



# Dynamic vapour sorption and thermoporometry of polyamide fabrics coated with chitosan hydrogels



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## ABSTRACT

In this work, chitosan hydrogels crosslinked with genipin have been incorporated onto the surface of polyamide fabrics and the porous structure of these modified textiles have been studied. The successful hydrogel incorporation was confirmed by weight gain and evidenced by cryo-SEM. By dynamic vapour sorption (TG-DVS) the water absorption ability of the treated fabrics was studied. The results show that fabrics coated with hydrogel have higher moisture content than uncoated fabric, and they are able to absorb more water at high relative humidity. Also, the pore distribution of fabrics was measured by thermoporometry, which allows the study of pore structures of materials in presence of water. These results show that the hydrogel coating provides new pores smaller than 100 nm, which enhance the water retention.

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## 1. Introduction

The surface modification of polyamide fabrics by hydrogel coating can affect the moisture absorption capacity and also the intrinsic porosity of fabrics. Polyamide is a widely used polymer in the textile industry. Different methods have been reported in the literature to increase its hydrophilicity and therefore their moisture sorption capacity which is related to comfort perception [1,2]. Hydrogel coating, plasma treatment and enzymatic hydrolysis are the most commonly methods used [3]. Among them the incorporation of hydrogels on textile surfaces is an interesting strategy not only to increase fabric comfort but also to incorporate an active component into hydrogel which could be released to the skin.

The sorption properties of polyamide coated fabrics can be studied by the dynamic vapour sorption technique (DVS) which can provide accurate isotherms over a wide range of relative humidity [4].

Another important parameter which could be influenced by hydrogel coating is porosity. Porous structure of fabrics is important since porosity influences some important physical and mechanical properties of textiles such as moisture uptake, wettability, softness and thermal insulation among others [5]. Moreover, pore size distribution is a prerequisite to investigate any transport phenomena,

especially in a porous structure [6]. There are different techniques to study porosity [7,8]. The most commonly used are mercury porosimetry [9] and nitrogen adsorption-desorption isotherms. Depending on the pore size one method or another will be selected. However, the methods above mentioned could be inappropriate for fabrics coated with hydrogels since they should be dried and this process could modify the original pore structure of hydrogel. For this reason, in this work thermoporometry has been chosen to measure the porosity of textiles coated with hydrogels because this technique allows the study of pore structure of materials in the liquid state. This is an appropriate method to measure the porosity of hydrogels, since the original porous structure can be preserved.

Hydrogels can be obtained from synthetic and also from natural polymers like chitosan which is a polysaccharide-based cationic biopolymer composed of units of *N*-acetylglucosamine and *D*-glucosamine joined by  $\beta$ -[1  $\rightarrow$  4] links. It is obtained as a result of deacetylation of chitin, which is widely present in nature as a structural component in the exoskeleton of arthropods and in the cell wall of fungi and yeasts [10]. Chitosan is one widely used polymer because it is hypoallergenic and possesses some extraordinary features, such as biodegradability, antimicrobial activity [11], non-toxicity and excellent biocompatibility, since their degradation products are natural metabolites.

Many of the properties of chitosan rely on its cationic nature, which allows it to interact with negatively charged molecules. This polymer has been used as textile finishing to confer antibacterial

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properties [12,13], as adsorbent of anionic dyes [3,10,12,14] or as shrink-resist agent in wool [15,16] among other applications.

Chitosan ability to form hydrogels is widely known from the last two decades. The structure stability of such hydrogels can be improved through a crosslinking process due to chitosan solubility in acidic conditions (below ca. pH 6.5) to form a viscous solution. Chitosan hydrogels can be obtained by various mechanisms of chemical or physical crosslinking such as covalent [17], ionic [18], hydrogen bonding [19] or hydrophobic association [20]. Commonly used chemical crosslinkers include aldehydes (formaldehyde, glutaraldehyde, glycerinaldehyde [21], tripolyphosphate, ethylene glycol, diglycidyl ether [22–25] and carbodiimides [26]). The main limitation in the use of toxic chemical crosslinkers arises from the presence of some unreacted crosslinker inside the hydrogel. For this reason, much interest has been addressed toward naturally derived crosslinking agents, with a low toxicity such as genipin [27]. This crosslinker is obtained from its precursor, geniposide, via enzymatic hydrolysis with  $\beta$ -glucosidase [28].

In this work, polyamide fabrics have been coated with chitosan hydrogels crosslinked with genipin and their effect in terms of moisture adsorption capacity and porosity has been studied. In order to increase hydrogel deposition on fabric surface, low temperature plasma treatment has been carried out before hydrogel coating. Also, the influence of ultraviolet treatment after hydrogel coating was evaluated. Dynamic vapour sorption (DVS) and thermoporometry by differential scanning calorimetry are two thermal analytical techniques that probe complementary dimensions of water interaction with polyamide.

## 2. Experimental

### 2.1. Materials

Chitosan with a degree of deacetylation of 85% and molecular weight of 300 kDa was obtained from Sigma-Aldrich (Steinheim, Germany). Genipin with an average molecular weight of 226 g/mol, was from Challenge Bioproducts Co. (Taichung, Taiwan). All other reagents and solvents used were of reagent grade. Polyamide fabrics with 86.21 g/m<sup>2</sup> weight was kindly supplied by Textile Industry Research Association (AITEK).

### 2.2. Synthesis of genipin crosslinked chitosan hydrogels

Chitosan hydrogels crosslinked with genipin were prepared as described in a previous work [29]. Briefly, chitosan solution was freshly prepared by dissolving 1% w/w in distilled water containing of acetic acid (1% v/v) with continuous stirring for 24 h. Genipin solutions were prepared at 0.05% w/w by dissolving genipin in phosphate buffer pH 7.4. The reaction of chitosan and genipin occurred after mixing both solutions at a ratio of 1:1 (w/w).

### 2.3. Hydrogel application on polyamide fabric

Chitosan hydrogel crosslinked with genipin was applied on polyamide fabrics by the padding technique. Fabrics were immersed in hydrogel solution and run three times through squeeze rolls with an HVF laboratory padder (Mathis, Switzerland) at a padding speed of 3 m/min and a squeeze roll pressure of 3 bar, and left to dry at room temperature. With the aim to increase hydrogel presence on fabric surface, the padding cycles were repeated two times after conditioning the samples at 22 °C and 50% relative humidity (RH). Also a plasma pre-treatment, before hydrogel coating, was carried out in order to activate textile surface. A dielectric barrier discharge reactor operating at atmospheric pressure was used. The distance between the electrodes was 1 cm. The incident power in the plasma reactor was kept constant at 30 W and the

plasma treatment was 120 s on each side of fabric. On the other hand, a UV post-treatment was carried out with the aim to increase hydrogel adherence on fabric. Ultraviolet radiation treatment was performed in a reactor equipped with a mercury lamp with a maximum emission around 320 nm. Fabrics were coated with chitosan pre-hydrogel solution and submitted to radiation for 3 h.

### 2.4. Characterization methods

Weight gain was determined after hydrogel incorporation and conditioning at 22 °C and 50% RH.

$$\text{Weight gain (\%)} = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (1)$$

where  $W_1$  is sample weight before hydrogel application and  $W_2$  after hydrogel application.

The hand feeling of fabrics was determined by a subjective method by five panellists who have conducted sensory tests. To appreciate the handle, the panellist stroked the fabric surface with one or several fingers.

The surface characterization of polyamide fabrics were by Cryo-scanning electron microscopy (Cryo-SEM) using a Jeol JSM-840 microscope with a cryo-chamber. Swollen fabrics were frozen and sputter-coated with gold before observation by Cryo-SEM analysis.

The water absorption ability was evaluated by Dynamic Vapour Sorption (DVS). Adsorption/desorption isotherms were obtained in a thermogravimetric balance equipped with a controlled humidity chamber Q500SA Sorption Analyzer (TA Instruments, New Castle, USA). The fabric samples were kept under humidity controlled conditions (22 °C and 50% RH) for 48 h before measuring. The measurements were performed at 25 °C by using the following procedure:

1. Conditioning step: samples were conditioned at 0% RH for 2 h.
2. Absorption: the relative humidity was increased and equilibrated stepwise from 0% to 95% at 5% RH interval. The sample remained in each step until the moisture content change was less than 0.02% per minute for 10 min.
3. Desorption: the atmospheric moisture content was decreased and equilibrated stepwise at 95% up to 0%. The sample remained in each step until the moisture content change was less than 0.02% per minute for 10 min.

Experimental moisture content values obtained from desorption isotherms were fitted to Guggenheim, Andersen and de Boer (GAB) model (Eq. (2)).

$$X = \frac{X_m C K a_w}{[(1 - K a_w)(1 - K a_w + C K a_w)]} \quad (2)$$

The parameters are the following:

X: equilibrium moisture content at  $a_w$  in g sorbed/100 g of sorbent on dry basis.

$X_m$ : monolayer moisture content in g sorbed/100 g of sorbent on dry basis.

$a_w$ : water activity expressed as vapour relative pressure  $p/p_0$ , where  $p_0$  is the saturated vapour.

C: energy constant related to the difference between the free enthalpy of the water molecules in the pure liquid state and in the monolayer. This is proportional to the rate between both the attachment and the escape rate constants for the primary sites.

K: ratio between the standard vapour pressure of the liquid and the vapour pressure of the sorbate in the secondary (upper) layers. It is proportional to the rate between the attachment rate constant and the escape rate for all higher layers.

Water activity corresponding to the monolayer moisture ( $a_w$ )<sub>m</sub> was determined from the GAB equation. Moisture is strongly linked

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