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To cite this article: C Colleoni *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **254** 122002

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Ceramic coatings for water-repellent textiles

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Abstract. In recent years, ceramic coatings have been widely studied for their potential performance in many scientific and technological fields. Ceramic coatings are also used as a textile-finishing agent to impart several properties such as anti-bacterial, anti-abrasion, flame retardant. In this study, fluoro free water repellent finishings have been developed to assess the features of the silica films on the textile fabrics. The water repellency of the treated samples has been evaluated by different tests such as water contact angle, water uptake and drop test.

1. Introduction

During the last few years, the increasing demand toward environmental friendly and non-toxic textile finishings has attracted considerable interest with respect to both academic and industrial research in the field of fashion and textiles [1, 2]. This is also the outcome of the response of the textile sector to the textile regulations such as E.U. REACH and to several initiatives to reduce the negative impacts of chemicals in the textile production chain. The Roadmap to Zero Discharge of Hazardous Chemicals (ZDHC 2014) and the Chemicals Management Working Group (CMWG) (Outdoor Industry Association, 2014) are the most internationally known initiatives. In this context, considerable attention has been dedicated to study new hydrophobic and super-hydrophobic [2, 3] coatings.

Water/oil repellent textiles are mostly based on polymeric per- and polyfluoroalkyl substances (PFASs), more precisely “side-chain fluorinated polymers” due to the high repellent performance both against water and oil. The use of fluorochemicals is at present the most favourable treatment, because they greatly decrease the wettability of the textile substrate by forming a water-repellent and oil-repellent film on its surface.

However, the disadvantages of fluoroalkyl compounds are the high cost of materials and a potential risk for human health as well as environmental concern [2, 4]. In particular, perfluorooctanoic acid (PFOA) and perfluorooctane sulphonate (PFOS) are being replaced by other lower fluorocarbon alternatives, even if short fluorocarbon chains could also be considered potentially dangerous, due to the high strength of carbon–fluorine chemical bond [4-5]. Commercially available non-fluorinated chemicals are unable to provide the desired performance requirements, especially in situations where extremely low surface tension is needed. For this reason, non-fluorinated surface modification using sol–gel technique has been proposed as an alternative approach to confer water repellency. The sol–gel represents a versatile two-step reaction (hydrolysis and condensation), that is able to confer, by the formation of an inorganic or organic–inorganic film, different textiles with anti-abrasion, antimicrobial, sensing and flame retardant properties [2, 6-12]. Currently, the sol–gel technique has



been reported as a promising tool for the preparation of water-repellent coatings for application on paper, textiles or wood [2].

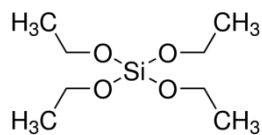
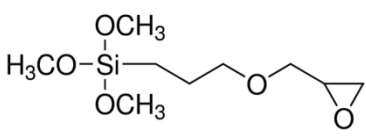
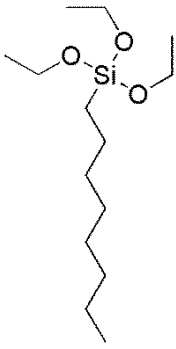
In this study, the sol-gel technique was used to develop hydrophobic ceramic finishing for textile applications using non fluorinated additives both for cotton and poly(ethylene)terephthalate (PET) fabrics to explore new routes in order to increase water repellency. For these reasons, different silane solutions were synthesized at room temperatures using different precursors (e.g. TEOS, GPTES, etc.) and then applied singularity and in combination.

2. Experimental part

2.1. Materials

Scoured and bleached 100% plain-weave cotton fabric and 100% PET were supplied by Mascioni Spa, Cuvio (Va), Italy. The fabrics were washed in 2% non-ionic detergent at 40°C for 20 min, and then rinsed several times with de-ionized water, dried and put into drier for storage. The cleaned samples were conditioned under standard atmospheric pressure at $65 \pm 4\%$ relative humidity and $20 \pm 2^\circ\text{C}$ for at least 24 h prior to all the experiments. All chemical reagents were purchased from Sigma Aldrich or Carlo Erba and used as received (Table 1).

Table 1. Name, code and chemical structures of some precursors.

Name	Code	Chemical formula
Tetraethyl orthosilicate	TEOS	
(3-Glycidyloxypropyl)trimethoxysilane	GPTMS	
Octyltriethoxysilane	OTES	

2.2. Methods

Silica sols were synthesized at room temperature in hydro/alcoholic solution at different precursor concentrations in presence of HCl as catalyst. The sols were vigorously stirred at room temperature for 4 hours before the application to complete the hydrolysis of alkoxy silane. The cotton specimens (20 cm x 30 cm) were impregnated with the sols and afterward were passed through a two-roll laboratory padder (Werner Mathis, Zurich, Switzerland) working with 3 bar nip pressure and obtaining about 70%-90% of wet pick-up. After applying the fabrics were thermal treated at 80°C for 10 min and,

then, polymerized at 170°C for 2 min in a gravity convection oven. In order to investigate the nature of the hybrid coating and the interactions between ceramic film and polymer substrate, Thermo Avatar 370 FT-IR spectrometer, equipped with an attenuated total reflection (ATR) accessory (using a diamond crystal), was used. Three replicate spectra were acquired at a resolution of 4 cm⁻¹ and 128 scans for each sample over a frequency range of 650 to 4000 cm⁻¹. The samples were collected at room temperature. The water repellency of treated and pristine samples was tested by contact angles measurement and modified AATCC 193-2009 Test Method, water uptake test. To evaluate durability of water repellency, water contact angle and infrared spectra of treated textile fabrics were collected after washing cycle performed according to AATCC Test Method 61-2006, at 40°C for 30 min.

3. Results and discussion

In this study, the sol-gel technique was used to develop water repellent ceramic finishings for textile applications using non fluorinated additives both for cellulosic (cotton) and polyester (poly(ethylene)terephthalate, PET) fabrics. Different silane solutions were synthesized at room temperatures using different precursors to investigate several parameters, in particular, i) nature and concentration of the precursors, ii) substrate iii) washing fastness. The FT-IR ATR spectra of the untreated and treated cotton fabrics by precursors (TEOS, GPTES, OTES) are shown in Figure 1. The spectra of the treated textiles were compared with that of the untreated cotton fabric in order to more easily locate the characteristic peaks of the sol deposited. The spectral intensity in the ranges 3500–3000 cm⁻¹, 2980–2800 cm⁻¹, 1435–1425 cm⁻¹, characteristic of hydrogen bonded O-H stretching, C-H stretching and C-H wagging of cellulose, respectively, remained essentially unchanged except for GPTES and OTES spectrum in which an increasing at about 2850 cm⁻¹ is due to the presence of $\nu(\text{CH}_2)$ bonds. The presence of the thin silicon film covering the surface of cotton fibers is strongly evidenced by a significant intensity increasing in the fingerprint spectral region at about 1300 cm⁻¹, due to overlapping of the main cellulose and silicon absorptions. The ceramic coating formation is confirmed by the presence at around 1200 cm⁻¹, 950 cm⁻¹, and 800 cm⁻¹ of an absorption bands assigned to Si-O stretching vibration shoulder, Si-OH stretching, and Si-O-Si symmetric stretching, respectively. The characteristic band of a ceramic coating, expected at 1020 cm⁻¹, is overlapped with a broad band between 1050 and 980 cm⁻¹ attributed to the characteristic peaks of cellulose.

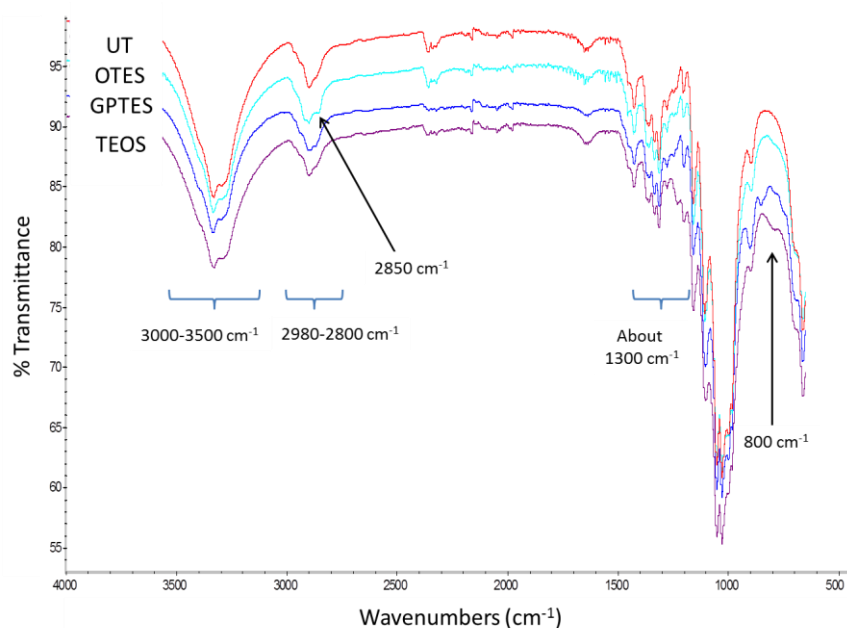


Figure 1. FT-IR spectra of untreated (UT) and treated cotton samples (TEOS, GPTES, OTES).

The wettability of treated samples decreases after the deposition of ceramic coating, independently from the kind of the precursor used (Figure 2). However, as expected, the nature of the precursor plays an important role in the water repellency. Water contact angle increases dramatically in presence of a long alkyl chains (OTES).

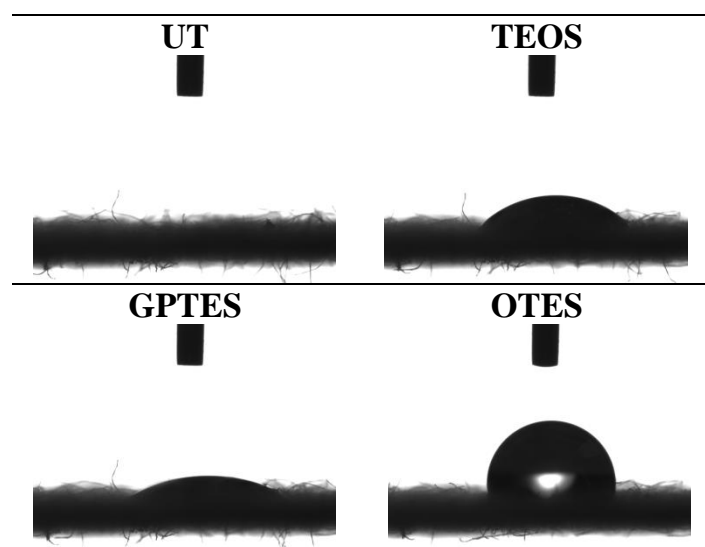


Figure 2. Water contact angle of untreated (UT) and treated cotton samples (TEOS, GPTES, OTES).

Furthermore, an increase of the water repellency is observed when precursors are used together. A possible hypothesis could be related to the better orientation of the alkyl chains, improved by the ceramic coating and to a changing of the textile surface roughness.

Because of the nature of the textile surface and precursors, the modified silica sol system shows a good adhesion on the cotton fabric as indicated by water contact angles after home launderings (Figure 3). These performance could not be obtained on PET samples due to the low interaction between the finishes and the surface.

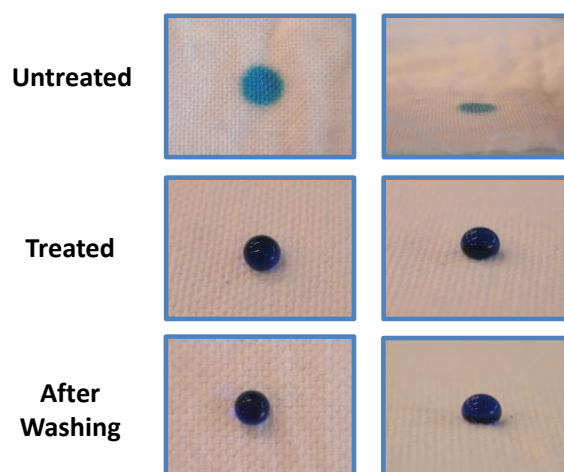


Figure 3. Water repellency of untreated and treated cotton fabrics by sol-gel finishing.

4. Conclusions

Ceramic coatings can provide an easy alternative to conventional methods for the manufacturing of water repellent textile fabrics, in substituting of fluoro-based. The nature and the concentration of the

silane precursor plays an important role in the water repellency of the treated textiles as well as the nature of the textile fabric.

Acknowledgments

Authors wish to thank Franco Belotti for technical support and useful discussion.

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