Influence of crosslinker structure on performance of functionalised organic-inorganic hybrid sol-gel coating

J Vasiljević[1], M Zorko[2], D Štular[1], B Tomšič[1], I Jerman[2], B Orel[2], J Medved[1] and B Simončič[1]

[1]University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva 12, 1000 Ljubljana, Slovenia
[2]National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

e-mail: barbara.simoncic@ntf.uni-lj.si

Abstract. This research aimed to investigate the influence of the co-condensation of the three different organofunctional trialkoxysilane precursors with two different crosslinkers, i.e. tetraethoxysilane or organocyclotetrasiloxane on the performance and the washing fastness of this multicomponent multifunctional sol-gel coating on cellulose fibres. To this aim, a three-component equimolar sol mixture (MC), which included 1H,1H,2H,2H-perfluorooctyltriethoxysilane (SiF), 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (SiQ) and P,P-diphenyl-N-(3-(trimethoxysilyl)propyl) phosphinic amide (SiP) in combination with two different concentrations of TEOS (T and 3T) or organocyclotetrasiloxane 2,4,6,8-tetrakis(2-(diethoxy(methyl)silyl)ethyl)-2,4,6,8-tetramethyl–cyclotetrasiloxane (T_4) as crosslinkers, was applied to the cotton fibres by a pad-dry-cure process. The functional properties of the coated samples before and after repeated washing were investigated by the water θ (W) and n-hexadecane θ (C16) static contact angle as well as water sliding (roll-off) (α) angle measurements. The inclusion of both TEOS and T_4 into the MC sol increased the hydrophobic affect and simultaneously decreased the oleophobic effect of the MC coating. These phenomena were more pronounced for higher concentration of TEOS and T_4 crosslinker. The inclusion of T_4 into the MC sol improved the coating washing fastness to a significantly higher extent than the inclusion of TEOS, with respect to the applied concentrations.

1. Introduction

Organoalkoxysilane and organofunctional alkoxysilane sol-gel precursors are widely used for the surface functionalization of textile fibres through the deposition of thin hybrid films from the liquid phase [1,2]. Even more, the sol-gel application of a mixture of three or more organofunctional trialkoxysilane precursors represents an exceptional and simple method for the development of a multifunctional multicomponent coating with selected protective properties. Following this approach, we previously reported [2] the fabrication of a novel multifunctional water and oil repellent, antibacterial and flame retardant sol-gel film on a cotton fibre surface. However, the coating washing fastness was poor which could be assigned to the reduced adhesion between coating and fibre surface.

Effect of the increased steric hindrance of bulky organofunctional groups can deteriorate the polymerisation process and the orientation of functional groups in the coating, consequently reducing the coating washing fastness as well as its functional properties [3]. The performance of the hybrid

sol-gel coatings can be improved by assisted condensation with crosslinkers [4,5]. Nonetheless, this assisted crosslinking can be followed by the side effect, i.e. a reduction of the coating's functional properties. Since the later phenomenon is influenced by the structure of the crosslinking agent, the main objective of this study was to investigate the influence of crosslinkers tetraethoxysilane (TEOS) of two different concentrations (T and 3T) and organocyclotetrasiloxane 2,4,6,8-tetrakis(2-(diethoxy(methyl)silyl)ethyl)-2,4,6,8-tetramethyl–cyclotetrasiloxane (T_4) on the orientation and durability of the multifunctional water- and oil repellent, antibacterial, and flame-retardant coating including 1H,1H,2H,2H-perfluorooctyltriethoxysilane (SiF), 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (SiQ) and P,P-diphenyl-N-(3-(trimethoxysilyl)propyl) phosphinic amide (SiP).

2. Experimental

2.1. Materials

The alkaline-scoured, bleached, and mercerised plain-weave 100 % cotton (CO) woven fabric with a weight of 119 g/m^2 (warp density: 50 threads/cm; weft density: 31 threads/cm) was kindly supplied by the Slovenian textile company Tekstina d.d. Ajdovščina (Ajdovščina, Slovenia).

The commercially available 1H,1H,2H,2H-perfluorooctyltriethoxysilane (SiF, 97 %, ABCR), 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (SiQ, 40 %, ABCR), hexadecyltrimethoxysilane (SiH, 90 %, ABCR) and P,P-diphenyl-N-(3-(trimethoxysilyl)propyl) phosphinic amide (SiP), which was synthesised according to a procedure reported in the literature [6], were used as organofunctional-trialkoxysilane precursors.

Tetraethyl orthosilicate (TEOS), ethanol (EtOH), 2-propanol (i-PrOH), and a 25 % ammonia solution [NH3 (aq)] were purchased from Sigma Aldrich Corporation, and 97 % 1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane and 97 % methyldichlorosilane were purchased from ABCR Gute Chemie. The chemical structures of the SiF, SiQ, SiP, T and T_4 precursors are presented in our previous work [7].

Organocyclotetrasiloxane 2,4,6,8-tetrakis(2-(diethoxy(methyl)silyl)ethyl)-2,4,6,8-tetramethyl–cyclotetrasiloxane (T_4) was synthesised from tetramethyltetravinyl-cyclotetrasiloxane and methyldichlorosilane, followed by controlled ethanolysis in the presence of a base. The chemical structures of the TEOS and T_4 precursors are presented in Fig. 1.
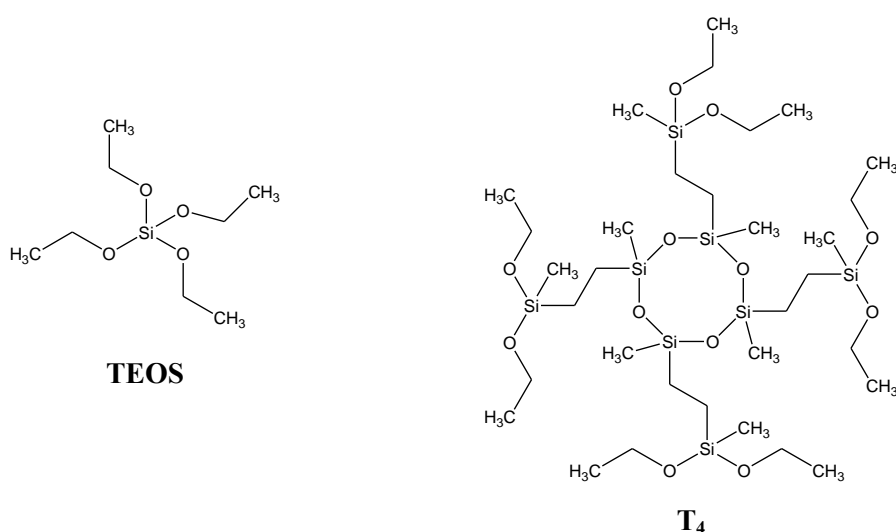

Figure 1. Chemical structures of TEOS and T_4

2.2. Sol-gel coating

Four different multicomponent sol mixtures of the hydrolysed precursors SiF, SiQ, SiP, T and T4 were prepared in ethanol and applied to cotton fabric samples by the pad-dry-cure method as described in our previous work [7]. The concentration of the components in the sol mixtures and the corresponding codes are presented in Table 1.

Table 1. Codes of the multicomponent hybrid coatings, and concentration and molar ratio of the components in the corresponding sol mixtures.

Sol mixture code	Concentration of the components in sol mixture (%)					Molar ratio
	SiF	SiQ	SiP	TEOS	T_4	
MC	4	3.9	3	-	-	$n(SiF):n(SiQ):n(SiP) = 1:1:1$
MC+T	4	3.9	3	1.6	-	$n(SiF):n(SiQ):n(SiP):n(TEOS) = 1:1:1:1$
MC+3T	4	3.9	3	4.8	-	$n(SiF):n(SiQ):n(SiP):n(TEOS) = 1:1:1:3$
MC+T_4	4	3.9	3	-	6.9	$n(SiF):n(SiQ):n(SiP):n(T_4) = 1:1:1:1$

2.3. Analyses and measurements

The surface morphology of the fabric samples was observed using a scanning electron microscope (SEM) (FE-SEM Zeiss SUPRA 35VP), which was operated with a primary electron beam at an accelerating voltage of 1 kV.

Fourier-transform infrared (FT-IR) spectra were obtained on a Spectrum GX I spectrophotometer (Perkin Elmer, Great Britain) equipped with an attenuated total reflection (ATR) cell and a diamond crystal (n = 2.0). The spectra were recorded over a range of 4000 cm^{-1} to 600 cm^{-1} using 32 scans at a resolution of 4 cm^{-1}.

The fabric samples were washed repeatedly in an AATCC Atlas Launder-O-Meter standard instrument (SDL Atlas, USA). One washing cycle in a Launder-O-Meter (ISO 105-C06 standard method) with ten steel balls provides an accelerated washing treatment that corresponds to 5 domestic washes. The finished fabric samples were washed repeatedly up to 4 times. The washed samples were coded by adding the suffix –1W, –2W, –3W and –4W to the assigned codes, according to the number of washing cycles.

The static contact angles, θ, were measured with water (W) and n-hexadecane (C16) on the fabric samples using a DSA 100 contact angle goniometer (Krüss, Germany). The static contact angle, θ, of a liquid droplet was determined using the Young-Laplace fitting method. Ten measurements, which were performed with 5-μl liquid droplets at different points on the fabric samples, were used to calculate the average contact angle values and standard errors. All the values reported here correspond to contact angles that were obtained under stationary conditions, i.e., 30 s after the liquid droplet was placed on the fabric.

The water sliding (or roll-off) angles, α, were measured in the warp direction and determined as the critical angle at which the 50-μl droplet began to slide or roll off the gradually inclined fabric surface. Five measurements were performed for each fabric sample, and the mean values were calculated.

Because of the direct influence of coating orientation or damage of the polymeric film by repeated washing on the water and oil repellent properties, we used the water θ (W) and n-hexadecane θ (C16) static contact angle as well as water sliding (roll-off) (α) angle measurements. Furthermore, from the values of the contact angles we calculated the work of adhesion, W_A, by using the following equation:

$$W_A = (1 + \cos \theta) \times \gamma_L \qquad (1)$$

where θ is the static contact angle of the tested liquid and γ_L is the liquid surface tension (γ_L is equal to 72.8 mJ/m^2 and 27.5 mJ/m^2 for water and n-hexadecane, respectively) [8].

3. Results and discussion

3.1. SEM and ATR FT-IR characterisations
The representative SEM images of the applied coatings on the cotton fibre surface are presented in Fig. 2. As observed in Fig. 2, the MC, MC+T, MC+3T and MC+T4 coatings with a nanoscale thickness were uniformly deposited on the cotton fibre surface. The ATR FT-IR spectra of the CO, CO/MC, CO/(MC+T), CO/(MC+3T) and CO/(MC+T4) samples are presented in Fig. 3.
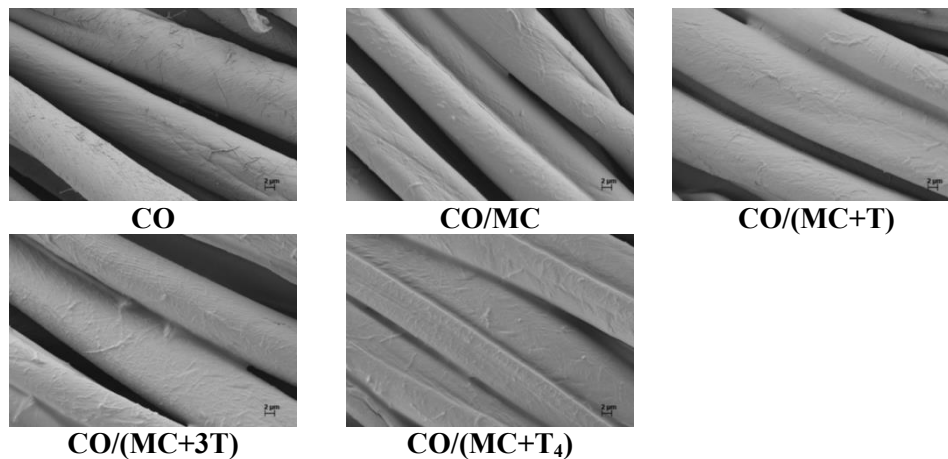

CO   **CO/MC**   **CO/(MC+T)**

CO/(MC+3T)   **CO/(MC+T$_4$)**

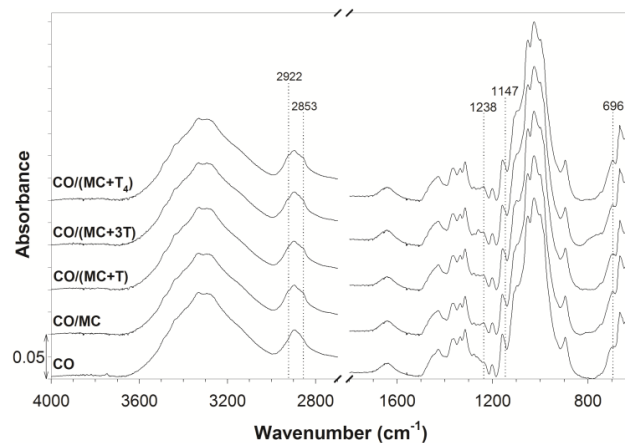**Figure 2.** Representative SEM images of the unfinished and CO-coated samples

Figure 3. ATR FT-IR spectra of the unfinished and CO-coated samples

The cellulose fingerprint in the 1500-800 cm^{-1} spectral region, a broad absorption band in the 3500–3200 cm^{-1} spectral region due to the hydrogen-bonded O–H stretching in cellulose and the absorption band at 1647 cm^{-1}, which is related to the O–H bending of absorbed water molecules were observed in the spectra of all CO samples [9,10]. The bands at 1238 cm^{-1} and 1147 cm^{-1}, assigned to CF$_2$ valence asymmetrical stretching mixed with CF$_2$ rocking and CF$_2$ valence symmetrical stretching, respectively [7], confirmed the presence of the SiF component in all the examined samples. The bands at 2922 and 2853 cm^{-1} assigned to the asymmetric and symmetric stretching vibrations of the C–H bonds of the octadecyl group [9,11] and the band at 696 cm^{-1} related to the benzene ring [9,12] indicated the presence of the SiQ and SiP components, respectively, in all the examined samples.

3.2. Hydrophobic, oleophobic and washing fastness performance of the coatings

We previously reported [2,7] the fabrication of a novel multifunctional sol-gel coating on a cotton fibre surface through the sol-gel application of an equimolar three-component sol mixture, which included SiF, SiQ and SiP. The created multifunctional coating simultaneously preserved the water and oil repellency, excellent antibacterial activity and enhanced their thermo-oxidative stability of the cotton fibres. The influence of the co-condensation of the organofunctional trialkoxysilane SiF, SiQ and SiP precursors with two different crosslinkers, i.e. tetraethyl orthosilicate (TEOS) or organocyclotetrasiloxane (T_4) on the performance and the washing fastness of this multifunctional sol-gel coating on cellulose fibres was investigated by using water and n-hexadecane static contact angle measurements. These measurements were chosen, because it was assumed that inclusion of the crosslinkers into the coating would influence the steric hindrance and consequently, the orientation of functional groups and the coating arrangement, which directly influence the hydrophobic and oleophobic properties of the surface.

The results from the water and n-hexadecane static contact angle and water sliding (roll-off) angle measurements as well as the calculated values for the work of adhesion are presented in Fig. 4.
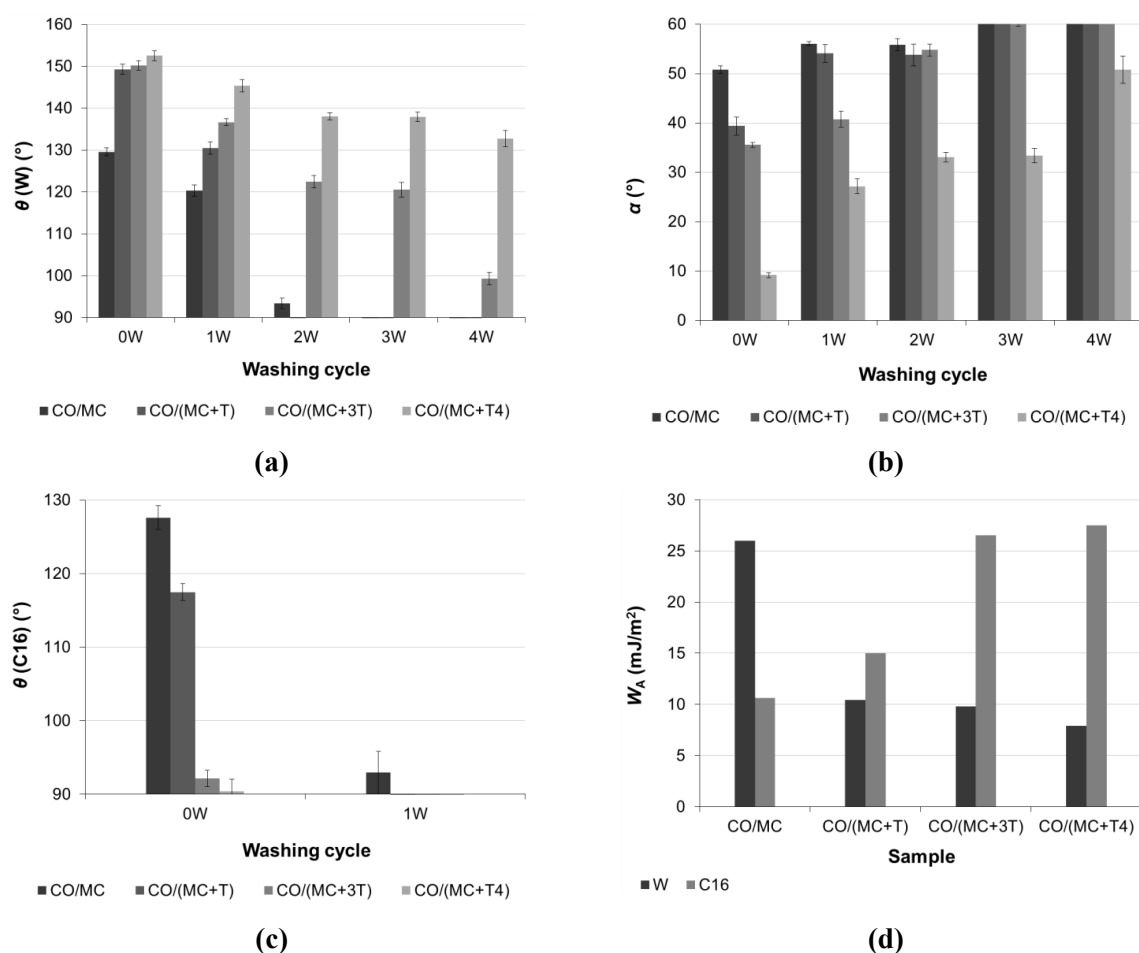

(a)

(b)

(c)

(d)

Figure 4. Static contact angles, θ(W), of water (**a**), water sliding (roll-off) angles, α, (**b**), static contact angles, θ(C16), of n-hexadecane (**c**) obtained before and after repeated (1, 2, 3 and 4W) washing cycles, and work of adhesion (**d**) between different liquid (water and n-hexadecane) and fabrics

The presence of T, 3T and T_4 in the coating increased θ(W) and decreased α in the raw CO/MC < CO/(MC+T) < CO/(MC+3T) < CO/(MC+T4), meaning that compared to TEOS, with the respect to

the applied concentrations, organocyclotetrasiloxane (T_4) more contributed to the increase of the the hydrophobic effect of the multicomponent coating (Fig 4 (a) and (b)). Even more, the inclusion of T_4 in the multicomponent multifunctional coating enabled achievement of the noteworthy ''lotus effect'' on the cotton fabric surface. However, the oleophobicity decreased in the raw CO/MC < CO/(MC+T) < CO/(MC+3T) < CO/(MC+T4) (Fig 4 (c)). These phenomena were followed by the corresponding trend for the work of adhesion, which is directly related to the adhesion forces between a solid and a liquid (Fig 4 (d)). The inclusion of the crosslinkers into the polymer network backbone and increased concentration of TEOS caused its expansion, decreased the steric hindrance of the site groups and allowed greater arrangement of the functional groups on the fibre surface. However, the T_4 crosslinker and increased concentration of TEOS had pronounced negative effect on the coating oleophobicity, which may be assigned to a decrease in the surface concentration of the perfluoroalkyl chains as well as to the directionally specific embedment of the oleophobic C-F groups in the deposited coating.

Whereas the inclusion of TEOS at lower concentration into the coating insignificantly influenced the coating washing fastness, increased concentration of TEOS as well as T_4 crosslinker greatly improved washing fastness of coatings compared to that of the MC coating. Compared to TEOS, T_4 crosslinker increased the washing fastness of the coating to a significantly higher extent.

4. Conclusion
The presence of the crosslinkers in the polymer network backbone influenced the coating performance, which was dependent on the chemical structure of the crosslinkers. Higher concentration of TEOS (3T) increased the hydrophobic effect of the MC coating to a higher extent than lower concentration (T). Compared to TEOS, with respect to the applied concentrations, the presence of T_4 in the multicomponent multifunctional coating increased the hydrophobic effect to a higher extent and even enabled achievement of the ''lotus effect'' on the cotton fabric surface. However, the crosslinkers reduced the oleophobic effect of the MC coating and this phenomenon was more pronounced for higher concentration of TEOS and T_4 crosslinker. Besides their influence on the coating orientation and arrangement, the crosslinkers also influenced the coating washing fastness. Whereas lower concentration of TEOS insignificantly influenced washing fastness of the MC coating, higher concentration of TEOS (3T) increased washing fastness of the MC coating to a higher extent. Compared to TEOS, the presence of organocyclotetrasiloxane T_4 in the MC coating increased the coating washing fastness to a significantly higher extent.

References
[1]   Mahltig B, Haufe H and Böttcher H 2005 *J. Mater. Chem.* **15** 4385
[2]   Vasiljević J, Tomšič B, Jerman I, Orel B, Jakša G and Simončič B 2014 *Cellulose* **21** 2611
[3]   Kumar N, Jyothirmayi A, Soma Raju KRC and Subasri R 2012 *Ceram. Int.* **38** 6565
[4]   Roe B and Zhang X 2009 *Text. Res. J.* **79** 1115
[5]   Mahltig B and Böttcher H 2003 *J. Sol-Gel Sci. Technol.* **27** 43
[6]   Yang Z, Fei B, WANG X, Xin JH 2012 *Fire Mater* **36** 31
[7]   Vasiljević J, Zorko M, Štular D, Tomšič B, Jerman I, Orel B, Medved J, Kovač J and Simončič B 2017 *Cellulose* **24** 1511
[8]   Černe L, Simončič B and Željko M 2008 *Appl. Surf. Sci.* **254** 6467
[9]   Socrates G 2001 Infrared and raman characteristic group frequencies: Tables and charts. Wiley, Chichester
[10]   Tomšič B, Simončič B, Vince J, Orel B, Vilčnik A, Fir M, Vuk AŠ, Jovanovski V 2007 Tekstilec 50 3
[11]   Pardal AC, Ramos SS, Santos PF, Reis LV, Almeida P 2002 *Molecules* **7** 320

[12]   Vasiljević J, Hadžić S, Jerman I, Černe L, Tomšič B, Medved J, Godec M, Orel B, Simončič B
       2013 Polym. Degrad. Stabil. 98 2602