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Surface modification of polyamide 6.6 fibers by enzymatic hydrolysis

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ABSTRACT

Synthetic fibers are used extensively in textile industry, however, their high hydrophobicity is a drawback that needs to be considered. The decrease of hydrophobicity can be achieved via a "green" root using enzymes as biocatalysts. In this study, the enzymatic surface modification of polyamide (PA) 6.6 fabric was studied with the use of the commercial protease Alcalase 2.4 L at optimal conditions. The modified fabrics were studied via dyeing parameters K/S and ΔE values. For treatment at 40–60 °C and pH 8 ΔE was found to be approximately 14 and K/S was 1.24-fold increased. Additionally, the enzymatic surface modification of PA textile was justified using different spectroscopy techniques, such as FTIR-ATR and XPS. FTIR-ATR indicated alterations of C=O and N—H band intensities, while via XPS, there proved to be differences in relative intensities of carbon component peaks. Finally, thermogravimetric and mechanical tests were also conducted to prove the non-degradation of the properties of the bulk material. In conclusion, the investigated enzymatic process increased the hydrophilicity with 2.7-fold increased water absorbency and 1.24-fold enhanced color strength of PA textiles, while maintaining the thermal and mechanical properties of the bulk synthetic material.

1. Introduction

Synthetic fibers play an important part in textile industry as they are used in numerous applications, where cotton fibers cannot meet up due to their properties. Synthetic fabrics present several advantages such as strength, and elasticity, less wrinkles, lightness and fast drying [1], making them highly suitable for use in sportswear, however, their high hydrophobicity consists a problem that seeks attention, since it hinders the process of dyeing, permeability and sweat evaporation [2–4]. In addition, hydrophobicity is responsible for detainment of stains and static charges [5]. Therefore, the increase of hydrophilicity of synthetic fibers is crucial in order to improve certain properties and expand to further applications.

Enzymatic surface modification of synthetic fabrics is a modern and "green", eco-friendly procedure, which is more advantageous compared to chemical hydrolysis since no degradation of the fabric's bulk properties occurs due to the large size of biocatalyst that prevents it from penetration [5,6]. Modification of polyamide (PA) 6.6 fibers focuses on the surface hydrolysis of the amide bonds releasing carboxyl- and amino- end groups [7]. Furthermore, the partial hydrolysis of PA fibers could aid, in a second stage, in the functionalization of the polymer [8]. According to literature, the most suitable enzymes for PA modification are esterases, cutinases and proteases [9,10].

In the present study, the ability of Alcalase 2.4 L, which is a commercial protease from bacterium *Bacillus licheniformis*, was investigated for the modification of PA 6.6 fibers. Initially, the hydrolytic potential of the enzyme preparation was tested on adipic acid bishexyl-amide model substrate, a PA model that mimics the PA 6.6 surface. Subsequently, the surface modification of PA 6.6 textile was carried out at the optimal conditions provided by Novozymes [11]. The extent of the enzymatic treatment on the PA model was monitored by the quantification of amino-groups released in reaction supernatant. The modification of the polymeric material was analyzed via dyeing tests and was further justified through different spectrometric and physicochemical analysis methods such as Fourier Transform Infrared Spectroscopy in the

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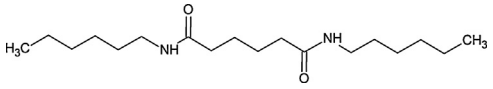

Fig. 1. Structure of adipic acid bishexyl amide model substrate.

Attenuated Total Reflectance mode (FTIR-ATR), Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA) and various mechanical tests.

2. Materials and methods

2.1. Materials, chemicals and enzyme

Commercial PA (100% PA 6.6) woven fabric was obtained from Colora S.A (Thessaloniki, Greece) with density 12 warp cm^{-1} and 11 weft cm^{-1}, 912.9 Denier, weight 238.67 g/m^2 and thickness 359 μm. The PA fabric was washed with detergent Felosan NFG before use for the removal of paraffins used during weaving. Hexylamine and dimethyl adipate were purchased from Sigma (St. Louis, MO). Alcalase 2.4 L (protease from bacterium *B. licheniformis*) was kindly provided by Novozymes (Bagsvaerd, Denmark). The reactive dye Remazol Brilliant Blue R Special (CI Reactive Blue 19) and 2,4,6-trinitrobenzenesulfonic acid (TNBS) were obtained from Sigma (St. Louis, MO). The reactive dye Novacron Deep Cherry S-D was purchased from Huntsman (Everberg, Belgium). All other chemicals were of analytical grade.

2.2. Chemical synthesis and enzymatic hydrolysis of PA model substrate

The synthesis of the PA model substrate adipic acid bishexylamide (Fig. 1) was carried out using hexylamine and dimethyl adipate as previously described [12]. The structure of the synthesized PA model was confirmed by ^1H NMR with a Bruker DRX 400 NMR spectrometer, equipped with a 5 mm $^1H/^{13}C$ dual inverse broad probe operating at 400 MHz (data not shown).

Alcalase 2.4 L concentration was measured with Bradford method, using bovine serum albumin as standard [13]. Indicatively, in 1.25 mL of Bradford solution 0.025 mL of diluted enzyme solution was added, incubated for 10 min and then measured spectrophotometrically at 595 nm. Alcalase 2.4 L concentration was found to be 93 mg mL^{-1}. Regarding Alcalase 2.4 L activity, in 1 mL of 0.2% (w/v) azocasein solution prepared in Tris-HCl buffer pH 8, 0.025 mL of diluted enzyme solution was added and incubated at 40 °C for 10 min, as previously described [14]. Subsequently, 1 mL of 0.1 M TCA was added and centrifuged to remove protein. In 1 mL of the supernatant 1 mL of 0.5 M NaOH was added, incubated for 5 min and measured spectrophotometrically at 440 nm. One unit of activity was defined as the amount of enzyme required to produce an increase in absorbance at 440 nm of 0.1 at certain pH and temperature conditions. The enzymatic activity was found 38.21 kU mL^{-1}.

The hydrolysis of PA model occurred as followed: 50 mg of the model was treated with 4.65 mg of Alcalase 2.4 L in 1.5 mL potassium phosphate buffer pH 8, at 40 °C, overnight. Subsequently, the samples were filtered to obtain the soluble fraction of the hydrolysis and analyzed with the TNBS method as previously described [15]. This method is based on the reaction of the primary amino groups with the sodium salt of TNBS leading to the formation of a complex that can be measured spectrophotometrically at 420 nm. 1 mL of the reaction's supernatant was incubated with 25 μL of 30 mM aqueous TNBS for 30 min at 30 °C. For the quantification of amino-groups that is indicative of the enzymatic hydrolysis of the PA model, the absorbance was read against the two controls, one with model and buffer and one with enzyme and buffer at 420 nm in a BOECO S-20 Spectrophotometer. A calibration curve was prepared using hexamethylenediamine as a standard solution in different concentrations. The blank with the enzyme also absorbs at 420 nm, due to the commercial enzyme's crude status, yet the PA model is hydrolyzed to a certain extent and there is a distinctive difference between the blank and the reaction sample, presenting a tendency for increase, when enzymatically treated.

2.3. Enzymatic treatment of PA fabric

PA fabrics were cut into pieces of 0.5 g (4.5 × 4.5 cm^2) and were incubated in glass vessels with textile:liquor ratio 1:50, 24 h, at 40–60 °C, pH 8 under stirring (170 rpm) with different concentrations of enzyme loading. Controls without enzyme and with thermal deactivated enzyme (boiled for 30 min) were also prepared. After enzymatic treatment the fabrics were washed with 2 g L^{-1} $NaCO_3$ at 60 °C for 1 h and afterwards double-washed with deionized water for 1 h. All experiments were performed in duplicate.

The dyeing of the PA fabrics occurred in 390 cm^3 glass tubes in a Ahiba Texomat machine (Datacolor, Lawrenceville, NJ, USA). According to dyeing procedure, 55 g L^{-1} of Na_2SO_4 and 2% (w/w) of each dye were dissolved and introduced in the glass tubes along with the fabrics. The dye bath was heated up to 60 °C and after 20 min, 5 g L^{-1} Na_2CO_3 were added. Finally, 0.4 g L^{-1} of NaOH were introduced 30 min before the end of the dyeing procedure. For the fabric neutralization to pH 6 a small amount of HCOOH was added after removing the fabrics from each dye bath. In Fig. 2 the dyeing process is given, after which a wash procedure followed at 95 °C with soap (Cibapon R) for 1–2 h, in order to remove the non-reacted dye.

Color co-ordinates were evaluated according to CIE L*a*b* System, established by the "Commission Internationale de l'Eclairage – CIE" according to ASTM D 2244-68, with the use of a color tristimulus colorimeter (Data Color International, Spectraflash SF450) (Lawrenceville, NJ, USA). For each sample, four repeated measurements were taken to determine color coordinates L, a, b. Color change ΔE and color strength K/S were calculated as described before [16].

2.4. Fabric hydrophilicity measurement

Fabrics' hydrophilicity was determined by measuring the wicking height against gravity along the warp and weft direction of the fabric. The test was conducted using a vertical wicking tester according to DIN 53924 method. A strip of fabric (200 × 5 mm^2) was suspended vertically with its lower end (30 mm) immersed in a reservoir of distilled water, to which 1% reactive dye was added for tracking the movement of water and at a regular time interval. The time was measured on pre-marked samples according to the DIN.

2.5. Fabric mechanical properties study (tensile-bending-compression-shearing pilling)

Tensile tests were carried out by an STL Atlas tensile test machine, according to the EN ISO 13934. All measurements were performed on 5 × 20 cm^2 specimens at 25 °C.

The Kawabata Evaluation System (KES) was also used to assess the handle properties of the fabrics. KES measures mechanical properties at low stresses that correspond to deformation of fabrics in hand manipulation and includes five highly sensitive instruments that measure fabric bending, shearing, tensile and compressive stiffness, as well as the smoothness and frictional properties of a fabric surface. Standard specimens of 20 × 20 cm^2 were used. All measurements were directional, except for com-