Sorption properties during dyeing of enzyme-treated polyester fibers

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In this paper the process of sorption of a disperse dye on enzyme hydrolyzed polyester knitted fabric was researched. Hydrolysis with the enzyme esterase changes the surface morphology of the fibers, i.e., the peeling of the surface occurs, making the fibers more hydrophilic, which improves the sorption properties during dyeing. The process of dyeing hydrolyzed polyester knitted fabric gives better results compared to dyeing non-hydrolyzed fabric. A higher percentage of dye exhaustion occurs at the beginning of the dyeing process, while the percentage of dye exhaustion slows down over time. By increasing the dye concentration, the dye exhaustion on the fiber is reduced. A greater amount of dye in the solution or a longer dyeing time results in a greater amount of dye absorbed per unit mass of the textile, i.e., the highest absorption occurs at the highest dye concentration and the longest dyeing time.
Keywords: *sorption, dyeing, polyester, disperse dye, esterase*

1. Introduction

PET, poly(ethylene-terephthalate) is the most widely used synthetic fiber and accounts for nearly 80% of total synthetic fiber production. Due to its chemical composition and molecular structure, polyester fibers are very hydrophobic. The poor sorption properties and low ability to remove stains are the main reasons for the poor wearing comfort of clothes made of these fibers. These shortcomings can be overcome by increasing the hydrophilicity of the surface of polyester fibers, which can improve the efficiency of dyeing, finishing and functionalization [1].

Hydrophilicity can be achieved by various methods, such as: physical impregnation, plasma treatment, glow discharge, sol-gel process, macromolecule grafting, chemical treatment, etc. These methods require high energy consumption or the use of strong chemicals and are also not easily feasible [2].

Research into the application of biotechnology, i.e., enzymes, to improve the hydrophilicity of polyester fibers has become increasingly important in recent years because such hydrolysis process is environmentally friendly.

Recently, hydrolases of fungal and bacterial origin were reported to

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exhibit hydrolytic activity towards PET films and fibers. Among hydrolases, cutinases, lipases, esterases and their homologs showed the greatest potential for hydrolysis of PET [3-13].

Esterases act on glycerol esters of shorter fatty acids and, unlike most lipases, do not exhibit interfacial activity and lid structure. Apart from serine esterase originated from *Pseudomonas spp*. Or p-nitrobenzyl esterase from *Bacillus subtilis*, there are not many articles on the ability of esterases to hydrolyze PET [2,4]. Moreover, the use of esterases (which are closely related to lipases) enhances the absorption of chemical agents on polyester fabric, such as finishing agents, dyes, antistatic agents, antistain agents, antimicrobial agents, antiperspirants, etc. [5].

For example, samples of PET, nylon 6.6 and poly(methyl-methacrylate) were exposed to numerous enzyme solutions *in vitro*. PET was attacked by esterase and papain, although in different ways, but not by trypsin or chymotrypsin. Nylon 6.6 was not attacked by esterase but was degraded by the other three enzymes. None of these enzymes affected poly(methyl methacrylate). This suggests that some polymers are more sensitive to degradation by enzymes under certain conditions due to their structure, while others are not [6].

In this paper, a commercial esterase was used to modify PET knitted fabrics. The effect of hydrolysis was tested using the dyeing process of PET, which is an indicator of the hydrophilicity of the fibers, since the greater sorption of the disperse dye is a consequence of the greater hydrophilicity of PET. Therefore, the influence of enzymatic hydrolysis of PET on its dyeing properties was analyzed under lower temperature, atmospheric and no carrier conditions.

2. Experimental part

In this work, an untreated, undyed knitted fabric composed of 100% poly(ethylene-terephthalate) was used. The characteristics of the knitted fabric are: interlock knit, yarn fineness 10 tex, number of lines and strings per 1 cm is 16 and surface mass is 150 g/m^2.

The fabric was hydrolyzed with esterase from *Bacillus stearothermophilus* (Merck KGaA, Germany). Characteristics of the enzyme are: lyophilized form, specific activity ≥0.2 U/mg, thermostable. Hydrolysis was performed for 180 min with a bath ratio (0.1 M Tris-HCl buffer solution, pH 8) of 1:100 at a temperature of 70°C. The procedure was carried out in steel cuvettes with simultaneous agitation of solution and textile material (Linitest Hanau apparatus). Enzyme inactivation was then performed by immersing the polyester samples in hot water (90°C) at a bath ratio of 1:40 for 30 min. The fabric was then washed with a large amount of cold water and dried in a dryer at 80°C.

The morphology of polyester fibers was observed using a JEOL JSM 5300 scanning electron microscope (SEM) at 2000x and 5000x magnification.

The hydrolyzed PET knitted fabric was dyed with disperse dye C.I. Disperse Red 13. This dye is a monoazo dye with a molar mass of 348.8 g/mol. The structural formula of the dye obtained by software modeling (ChemBio Draw Ultra 14.0) is shown in Fig.1.

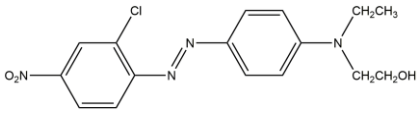


Fig.1 Structural formula of the disperse dye C.I. Disperse Red 13

The dye adsorption test was performed in such a way that 1 g mass sample of the knitted fabric was dyed in a solution with constant volume of 0.1 dm^3; the dye concentration was 50, 100, 200, 300 and 400 mg/dm^3. Distilled water was used for dyeing. The dyeing time was 10, 20, 30, 40, 50 and 60 min. The final time was 60 min, as it was shown that the degree of dye exhaustion did not change significantly with longer dyeing time. The aqueous dye solution contained a dispersing agent (CHT dispersant SMS), 1.5 g/dm^3 and formic acid (pH= 4.5), and the dyeing temperature was 100°C. The untreated sample was stained in the same way and was used to compare the results.

The dye exhaustion [7] was calculated according to the following equation:

$$\text{Dye Exhaustion} = \frac{C_0 - C_t}{C_0} \cdot 100 \ (\%) \quad (1)$$

where:

C_0 and C_t (mg/dm^3) are the initial concentration and the dye concentration at time t, respectively.

The amount of dye adsorbed [7] or sorption capacity is calculated using the following equations:

$$q_t = \frac{C_0 - C_t}{w} \cdot V \quad (2)$$

and

$$q_e = \frac{C_0 - Ce}{w} \cdot V \quad (3)$$

where:

q_t (mg/g), mass of adsorbed dye per unit mass of fabric at dyeing time t; q_e (mg/g), mass of adsorbed dye per unit mass of knitted fabric at equilibrium; C_0 (mg/dm^3), initial dye concentration; C_t (mg/dm^3), dye concentration in solution during dyeing time t; C_e (mg/dm^3), equilibrium concentration of dyes in solution; w (g), weight of knitted fabric; and V (dm^3), volume of dyeing solution.

3. Results and Discussion

Enzymatic hydrolysis of polyester by esterases results in the formation of polar hydroxyl and carboxyl groups on the surface due to the hydrolysis of ester bonds [8,9]. Enzymatic hydrolysis does not have a significant effect on the decrease in tensile strength, resulting in good mechanical properties, as the enzyme cannot penetrate into the fiber and therefore can only act on the surface, which also increases the wettability of the textile surface.

Esterase from *Bacillus stearothermophilus* is thermostable up to 70°C. This temperature is very close to the glass transition temperature of polyester, at which the amorphous regions of PET become more flexible and accessible to enzymes. In fact, enzymatic hydrolysis at a temperature close to T_g resulted in favorable effects on polyester, since at temperatures above 65°C (the glass transition temperature of PET), the amorphous parts of the polymer become more flexible and accessible to enzyme action.

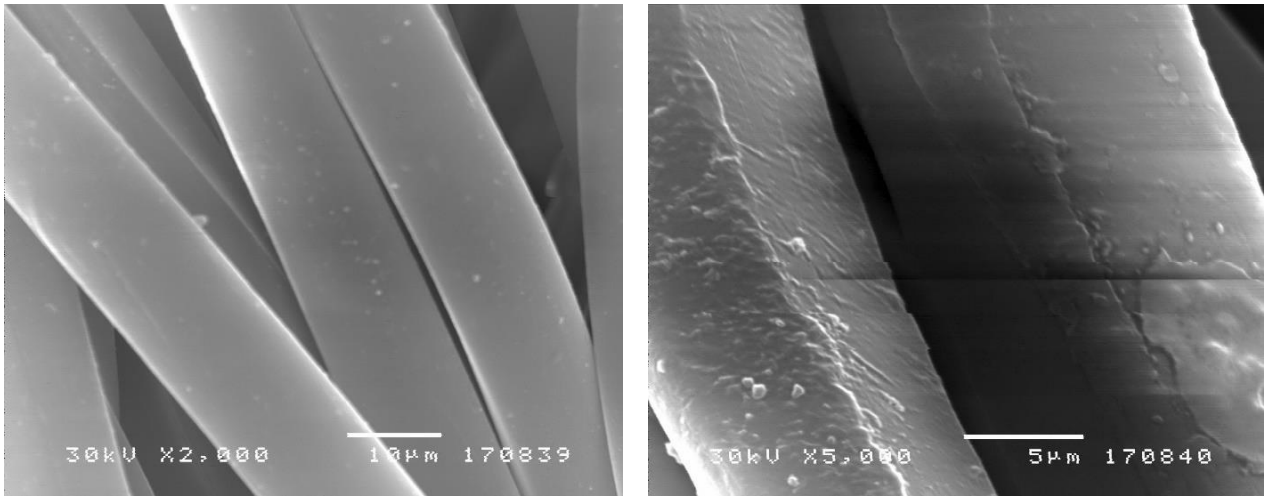
The effects of esterase hydrolysis of polyester can be tested by direct or indirect (by sorption of the dispersed dye during dyeing) method. Namely, if the dye sorption of the hydrolyzed sample is higher than that of the non-hydrolyzed sample, the esterase activity is confirmed because the fiber has become more hydrophilic. In this sense, hydrolyzed polyester fibers absorb more liquid, are less statically charged, have better touch, have less tendency to staining, etc.

Fig.2 shows surface micrographs of PET fibers before and after esterase hydrolysis with magnification of 2000x and 5000x, respectively. In contrast to the smooth surface of the non-hydrolyzed fibers, the changes on the surface of the hydrolyzed fibers are very noticeable because the peeling appears on the surface. The peeling of the surface improves the hydrophilicity of the fibers and changes the tactile properties of the knitted fabric so that touch of the fabric becomes similar to textiles made from natural fibers, as opposed to the characteristic tactile properties of synthetic textiles.

Compared to conventional alkaline hydrolysis, esterase hydrolysis is not only more environmentally friendly, but also better at maintaining the integrity of polyester fibers and their mechanical properties.

The influence of disperse dye concentration and dyeing time on the degree of dye exhaustion after enzymatic hydrolysis is shown graphically in Fig.3. A continuity of changes over time is shown, i.e., the longer the processing time, the higher the degree of dye exhaustion. At the beginning of the dyeing process, the percentage of dye exhaustion is higher, while it decreases with time. The linear parts of the curve represent diffusion in the surface layer, while the elevated parts of the curve correspond to diffusion in the pores. Increasing the dye concentration decreases the dye exhaustion on the fiber. Increasing the dye concentration in the solution initially results in a slightly greater decrease in the percentage of exhausted dye, but by the end of dyeing this decrease is 8-15% less for each individual dyeing time of 10 to 60 min.

The greater dye exhaustions can be explained by the well-known fact that the crystallinity of polyester fibers changes during hydrolysis, especially in the temperature range close to the glass transition temperature of polyester. The peeling of the surface promotes the diffusion of dye molecules into the free volume inside the fibers. The free volume changes due to both the thermal movement of the chains and the entry of dye molecules that enter this free space.



a) b)

Fig.2 Morphology of PET fibers a) before and b) after hydrolysis by esterases

The results of the change in the amount of absorbed dye on the enzyme hydrolyzed knitted fabric for different dye concentrations and dyeing times are shown graphically in Fig.4. A larger amount of dye in the solution or a longer dyeing time results in a larger amount of absorbed dye per unit mass of the textile, i.e., at the highest dye concentrations and the longest dyeing time, the maximum absorption occurs during the dyeing time.

In the literature, the possibility of using a commercial lipase enzyme as well as an enzyme produced in the laboratory from the microorganism *Penicillium sp*. OIL1 to modify polyester fabrics was researched. The results showed surface changes on the polyester fiber, i.e., improved sorption properties and dyeing. Dyeing with disperse dyes showed better binding of the dyes to the fiber, i.e., better exhaustion of the dyes from the dye baths. Since the enzymes are biodegradable and operate under mild conditions, such treatments represent a potential application for biodegradation of other polyester products due to their environmentally friendly properties [7, 10-13].

Comparison curves of the exhaustion and sorption capacity of non-hydrolyzed and enzyme hydrolyzed PET are shown in Fig.5. In both cases, the non-hydrolyzed sample has a lower dye sorption capacity.

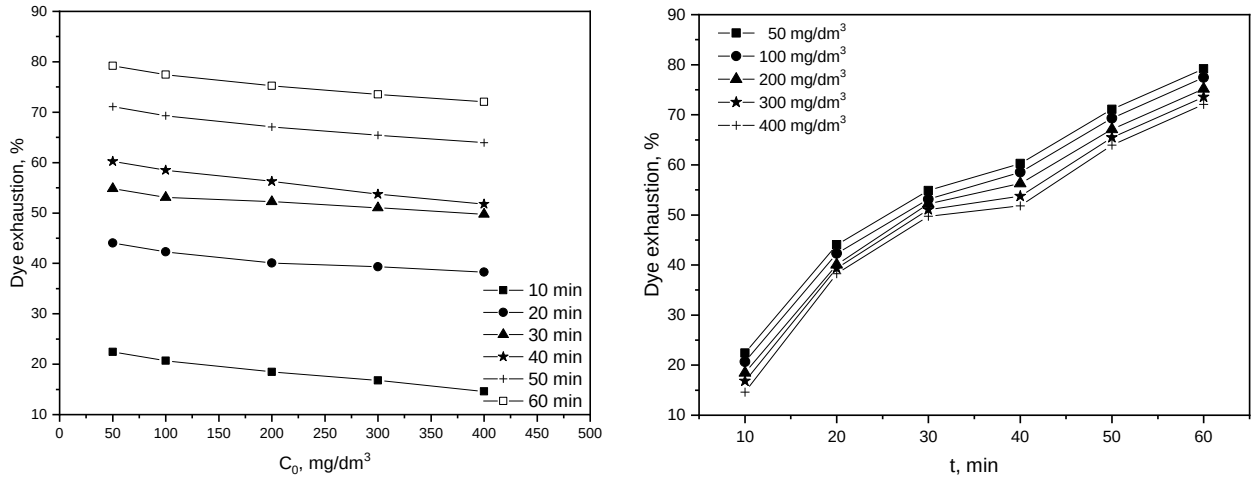


Fig.3 Influence of a) dye concentration and b) dyeing time on the degree of dye exhaustion after enzymatic hydrolysis of PET

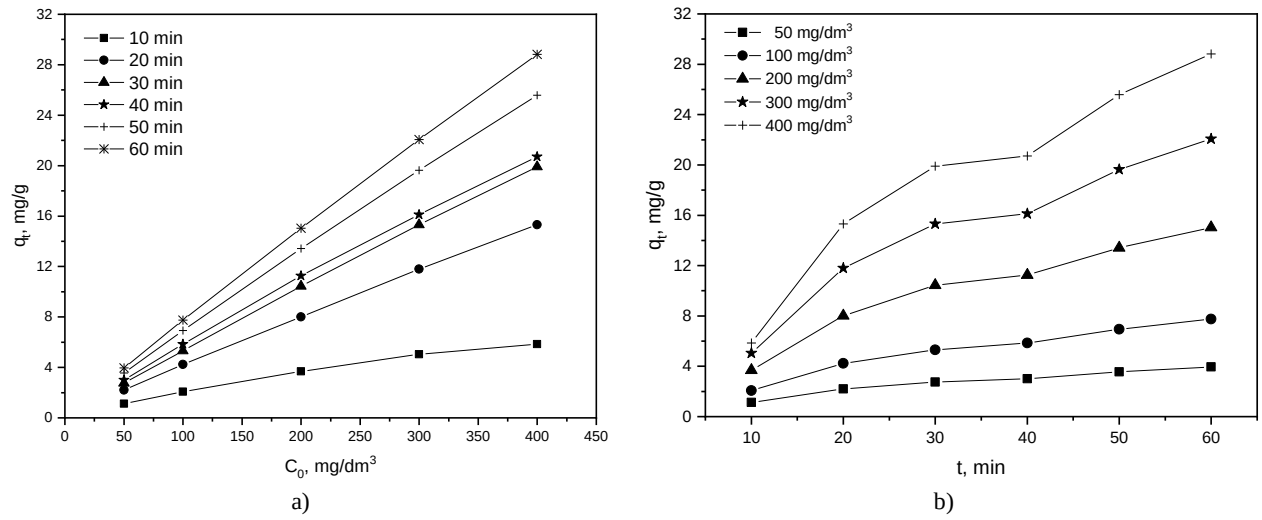
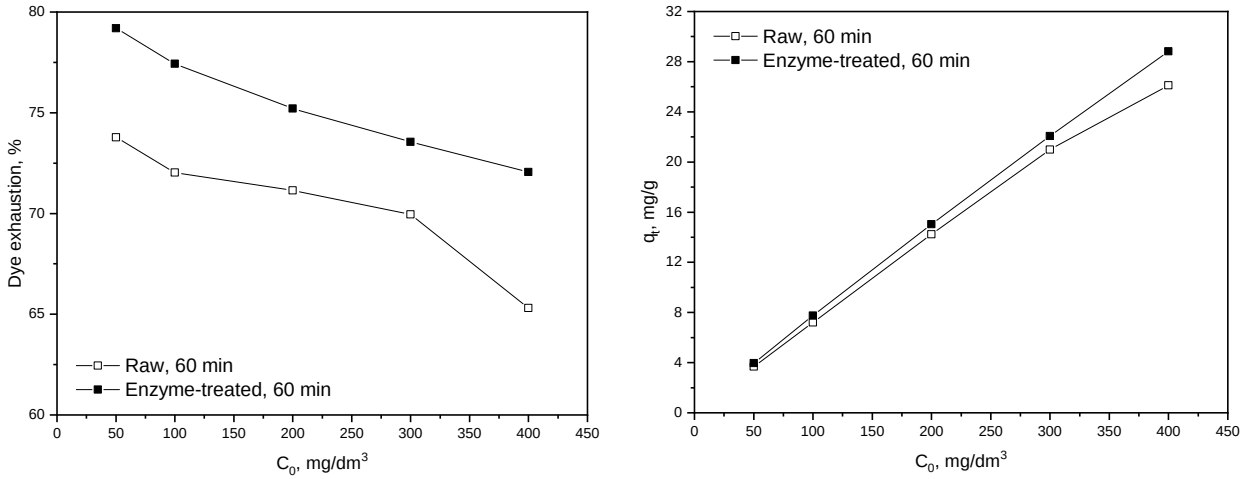


Fig.4 Influence of a) dye concentration and b) dyeing time on the amount of absorbed dye on the fabric after enzymatic hydrolysis of PET



a) b)

Fig.5 Comparison curves of sorption parameters of unhydrolyzed and enzyme hydrolyzed PET, a) dye exhaustion, b) the amount of absorbed dye vs. dye concentration

In Fig.5a the difference between untreated and hydrolyzed PET is larger, than in Fig.5b. The largest differences in sorption parameters were found at the highest concentration of 400 mg/dm^3.

It is considered that at higher dye concentrations, the peeled surface of the enzyme-hydrolyzed fibers absorbs more dyes due to the large amount of dyes around the fibers, taking into account the presence of a large concentration gradient between the solution and the fibers.

5. Conclusion

Hydrolysis with esterases enables the improvement of sorption properties of polyester textiles with an environmentally friendly approach.

The use of enzymes in textile technology is justified from an economic and sustainable point of view as well as for environmental reasons.

Hydrolysis of poly(ethylene-terephthalate) esterase showed the desired effects on the fibers, which was confirmed by microscopic images on electron microscope and by staining, taking into account the values of sorption parameters such as the degree of exhaustion. The enzyme hydrolyzed polyester exhibits better sorption parameters compared to the non-hydrolyzed sample, which suggests that the use of this type of esterase enzymes to increase the hydrophilicity of polyester is justified.

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