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Preparation of durable insecticide cotton fabrics through sol–gel treatment with permethrin

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ABSTRACT

This paper presents the development of an industrially viable procedure for the fabrication of durable insecticide textiles based on the sol–gel technique. Permethrin was incorporated on cotton fabrics by a silicon oxide nanocoating applied by conventional padding followed by curing. The effect of the sol–gel process parameters, such as silica solid content and the permethrin/tetraethyl orthosilicate (TEOS) ratio on the insecticide activity and on the textile properties of the resulting fabrics was evaluated. The application of the nanosol coating results in textiles with a high anti-mosquito effect without altering their flexibility and softness. Moreover, this method allows the insecticide content to be controlled by simply adding the proper amount of it to the coating bath. The washing fastness was assessed on a textile with a permethrin loading close to 500 mg/m^2 of fabric showing a good insecticide effect even after 50 washing cycles.

1. Introduction

The application of functional finishes to textile fabrics has led to the development of textile products with advanced properties, such as antibacterial [1–4], UV protection [5,6], fire protection (flame retardant textiles) [7], self-cleaning [8], hydrophobicity [9] or combinations of various properties in one fabric (multifunctional textiles) [10].

Sol–gel nanocomposite hybrids [11–13] have been shown to enable the chemical modification of natural fibres like cotton. Mild processing conditions are required and single-step processing, employing conventional machinery used in industrial textile finishing, such as pad application or exhaust processes, is usually enough to impart multifunctional properties to the finished fabrics [14]. Importantly, sol–gel nanocoatings exhibit excellent adhesion on cotton, attained through condensation between the –OH groups of the hydrolyzed silanes and those present on the surface of cellulose [12,14].

The resulting transparent oxide layers can act as a carrier for embedded functional additives, such as organic compounds, inorganic particles or polymers [13]. The additives or active substances can be homogeneously incorporated into and immobilized in the sol–gel nanosol coatings, leading to new applications for functional fabric finishes, like the slow release of insecticides in insect-repellent textiles [15].

Insect-borne diseases afflict hundreds of millions of people each year and represent a significant portion of overall infectious diseases, which globally rank second among all causes of death. Vaccines and therapeutic drugs have yet to be developed to treat many of these diseases, so preventive measures must be taken to control these insects and avoid contact with them. Public health agencies worldwide consider insect-repellent textiles to be an increasingly important component in reducing the incidence of insect-borne infectious diseases such as malaria, West Nile virus, encephalitis, dengue fever, Lyme disease and many others [16–20].

Permethrin is a synthetic insecticide/repellent commonly used to treat clothing, netting, camping gear and military uniforms and to provide protection from mosquitoes, ticks, sand flies, fleas and other such disease-bearing insects. In spite of being effective against all stages of insect growth, permethrin is one of the least toxic insecticides to humans and the only one registered by the US Environmental Protection Agency (EPA) for use on clothing and in agricultural and pharmaceutical applications in the United States [16,17].

Permethrin or other pyrethroid insecticides are generally incorporated into cotton based textiles either by dipping/spraying of the fabrics or by polymer-coating [18]. While the treatment by spraying is very simple, it results in a low laundering durability and it is difficult to control the quantity of permethrin on the textile. On the other hand, durable and effective insect-repellent coatings have been developed by using the polymer-coating method [19–21]. Nevertheless, these studies do not analyse the effect of the coatings on the textile properties, that is, handling and drapability, which are of crucial importance for clothing applications. In this sense, treatments with toxic formaldehyde-urea resins or other synthetic polymers dramatically alter the comfort and visual and tactile properties of cotton based fabrics.

In this study, we present an industrially viable procedure for the fabrication of comfortable and durable insecticide textiles based on the sol–gel technique. Permethrin was embedded into cotton fabrics by a silicon oxide nanocoating applied by conventional padding followed by curing

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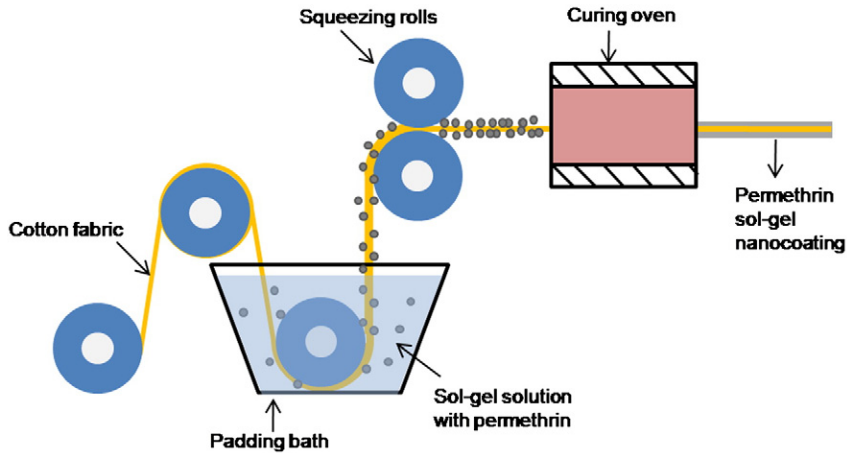

Fig. 1. Schematic illustration of the fabrication process for permethrin-loaded textiles.

(Fig. 1). The effect of the process parameters, such as silica precursor content and permethrin/silica precursor ratio, on the insect-repellent activity, textile properties and stability during washing was studied.

This new method provides the possibility of fine tuning the amount of insecticide incorporated. This point is critical since the maximum dosage of permethrin in clothing recommended by the World Health Organization (WHO) is 500 mg/m^2.

Thanks to the high laundering durability, strong anti-mosquito effect and ease of application, the permethrin-containing sol–gel coatings presented in this study, could be proposed as an alternative to well-established treatments for cotton textiles [16–21].

2. Materials and methods

2.1. Materials

The textile substrate used in this study was a satin weave cotton fabric bleached without optical brightener, purchased from *EMPA Test Materials*. The characteristics of the fabric were 24 yarns and picks/cm with a weight of 210 g/m^2.

Permethrin (provided by Zell Chemie Internacional, S.L) was used as the active principal substance. The most remarkable physicochemical properties are a density of 1.29 g/cm^3, a decomposition temperature of 252 °C, low solubility in water (0.006 mg/L at 20 °C) but soluble in ethanol (25 mg/mL). The maximum dosage of permethrin in clothing recommended by WHO is 500 mg/m^2.

Tetraethyl orthosilicate (TEOS) (98%), purchased from Sigma Aldrich, was used as the silica precursor. HCl (hydrochloric acid solution 0.1 mol/L) and ethanol from Scharlab were used as reagents for the sol–gel process.

2.2. Preparation of the permethrin-containing sol–gel solutions

The permethrin-containing sol–gel solutions were prepared in 2 steps. First, a 13 wt.% silica sol was synthesized by acid hydrolysis of TEOS with HCl 0.05 M for 3 h at r.t. In the second step, the silica sol was mixed at r.t. with a permethrin solution in ethanol (2 wt.%). The pick-up was 68%. Immobilization occurred during the formation of the silica matrix by physical entrapment of the permethrin molecules into the pores of the cross-linked network [15,22].

Various solutions with different wt.% of solid content (defined as the total mass of TEOS and permethrin with respect to the total mass of the solution) and permethrin/TEOS weight ratios were prepared. Moreover, sol–gel solutions without permethrin were prepared in the same conditions as the reference samples.

2.3. Fabric treatment

The samples were dipped into the sol–gel solution and passed through a laboratory padding machine (Foulard Roaches FHP) at a speed of 3 m/min under a pressure of 2.75 kg/cm^2. The padded fabric samples were dried at 105 °C for 2 min and cured in an oven at 140 °C for 1 min. All the samples were conditioned at 20 °C and 65% relative humidity for at least 24 h before characterization.

2.4. Fabric characterization

The permethrin content of the textiles was determined by HPLC after Soxhlet extraction of textile fabrics with methanol. Both isomers, *cis* and *trans*, were taken into account to quantify the total permethrin content.

The morphology of sol–gel treated fabric was analysed using scanning electron microscopy (SEM, Hitachi H-4100FE) after coating the samples with carbon to minimize the charging effect.

The textile properties were assessed before and after the sol–gel coating. The bending rigidity (S) was determined first on the warp and weft directions using a Shirley stiffness meter. The bending rigidity of the warp or weft directions is defined as Eq. (1):

$$S_{warp,weft} = mc^3_{warp,wef} \quad (1)$$

where c is the bending length measured in the warp or weft direction and m is the fabric weight per unit of area. The values reported for the warp and weft directions are the averages of 10 repeated measurements in each face of the fabric.

The bending rigidity is obtained from Eq. (2):

$$S = \sqrt{S_{warp} \times S_{weft}} \quad (2)$$

The recovery from creasing was determined by measuring the recovery angle (α) of a horizontally folded specimen loaded with 1 kg for 5 min according to UNE-EN 22313. The values reported are the averages of 10 repeated measurements in the warp and weft directions and in each face of the fabric.

To evaluate the durability of the treatment to repeated laundering, the textiles were washed in a Wascator (Type A) at 40 °C in agreement with the standard UNE-EN ISO 6330 washing procedure. The detergent used was an ECE washing powder with the following composition: 77% IEC-A, 20% tetrahydrated sodium perborate and 3% tetra-acetylenediamine.

The insecticide activity of the treated fabrics was assessed by performing bioassay tests following a protocol proposed by WHO [23]. A known amount of *Aedes aegypt* mosquitoes, used as the model specie,