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Application of fluorinated compounds to cotton fabrics via sol–gel

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ABSTRACT

The aim of this work was the study of the surface modification of cotton fibers to confer hydro and oil repellency to the fabrics. A surface treatment not involving the bulk of the fibers was chosen, so fabrics can maintain comfort properties. Moreover the study focused on an economical and environmental friendly process, in order to obtain an effective treatment with good fastness to washing.

A modified silica based film was applied on fibers surface by sol–gel, comparing laboratory grade reagents with a commercial product as precursors and optimizing process parameters.

From obtained results sol–gel can be indicated as a promising process to confer an effective and durable finishing to cotton fibers with low add-ons. Long impregnation times can significantly improve the treatment fastness, while ironing the washed samples can restore, at least partially, hydro and oil repellency lost after the washing. Obtained results were supported by a deep surface characterization of untreated, treated and washed samples.

The best results were obtained using the commercial product as the only precursor. This is interesting for an industrial application, due to the low cost of this product if compared with the laboratory grade reagents investigated.

Some applications of finished textiles can be for household use, technical garments, umbrellas or outdoor textiles.

1. Introduction

In the last decades the number of new applications of textile materials has strongly increased. Especially the market of technical textiles is showing high rates of economic growth and the demand for materials with new or additional properties is becoming crucial. Water and soil repellency or superhydrophobicity, in particular, are among the most desirable textile properties for consumers [1].

In many cases a water barrier is achieved by completely covering the open structure of a textile with a dense polymer layer or by producing laminates by incorporation of certain membranes like Gore-Tex® or Sympatex®. Nevertheless, these treatments can compromise the peculiar characteristics of natural fabrics, such as softness or breathability. Due to this reason, the surface modification of fiber materials is an important topic of textile research worldwide.

The surface modification of textile fibers is carried out by commonly used chemical or electro-chemical application methods. Dyestuffs, polymers or monomers are applied to the fibers and are bonded either in a permanent or often only in a temporary way.

However more recent techniques are applied more and more in addition to these [2]. Plasma treatment, for instance, can add a huge number of functional groups to the polymer surface, depending on the process gases in the plasma chamber. The literature reports, for example, the deposition of fluorine rich surfaces, leading to highly repellent fabrics [3,4]. Plasma techniques offer far-reaching possibilities, but the technical effort is comparatively high due to the fact that the processes often have to be carried out under reduced pressure or at least under oxygen-free atmosphere. Besides plasma treatments, electron beam technologies as well as different photonic technologies, namely UV-grafting [5–8] or laser treatment, are applied to achieve a specific functionality [9].

In this scenario, nanotechnology shows real and great potential in the textile industry, especially considering that the conventional methods used to impart specific properties to fabric textiles do not often yield permanent effects against wearing or washing. The application of nanotechnology has been proven to give high durability to fabric modifications and to improve the overall fabric performance, thanks to the nanomorphology of the fillers used [10].

Among the new approaches, the sol–gel technology is probably one of the most important developments in material science during

Abbreviations: TEOS, Tetraethoxysilane; FOS, 1H,1H,2H,2H-Fluorooctyltriethoxysilane.

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the last decades. Sol–gel technology enables the possibility to tailor surface properties to a certain extent, and to combine different functionalities in a single material. At the same time, the application of sols can be carried out with techniques commonly used in the textile industry [1,11].

An important issue in the application of nanosol coatings to textiles is the adhesion to the fiber surface in order to prevent the coating from flaking off during use or washing [12]. In the case of cellulose materials like cotton, the adhesion of the sol–gel coating is easily improved by chemical condensation of silanol groups with the hydroxyl groups on the textile surface. The chemical condensation of pre-hydrolyzed alkoxysilanes on cellulose is known to occur after thermal treatment at above 100 °C [9,13].

Cotton has always been the principal fiber for clothing due to its attractive characteristics. However, its high absorbency, as a result of the high amount of hydroxyl groups on the surface, compromises stain-resistance and water repellency. Therefore, additional finishes are mainly required to impart superhydrophobicity and self cleaning properties to cotton textiles.

Generally pure laboratory grade alkoxysilanes are used as sol–gel precursors. A hybrid framework composite can be obtained by mixing alkoxysilanes with organic precursors and the final properties of the coating can be tailored on purpose by choosing proper precursors. TEOS is the most widely used precursor in sol–gel processes [14], nevertheless it can be partially or totally replaced by fluorinated alkoxysilanes to confer hydro and oil repellency typical of these compounds [15–19].

In a previous study it was investigated the finishing of cotton fabrics by a TEOS nanosol modified with FOS, obtaining quite good results [20]. However, pure fluoroalkyl compounds have the significant disadvantage of high cost, making them unsuitable for wide industrial applications.

In the present work, a process improvement is proposed by replacing FOS with the cheaper commercial product Fluorolink S10, already used to prepare organic-inorganic hybrid coatings on glass by sol–gel in presence of TEOS [21]. Moreover the possibility to avoid TEOS introduction in the sol–gel process was investigated.

In this way, an improved resistant superhydro and oil repellent cotton can be obtained by a cheap and significantly simplified process.

2. Materials and methods

2.1. Samples preparation

Tetraethoxysilane (TEOS), 1H,1H,2H,2H-Fluorooctyltriethoxysilane (FOS), both pure laboratory grade reagent purchased from Sigma–Aldrich (Italy), and Fluorolink® S10, commercial product from Solvay Solexis (Italy) were used as precursors. In Fig. 1 the molecular structures are reported; in particular that of Fluorolink was taken from literature [22] and the Mw of the reagent used was in the range 1750–1950 g/mol.

Ethanol 96% vol from Sigma–Aldrich and deionized water were used as dilution media while the acidity was adjusted by addition of reagent grade hydrochloric acid.

Three different nanosols were prepared, using FOS or Fluorolink alone or Fluorolink mixed with TEOS as precursors. At first sol–gel precursors were dissolved in alcoholic media, then aqueous 0.01 M hydrochloric acid was added so that hydrolysis and condensation reactions occurred forming a nanosol by vigorously stirring, for 24 h at room temperature. FOS and Fluorolink nanosols were prepared both with 50% w/w of the respective precursor, 46% w/w of ethanol and 4% w/w of 0.01 M HCl, while that of Fluorolink plus TEOS was 17% w/w Fluorolink, 19% w/w TEOS, 58% w/w ethanol and 6% w/w 0.01 M HCl.

The cotton fabric was dipped in the respective suspension, suitably diluted with ethanol (1:2 w/w), in order to adsorb the nanoparticles on the fiber surface; weights on were fixed to about 5% or 10% o.w.f. (over weight fiber) and the influence of different impregnation times (1 min, 2 h and 24 h) on FOS nanosol was investigated. The best results were obtained with 24 h impregnation, so with Fluorolink only this time was adopted. Finally, drying and curing were carried out at 120 °C for 1 h.

The textile substrate used was Cotton ISO 105-F02 woven fabric, 105 g/m^2 weight. The area of treated samples was about 100 cm^2.

2.2. Samples characterization

Hydro and oil repellency were tested using HPLC grade water and paraffin oil (Sigma–Aldrich), with surface tension of 72 mN/m and 31.5 mN/m respectively. The wettability of untreated, treated and washed samples were investigated by a DSA20E "Easydrop standard" drop shape analysis tensiometer from Krüss, (Germany) equipped with DSA software, using the sessile drop method for fitting. Measuring liquid drops were deposited from a glass syringe on the fabrics surface by means of the software controlled dosing. The contact angles were the average of at least 5 measurements for each sample with a standard deviation of about 2–3%.

Moreover, the time necessary for the total absorption of both water and oil drops was measured.

Investigation on fastness behavior of treated samples to domestic laundering was performed by washing the treated samples at 40 °C for 30 min using 5 g/l ECE detergent according to ISO 105 C01 standard. Contact angles and drop absorption times were measured after 5 washing cycles.

FTIR-ATR analyses were performed on a Nicolet FTIR 5700 spectrophotometer equipped with a Smart Orbit ATR single bounce accessory mounting a diamond crystal. Each spectrum was collected directly on treated samples by cumulating 128 scans, at 4 cm^{-1} resolution and gain 8, in the wavelength range 4000–600 cm^{-1}.

Surface chemistry of the fabrics was analyzed before and after the treatment by X-ray photoelectron spectra (XPS) with a PHI 5000 Versa Probe system (Physical Electronics, MN) using a monochromatic Al radiation at 1486.6 eV, 25.6 W power, with an X-ray beam diameter of 100 μm. The energy resolution was about 0.5 eV. XPS measurements were performed at a pressure of 1.0×10^{-6} Pa. The pass energy of the hemisphere analyser was maintained at 187.85 eV for survey scan and 29.35 eV for high-resolution scan while the takeoff angle was fixed at 45°. Since the samples are insulators, an additional electron gun and an Ar^+ ion gun were used for surface neutralization during the measurements. Binding energies of XPS spectra were corrected by referencing the C1s signal of adventitious hydrocarbon to 285 eV. XPS data fittings were carried out with PHI multipakTM software using the Gauss-Lorenz model and Shirley background.

The surface morphology of the fabrics was examined by SEM with a Leica (Cambridge, UK) Electron Optics 435 VP scanning electron microscope with an acceleration voltage of 15 kV, a current probe of 400 pA, and a working distance of 20 mm. The analysis was carried out on the samples treated with 10% Fluorolink and an impregnation time of 24 h. The samples were mounted on aluminum specimen stubs with double-sided adhesive tape and sputter-coated with gold in rarefied argon using an Emitech K550 Sputter Coater with a current of 20 mA for 180 s.

3. Theory

In general, the wettability of solid surfaces is governed by both chemical composition and topography. Repellent finishes achieve