Organofunctional Trialkoxysilane Sol-Gel Precursors for Chemical Modification of Textile Fibres

1 Introduction

Organofunctional trialkoxysilanes are organically modified silicon alkoxides that belong to a group of organic-inorganic hybrid (OIH) molecular precursors that include organic and inorganic components that are intimately mixed on the molecular scale. Depending on the type of interactions that connect the organic and inorganic components, hybrid materials can generally be divided into two classes (Figure 1). Class I hybrid materials are characterised by weak bonds (hydrogen, van der Waals or...
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ionic bonds) between the organic and inorganic phases. Examples of this class include the blends of inorganic particles with organic polymers and interpenetrating inorganic and organic networks. In contrast, in the case of Class II hybrid materials, organic and inorganic phases are linked via covalent, ionic-covalent or coordination bonds [1–3].

The most explored representatives of Class II hybrid materials include (i) organofunctional alkoxysilane precursors with the general chemical structure of $R'_n-Si(OR)_{4-n}$ where $R'$ represents an alkyl or organofunctional group and $R$ represents primarily methyl, propyl or butyl groups; (ii) bridged silsesquioxane precursors with the general chemical structure of $(OR)_{3}Si-R''-Si(OR)_{3}$, where $R''$ represents an organic spacer [1, 2, 4–6]; and (iii) polyhedral oligomeric silsesquioxanes (POSS) with the general chemical structure of $(R'-SiO_{3/2})_{n}$ ($n = 6, 8, 10, \ldots$) [7, 8].

Among the organofunctional alkoxysilanes, organofunctional trialkoxysilanes, $R'-Si(OR)_{3}$ (Figure 2) are of great importance for textile applications since their unique structure of three polymerisable groups enables them to form a highly oriented polymer network structure with an incorporated organic moiety. Depending on the molecular structure, the organic moiety, $R'$, can act as a network former or a network modifier [1, 9]. The network-forming organic moieties are polymerisable groups, such as vinyl, methacryloxy, and epoxy groups. The network-modifying moieties are non-hydrolysable and non-polymerisable organic groups which decrease the crosslinking degree and enable the formation of open network structures. Depending on the chemical structure of the network-modifying moiety, different functional properties can be tailored on the textile surface. Some of the most important chemical structures of the precursor organic groups are presented in Table 1.

The “soft chemistry” or “chimie douce” of the sol-gel processing of hybrid organofunctional trialkoxysilane precursors [9] is an exceptional strategy for environmentally friendly surface functionalisation of textile fibres that involves the deposition of thin hybrid films from the liquid phase [18]. The nanosized thickness of the hybrid polysilsesquioxane network ensures a high optical transparency [19], whereas the inorganic backbone does not influence the solid-state physical properties of the fibres, such as their crystallinity [20]. This process enables the development of novel, upgraded high-performance and durable textile-protective functionalities, such as water and oil repellency, soil repellency, antimicrobial
properties, anti-static properties, conductivity and flame retardancy. The outstanding advantage of these innovative hybrid systems provides an opportunity for sol-gel applications of mixtures of different organofunctional trialkoxysilane precursors, and this represents a simple method for the development of a multifunctional and multicomponent coating with selected protective properties.

2. Sol-gel processing of organofunctional trialkoxysilanes on textile fibres

The sol-gel fabrication of a hybrid organofunctional silsesquioxane polymeric film on the textile fibre surface is a two-step process. The first step begins

Table 1: Examples of functional properties provided by the specific organic group, R', in the precursor

<table>
<thead>
<tr>
<th>Property of R'</th>
<th>Structure of R'</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Network forming</td>
<td>H₂C—CH—vinyl</td>
<td>[1]</td>
</tr>
<tr>
<td></td>
<td>H₂C═C—C—O—(CH₂)₃ methacryloxypropyl</td>
<td>[10]</td>
</tr>
<tr>
<td></td>
<td>O—CH₂—O—(CH₂)₃ glycidoxypropyl</td>
<td>[11, 12]</td>
</tr>
<tr>
<td></td>
<td>H₂C—(CH₂)n alkyl</td>
<td>[11]</td>
</tr>
<tr>
<td></td>
<td>F₃C—(CF₂)n—(CH₂)₂ perfluoroalkyl</td>
<td>[13]</td>
</tr>
<tr>
<td></td>
<td>OCH₂CH₃</td>
<td>[14]</td>
</tr>
<tr>
<td></td>
<td>O═P—CH₂CH₂</td>
<td>diethyl(2-ethyl)phosphonate</td>
</tr>
<tr>
<td></td>
<td>Cl⁻</td>
<td>[15]</td>
</tr>
<tr>
<td></td>
<td>H₂C—(CH₂)n—N⁺</td>
<td>alkylidimethylammonium chloride</td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>[16]</td>
</tr>
<tr>
<td></td>
<td>1-(3-(1H-pyrrole-1-yl)propan-2-ol)-aminopropil</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂N—(CH₂)n aminoalkyl</td>
<td>[17]</td>
</tr>
</tbody>
</table>
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3 Functional properties

3.1 Water and oil repellency

Water- and oil-repellent surfaces of textile fibres can be efficiently fabricated via sol-gel processing of organofunctional trialkoxysilane precursors in which the organic moiety is hydrophobic or oleophobic in nature [35]. The representative hydrophobic organic moieties are alkyl groups with 12 to 18 carbon atoms in the chain, and hydrophobic and oleophobic organic moieties include perfluoroalkyl groups. Their structures are presented in Figure 3. The hydrophobicity and oleophobicity of the alkyl- and perfluoroalkyl-functionalised polysilsesquioxane coatings result from their low surface free energy with respect to the effect of the surface topography parameters [36]. The presence of perfluoroalkyl groups provides lower surface free energies for the
coating and a weaker adhesion between the coating and the liquid compared with those of the alkyl groups. Namely, the coating created by the alkyltrialkoxytitanates precursor can lower the critical surface tension of bleached cotton from 60–70 mN/m to 24–30 mN/m, whereas perfluoroalkyltrialkoxytitanates can lower the critical surface tension to lower than 10 mN/m. The extremely low surface free energy of the perfluoroalkyl groups originates from the stability of C–F bonds and is related to the number of fluorine atoms [35, 37–39]. When the perfluoroalkyl group is longer, the surface free energy is lower. This value is not only lower than the surface tension of water but also lower than the surface tension of oils, such as paraffin oil, motor oil, and olive oil (γ_{oil} \approx 30 \text{ mN/m}). In contrast to perfluoroalkyltrialkoxytitanates, alkyltrialkoxytitanates cannot provide the oleophobicity of the coating [13, 19, 40, 41]. A low surface energy alkyl- and perfluoroalkyl-functionalised coating has been reported to be able to induce additional functional properties, e.g., passive antibacterial activity of the coated fibres due to the lowered adhesion of bacteria [13, 15, 42] and improved anti-icing/de-icing properties of the coated fabric [43] (i.e., the icophobicity because of the low solid–ice adhesion and low shear strength of ice) [44].

The use of precursors with longer perfluoroalkyl groups also has an important disadvantage. Namely, the degradation of perfluoroalkyl groups with more than seven fluorinated carbons leads to the release of toxic, biopersistent, and bioaccumulative perfluoroalkyl acids (e.g., perfluoroctanoic acid or perfluorooctanesulphonic acid) into the environment where these chemicals can cause serious ecological problems and adverse human and animal health outcomes [45–48]. Due to concerns regarding the environmental effect of these compounds, the use of perfluoroalkyl groups with shorter chains is recommended.

In addition to chemical structure of the precursors organic moiety, the hydrophobicity and oleophobicity increased as the contact area between the coating surface and the liquid decreased, which is directly influenced by the coating topography. The fabrication of coatings on naturally micro-roughened textile fibre surfaces produces specific surface nano-modifications, which significantly contribute to water- and oil-repellent properties. Accordingly, an increase in the fibre surface roughness by plasma surface etching [49–57], prior the formation of the repellent sol-gel coating, enables the creation of a dual micro- to nano-structured fibre topography with low adhesion super hydrophobicity, very high oleophobicity and self-cleaning properties. Such surfaces are characterised by a water static contact angle that is higher than 150°, an n-hexadecane static contact angle that is higher than 140° and a water roll-off angle that is lower than 7°, which allows water droplets to roll off fabric surfaces very easily, thus removing solid particles of dirt from the fibres. This phenomenon is known as the “Lotus effect”.

Another method to increase the roughness of the fibre surface includes the surface deposition of silica particles of different sizes that are prepared via the Stöber method [22, 58]. The surface deposition of monodispersed, nano-sized Stöber silica particles onto cotton fibres has been shown to significantly improve the performance of alkyl- and perfluoroalkyl-functionalised polysilsesquioxanes and has enabled the achievement of a high hydrophobicity or superhydrophobicity via the creation of dual-scale-length roughness (Figure 4) [59–67]. Furthermore, the creation of triple-length-scale roughness by adsorbing silica nanoparticles onto microparticle-covered fibres via electrostatic attractions prior to the modification with perfluoroalkyl silane results in superhydrophobicity and proves to be essential for achieving superoleophobicity [68]. Another approach to create highly repellent cotton is to conduct surface deposition of previously alkyl- or perfluoroalkyl-modified silica nanoparticles via dipping [61, 69] or spraying [70].

Figure 3: Structures of water- and oil-repellent organo and organofunctional trialkoxytitanates: hexadecyltrioctothoxysilane (A) [40] and 1H, 1H, 2H, 2H-perfluorooctyltrioctothoxysilane (B) [40]
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The in situ growth of microsized silica particles on a cotton fibre surface with subsequent modification using perfluoroalkyl silane is an efficient method for achieving superhydrophobicity and high oleophobicity [71]. In situ processes were also used for the application of previously hydrophobically functionalised silica particles [72, 73]. The hierarchically roughened bumpy surface topography of cotton fibres that were fabricated by applying a fluoroalkyl functional oligosiloxane coating after the surface deposition of Stöber particles and the in situ growth of a TEOS-based particle-containing polysiloxane layer resulted in a long-lasting “Lotus effect” accompanied by an exceptionally high oleophobicity with an excellent washing fastness performance [74]. The stability of the water- and oil-repellent hybrid polysilsesquioxane coatings towards repeated washings was improved by assisted condensation with sol-gel precursors as cross-linkers, i.e., 3-glycidoxypropyltriethoxysilane (Table 1) [11, 12], the bridged silsesquioxane precursor, 1,2-bis(triethoxysilyl)ethane [61], and 2,4,6,8-tetakis(2-(diethoxy(methyl)silyl)ethyl)-2,4,6,8-tetramethyl–cyclotetrasiloxane [75]. The adhesion between the cellulosic surface and polysilsesquioxane was also enhanced with the formation of interfacial ester bonds by polycarboxylic acids, e.g., 1,2,3,4-butanetetracarboxylic acid, which can esterify with cellulosic hydroxyl groups and co-condense with silanol groups [76].

3.2 Flame retardancy

Organofunctional trialkoxysilane precursors with phosphorus- and phosphorus-nitrogen-based organo-moieties represent very promising “green” competitors for the creation of the flame retardant functionalities on textile fibres. Some of them are presented in Figure 5. Sol-gel processing enables the formation of a hybrid silsesquioxane polymeric film in which the flame retardant organic groups face outward from the surface. In addition to acting as a cross linker between the fibre surface and the flame-retardant organic groups, the silsesquioxane polymeric film is considered to act synergistically with phosphorus or phosphorus–nitrogen as a thermo-insulating barrier [14, 77–85]. The hybrid polysilsesquioxane coating formed on the cotton fibres by the $P,P$-diphenyl-N-(3-(trimethoxysilyl)propyl) phosphinic amide is schematically illustrated in Figure 6.

The flame retardant mechanism of OAH precursors has been the most comprehensively studied on cellulose fibres, but it has been rarely studied on other fibres. In the case of cellulose fibres, all of the examined flame retardant hybrids decreased the starting thermo-oxidative decomposition temperature and promoted dehydration and formation of the crosslinked aliphatic char, which was thermally more stable compared to that of untreated cellulose [14, 78, 80, 83, 84, 86]. The formed char protected the underlying cellulosic material, therefore reducing the weight-loss percentage and rate during the first decomposition stage and shifting further degradation towards higher temperatures compared with untreated cotton due to an enhanced aromatisation effect. Consequently, this increased the residue percentage at 800 °C. The promoted dehydration and crosslinking due to the phosphorylation of C(6) hydroxyl groups during the first decomposition stage resulted in an increased intensity of the released $H_2O$ [78, 81]. The enhanced evolution of $H_2O$ and the formation of thermally stable aromatic char during the second decomposition stage inhibited the production of flammable volatiles [80, 81]. Additionally, the chemical structure of the organic moiety plays an important role in the modification of the cellulose burning behaviour. The sol-gel coating fabricated via the application of 10-(2-trimethoxysilyl-ethyl)-9-hydro-9-oxa-10-phosphaphenanthrene-10-oxide retarded the combustion of cotton in an air atmosphere by decreasing the rate of the flaming combustion, whereas the application of diethylphosphateethyltriethoxysilane [14] and $P,P$-diphenyl-N-(3-(trimethoxysilyl)propyl) phosphinic amide [85]...
reduced the total burning time. Flaming combustion may be followed by glowing combustion, during which char smouldering occurs [78]. The formation of a carbonaceous-siliceous aromatic charred protective layer prevented the complete combustion of the underlying carbon-rich material [82–84].

A combination of two precursors, i.e., $P,P$-diphenyl-$N$-(3-(trimethoxysilyl) propyl) phosphinic amide and $1H,1H,2H,2H$-perfluorooctyltriethoxysilane, was used to create a functional coating that had flame retardant and water- and oil-repellent properties [87]. The cooperative action of both precursors in the coating provided a cotton fabric with an exceptional high-performance multifunctionality, including simultaneous superhydrophobicity and high oleophobicity, good ice-releasing properties of the surface, improved thermo-oxidative stability, and “glow” retardancy.

Figure 5: Structures of flame retardant organofunctional trialkoxysilanes: $P,P$-diphenyl-$N$-(3-(trimethoxysilyl) propyl) phosphinic amide (A), 10-(2-trimethoxysilyl-ethyl)-9-hydro-9-oxa-10-phosphaphenanthrene-10-oxide (B), 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-isophorone disocyanate-(3-aminopropyl)trioctoxysilane (C), $P$-ethoxy-$P$-phenoxy-$N$-(3-(triethoxysilyl)propyl) phosphinic amide (D), diethylphosphatoethyltriethoxysilane (E) [78–82, 84, 85]
3.3 Antimicrobial properties

Two different organic moieties are important for the preparation of organofunctional trialkoxysilane precursors with antimicrobial properties, i.e., quaternary ammonium salt (QAS) and N-halamine. The processing of QAS-functional trialkoxysilanes (Figure 7) enables covalent fixation of antimicrobial quaternary ammonium groups to the fibre surface via the creation of the QAS-functionalised polysilsesquioxane coating (Figure 8). Because the cationic alkyl ammonium group is coupled to the polysilsesquioxane coating, the coating does not release toxic compounds into the surroundings.

Among QAS-functional trialkoxysilanes, 3-(trimethoxysilyl)-propyltrimethylammonium chloride has been primarily investigated [15, 88–92]. The results show that the coating created on the cellulose fibres provides a durable, nonleachable, and environmentally friendly bio-barrier with excellent protection against a broad spectrum of both gram-positive and gram-negative bacteria as well as against algae and fungi.

QAS-functional trialkoxysilanes were also applied in combination with other functional precursors. Accordingly, to develop multifunctional antibacterial, water- and oil-repellent, and flame-retardant cotton fibres, 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride, 1H,1H,2H,2H-perfluoroctyltrimethoxysilane, and P,P-Diphenyl-N-(3-(trimethoxysilyl) propyl) phosphinic amide were combined [93]. The high-performance multifunctionality of the coating on the cotton fibre exhibited

\[\text{Figure 7: Structures of the antimicrobial organofunctional trialkoxysilanes: 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride (A), perfluoroctylated quaternary ammonium silane coupling agent (B) [65, 88]}\]
an excellent cooperation between all three organic groups in the polysilsequioxane film. Organofunctional trialkoxysilane precursors with incorporated N-halamines that have antimicrobial properties are presented in Figure 9. The antimicrobial activity of N-halamines is based on the controlled release of antimicrobial \( \text{Cl}^+ \) cations that are a result of the electrophilic substitution of Cl in the N-Cl bond with H in the presence of water. Because the N-H bond has no antimicrobial properties, the N-Cl bond should be regenerated with the exposure of the coating to dilute sodium hypochlorite to reactivate its antimicrobial activity.

3.4 Electrical conductivity and antistatic property

Textiles with electrical conductivity could be designed via the sol-gel processing of organofunctional trialkoxysilane with a pyrrole (PY) organic moiety (Figure 10 A). After the formation of a pyrrole-functionalised polysilsequioxane film on the fibre surface, \textit{in situ} oxidative chemical polymerisation of Py should be performed to create its oxidised derivatives that have good electrical conductive properties (Figure 10 B). Their main applications are as antistatic agents or chemical sensors. The electrical conductivity of the polypyrrole (PPy) layer is influenced by many factors, among which the preparation technique, precursor concentration, solvent, oxidant, polymer additive, time and temperature of the reaction are crucial.

Another study showed that the creation of a pyrrole-functionalised polysilsequioxane film on the surface of polypropylene and viscose using 1-([3-(triethoxysilyl)propylamino]-3-(1H-pyrrole-1-yl)propan-2-ol and subsequent formation of an outer conducting polypyrrole layer facilitated the preparation of thick and highly ordered polypyrrole chains with an increased washing fastness for the conductive layer [16]. The washing fastness of the polypyrrole layers was also affected by the fibre morphology and was more pronounced in the case of the polypropylene than of viscose because pyrrole penetrated into the viscose substrate during its polymerisation reaction.

Antistatic properties of textile fibres can also be improved via the sol-gel processing of aminoalkyl-functionalised trialkoxysilane precursors, i.e., aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane and 3-[2-(2-aminoethy lamino)ethylamino]propyltrimethoxysilane (Figure 11). Furthermore, it was found that the application of aminoalkyl-functionalised trialkoxysilanes in combination with tetraethoxysilane and different alkyltrialkoxysilanes on the surface of polyester or polyester/cotton blended fabrics represents a promising approach for the preparation of water-repellent coatings with simultaneous antistatic properties [17].

![Figure 9: Chemical structures of N-halamine siloxanes: 5,5-dimethyl-3-(3’-triethoxysilyl)pyrrole-hydantoin (A), 4-[3-triethoxysilylpropyl]-2,2,6,6-tetramethylpiperidine (B), 3-(3’-triethoxysilyl)propyl]-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione (C) [94–97]](image-url)
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4 Future trends

The chemical modification of textile fibres with organically modified trialkoxysilanes is increasingly gaining importance since it represents an environmentally friendly nanotechnology process that enables the development of novel, upgraded high-performance textile functionalities. To increase the practical importance and commercialisation of the sol-gel process, additional research is required as follows:

- synthesising organically modified trialkoxysilanes with novel functionalities,
- preparing multifunctional properties of the coatings,
- achieving a synergistic effect of the functional properties of the components in the multicomponent multifunctional films,
- structural optimisation of multicomponent coatings to improve their washing fastness, and
- transferring laboratory processes to industrial production.

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