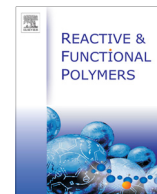




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Chemical functionalization of polyamide 6.6 fabrics

Alexandre Kisner^{a,b}, Karine Thaise Rainert^a, Fernanda Ferrari^a, Carla Tatiana Nau^a, Ivonete Oliveira Barcellos^a, Sérgio Henrique Pezzin^c, Jürgen Andreas^{a,*}^a Department of Chemistry, Regional University of Blumenau, 89010-971 Blumenau, Brazil^b Institute of Chemistry, Universidade Estadual de Campinas, 13083-870 Campinas, SP, Brazil^c Department of Chemistry, Center of Technological Sciences, Santa Catarina State University, 89223-100 Joinville, Brazil

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ABSTRACT

Polyamide 6.6 (PA 6.6) fibers, produced from adipic acid and hexamethylenediamine, are among the most consumed synthetic textile fibers used for garments. Fibers are hydrophobic, which makes dyeing difficult and affects wearing comfort. In the present work, chemical treatments of PA 6.6 fibers were carried out and compared with respect to their effect on fiber properties and obtained surface modifications. Scoured knitted PA 6.6 fabrics (opaque) were treated with hydrochloric acid (0–3 M) and sodium hydroxide (3 M) for up to 3 h at 60 °C. The fibers were characterized with respect to bulk and surface modifications such as amino and carboxyl end groups, superficial dyeing below the T_G of the fiber, surface structure with SEM and AFM analysis. Furthermore a new analytic procedure for the determination of surface amino groups was tested. Both chemical treatments resulted in a significant increase in the amount of amino groups on the fiber, but especially the treatment with HCl 3 M caused a more drastic surface modification of the fibers, however, not only restricted to the fiber surface. AFM and SEM analysis have shown a significant change in surface roughness on the nanoscale, which in addition to the creation of surface functional groups increases the fiber's hydrophilicity and reactivity.

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1. Introduction

Polyamide 6.6, also known as nylon 6.6, is the polyamide fiber of major commercial importance in textile industry used for the production of yarns, garments, industrial textiles and carpets. Polyamide fibers are relative hydrophobic, and have a low surface energy which makes dyeing difficult and affects wearing comfort of garments and their use in industrial applications [1]. Surface modifications or partial degradation of synthetic fibers through the hydrolytic or oxidizing action of chemicals or biological catalysts might result in improvements of fiber properties and provide better possibilities for grafting [2] or adherence of coatings [3]. While chemical treatments with acids or alkali require harsh conditions such as high concentrations and temperatures and in general are more difficult to control and may damage the polymers [4–7], biocatalytic processes with enzymes are carried out under moderate conditions and with less water consumption [8,9].

Polyamide 6.6 is produced by polycondensation of hexamethylene diamine and adipic acid resulting in polymers with amine and carboxyl end groups derived from the constituent monomers. The

relative number of both end groups can be controlled by proper termination of the growing chain with a monofunctional acid or base [10]. The wettability of polyamide 6.6 depends on the quantity of amine and carboxyl end groups on the polymer surface as well as on the crystallinity of the material. Since the fibrous filaments are stretched (drawn) to four or five times from their original length during the fiber spinning process, the molecules gather together in a more regular manner with hydrogen bonding between adjacent chains, resulting in a fiber with a high degree of crystallinity and a strong orientation of polymer molecules along the fiber axis. These changes reduce the accessibility of the fiber and decrease its wettability and consequently its affinity for acid dyes [11].

In order to provide changes in the fiber surface characteristics and to improve the fibers processing and application properties as a substitute to chemical methods, treatments with enzymes such as manganese peroxidase [12], proteases [13,14] and cutinases [13,15,16] have been proposed. Due to the size of biocatalysts it is supposed that enzymatic treatments are only superficial. Enzymatic treatments may provide specific modifications on the polymer and improve the dyeability and the wettability properties of polyamide 6.6 [8,16,17] without causing negative environmental impacts such as the hazardous use of harsh chemicals.

Despite of these efforts to modify the surface of synthetic fibers with biocatalytic processes, only a few attempts to analyze and

* Corresponding author. Address: Department of Chemistry, Universidade Regional de Blumenau – FURB, Rua Antônio da Veiga 140, 89010-971 Blumenau, Brazil. Tel.: +55 47 33210544; fax: +55 47 33228818.

E-mail address: jandr@furb.br (J. Andreas).

understand the surface modifications of polyamide 6.6 fibers by chemical methods and their influence on fiber properties have been made [4,18–20]. This information can be useful for further investigations with enzymes and provide insights about the actual possibilities of biocatalytical processes for polyamide fibers.

In the present work, we addressed this issue by analyzing the modification of polyamide 6.6 fibers with chemical methods in two stages. In a first stage PA 6.6 fabrics were treated with hydrochloric acid varying acid concentration and treatment time and fibers were analyzed concerning their physical and chemical surface and bulk modifications. In a second stage PA 6.6 fibers were treated with 3 M HCl and NaOH and results were compared with respect to the obtained surface modifications. Furthermore a new analytical procedure for the determination of surface amino groups has been elaborated and tested on the treated fabrics.

2. Materials and methods

2.1. Fabric preparation

In all experiments knitted polyamide 6.6 fabric of plain single jersey structure (180.55 g m^{-2}) made from opaque filaments (80 f 68 dtex), kindly supplied by Rhodia Poliamida e Especialidades Ltda. (Brazil), was used. In order to remove lubricants, spinning and knitting oils and other adsorbed impurities the fabric swatches were previously scoured in a KIMAK Washtester (Kimak, Indústria de Máquinas Knihs Ltda., Brusque, Brazil) at 80°C for 30 min at a liquor ratio (LR) 1:20 with $2 \text{ g L}^{-1} \text{ Na}_2\text{CO}_3$ and 2 g L^{-1} surfactant Effectol BRD (Thomas Boehme Chemie, Brazil) or Hostapal PYD.BR liqu. (Clariant S.A., Brazil), then neutralized with a 1% CH_3COOH solution and rinsed exhaustively with distilled water at 60°C . Hydrochloric acid (HCl) used in the experiments was acquired from Merck. All chemicals were reagent grade.

Fabrics used in 3 M HCl and NaOH treatments had a weight of $3.1 \pm 0.01 \text{ g}$. After scouring, fabrics were rinsed with tap water and washed again with distilled water at a liquor ratio (g fabric/mL treatment bath) of 1:20 in a KIMAK Washtester for 30 min at 80°C and finally air dried.

2.2. Treatment of PA 6.6 fabrics with different acid concentrations

The pre-scoured (pre-washed) nylon 6.6 swatches ($7.00 \pm 0.05 \text{ g}$) were treated with HCl solution (0.5 M, 1.0 M and 3.0 M) at a liquor ratio of 1:20 in closed Erlenmeyer flasks for 10, 35, 60 and 240 min at 60°C on a Rotary Shaker Te-420 at 150 rpm (Tecnal, Brazil). Additionally, control experiments with only distilled water were performed under the same conditions. Experiments were carried out in duplicate. At the end of each experiment the swatches were rinsed exhaustively with distilled water at room temperature, washed for 15 min at 60°C with $1 \text{ g L}^{-1} \text{ Na}_2\text{CO}_3$ under agitation (150 rpm) in a Erlenmeyer flask and then neutralized by adding sodium carbonate solution until the pH remained between 6.5 and 6.8. Then swatches were washed in an Erlenmeyer flask with distilled water at 60°C for 10 min. Afterwards, all fabrics including control samples were neutralized together in a single flask with a 10% acetic acid. After 1 h, the samples were transferred to a new flask with distilled water and left for 80 min. At the end of the period, the pH of the solution with all the fabrics was 6.9. Then, the samples were air dried.

2.3. Chemical treatments with 3 M HCl and NaOH

Swatches of 3.1 g previously scoured (as described above) knitted PA 6.6 fabric (opaque, Rhodia) were treated at a liquor ratio of 1:10 with 3 M HCl or 3 M NaOH during 1–3 h at 60°C at constant

shaking (140 rpm; Rotary Shaker Te-420, Tecnal, Brazil). A control experiment was carried out under the same conditions with distilled water. After the chemical treatment, the fabrics were rinsed with tap water, washed for 30 min at 80°C in a neutralizing bath (1% acetic acid or 1% sodium carbonate) on a Kimak Washtester (40 rpm; liquor ratio 1:20), rinsed thoroughly with tap water and washed for another 30 min with distilled water on the Kimak washtester under the same conditions (80°C , 40 rpm; liquor ratio 1:20). Finally, swatches were rinsed with distilled water and air dried. Treatments were carried out in duplicate.

2.4. Fabric analysis

2.4.1. Determination of amino groups on the fiber surface

For the determination of amino groups on the fiber surface a new method, adapted from the TNBS methods described before [15,21,22] was used. Therefore $0.1 \text{ g} \pm 0.02 \text{ g}$ of the water and acid and base treated PA 6.6 fabrics were reacted with 4 mL borate buffer ($\text{Na}_2\text{B}_4\text{O}_7/\text{HCl}$ 0.05 M, pH 8.5) and 100 μL of 30 mM 2,4,6-trinitrobenzenesulphonic acid (TNBS); for 2 h at 37°C . An aliquot of 3 mL was withdrawn and reacted with 1.5 mL of 0.2 M glycine for 30 min and subsequently absorption was measured at 420 nm. A standard curve was prepared under the same experimental conditions using instead of 100 μL of a 30 mM solution different TNBS concentrations (0–5 mM). Amino groups on the PA 6.6 fabric were calculated considering a 1:1 TNBS-amino group stoichiometry for the reaction. Amino groups detected on control fabrics treated in water for 0–3 h were subtracted. Analyses were carried out in duplicate and measurements in triplicate.

2.4.2. Determination of water absorption

In order to evaluate the wetting behavior of the acid treated PA 6.6 fabrics the vertical wicking height (rising height) was measured with an assay adapted from the Italian standard ICEC TS 304 for leather and similar to DIN 53924 (“Bestimmung der Sauggeschwindigkeit von textilen Flächengebilden gegenüber Wasser”) based on the capillarity phenomenon. Differently treated PA 6.6 fabrics strips with dimensions of $3 \text{ cm} \times 17 \text{ cm}$ (width and length respectively) were prepared and conditioned at 67% relative humidity (RH) and 24°C in a dry closed box over a saturated solution of CuCl_2 for at least 24 h. The conditioned polyamide fabrics were attached to a metal wire and carefully suspended vertically so that 3 mm were immersed in deionized water (Milli-Q™, $\rho > 18 \text{ M}\Omega \text{ cm}$). The rising height of water in the vertically suspended samples was measured after 15 min. The rising height of the 3 M HCl and NaOH treated fabrics was measured under very similar conditions with fabric pieces of $1 \text{ cm} \times 13 \text{ cm}$ size in distilled water (pH 8.35) and at a relative humidity of 55% and 32.5°C ambient temperature. Rising height was measured after 5, 10 and 30 min. All measurements were carried out at least in duplicate.

2.4.3. Superficial dyeing of the PA 6.6 fabrics (below T_C)

The samples of the acid treated polyamide fabrics were stained with three different dyes. Dyeing with the wool reactive dye Lanazol Red 5B (Ciba; C.I. Reactive Red 66) was carried out with 1 g of each fabric sample with 2% o.w.f. (on weight fabric) of the dye in 25 mL (liquor ratio 1:25) of aqueous solution. The acid treated fabrics presented in Figs. 5 and 6 were dyed at 30°C for 60 min in Erlenmeyer flasks on a rotary shaker in a dye solution containing $5 \text{ g L}^{-1} \text{ NaCl}$. In order to remove unfixed dye fabrics were washed with a neutral solution of 2 g L^{-1} Lutensol AT 25 (BASF, Ludwigshafen, Germany) at 60°C for 30 min (liquor ratio 1:25) and washed again with an alkaline solution containing 2 g L^{-1} Lutensol AT 25 (BASF) and $2 \text{ g L}^{-1} \text{ Na}_2\text{CO}_3$ at 90°C for 30 min. Finally fabrics were rinsed with water and dried at room temperature.

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