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Eco-friendly surface modification on polyester fabrics by esterase treatment

Jindan Wu, Guoqiang Cai, Jinqiang Liu, Huayun Ge, Jiping Wang*

MOE Key Laboratory of Advanced Textile Materials & Manufacturing Technology, National Base for International Cooperation in Science & Technology of Textiles and Daily Chemistry, MOE Engineering Research Center for Eco-Dyeing and Finishing of Textiles, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, China

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ABSTRACT

Currently, traditional alkali deweighting technology is widely used to improve the hydrophilicity of polyester fabrics. However, the wastewater and heavy chemicals in the effluent cause enormous damage to the environment. Esterase treatment, which is feasible in mild conditions with high selectivity, can provide a clean and efficient way for polyester modification. Under the optimum conditions, the polyester fabric hydrolysis process of esterase had a linear kinetics. X-ray photoelectron spectrometry (XPS) results showed that hydroxyl and carboxyl groups were produced only on the surface of modified fiber without changing the chemical composition of the bulk. These fibers exhibited much improved fabric wicking, as well as greatly improved oily stain removal performance. Compared to the harsh alkali hydrolysis, the enzyme treatment led to smaller weight loss and better fiber integrity. The esterase treatment technology is promising to produce higher-quality polyester textiles with an environmental friendly approach.

1. Introduction

Surface hydrophilicity is a key property of materials which is related to their adsorbing capacity [1,2], antifouling ability [3], biocompatibility and bioreactivity [4]. For example, polymeric materials are often used as separation membranes for water purification but the fouling phenomena ubiquitously exist. As a result, the efficiency will be lowered or even lost with reduced sensitivity and blocked filters [5,6]. The improvement of hydrophilicity can efficiently prevent the fouling behavior by increasing the surface energetic barrier for adhesion. Surface wettability is also related to the moisture conductivity of the textiles [7]. PET (polyethylene terephthalate) fiber is the most widely used synthetic fiber which accounts for nearly 80% of total synthetic fiber output. However, due to its chemical composition and molecular structure, polyester fibers are usually hydrophobic. The low moisture permeation and stain removing ability are the main causes of poor wear comfort. Fortunately, these problems can be solved by improved surface hydrophilicity. In addition to these benefits, improved hydrophilicity also makes polyester fibers more efficient in dyeing, finishing and functionalization.

Surface hydrophilization is an important step in the manufacturing process of materials. Many technologies have been developed to improve the hydrophilicity of various kinds of materials, including physical coating, plasma treatment [8,9], glow discharge [10], silanization [11], macromolecule grafting [8,12], chemical processing [13,14] etc. These methods mainly depend on high energy input or harsh chemicals and they are always complicated to handle. For example, plasma treated materials are instable since the surfaces will return to hydrophobic in a few days time [15]. Alkali deweighting is the most commonly used method for PET surface modification in industry because of its low cost. However, the wastewater causes enormous damage to the environment.

Recent studies have reported a new way for surface modification of synthetic polymers: enzymatic treatment [16,17]. Enzymes are catalysts for reactions with high selectivity and specificity in mild conditions. From an economic and ecological point of view, new processes using lipase [18], proteases, papain, glycosidases etc. are safe with low energy consumption. It may lead to huge developments and wide applications of enzymes in the functionalization of polymer surface [19]. As first reported by Tokiwa et al. in 1977 [20], aliphatic polyester particles were treated by enzymes and a significant degradation of the polyester was found. In 1987, Smith et al. found that PET can be slightly degraded by esterase and papain [21]. In 1998, Hsieh et al. reported that the wettability and water absorption effect of PET fabric could be improved by lipase treatment [22]. Cutinase, as a new tool for polyester modification, has not been widely studied. It is an α/β hydrolase [23], which has a catalytic serine with high activity and low specificity for cutin

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* Corresponding author at: Zejiang Sci-Tech University,College of Materials and Textiles, Xiasha Higher Education Park 2 St., Hangzhou, Zhejiang 310018, China. Tel.: +861373588304.
E-mail address: jipingwanghz@gmail.com (J. Wang).

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degradation. In addition, cutinase has some benefits over the commonly used esterase. First, most of its outer amino acid residues are hydrophobic and the enzyme-fiber interaction can be enhanced [24]. Second, cutinase is known as a nonspecific esterase which can act on several kinds of soluble and insoluble esters. What's more, polymers like polyamide, polyurethane and polyacrylonitrile also can be hydrolyzed by cutinase [25]. Currently, researchers are still not clear about how cutinase works. It was reported that cutinase may have different modes of action and different activities on various kinds of polymers [26]. Furthermore, researchers are interested in the benefits in material performance brought by cutinase treatment compared to chemical hydrolyzing technologies.

In our study, cutinase was used for polyester modification. The mechanism of the hydrolysis was deeply explored by studying the kinetics of hydrolysis process and the surface properties of polyester. As an efficient and economic process for potential industry applications, the cutinase treatment technology for PET fiber was systematically studied together with traditional alkali treatment technology.

2. Experimental

2.1. Materials

A polyester fabric (Knitting, white, 150D/48F) was purchased from the market in Shaoxing, China. A cutinase (12 mg/mL) was provided and stored at 4 °C before application. Four used surfactants were fatty alcohol ethoxylates (AEO7, AEO3), fatty alcohol polyoxyethylene ether sulfate (AES) and sodium dodecyl sulfate (SDS). Poly(ethylene glycol) methacrylate (PEGMA) (MW = 950) was purchased from Sigma-Aldrich Company. Tide laundry detergent was purchased from the market. Sodium hydroxide and hexadecyltrimethyl ammonium bromide (CTAB) were purchased from Gao Jing Fine Chemical Co., Hangzhou and Bodi Chemical Co., Tianjin, respectively. All the chemicals were used as received.

2.2. Fabric pretreatment

The polyester fabric was dry-cleaned in decamethylcyclopentasiloxane (D5) for 30 min at 60 °C, and spun in a laundry washing machine. After 3 cycles, the fabric was dried in an oven at 80 °C. They were then washed in water (bath ratio was 1:100, 1 g/L detergent) using a Haier washing machine for 15 min at 60 °C. They were then rinsed in water twice (each time 3 min) and spun for 3 min. After 3 cycles, the fabric was dried at 80 °C.

2.3. Enzyme activity measurement

An aqueous solution with 2 mg/mL PEGMA, 200 ppm surfactant and a certain concentration of cutinase was prepared. The reaction was performed with different temperatures and pH values in a shaking bath for a certain time. 50 mL of the solution was then taken out and titrated with 0.1% sodium hydroxide solution. The amount of acid produced by the hydrolysis was determined and the enzyme activity was calculated. The enzyme activity (U) is defined as the amount of acid (μmol) produced per milligram cutinase per minute.

2.4. Cutinase/alkali treatment on polyester

The fabric was placed into the aqueous solution with cutinase and 200 ppm AEO7 (pH 6.5). The reaction was performed at 60 °C in a shaking bath for 3 h. For the alkali deweighting treatment, fabric was hydrolyzed in a solution containing 5 g/L NaOH and 1 g/L CTAB. The bath ratio was 1:50 and the process was undertaken at 90 °C for 1 h. Finally, fabric was rinsed with a large amount of water and dried at 80 °C.

2.5. Surface chemical composition analysis

The chemical composition was measured using infrared spectroscopy under attenuated total reflection (IR-ATR) mode (AVATAR 5700, Nicolet, America) and X-ray photoelectron spectrometry (XPS, Axis Ultra from Kratos Analytical, UK). XPS instrument had a monochromated Al Kα source at pass energies of 160 eV for survey spectra and 80 eV for core level spectra. The peaks were differentiated and fitted using XPS Peak analysis software and the binding energy was corrected by setting C 1s peak ($\underline{C}$—C) at 284.6 eV.

2.6. Surface wettability test

The contact angle was measured by a high-speed camera (PCO 1200hs, Germany). In detail, a droplet of water (4.5 μL) was dripped onto the surface. Before it penetrated into the fabric, the wicking process was videotaped by high-speed camera with an exposure time of 0.6 ms (1666 fps). Images of water droplets were analyzed using Image-Plus 5.0 software and contact angles at different times were calculated. By counting the number of pictures recorded in each wicking process, the wicking time was calculated. The thin layer wicking (TLW) measurements were performed according to Chinese national standard FZ/T 01071-2008. Fabric was cut into pieces in the size of 30 cm × 5 cm. They were fixed on a support stand and vertically dipped into a beaker of water. Once the lower side was immersed into water, the liquid climbed up along the fabric to a certain distance. After a period of 30 min, the height of water climbed was recorded. The moisture regain was measured referring to Chinese national standard GB 9994-2008. Fabric was weighted before and after being balanced in the standard condition (20 °C, 65% RH). The value was measured using Eq. (1).

$$\text{Moisture regain} = \frac{m_1 - m_0}{m_0} \times 100\% \tag{1}$$

here, m_1 is the weight of fabric balanced in the standard condition and m_0 is the weight of fabric dried in the oven.

2.7. Fiber integrity measurement

The surface morphology of fibers was studied using scanning electron microscopy (SEM, JSM-5610Lv, Japan). The crystallinity was measured by X-ray diffraction (XRD, ARL XTRA, Switzerland) and analyzed using Jade 5.0 software.

The fibers were weighted before and after cutinase/alkali treatment and the weight loss was calculated using following Eq. (2).

$$\text{Weight loss} = \frac{m_0 - m_a}{m_0} \times 100\% \tag{2}$$

here, m_0 and m_a are the weight of fibers before and after treatment, respectively.

2.8. Mechanical property measurement

Investigation of the mechanical strength of fibers was taken by bursting strength measurement referring to Chinese national standard GBT 19976-2005. The specimen was mounted on a circular clamp folder followed by moving ball plunger (diameter of 25 mm) vertically towards the specimen at a constant speed (300 mm/min).The fabric was forced to deform until rupture and the value of the bursting strength was recorded. Samples were not folded and wrinkled, and the test was repeated at least 5 times using different parts of the fabric.