uz činjenicu da obrade ne uzrokuju veća oštećenja površine kao i veću reorganizaciju u površinskim slojevima vlakana, što se potvrđuje i zadovoljavajućim mehaničkim osobinama.

Ključne reči: Poliestersko vlakno, Tkanina, Lipaze, SEM, Jačina, Izduženje, Otpornost na habanje, Penetracija vode, Adsorpcija vode.