Microbial Modification of Polyethylene Terephthalate Fabric

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ABSTRACT: A great disadvantage of synthetic fibers is their low hydrophilicity. Polyester fibers are particularly hydrophobic. In the first place, this affects the processability of the fibers. The surfaces are not easily wetted, thus impeding the application of finishing compounds and coloring agents. In addition, a hydrophobic material hinders water from penetrating into the pores of fabric. An additional advantage is a decrease in build-up of electrostatic charge. Besides an improved processability of hydrophilic textiles, a number of advantages from the consumer's point of view are improved washability, as the water can remove hydrophobic stains more easily, and enhanced wearing comfort due to greater water absorbency. For these reasons, hydrophilicity of polyester fabrics was improved using *Trametes versicolor*. Incubation conditions were determined as; the polyester fabrics were incubated for 10 days at 28°C and 175 rpm. The modification medium was contained 1 g/L glucose and pH of medium was 4. The modification degree was determined according to the contact angle measurements. Water retention values were compatible with contact angle values. FTIR and SEM images showed that the modification occurred on the PET fabric surface. More hydrophilic PET fabric was made by *T. versicolor*. J Appl Polym Sci 121: 690–695, 2011

Key words: polyesters; modification; hydrophilic polymers; *Trametes versicolor*

INTRODUCTION

The classical chemical modification of synthetic polymers requires high amounts of energy and chemicals, which are partially discharged to the environment. Furthermore, some of the substances used during the processing of fibers are released from the end products due to weak bonding, causing serious health risks and reducing the technical life-time of the products.[1,2]

Polyester fibers made of polyethylene terephthalate (PET) are important synthetic fibers used for the production of textiles. The fibers show excellent strength properties, a high hydrophobicity and resistance to chemicals together with low abrasion and shrinking properties. However, for desired textile features such as a high wearing comfort and improved dyeability with water-soluble dyes, an increased hydrophilicity of the surface of the fibers is necessary. PET can be hydrolyzed under strong alkaline conditions resulting in a hydrophilic fiber. However, this treatment is resulting in drastic weight and strength losses and is not an environmentally benign industrial process.[3–8] PET is known to be very hydrophobic and insoluble in water as well as in most organic solvents, which makes an enzymatic reaction at the surface of the polymer rather unlikely. Concerns regarding health, energy, and the environment drive the improvement of enzyme technology in the textile industry.[9] Several enzymes have been found to carry out hydrolysis reactions at the PET surface. Especially, microbial enzymes are suitable for this purpose. Instead of one type of enzyme, much more enzyme could be used to modify PET surface and this system can be made by microorganisms. Microorganisms as enzyme source can modify surface of PET. Modification leads to an increase of free hydroxyl end groups and carboxylate end groups changing the surface properties of the treated material.[10–14] This introduction of charged and functional groups directly leads to an increased hydrophilicity. Furthermore, the increased amount of carboxylate and hydroxyl end groups facilitates the attachment of cationic dyes and could allow furthermore a reduction of coupling agents in special textile applications.[15] Instead of chemical modification, enzymatic modification is suitable to change properties of PET fabric because of environment and energy. Hydrophilicity of PET fabric can be made low-cost by microorganisms as an enzyme source. *T. versicolor,* which is a white-rot fungi (WRF) have ligninolytic enzyme system, which could oxidize synthetic polymers like PET fabric. The purpose of this paper is to investigate the conditions of the treatment using *T. versicolor* to improve the hydrophilicity of the PET fabrics.

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MATERIALS AND METHODS

Chemicals, organism and PET fabric

All chemicals were commercially available and of reagent grade. *Trametes versicolor* (ATCC 11235; FRPL 28A IMI, EGHAM SURVEY). PET fabric was double fabric palin weave 100% PET, 34 threads/cm in warp, 25 threads/cm in weft directions and unit weight was 223 g/m^2 and purchased from BOYTEKS (Kayseri, Turkey).

Culture conditions

The WRF *T. versicolor* was maintained on 2% (w/v) malt extract agar slants at 4°C and the fungus was activated at 26°C, for 4 days. The mycelium were harvested with sterile 0.9% NaCl solution and then inoculated into 100 mL 2% malt extract broth in 250 mL erlenmeyer flasks at 26°C and 175 rpm for 4 days. Pellets were inoculated into 50 mL modification medium consisting of 10 g glucose, 1.0 g of $NH_4H_2PO_4$, 0.05 g of $MgSO_4.7H_2O$, 0.01 g of $CaCl_2$, 0.025 g of yeast extract.[16] Cultivation was carried out in an orbital shaker incubator, at 28°C and 175 rpm. All mediums were autoclaved for 20 minutes at 121°C.

Modification process

PET fabrics and *T. versicolor* of 10 × 10 cm^2 were used for modification. PET fabrics were placed in a 250 mL glass beaker, which contained 50 mL modification medium. The PET fabrics were incubated for 10 days at 28°C and 175 rpm. The modification degree was determined according to the contact angle measurements.

Optimization of modification process

The effect of incubation temperature, pH, times, shaking speed, glucose concentration in the modification medium, and chemicals on modification were tested.

- Incubation Temperature: 26, 28, and 30°C.
- Shaking Speed: 0, 150, 175, 200 and 225 rpm.
- Glucose Concentration: 0, 1, and 10 g/L.
- Chemicals: TEMPO (2,2,6,6-Tetramethylpiperidine 1-oxyl), violuric acid (VA), and phenol (10 mg/L).
- Incubation pH.: 4, 5, 6, 7, and 8.
- Incubation Times: 10 and 20 days.

TABLE I
Contact Angle Values of Unmodified PET Fabric

	1 Second	2 Seconds	3 Seconds	4 Seconds	5 Seconds
Contact Angle (°)	130.431	128.241	125.743	121.527	117.052

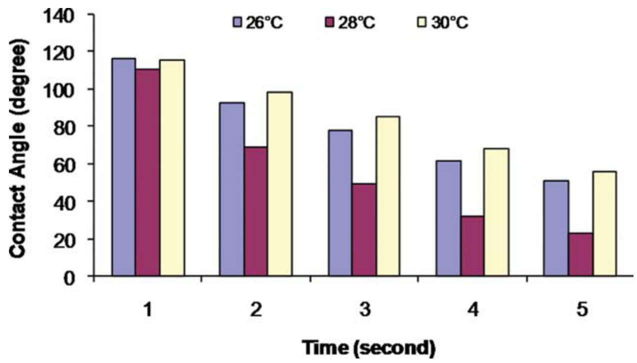

Figure 1 Effect of incubation temperature to microbial modification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Contact angle measurements

Contact angle measurements of a drop of glycerin on unmodified and modified PET fabrics were carried out using the sessile drop method with a CAM 100 KSV (KSV, Finland). Recording the drop profile with a CCD video camera allowed monitoring changes in wetting. All reported data were the average of at least five measurements at different locations of the fabric surface. The experiments were conducted at 25 ± 1°C. The volume of the drops was always about 2 μL. The piston is moved by a micrometer to obtain good control in applying liquid to the surface.

FT-IR spectroscopic measurements

A fourier transform infrared spectrophotometer (Perkin Elmer Spectrum 100 Series) was employed for the entire study. One milligram of PET fibers were ground into powder with high purity infrared grade KBr powder (100 mg) and pressed into a pellet for measurement. Each spectrum was recorded in the range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1}. Modified PET fabric was prepared at optimized incubation conditions (T = 28°C, 1 g/L of glucose, 175 rpm, incubation time: 10 days for incubation time, pH 4).

SEM observation

Scanning electron microscope (JEOL JSM 5200 SEM, Tokyo, Japan) was used for surface imaging of the PET fabrics. Samples were observed at 10 kV acceleration voltages, after gold coating under reduced argon atmosphere. Modified PET fabric was prepared at optimized incubation conditions (T = 28°C, 1 g/L of glucose, 175 rpm, incubation time: 10 days for incubation time, pH 4).

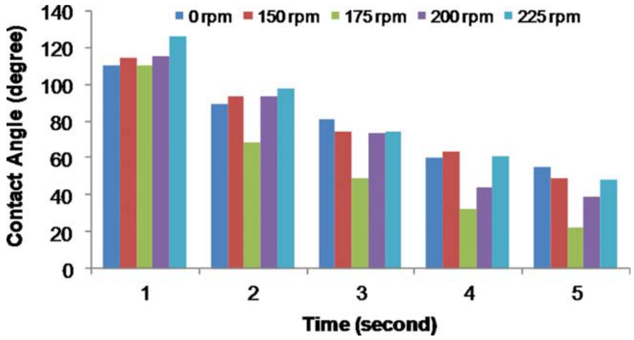

Figure 2 Effect of shaking speed to microbial modification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

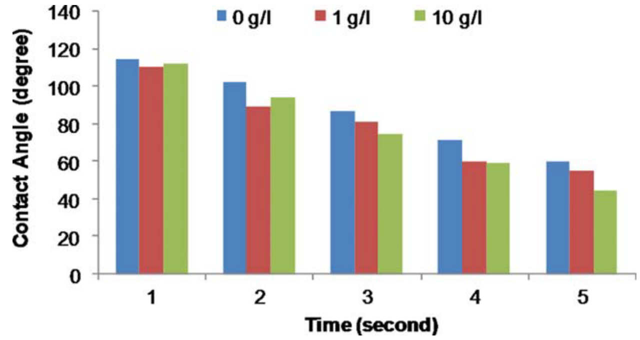

Figure 4 Monitoring of contact angles of PET fabrics incubated in different glucose concentrations at fixed culture. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water retention values

Modified and unmodified PET fabrics of 0.5 g were accurately weighed and immersed in deionized water for 24 h at ambient temperature, then removed and centrifuged at 4000 × g for 10 min after which the wet specimens were reweighed (W_w). The wet specimens were dried in an oven for 4 h at 105°C, allowed to cool in a desicator, and the weight of the dried specimen was recorded (W_d). The water retention value (WRV) was calculated according to eq. (1).

$$\mathrm{WRV} = (W_w - W_d)/W_d$$

RESULTS AND DISCUSSION

Optimization of modification process

PET fabrics, which were incubated with *T. versicolor*, were dried and contact angle measurements were performed. When contact angle is high, the PET fabric is hydrophobic. Lower contact angle values shows PET fabric is more hydrophilic than initial form of it.[17] Dynamic contact angles of modified and unmodified PET fabrics were measured. Contact angles values of unmodified PET fabrics were given in Table I.

In all experiments, contact angle values of modified PET fabrics were obtained lower than contact angle values of unmodified PET fabrics. Contact angle values showed that modified PET fabrics were more hydrophilic.

One of the most important parameter is temperature for microbial growth and enzyme production. Optimum temperature definition is highest rate of growth at a certain temperature. Metabolism of microorganisms decelerates at lower values of optimum temperature. At higher values of optimum temperature, enzyme degradation rate increases. So the rate of growth decreases. This case is suitable for microbial growth. But optimum temperature for enzyme activity could be a different temperature.[18] PET fabrics were incubated at 26, 28, and 30°C. PET fabrics, which were incubated at 26 and 30°C, were more hydrophobic than PET fabric that was incubated at 28°C (Fig. 1). Optimum temperature for incubation was determined as 28°C and this temperature is also optimum for *T. versicolor* growth.[19]

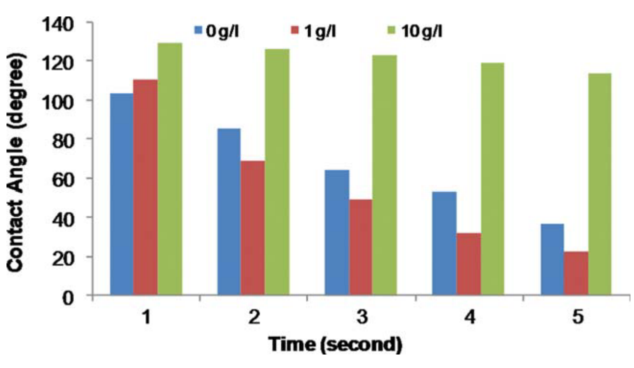

Figure 3 Contact angle values of PET fabrics incubated in different glucose concentrations at 175 rpm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

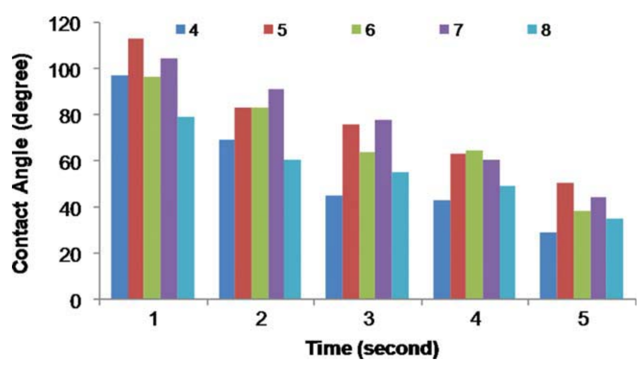

Figure 5 Effect of media pH to microbial modification. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

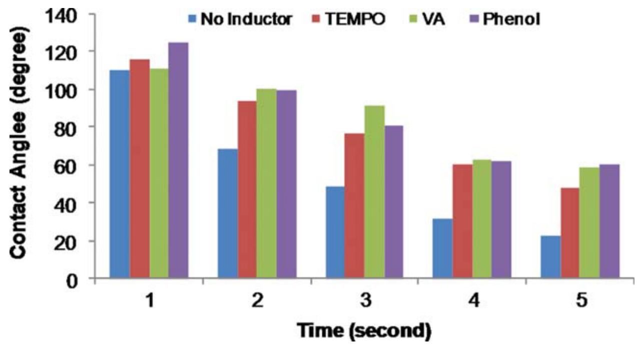

Figure 6 Contact angle values of PET fabrics incubated with laccase inductors. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

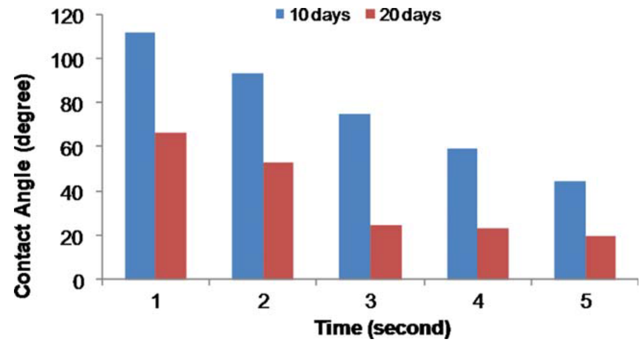

Figure 7 Monitoring of contact angles of PET fabrics incubated at 10 and 20 days. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The PET fabrics were incubated at 0, 150, 175, 200, and 225 rpm. The optimum shaking speed for incubation was determined as 175 rpm (Fig. 2).

Fixed and shaking cultures were compared. Modification in shaking culture was more effective than fixed culture. At 150 rpm, pellets bound to each other and the surface area contracted. Diffusion of glucose, oxygen, and nutrients from medium to cells might be limited. Enzymes and/or enzyme systems secretion might also be limited from cell to medium. At 200 and 225 rpm shaking speed values, pellets scraped to PET fabrics. Because of scraping, the cells might suffer damage and some of them might be died. This might cause to decrease the amount of enzymes. The contact angle values of them might be lower because of lower amount of enzyme.

To determine glucose concentration effect to hydrophilicity, PET fabrics were incubated in 0, 1, and 10 g/L glucose concentrations at fixed and shaking culture. For shaking culture, best result was taken for 1 g/L glucose concentration (Fig. 3).

The contact angle changed a little for containing 10 g/L glucose. The cells might be oriented to grow, not to product enzymes that were responsible for modification. Optimum glucose concentration was determined as 1 g/L. For 0 g/L sample, the cells were not effective. Activity of enzyme(s), which modified PET fabric, increased at limited concentration of glucose. This result could be explained with monod model. According to the monod model, when growth of microorganisms were limited, some of metabolites production increases. In this case, limited concentration of glucose was caused that production of PET modification enzymes was increased. For 1 g/L of glucose concentration, the fixed and shaking culture results showed that modification was more effective at shaking culture (Fig. 4). For fixed culture, the contact angles were changed little for all glucose concentrations.

Other the most important parameter is pH for microbial growth and enzyme production. Microorganisms produce enzymes maximum level at certain pH values. But enzymes might catalysis reactions at different pH value from enzyme production pH. Enzymes work highest activity at optimum pH values.[20] PET fabrics were incubated with *T. versicolor* at pH 4–8. PET fabrics, which were incubated at pH

TABLE II
WRV Values of Modified and Unmodified PET Fabrics

WRV of Unmodified PET	0.020				
Temperature (°C)	26	28	30		
WRV	0.037	0.061	0.025		
Shaking Speed (rpm)	0	150	175	200	225
WRV	0.025	0.021	0.062	0.022	0.021
Glucose Concentrations (175 rpm) (g/l)	0	1	10		
WRV	0.021	0.063	0.026		
Glucose Concentrations (0 rpm) (g/l)	0	1	10		
WRV	0.026	0.040	0.024		
pH	4	5	6	7	8
WRV	0.074	0.023	0.022	0.034	0.062
Inductor	No inductor	TEMPO	VA	Phenol	
WRV	0.075	0.022	0.024	0.023	
Time (days)	10	20			
WRV	0.077	0.103			

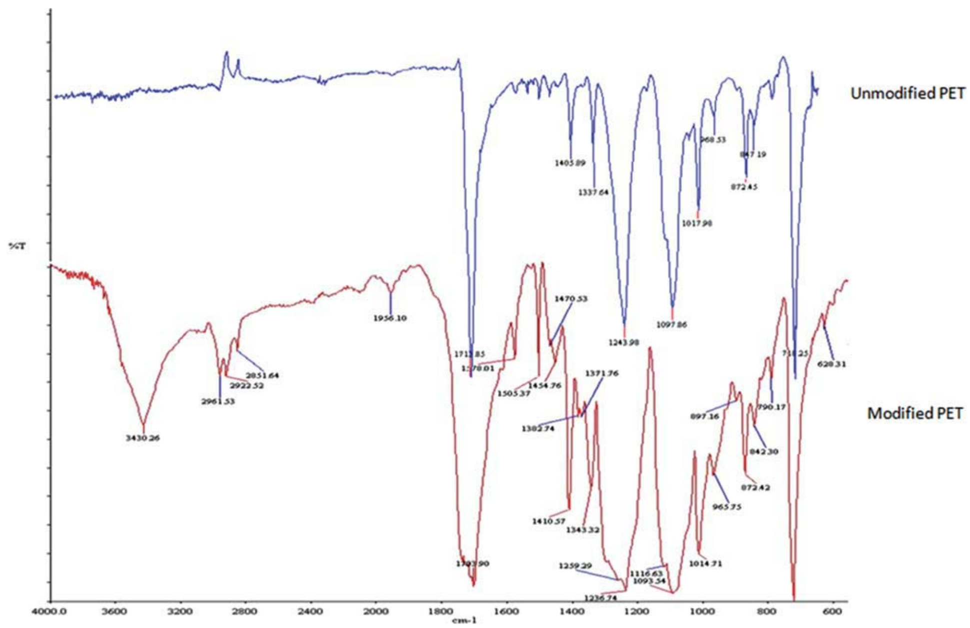

Figure 8 FTIR spectrum of unmodified and modified PET fabrics. The experimental conditions were 28°C for incubation temperature, 1 g/L for glucose concentration 175 rpm for shaking speed, 10 days for incubation time and pH 4 for incubation medium. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

4, were more hydrophilic. Optimum pH for incubation was selected pH 4 (Fig. 5).

Some chemicals could be worked as inductor for enzyme production and mediator for enzyme. TEMPO, VA, and phenol of 10 mg/L were added to modification medium to develop modification effect. These chemicals are inductors of laccase and Laccase catalysis oxidation reactions. These chemicals were used but no effect of them was determined to contact angles. This might show that the modification was not made by oxidation reactions (Fig. 6).[21,22]

Incubation time is another important parameter. If process of PET modification time is short, cost will be decreased. PET fabrics were incubated for 10 and 20 days. The results were given at Figure 7. The

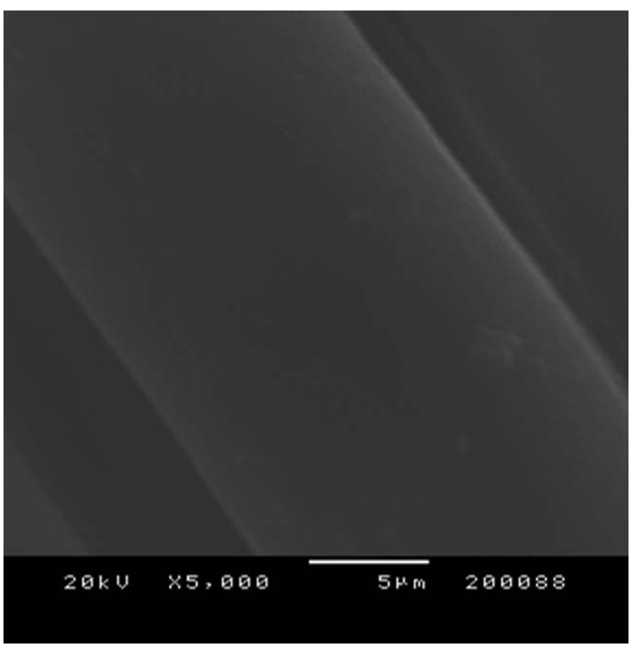

Figure 9 SEM image of unmodified PET fabric.

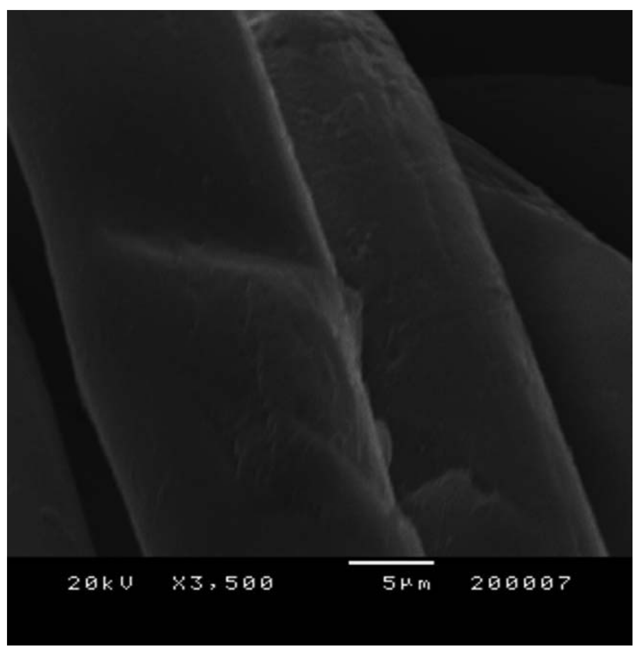

Figure 10 SEM image of modified PET fabric. The experimental conditions were 28°C for incubation temperature, 1 g/L for glucose concentration 175 rpm for shaking speed, 10 days for incubation time and pH 4 for incubation medium.

contact angle values of 20 days incubation sample was nearly half of 10 days incubation sample. This result might show that the modification effect was continuously. We selected 10 days for incubation.

Water retention values

Hydrophilic materials hold water. When the hydrophilic properties of materials increase, water retention values increase. All water retention values of modified PET fabrics were parallel with contact angle values (Table II). Modified PET fabrics held water more than unmodified PET fabric.

Infrared spectroscopic study

The band at around 966 cm^{-1} represents the —O—CH_2 stretching vibration of the ethylene glycol segment in PET. Hydroxylation of the degraded PET fabric is confirmed by the new peaks at 1371 cm^{-1} assigned to phenolic —OH. In the spectra of degraded PET samples, only the peak around 872 cm^{-1} remains confirming that substitution occurred on the terephthalic ring. The band at 3430 cm^{-1} represents the —OH stretching of diethylene glycol end group in the polymer. The carbonyl stretch C=O of a carboxylic acid appeared as an intense band from 1704 cm^{-1} (Fig. 8). The added polar groups to PET fabric structure from modification process made it more hydrophilic.

Microstructure of the PET fabric surface

If there were reactions taking place on the surface of PET fabric, there should be changes on the fiber surface. Scanning electron microscopy (SEM) was adopted to show the modifying effect on the PET fabric. Figure 9 showed the SEM images of the unmodified PET fabric.

The surface of unmodified PET fabric was very smooth. Additionally, from the analysis of FTIR of the modified PET fabric, it is concluded that the differences on the surface and rugged and cracked surface of the fiber should be the modification effect (Fig. 10).

CONCLUSION

The data from experiments indicated that the optimum incubation parameters were 28°C for incubation temperature, 1 g/L for glucose concentration 175 rpm for shaking speed, 10 days for incubation time and pH 4 for incubation medium. Results from FTIR and SEM showed that enzymatic reactions took place on the surface of PET fabric. FTIR results also showed that some new groups were added to PET structure and they made it more hydrophilic. By this modification process, less energy, chemicals, and cost could be spent according to traditional hydrophilization methods. Surface modification with enzyme and/or enzyme systems showed great potential for PET fabrics, and it also could find applications for other synthetic fibers. This experiment was supplied a new method for the surface modification of PET fabrics.

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