Lipases Improve the Grafting of Poly(ethylene terephthalate) Fabrics with Acrylic Acid

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ABSTRACT: In this study, poly(ethylene terephthalate) (PET) fabrics were modified with two types of commercial lipases, namely, Lipex and Lipolase, and grafted with acrylic acid (AA) to improve their absorption properties. The effects of the enzyme concentration, reaction temperature, time, and pH on the grafting of AA onto PET were investigated. The pretreatment of PET with lipases increased the amount of AA that was introduced to the PET fibers, whereas AA grafting onto the untreated PET fabrics led to lower graft yields. Fourier transform infrared spectroscopy and scanning electron microscopy were used to characterize the AA-grafted pretreated polyester fabrics. A new band appearing at 1546 cm^{-1} in the Fourier transform infrared spectrum implied that AA was introduced onto the PET fabrics. The surfaces of the fabric fibers presented in scanning electron microscopy micrographs clearly indicated the formation of a layer of grafted poly (acrylic acid). The results show that the density of surface grafting was improved by the lipase pretreatment. The increase in grafting was higher for Lipex than for Lipolase. The highest graft yield was obtained with 1% Lipex and Lipolase for 30 min at pH values of 7 and 5, respectively. There were no significant changes in the tenacity or weight reduction of the fabrics. The moisture content of the samples increased linearly with increasing graft yield. This was higher for the pretreated fabrics grafted with Lipex. A higher color strength was obtained for grafted PET samples that were pretreated with Lipex when they were dyed in alkaline aqueous solutions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 116: 203–209, 2010

Key words: enzymes; fibers; modification; polyesters

INTRODUCTION

Poly(ethylene terephthalate) (PET) is the most important polymer used for the production of synthetic textile fibers. Today, not only is the demand for PET textile fibers increasing but also the desire to improve its properties, such as wettability and hydrophilicity, is high. Furthermore, effects, such as a better dyeability with water-soluble dyes and surface fictionalization for special purposes such as the coupling of flame retardants, are desirable from the perspective of the textile industry.

Graft copolymerization is one effective method for the improvement of undesirable properties, such as low moisture regain, difficult dyeing, and poor antistatic properties due to its high crystallinity, and hydrophobicity, or to furnish PET with new properties. The essential fiber properties of the PET backbone are not affected; however, the fibers acquire new properties that depend on the grafted monomer or monomers. Vinyl monomers, such as acrylic acid (AA),[1–3] methacrylic acid,[4,5] polyaniline,[6] and acrylamide,[7] can be grafted onto PET fibers by chemical[1,3,4,7] or radiation initiation.[2]

In addition to graft copolymerization, the enzymatic modification of synthetic materials has immense potential for specialty applications, such as medical devices and electronics.[8,9] Enzymatic treatments have the advantage of lower energy consumption and the use of no harsh chemicals, compared with chemical surface treatment. Enzymes have been used for the improvement of the properties of natural polymers, such as polysaccharides, proteins, and lignocellulose materials, for many years.[10,11] Obviously, such enzymes have been isolated from microorganisms that are responsible for the decomposition of these natural polymers in the environment. Although such an approach is difficult for synthetic polymers, the potential of enzymes for their modification has been reported. Nitrilases have been used for the hydrolysis of nitrile groups and polyacrylonitrile,[12,13] and oxidative enzymes have shown potential for the modification of polyamide fibers.[14,15] Fundamentally, a great variety of enzymes could be used to modify the surface of PET. Among the hydrolytic enzymes, in addition to esterases and lipases, enzymes acting on natural polyesters, such as cutinases or polyhydroxyalkanoate depolymerases, could have potential use in fabric modification.[16–19]

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Previously, the treatment of PET with lipases was shown to improve the wetting and absorbency of PET fabrics with the retention of strength.[19] Compared to chemical hydrolysis by alkali treatment, enzymatic surface hydrolysis has the advantage of maintaining mechanical stability because this enzyme cannot penetrate into the fiber and is, therefore, restricted to reacting on the surface only. Improved stain resistance, wettability, and/or dyeability of PET-treated fabrics were reported with the so-called polyesterases (lipases, esterases, or cutinases).[20]

Although results from the modification of PET fibers with grafting copolymerization and enzymes have been obtained separately in different studies, more new investigations on the combination of both treatments would be effective for finding some new results of the graft yield efficiency. In this research, we tried to pretreat PET fabrics with lipases to modify the fabric surface and to place some reactive groups on the fabric surface, so it would easily accept AA for grafting on its surface. To this end, fabrics were pretreated by commercial lipases, namely, Lipex and Lipolase, and then grafted with AA. This study was undertaken, first, with a view of studying different parameters that affect the grafting of PET fabrics with AA, with benzoyl peroxide (Bz_2O_2) as an initiator, to determine the optimal graft polymerization conditions. Then, the effects of the enzyme concentration, reaction time, and temperature as a pretreatment process on grafting were investigated in detail and are discussed. The wettability, dyeability with water-soluble dyes, and mechanical properties of the grafted fabrics were determined. The grafted fabrics were also characterized pretreated pretreated with Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The fabric samples used were a plain-weave PET fabric (warp and weft: 110 dtex and 94.5 g/m^2, respectively). AA, Bz_2O_2, and other chemicals used in this study were obtained from Merck Chemical Co. (Darmstadt, Germany). The lipases (Lipex and Lipolase) were gifts from Novozyme, Inc. (Bagsvaerd, Denmark).

Methods

Before enzymatic treatment, fabrics were washed with an aqueous nonionic detergent solution (1 g/L) at 60°C for 30 min and dried in an oven at 40°C for 24 h.

The enzymatic treatments were carried out at 30, 60, and 70°C with Lipex and Lipolase at different concentrations of 0.5, 1, and 1.5% at pH's of 5, 7, and 9 for 15, 30, and 60 min with a reciprocal shaker at 50 rpm for agitation. The same preparation was applied for the fibers without enzyme as a blank sample. After the treatment, the fabrics were washed once with a sodium carbonate solution in double-distilled water and then with demineralized water, each for 30 min at room temperature. Each experiment was carried out three times, and the mean values are reported.

The grafting process was carried out with a mixture containing the polyester fabric (10 × 10 cm^2), monomer, and Bz_2O_2 at the required concentration. The effects of various experimental conditions, such as initiator and monomer concentrations, temperature, and monomer/mixture ratio, were investigated. PET fabric was placed in a 100-mL polymerization tube containing the required concentrations of monomer and initiator. The volume of the polymerization mixture was made up to 100 mL with distilled water, and then, the mixture was immediately placed into a water bath at the polymerization temperature. After the grafting procedure and desired polymerization time, the sample was taken out and washed with boiling distilled water for 4 h to be purified by extraction of the unreacted monomers and homopolymers. Finally, the sample was dried for 30 min at 110°C with a constant weight maintained. The graft yield percentage was calculated from the increase in the weight of the original PET after grafting and calculated by the following equation:

$$\text{Graft yield } (\%) = [(w_2 - w_1)/w_1] \times 100$$

where w_1 and w_2 denote the weights of the original PET and grafted PET, respectively.

The properties of the enzyme-treated samples were investigated by determination of the wettability, a measurement of the hydrophilicity of the PET fabrics. The BS 3449 method of testing for the wettability measurements and the time in seconds needed for a drop of water to sink into the fabric were used.[21] Five areas on each sample were tested, for three samples in all, to give a total of 15 measurements.

Handle properties, assessed by touch, depend on the fabric stiffness. The BS 3356 method was applied for the determination of the bending length of the fabrics.[22] The samples were each 25 mm wide and 200 mm long; there were three samples cut parallel to the warp and three samples cut parallel to the weft.

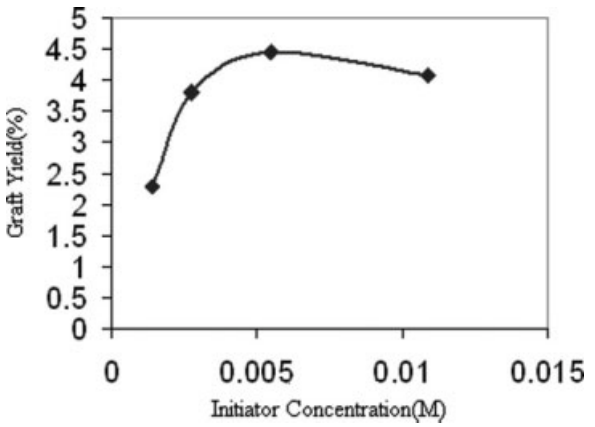

Figure 1 Effect of the Bz_2O_2 concentration on the grafting yield (AA concentration = 0.1 mol/L, time = 2 h, temperature = 85°C).

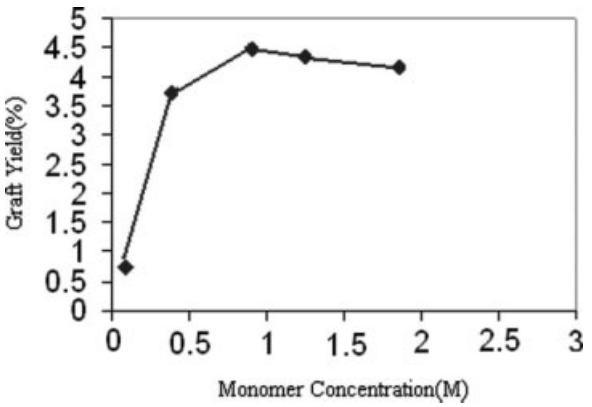

Figure 2 Effect of the AA concentration on the grafting yield (time = 2 h, temperature = 80°C).

To elucidate the surface morphology changes of the untreated, grafted, and enzyme-pretreated grafted fibers under different conditions, the micrographs of the investigated samples were examined by means of a Philips XL30 scanning electron microscope (Eindhoven, Netherlands) at 7 kV. The fibers were coated with a thin layer of gold to prevent charging in the microscope. The attenuated total reflectance technique was used. A Nicolet Nexus 670 FTIR spectrometer (USA) with a germanium crystal was used. The attenuated total reflectance/infrared spectra of the PET fabric surfaces before and after different treatments were obtained to evaluate the produced chemical changes. The spectra were recorded from 500 to 4000 cm^{-1}. Tensile tests were carried out with an Instron model TM-SM (USA). Five fabric samples were cut in the warp way to a size of 70 × 15 mm^2. The rate of extension was set to 12.5 cm/min. PET fabrics were dyed in a Atlas Linitest (USA) laboratory dyeing machine in the presence of the proprietary anionic leveling agent Levegal PEW (Dystar, Germany) (0.4 wt % of the fabric). A dye bath was prepared with a dispersing agent [Avolan IW and acetic acid (1.0 mL/L)] and adjusted to pH 4.5. A basic dye (Astrazon Blue FGGL, Ciba-Geigy, Switzerland) was used to dye the fabrics; the dye weight was 0.8% of the fabric. A certain weight of the fabric was immersed into the dyeing solution for 10 min at 70°C, The solution was then heated at a rate of 1°C/min to 96°C, and the temperature was kept constant for 50 min. The dyed specimens were fully washed with distilled water and then dried at room temperature for 24 h. The colorimetric properties of the samples were obtained by a ColorEye 7000A (USA). The average values of the lightness (L^*), redness–greenness (a^*), yellowness–blueness (b^*), and color difference with respect to a blank sample (ΔE) were recorded.

RESULTS AND DISCUSSION

Figure 1 shows the effect of Bz_2O_2 concentration on the rate of grafting obtained when AA was polymerized in the presence of the PET fabrics. The graft yield increased significantly with increasing initiator concentration up to 5.48 × 10^{-3} M and then decreased with further increases in the Bz_2O_2 concentration when the other variables, such as temperature, time of reaction, and concentration, were fixed. Because the number of radicals increased as a result of an increase in the concentration of the initiator, the number of active sites in the PET chain became greater, and the reaction increased as well. Further increases in the Bz_2O_2 concentration made the rate of terminal reactions increase. As shown in Figure 1, the maximum grafting was about 4.5%. The polymerization reaction was carried out at various concentrations of the monomer. Figure 2 shows the effect of AA concentration on the percentage grafting. The maximum yield of grafting was

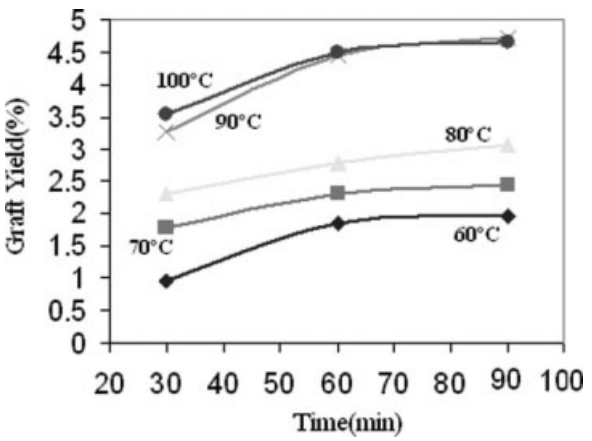

Figure 3 Graft polymerization of PET fabrics with AA at different temperatures and times.

TABLE I
Effects of the pH, Temperature, and Time on the Properties of the PET Fabrics Pretreated with 1% Lipolase

	pH at 60°C for 30 min		
	5	7	9
Weight loss (%)	1.23 ± 0.1	1.01 ± 0.1	0.50 ± 0.1
Weight gain with grafting (%)	7.03 ± 0.3	6.27 ± 0.3	5.14 ± 0.3
Strength loss (%)	2.31 ± 0.1	2.00 ± 0.2	1.73 ± 0.2
Moisture regain (%)	0.78 ± 0.05	0.77 ± 0.05	0.77 ± 0.05
	Temperature (°C) at pH 5 for 30 min		
	30	60	70
Weight loss (%)	0.87 ± 0.1	1.23 ± 0.1	1.27 ± 0.1
Weight gain with grafting (%)	6.31 ± 0.3	7.04 ± 0.3	7.10 ± 0.3
Strength loss (%)	1.89 ± 0.2	2.37 ± 0.2	2.47 ± 0.2
Moisture regain (%)	0.77 ± 0.05	0.78 ± 0.05	0.78 ± 0.05
	Time (min) at 60°C and pH 5		
	15	30	60
Weight loss (%)	0.70 ± 0.1	1.22 ± 0.1	1.31 ± 0.1
Weight gain with grafting (%)	6.11 ± 0.2	6.98 ± 0.2	7.01 ± 0.2
Strength loss (%)	1.80 ± 0.2	2.31 ± 0.2	2.69 ± 0.2
Moisture regain (%)	0.77 ± 0.05	0.78 ± 0.05	0.79 ± 0.05

TABLE III
Effects of the pH, Temperature, and Time on the Properties of the PET Fabrics Pretreated with 1% Lipex

	pH at 60°C for 30 min		
	5	7	9
Weight loss (%)	1.21 ± 0.1	1.86 ± 0.1	1.50 ± 0.1
Weight gain with grafting (%)	7.03 ± 0.2	9.11 ± 0.3	6.94 ± 0.2
Strength loss (%)	2.22 ± 0.1	2.79 ± 0.1	2.01 ± 0.1
Moisture regain (%)	0.78 ± 0.05	0.81 ± 0.05	0.77 ± 0.05
	Temperature (°C) at pH 5 for 30 min		
	30	60	70
Weight loss (%)	1.85 ± 0.1	1.45 ± 0.1	1.00 ± 0.1
Weight gain with grafting (%)	9.11 ± 0.3	7.37 ± 02	6.44 ± 0.2
Strength loss (%)	2.79 ± 0.1	2.34 ± 0.1	2.14 ± 0.1
Moisture regain (%)	0.81 ± 0.05	0.78 ± 0.05	0.77 ± 0.05
	Time (min) at pH 5 at 60°C		
	15	30	60
Weight loss (%)	0.98 ± 0.1	1.86 ± 0.1	1.92 ± 0.1
Weight gain with grafting (%)	7.08 ± 0.2	9.12 ± 0.3	9.09 ± 0.3
Strength loss (%)	2.00 ± 0.1	2.78 ± 0.1	3.01 ± 0.1
Moisture regain (%)	0.77 ± 0.05	0.81 ± 0.05	0.82 ± 0.05

obtained at a monomer concentration of 0.93*M*. A higher concentration of AA led to a small decrease in grafting.

Figure 3 shows the graft polymerization at five different temperatures ranging from 60 to 100°C for various times. When the temperature was increased, the grafting yields and rates of reaction increased. The higher grafting efficiency at higher temperatures may have been connected with a higher decomposition rate of Bz_2O_2 and a possible reaction between the macroradical of AA and the radical of PET. In addition, at a temperature higher than the glass-transition temperature of PET, the PET molecules went far from each other and were inflated. Therefore, the flexibility of the PET chain increased and led to higher grafting yield. An increase in the polymerization temperature from 90 to 100°C was accompanied by no significant enhancement in the rate of homopolymerization.

The most suitable time for the polymerization reaction was 60 min. After this time, the viscosity of environment increased because of a homopolymerization reaction in the system, and this provided less accessibility to the reactive groups of PET.

The results of the enzymatic pretreatment conditions (pH, temperature, concentration, and length of reaction time) on some properties of the fabrics, such as weight loss, weight gain after grafting, strength loss, and moisture regain, are shown in Tables I and II and Tables III and IV for Lipolase and for Lipex, respectively.

The results in Table I show that the maximum weight loss and weight gain after grafting with AA occurred with Lipolase at pH 5. The density of surface grafting for Lipolase-pretreated samples at 70°C was higher than that of the other samples (Table I).

TABLE II
Effects of the Pretreatment Lipolase Concentration on the Properties of the PET Fabrics at pH 5 and 60°C for 30 min

	Concentration (%)		
	0.5	1	1.5
Weight loss (%)	0.64 ± 0.1	1.23 ± 0.1	1.29 ± 0.1
Weight gain with grafting (%)	5.49 ± 0.2	6.98 ± 0.3	7.05 ± 0.3
Strength loss (%)	1.79 ± 0.1	2.31 ± 0.1	2.33 ± 0.1
Moisture regain (%)	0.76 ± 0.05	0.78 ± 0.05	0.78 ± 0.05

TABLE IV
Effects of the Pretreatment Lipex Concentration on the Properties of the PET Fabrics at pH 5 and 60°C for 30 min

	Concentration (%)		
	0.5	1	1.5
Weight loss (%)	1.05 ± 0.1	1.86 ± 0.1	1.88 ± 0.1
Weight gain with grafting (%)	7.32 ± 0.2	9.11 ± 0.3	9.15 ± 0.3
Strength loss (%)	2.09 ± 0.1	2.79 ± 0.1	2.83 ± 0.1
Moisture regain (%)	0.77 ± 0.05	0.81 ± 0.05	0.81 ± 0.05

TABLE V
Different Properties of the Untreated PET Fabrics and PET Fabrics Pretreated with Enzymes

Sample	Test results						
	Graft yield (%)	Wetting time (s)	Bending length (cm)		Moisture regain (%)	Breaking load (kgf)	Elongation at break (%)
			Warp way	Weft way			
Raw	0	95.8 ± 6	2.6 ± 0.09	1.5 ± 0.05	0.43 ± 0.05	2 ± 0.9	38.1 ± 2.1
Without pretreatment	3.81	82.3 ± 3	2.5 ± 0.05	1.4 ± 0.04	0.57 ± 0.07	2.4 ± 1.1	35.7 ± 1.9
Pretreated with Lipolase	6.98	70.2 ± 4	2.3 ± 0.04	1.2 ± 0.06	0.78 ± 0.07	4.1 ± 0.7	33.5 ± 1.3
Pretreated with Lipex	9.11	44.6 ± 3	2.2 ± 0.05	1 ± 0.12	0.81 ± 0.05	4.9 ± 0.5	30.4 ± 1.7

A 1% enzyme concentration at 30°C for 30 min was used for the pretreated fabrics.

There were also no significant changes in weight gain after grafting and moisture regain for samples treated for 30 and 60 min (Table I). It seemed very close at both 70 and 60°C. There was no significant difference in the amount of graft yield between enzyme concentrations of 1 and 1.5% (Table II).

As shown in Table III, the maximum weight loss of the Lipex-pretreated samples was at pH 7. The greatest surface grafting density and moisture regain for Lipex occurred at 30°C (Table III). There was no significant difference between the amount of graft yield and moisture regain for fabrics pretreated with enzyme for 30 and 60 min (Table III). The results obtained with 1 and 1.5% enzyme concentrations for the grafting yield and the moisture regain were very close to each other (Table IV).

Table V shows some important properties of the untreated and enzyme-pretreated PET fabrics under the optimal conditions (1% concentration at 30°C for 30 min).

The polyester fabrics pretreated with enzyme clearly showed improved water wettability. The Lipex-type enzyme improved the water wetting and absorption of the polyester fabrics more than the Lipolase-type enzyme. The enzyme reaction was also shorter. The improved water wettability was accompanied with strength, and there were no significant changes in the tenacity and weight loss of fabrics because of the enzyme surface modification of the fibers. The moisture content increased with increasing graft yield. This property in the grafted fabrics pretreated with Lipex was much higher than in the other samples. The results also show that the density of surface grafting was enhanced by enzyme pretreatment. This enhancement by Lipex enzymatic treatment was more efficient than that of Lipolase. The greatest graft yield was obtained by a 1% concentration and a 30-min treatment time for the Lipex and Lipolase enzymes at pH values of 7 and 5, respectively. The SEM micrographs (Fig. 4) well confirmed the aforementioned results. Figure 4(a) shows the SEM micrograph of the untreated PET fibers, and Figure 4(b,c) summarize the results of enzyme-pretreated AA-*graft*-PET for two types of enzyme. The smooth surface of the original PET fiber turned rough.

Figures 5 and 6 show the FTIR spectra of the untreated and treated PET fabrics. The results obtained from the FTIR spectrum of the grafted PET show a peak at 1546 cm^{-1} related to RCOO groups. As shown in Figure 5, the absorption band in this region appeared to weaken for the untreated sample. There was a significant intensity change in this band for the enzyme-pretreated samples. This suggests that more polar groups of COOH in the AA structure grafted to the PET chain existed in the enzyme-pretreated samples. The intensity of this band was

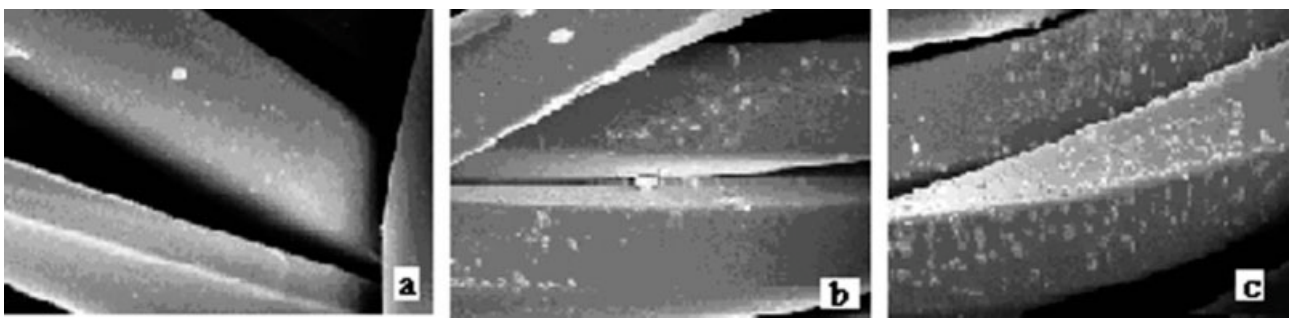

Figure 4 SEM micrographs of PET fibers: (a) untreated, (b) grafted with AA, and (c) pretreated with an enzyme (Lipex) and grafted with AA.

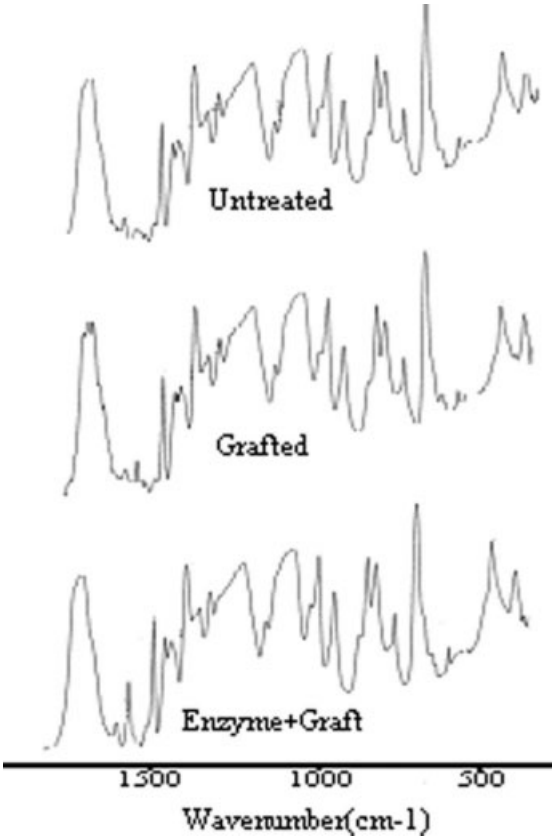

Figure 5 FTIR spectra of untreated and treated PET fabrics.

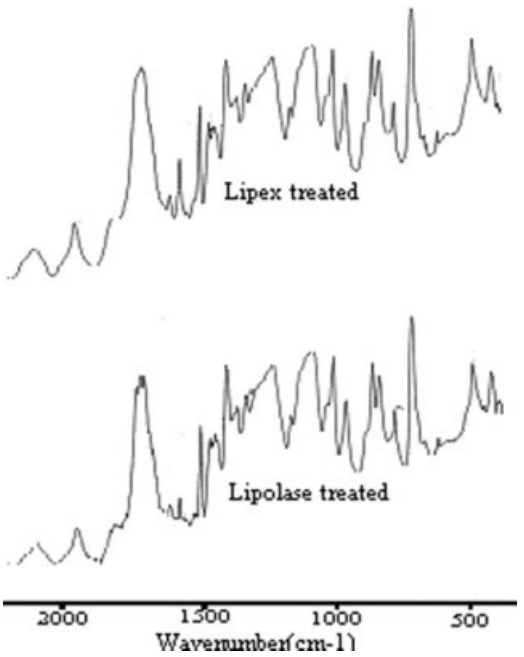

Figure 6 FTIR spectra of PET fabrics pretreated with different enzymes.

higher for the Lipex-pretreated samples than for the Lipolase-pretreated samples.

PET fibers do not contain chemically reactive groups. Hence, this material cannot be dyed with ionic dyes. When AA was introduced into the PET, some carboxylic groups linked to the PET surface. Therefore, the dyeability of the PET fibers was investigated with the use of a basic dye. The results showed that when the percentage of grafted products was increased, their dyeability increased. Because the graft yield percentage of enzyme-pretreated PET fabrics was higher than that of other samples, the dyeability was improved.

Table VI shows the average ΔE values (in Commission Internationale de l'Eclairage $L^*a^*b^*$ color coordinates) of the polyester fabric dyed with different treatments. The average ΔE value of the dyed fabric with enzymatic pretreatment was smaller than that of the dyed fabric without pretreatment.

As shown in Table VI, L^* decreased with the grafting of PET by AA. A remarkable point was the improvement of the basic dyeability of the enzyme-pretreated samples with Lipex.

CONCLUSIONS

The results suggest that it is practicable and effective to improve the grafting of AA onto polyester fabrics by means of enzymatic pretreatment. FTIR and SEM were used to characterize AA-grafted pretreated polyester fabrics. A new band appearing at 1546 cm^{-1} in the FTIR spectrum implied that AA was introduced onto the PET macromolecules. Changes in the surface structure of fabric fibers presented in SEM micrographs made it clear that poly(-acrylic acid) was grafted onto the surface of the PET fibers. The results show that the density of surface grafting was enhanced by enzyme pretreatment. This enhancement by Lipex enzymatic treatment was more efficient than that by Lipolase. The highest

TABLE VI
Color Indices of Dyed PET Fabrics with Different Treatments

Sample	Graft yield (%)	L^*	a^*	b^*	ΔE^*
Raw	0	84.59	−2.71	−9.17	0
Without pretreatment	3.81	74.88	−1.97	−12.1	20.48
Pretreated with Lipolase	6.98	69.97	−1.17	−14.17	21.12
Pretreated with Lipex	9.11	65.82	−0.48	−19.50	27.96

graft yield was obtained with a 1% concentration and a 30-min treatment time at 30°C for Lipex and Lipolase at pH values of 7 and 5, respectively. There were no significant changes in the tenacity and weight loss of the fabrics because of the enzyme surface modification of the fibers. The moisture content increased with increasing graft yield. This property in the grafted fabrics pretreated with Lipex was much higher than that of other samples. Higher color strength values were obtained when grafted PETs (Lipex-pretreated samples) were dyed with the basic dye.

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