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THE INFLUENCE OF POLYESTER SURFACE MODIFICATION BY CUTINASE TO ITS ADSORPTION AND UV PROTECTION

Ivana Čorak, Tihana Dekanić, Lea Botteri, Anita Tarbuk
University of Zagreb Faculty of Textile Technology, Department of Textile Chemistry and Ecology, Zagreb, Croatia

Poly(ethylene-terephthalate) (PET) fabric has small absorption due to crystallinity of fiber. The conventional surface modifications, as alkali hydrolysis and aminolysis, are not eco-friendly, so the alternative methods have been researched. Since the application of enzymes is one of them, in this paper the cutinase surface modification of PET fabric was researched. The surface of light PET satin woven fabric was modified by cutinase (variation in concentration – 0.5, 1.5 and 15 g/l and temperature – 80 and 100°C) and compared to alkali hydrolysis. The adsorption of Fluorescent Brightener 135 (Ciba) was determined through fabric whiteness (W_{CIE}) according to ISO 105-J02:1997 on remission spectrophotometer Spectraflash 300, Datacolor. Fabric's air permeability was determined using M021S Air Permeability Tester, SDL ATLAS according to ISO 9237:1995. UV protection was determined on transmission spectrophotometer Cary 50/Solascreen, Varian according to AS/NZS 4399:1996. The cutinase treatment led to the PET fabric functionalization giving the same or even better results than alkali hydrolysis considering fabric whiteness and UV protection. The cutinase concentration of 0.5% owf proved to be enough if applied **at the** temperature higher than 100°C. If the temperature lower than of 80°C was applied, than the concentration of 1.5 g/l owf is optimal one.

Keywords: PET, cutinase, hydrolysis, UV protection, fabric whiteness

INTRODUCTION

Polyester fabric made of poly (ethylene-terephthalate) (PET) has low adsorption ability because it has extreme crystallinity and therefore small quantity of free active groups. To improve adsorption of dyestuff and auxiliaries surface modification is necessary. The conventional surface modifications, as alkali hydrolysis and aminolysis, are not eco-friendly, so the alternative methods have been researched [1-4]. Alkali hydrolysis of PET fabric is used for modification of its surface to achieve silk like material of improved comfort [2]. Hydroxyl anions are responsible for hydrolytic cleavage of ester bonds and removal of small PET monomers/oligomers from polymer material. It is

known that the alkali treatment is limited on PET surface that is exposed to liquid because high ionized components as liquid sodium hydroxide don't allow diffusion into the fabric owing to strong nonpolar environment of PET [3]. Aminolysis, ie using ethylene-diamine (EDA) results in creation of both amine and carboxylic acid functional groups on the polyester fiber surface [4].
Recently, it was discovered that aliphaticaromatic copolyesters and even aromatic polyesters, can be attacked and modified by lipolytic enzymes. Because of its size, enzymes are active on the surface of fabric so that the main characteristic of the fiber remains unaltered. Reactions take place in mild conditions, no complicated mechanism is required, as for example for the plasma or etching process and it is necessary to add little or no chemicals. Enzymes active on PET substrates include various cutinases, lipases, and esterases [5-7].

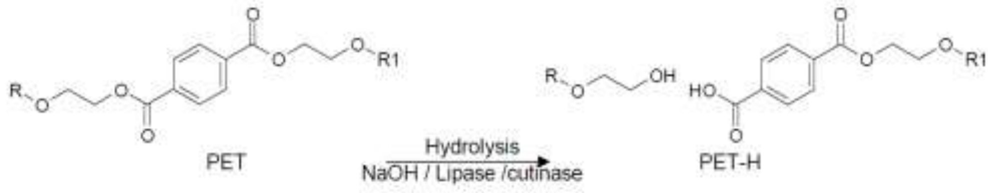


Figure 1. Hydrolysis of poly(ethylene terephthalate) [7]

For that purpose, in this paper the modification of surface of PET fabric with cutinase was researched to achieve better absorption, whiteness and UV protection in comparison to untreated and alkali hydrolyzed PET fabric.

MATERIALS AND METHODS

In this research light satin woven fabric of 100% poly (ethylene-terephthalate), PET, with a surface mass of 100 g/m^2 was used. The fabric was woven of textured multifilament yarns which are consisted of delustered fibers with trilobal cross section in warp and circular cross section in weft. Fineness of the yarn was 50 dtex (16f).
The surface of PET fabric was modified by cutinase (Novoenzymes) with the variation in enzyme concentration and process temperature (Table 1).

Table 1. Labels and treatment of PET fabrics

Label	Treatment / surface modification
PET	Untreated PET fabric
PET-H	Alkali hydrolyzed PET fabric
PET-conc.-T	Cutinase treatment: conc. = 0.5, 1.5, 15 g/l; T = 80 or 100°C

Fabric was treated in three enzyme concentrations 0.5, 1.5 and 15 g/l by batch wise method having LR 1:50, pH 7, at 80 or 100°C for 60 min in stainless-steel bowls (Linitest, Original-Hanau). After processing, it was firstly rinsed in hot water to remove oligomers and degradation products from surface, then warm and cold distilled water and air dried. Surface modification of PET fabrics was also modified by alkali hydrolysis which was performed in 1.5 mol/l NaOH with 2 g/l cationic surfactant Lyogen BPN (Sandoz) used as an accelerator by batch wise method, LR 1:50, for 10 min at 100°C in stainless-steel bowls (Linitest, Original-Hanau). It was rinsed in hot, warm and cold distilled water. Afterwards, it was neutralized using 1 wt% aqueous hydrochloric acid and rinsed with distilled water till pH 7 was achieved.

Air permeability of PET fabrics was determined using M021S Air Permeability Tester, SDL ATLAS according to ISO 9237:1995 *Determination of the Permeability of Fabrics to Air*. The size of the sample was 5,08 mm^2 ±1 mm^2 and the pressure 100 Pa.

The adsorption ability of modified PET fabric was determined indirectly from adsorption of fluorescent whitening agent (FWA) Uvitex ERN-P (Ciba) (Figure 2). Uvitex ERN-P, 2,2'-(1,2-ethenediyl)bis[5-methylbenzoxazole], Fluorescent Brightener 135, C.I. 45152 (Fig. 2) was applied in two concentrations of 1.2 and 2.4% owf by exhaustion method in stainless-steel bowls (Linitest, Original-Hanau), LR 1:50, 60 min at 120°C.

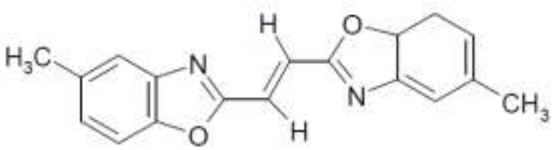


Figure 2. Fluorescent Brightener 135, C.I. 45152, Uvitex ERN-P (Ciba) [7]

From the measured remission on a remission spectrophotometer Spectraflash SF 600 PLUS-CT, tt. Datacolor, fabric whiteness (W_{CIE}) was calculated automatically according to ISO 105-J02:1997 *Textiles - Tests for colour fastness - Part J02: Instrumental assessment of relative whiteness.*

The UV protection ability of cutinase modified PET fabric was determined according to AS/NZS 4399:1996 *Sun protective clothing – Evaluation and classification* using transmission spectrophotometer Cary 50/ Solascreen, Varian.

RESULTS AND DISCUSSION

In this paper the cutinase surface modification of PET fabric was researched. The results are compared to alkali hydrolysis which is known as the best conventional modification of PET. Since the surface of light PET satin woven fabric was modified by cutinase, firstly the air permeability was determined. The results are presented in Figure 3. From the results it can be seen that untreated PET fabric has air permeability of 375 mm/s. Alkali hydrolysis degrade surface of fibers resulting in high air permeability, higher than 801 mm/s (limitation of instrument M021S Air Permeability Tester). Cutinase modified PET fabrics have improved air permeability. Fabrics modified at the temperature of 100°C have higher air permeability (>700 mm/s) than fabrics modified on lower temperature (>450 mm/s). By increasing the temperature, the air permeability increases, indicating higher effect of surface hydrolysis. The difference in air permeability regarding the cutinase concentration is not so meaningful.

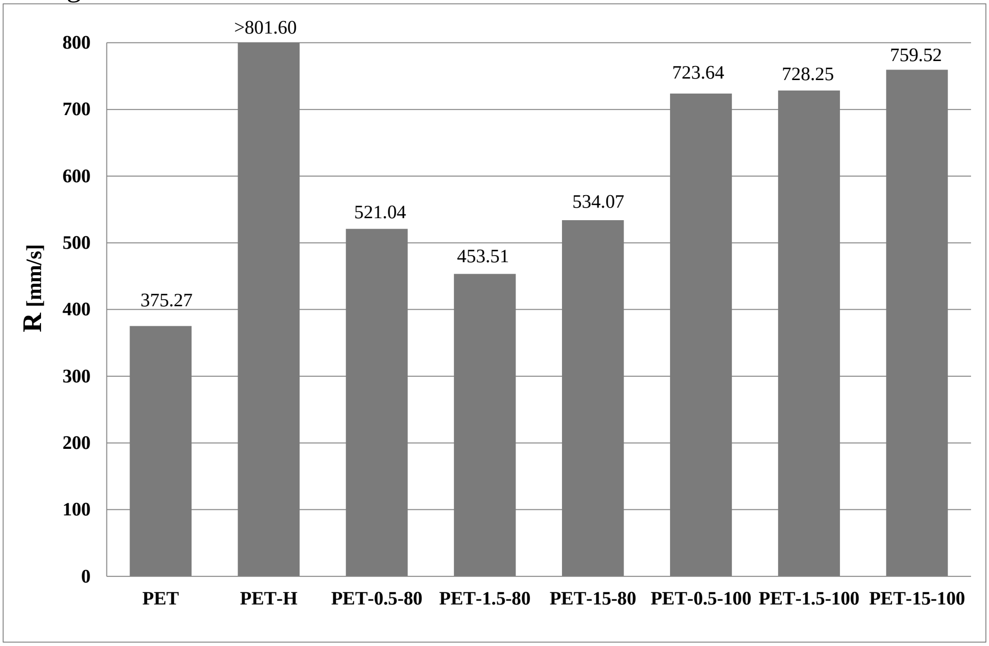
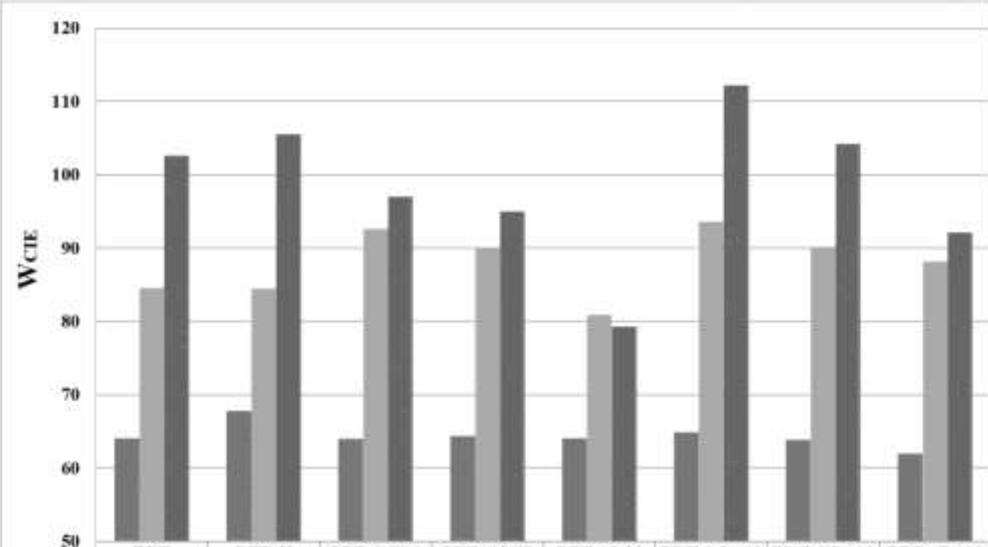


Figure 3. Air permeability through PET fabric after processing

The adsorption of Fluorescent Brightener 135 (Ciba) was determined through fabric whiteness (W_{CIE}) according to ISO 105-J02:1997 on remission spectrophotometer Spectraflash 300, Datacolor. For this FWA, according to literature [8] optimal concentration using exhaustion method for untreated polyester is 2.4% and for alkali hydrolyzed 1.2%. In order to determine adsorption ability of cutinase modified PET fabrics, FWA was applied in both concentrations 1.2 and 2.4% owf. The results are collected in Figure 4.

Untreated PET fabric shows whiteness degree according CIE (W_{CIE}) 64.1. Hydrolysis slightly changes whiteness. The alkali hydrolyzed fabric (PET-H) has the highest degree of whiteness 67.8, while cutinase treated have similar degree as untreated PET fabric. This shows that during alkali hydrolysis the best surface cleaning was achieved which led to improved whiteness.

Treatment with FWA results in higher whiteness regardless of applied concentration 1.2 or 2.4% owf. Untreated fabric has whiteness degree 84.6, which did not change on alkali hydrolyzed fabric, PET-H 84.5. However, treatment of all cutinase modified PET fabrics results in higher whiteness degree, indicating better adsorption. Considering the cutinase concentration, it is evident that 15 g/l results in the lowest whiteness degree suggesting not so good modification. The fabrics hydrolyzed by lowest cutinase concentration (0.5 g/l) shows the higher whiteness if compared to higher concentrations of cutinase (1.5 g/l and 15 g/l) through the same FWA concentration.



	PET	PET-H	PET-0.5-80	PET-1.5-80	PET-15-80	PET-0.5-100	PET-1.5-100	PET-15-100
0%	64.1	67.8	64.0	64.4	64.1	64.9	63.9	62.0
1.2%	84.6	84.5	92.6	89.9	80.9	93.6	90.2	88.2
2.4%	102.6	105.5	97.0	95.0	79.3	112.2	104.2	92.1

Figure 4. CIE whiteness of PET fabrics after the surface modification (0%) and FWA treatment (1.2 and 2.4% owf)

Considering applied temperature for modification it is evident that higher temperature of 100°C results in better surface activation. Such modified PET fabrics all have better whiteness suggesting higher adsorption of FWA. By increasing the concentration of the FWA, the whiteness increases. Optical brightening with 2.4% owf Uvitex ERN-P shows the highest whiteness degree, higher than 100.

Unmodified PET fabric treated with 2.4% owf FWA has W_{CIE} 102.6. Alkali hydrolyzed PET-H has better degree of 105.5 indicating better adsorption. Comparing cutinase treated PET fabrics to unmodified and alkali hydrolyzed it is evident that fabrics treated at lower temperature of 80°C have lower whiteness degree, whilst the ones treated on 100°C show higher. The highest whiteness degree of 112.2 has PET fabric treated with the lowest concentration of cutinase 0.5 g/l at 100°C, again suggesting the best adsorption is in modification with the lowest cutinase concentration on higher temperature.

Opposite to the opinion of most people that clothing provides UV protection, only 1/3 of summer clothing gives proper UV protection. It depends on a large number of factors such are type of fiber, fabric surface, construction, porosity, density, moisture content, type and concentration of dyestuff, fluorescent whitening agents (FWAs), UV-B protective agents (UV absorbers), as well as nanoparticles, if applied, which prevent transmission of UV-A and UV-B radiation through fabric [8-14]. By absorbing UV-A radiation optical brightened fabrics transform this radiation to blue fluorescence what leads to the better UV protection. Recently, the new fluorescent agents on the base of stilbene derivative were developed for UV-B protection as well, and can be used in textile finishing and care processes [12-14]. On the other hand, fabric porosity have influence as well [10]. The results of UV protection, determined on transmission spectrophotometer Cary 50/Solascreen, Varian according to AS/NZS 4399:1996 and expressed as Ultraviolet Protection Factor, UPF are presented in Tables 2-4.

Table 2. UV protection of PET fabrics after surface modification

Sample	**Mean UPF**	τ_{UVA}	τ_{UVB}	**St. dev.**	**St. error**	**UV Protection**	
PET	16.800	3.815	17.652	0.218	0.636	15	Good
PET-H	16.210	4.826	13.987	0.501	1.464	15	Good
PET-0.5-80	18.739	2.988	18.702	0.224	0.655	15	Good
PET-1.5-80	24.991	2.099	14.417	0.268	0.782	20	Good
PET-15-80	17.389	3.218	20.266	0.288	0.841	15	Good
PET-0.5-100	19.700	3.263	15.290	0.440	1.285	15	Good
PET-1.5-100	22.553	2.585	15.207	0.262	0.766	20	Good
PET-15-100	21.379	2.641	16.828	0.667	1.948	20	Good

Thou it is very light fabric of high porosity, due to benzene rings in the PET molecule which thanks to double bonds has the potential of adsorption of UV radiation, resulting in good UV protection. Hydrolysis results in porous fabric. As can be seen from the results of air permeability, porosity of alkali hydrolyzed fabric PET-H is high. However, even after treatment, it gives off good protection as well. The reason for that can be characteristic pits on surface which scatter UV-R [2]. Cutinase treated fabrics have higher UPF after treatment but give good UV protection as well. Since its surface is pealing, scattering is higher, regardless of increased porosity.

Table 3. UV protection of PET fabrics after treating with 1.2% Uvitex ERN-P (Ciba)

Sample	**Mean UPF**	τ_{UVA}	τ_{UVB}	**St. dev.**	**St. error**	**UV Protection**	
PET	41.291	1.343	7.735	1.288	3.761	35	Very good
PET-H	32.644	2.209	7.714	3.898	11.383	25	Very good
PET-0.5-80	30.425	1.831	10.713	0.987	2.883	30	Very good
PET-1.5-80	32.253	1.847	8.789	0.352	1.028	30	Very good
PET-15-80	21.666	3.025	12.497	0.508	1.483	20	Good
PET-0.5-100	33.190	1.808	8.538	0.746	2.178	30	Very good
PET-1.5-100	32.137	1.953	8.683	4.143	12.098	25	Very good
PET-15-100	25.387	2.641	10.149	1.791	5.229	20	Good

Table 4. UV protection of PET fabrics after treating with 2.4% Uvitex ERN-P (Ciba)

Sample	**Mean UPF**	τ_{UVA}	τ_{UVB}	**St. dev.**	**St. error**	**UV Protection**	
PET	24.728	2.895	8.847	1.042	3.044	20	Good
PET-H	22.810	3.457	8.048	0.472	1.378	20	Good
PET-0.5-80	28.127	2.388	8.556	0.237	0.692	25	Very good
PET-1.5-80	27.374	2.138	10.492	0.854	2.494	25	Very good
PET-15-80	24.745	2.657	10.993	1.589	4.639	20	Good
PET-0.5-100	27.529	2.565	7.933	1.423	4.154	25	Very good
PET-1.5-100	22.154	3.446	8.618	1.067	3.116	20	Good
PET-15-100	28.972	2.229	8.983	0.794	2.317	25	Very good

Treatment with FWA, regardless of concentration, results in higher UPF. It can be noticed that at fabrics that shown the highest whiteness the UPF is highest. The reason for that is in FWA mechanism. Based on electronically-excited state by energy of UV-R (usually 340-370 nm) the FWA molecules show the phenomenon of fluorescence giving to white textiles the high whiteness of outstanding brightness by reemitting the energy at the blue region (typically 420-470 nm) of the spectrum [14]. The highest UV protection is noticed at fabrics treated with 1.2% owf FWA suggesting that higher concentration is not necessary. However, whiteness degree is better in higher concentration of 2.4% owf.
Considering the temperature of cutinase treatment it can be seen from the results of UV protection there is no difference. Considering the concentration, once more, the lowest concentration of cutinase 0.5 g/l proved to be enough to achieve same results, or even the best UV protection.

CONCLUSIONS

The cutinase treatment led to the PET fabric functionalization giving the same or even better results than alkali hydrolysis considering fabric whiteness and UV protection. The cutinase concentration of 0.5% owf proved to be enough if applied on higher temperature of 100°C. If the lower temperature of 80°C was applied, the optimal concentration is 1.5 g/l owf.

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IZVOD

UTICAJ MODIFIKOVANJA POLIESTERSKE POVRSINE KUTINAZOM NA NJENU ADSORPCIJU I UV ZAŠTITU

Ivana Čorak, Tihana Dekanić, Lea Botteri, Anita Tarbuk
Univerzitet u Zagrebu, Tekstilno-tehnološki fakultet, Katedra za hemiju I ekologiju tekstila, Zagreb, Hrvatska

Poli(etilen-tereftalat) (PET) tkanina ima malu absorpciju zbog kristaliniteta vlakna. Konvencionalne modifikacije površine, kao sto su alkalna hidroliza i aminoliza, nisu ekološki podobne, pa se istražuju alternativni metodi. Pošto je primena enzima jedan od tih metoda, u ovom radu istraživana je modifikacija kutinazom površine PET tkanine. Površina svetle (ili lagane) PET satenske tkane tkanine modifikovana je kutinazom (varijacije u koncentraciji – 0.5, 1.5 i 15 g/l i temperature – 80 i 100^0 C) i uporedjivana sa alkalnom hidrolizom. Adsorpcija fluorescentnog posvetljivača 135 (Ciba) odredjena je kroz belinu tkanine (W_{CIE}) u skladu sa ISO 105-J02:1997 na remisionom spektrofotometru Spectraflash 300, Datacolor. Propustljivost tkanine na vazduh odredjena je korišćenjem M021S Air Permeability testera, SDL ATLAS u skladu sa ISO 9237:1995. UV zaštita odredjena je na transmisionom spektrofotometru Cary 50/Solascreen Varian, u skladu sa AS/NZS 4399:1996. Tretman kutinazom doveo je do funkcionalizacije PET tkanine dajući jednake ili čak bolje rezultate od alkalne hidrolize, u pogledu beline tkanine i UV zaštite. Koncentracija kutinaze od 0.5% owf pokazala se dovoljnom kad je primenjivana na temperaturi visoj od 100^0C. Ukoliko je korišćena temperatura niza od 80^0C onda je optimalna koncentracija bila 1.5 g/l owf.

Ključne reci : PET, kutinaza, hidroliza, UV zaštita, belina tkanine