



Review

Advances in biofilm control for food and beverage industry using organo-silane technology: A review



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ABSTRACT

Cell adhesion can be a potential problem as well as a valuable tool for microbiological engineering. It can lead to biofouling, contamination of product and corrosion. On the other hand, cell adhesion is purposely employed in fermenters and bioreactors to influence reactor performance. This paper presents an overview of organo-functional silanes – their chemistry, properties, use, and the main laboratory experiments that can be of interest to the food and beverage industry. The purpose is to introduce and explore possibilities for using organo-silane combinations to enhance or reduce microbial adhesion.

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1. Introduction

Food-processing environments provide a variety of conditions which might favor the formation of biofilm – for instance, the presence of moisture, nutrients and inocula of microorganisms from the raw material. Biofilms contribute to reduced heat transfer, loss of sensor sensitivity and filter plugging. Biofilms are also a potential source of food contamination which can lead to spoilage or transmission of foodborne pathogens (Myszka & Czaczyk, 2011). A consortium of microorganism-forming biofilms may produce aggressive substances such as acids, and the patchy nature of

biofilms can generate regions with different oxygen contents on the underlying surface. Both of these properties may contribute to the corrosion of various materials. This type of corrosion is called microbially influenced corrosion. It is not a new mechanism of corrosion, but merely indicates that bacterial activities have created conditions for normal corrosion to proceed (Kolari, 2003).

On the other hand, cell adhesion to an inanimate surface is often exploited as a convenient and cost-effective way of separating biomass from various fermentation products (Verstrepen & Klis, 2006). Cell immobilization has been applied in the production of enzymes, amino acids, organic acids, alcohol, aromas and in bioconversion processes as well as in bioremediation and effluent biotreatment (Gutiérrez-Correa & Villena, 2003). The technology of cell immobilization has been developed extensively over the last two decades.

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Therefore, the design of different food-contact materials with properties that modulate the adhesion of viable microorganisms is a longstanding goal. Suitable organo-silanes can be used to improve the physical, chemical and mechanical properties of such materials, which may be tailored either to prevent anti-biofouling or to stimulate microbial adhesion, and which can be used in a wide range of applications in the food and beverage industry (Materne, de Buyl, & Witucki, 2006).

2. Organo-silanes

2.1. Molecular structure and basic properties

Silanes are known as monomeric silicon chemicals. A silane that contains at least one silicon-carbon bond (e.g., Si-CH₃) is an organo-silane. The carbon-silicon bond is very stable and nonpolar, and in the presence of an alkyl group it gives rise to low surface energy and hydrophobic effects (Plueddemann, 1991).

Organo-functional silanes are hybrid compounds that combine the functionality of a reactive organic group and the inorganic functionality of an alkyl silicate in a single molecule. This special property means they can be used as 'molecular bridges' between organic substrates and inorganic materials (Antonucci, Dickens, Fowler, Xu, & McDonough, 2005) (Fig. 1).

An organo-functional group X is a non-hydrolyzable organic moiety. This moiety can be reactive toward another chemical (e.g., amino, epoxy, vinyl, methacrylate, sulfur) or nonreactive (e.g., alkyl). The organic group on the silane can be either a reactive organic group (i.e., an organofunctional group) or a non-reactive organic group. The groups can be hydrophobic or hydrophilic, with varying degrees of thermal stability. OMe is a hydrolyzable group. Like an alkoxy group (e.g., methoxy, ethoxy, isopropoxy) or an acetoxy group, it can react with various forms of hydroxyl group present in mineral surfaces or polymers, liberating alcohols (methanol, ethanol, propanol) or acid (acetic acid). These groups can provide linkages with inorganic or organic substrates. The organo-functional group is bound to the silicon via a carbon chain, called the spacer. The potential reactivity of the organo-functional group depends on its distance from the Si atom. If the organic spacer group is a propylene linkage (e.g., -CH₂CH₂CH₂-) or longer, then the organic reactivity of the organo-functional silane will be similar to its organic analog. Therefore, α -silanes with a methylene bridge instead of the usual propylene spacer between the silicon atom and the functional group are highly reactive and accordingly have huge application potential (Smits & Materne, 2005).

Depending on the nature of the hydrolyzable groups, the following categories of silane can be distinguished: chlorosilanes,

silazanes, alkoxy-silanes and acyloxy-silanes. The choice of functional group X will depend ultimately on the nature of the organic polymer. Nonreactive silanes are often used as dispersing or hydrophobing agents. They feature a nonreactive organic group (X) which is compatible with the matrix, and an alkoxy group (OMe) which reacts with the substrate. Reactive silanes are useful as 'coupling agents' to improve the adhesion of all kinds of coating (Materne et al., 2006) (Table 1).

The term 'silane coupling agent' was coined in the 1940s to refer to a category of organo-silane used to enhance adhesion and moisture resistance in glass fiber reinforced polymer composites. Glass-resin bonds did not provide the strength and stability necessary for durable adhesion, especially in water environments. Silane coupling agents are commonly deposited using a sol-gel reaction and form monolayers or multilayers depending on the kinds of sol-gel solution and substrate used (Plueddemann, 1991). Any application of organo-silanes as silane coupling agents requires hydrolysis and condensation reactions of the silane molecule. The Si-OR bonds hydrolyze rapidly in water environments and form reactive silanol Si-OH groups. This is the first step in the sol-gel process. Then silanol groups can condense with each other to form polymeric structures with very stable siloxane Si-O-Si bonds. They can also condense with metal hydroxyl groups on the surface of glass, minerals or metals to form stable Si-O-M bonds (M = Si, Al, Fe, etc). This allows surface treatment, coupling and assembling of chemically-dissimilar surfaces, such as between inorganic and organic materials (Arkles, Steinmetz, Zazyczny, & Metha, 1992; de Buyl, 2001) (Fig. 2).

The methoxy group on the carbon compound is stable as methyl ether, while its attachment to silicon produces a reactive and hydrolyzable methoxysilyl structure (Si-OCH₃). Because organo-silanes hydrolyze before reacting with each other or with the hydroxyl groups present on the substrate surface, it is important to understand the reaction kinetics. The hydrolysis reaction can be catalyzed using either an acid or a base. The optimum pH for hydrolysis is not optimum for condensation. Finding the best balance between hydrolysis and condensation is one of the keys to successful utilization of organo-silane chemistry in any application (Arkles et al., 1992; Materne et al., 2006).

Factors influencing silane surface modification selection include the concentration of surface hydroxyl groups, the type of surface hydroxyl groups, the hydrolytic stability of the bond formed and the physical dimensions of the substrate or substrate features. Surface modification is maximized when silanes react with the substrate surface and present a maximum number of accessible sites with appropriate surface energies (Arkles, 2006).

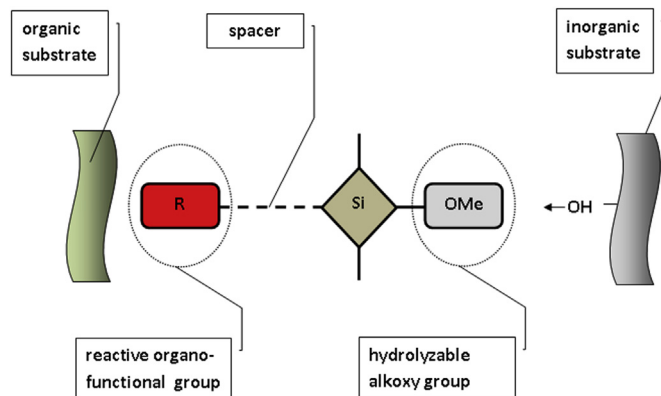


Fig. 1. Organo-functional molecule as molecular bridges.

Table 1
Examples of functional organo-silanes.

Organic group X	Alkoxy group OR	Chemical name
<i>Nonreactive silanes</i>		
methyl	methoxy	methyltrimethoxysilane
methyl	ethoxy	methyltriethoxysilane
methyl	methoxy	dimethyldimethoxysilane
propyl	methoxy	propyltrimethoxysilane
i-butyl	methoxy	isobutyltrimethoxysilane
phenyl	methoxy	phenyltrimethoxysilane
n-octyl	ethoxy	n-octyltriethoxysilane
<i>Reactive silanes</i>		
amino	methoxy	aminoethylaminopropyltrimethoxysilane
amino	ethoxy	aminopropyltriethoxysilane
epoxy	methoxy	γ -glycidoxypropyltrimethoxysilane
chloropropyl	methoxy	γ -chloropropyltrimethoxysilane
vinyl	methoxy	vinyltrimethoxysilane
vinyl	acetoxy	vinyltriacetoxy-silane
mercapto	ethoxy	mercaptopropyltriethoxysilane

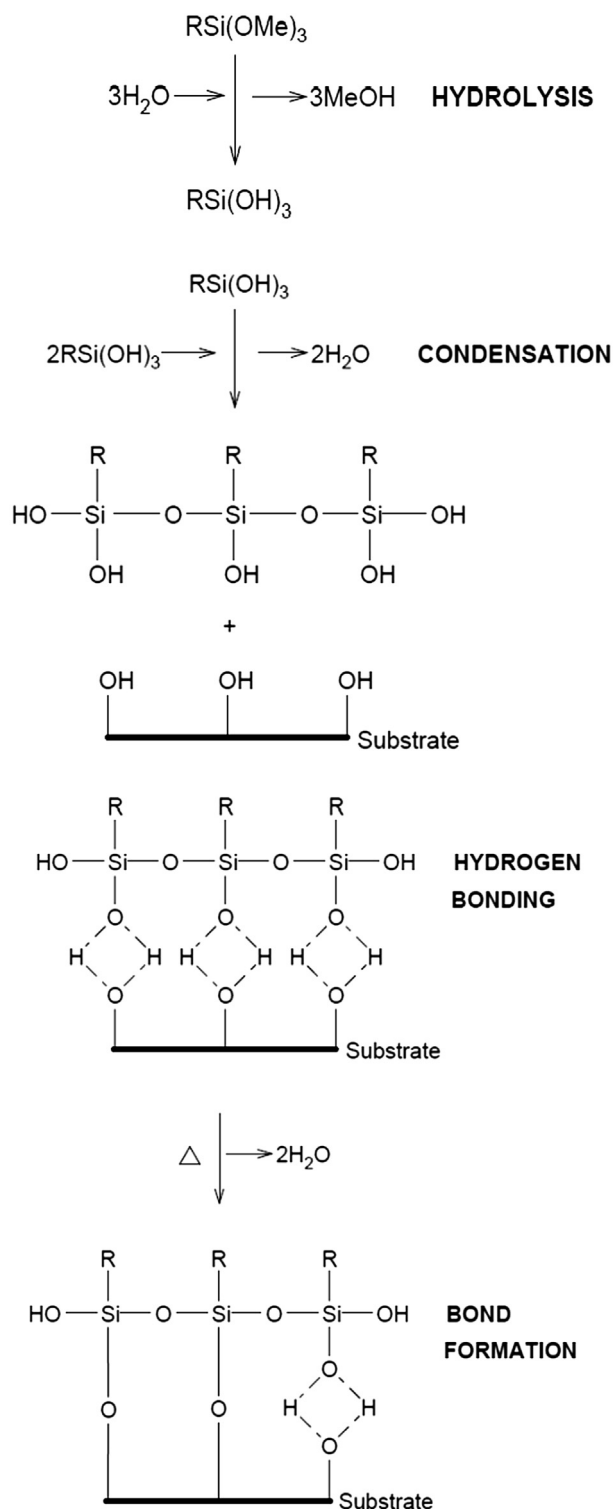


Fig. 2. The mechanism of hydrolysis, condensation and bonding of organo-silanes to an inorganic surface (sol–gel process).

Jenkins observed a clear relationship between increasing adhesion energy and increasing chain length of CH_3 -terminated silanes, and the opposite tendency of decreasing adhesion energy with increasing chain length for silanes with a vinyl end-group (Jenkins, Dauskardt, & Bravman, 2004). Moreover, nonpolar silanes show an orthogonal alignment, while polar silanes exhibit two different orientations at the solid surface,

heads up or tails down (Kornherr et al., 2006). These results indicate that organo-functionality and chain length are important factors in silane adhesion which should be considered in their selection and use.

2.2. Trends in application of organo-silanes

The bridge-building property of organofunctional silanes is particularly important in three fields of application: adhesion promotion, surface modification, and polymer crosslinking (Materne et al., 2006) (Table 2).

Charles Frieel and James Crafts discovered the first organo-silane compound in 1863. Since then, numerous organo-silanes and related compounds have been synthesized for use in a variety of applications. The main properties of surface modification include hydrophobicity, hydrophilicity, absorption, orientation, charge conduction (Materne et al., 2006).

Organo-silanes are relatively environmentally friendly, improve adhesion and provide better protection against corrosion. Surfaces on which they can be used include metal, plastic, glass, rubber, ceramic, porcelain, marble, cement, granite, tile, silica, sand, appliances that have been enameled, polyester, polyurethane, polyacrylic, resins that are melamine or phenolic, siliceous, polycarbonate and wood, as well as painted surfaces (Khranov, Balbyshev, Voevodin, & Donley, 2003). These compounds are effective adhesion promoters when used as integral additives or primers for paints, inks, coatings, adhesives and sealants. As integral additives, they migrate to the interface between the adhesive layer and the substrate. As a primer, the silane coupling agent is applied to the inorganic substrate before the product to be adhered. By using an appropriate organo-silane, a poorly adhering paint, ink, coating, adhesive or sealant can be converted into a material that will frequently maintain adhesion even if subjected to severe environmental conditions (e.g., high temperatures, underwater immersion or UV radiation). Since many organo-silane formulations naturally repel water and dirt, organo-silane mixtures are also used for cleaning (Materne et al., 2006).

Table 2
Typical organo-silane applications.

Type of application	Description
Coupling agent	Used to couple organic polymers to inorganic materials. Typical of this application are reinforcements, such as fiberglass and mineral fillers, incorporated into plastics and rubbers.
Adhesion promoter	Used as integral additives or primers for paints, inks, coatings, adhesives and sealants. As integral additives, they must migrate to the interface between the adhesive layer and the substrate to be effective.
Dispersing/hydrophobing agent	Used as durable hydrophobing agents in concrete construction applications, including bridge and deck applications. They are also used as hydrophobic inorganic powders to make them free-flowing and dispersible in organic polymers and liquids. Finally, they improve cure (by reducing catalyst inhibition) and electrical properties.
Crosslinking agent	Can react with organic polymers, resulting in grafting of the trialkoxysilyl group onto the polymer backbone, to crosslink the silane into a stable, three-dimensional siloxane structure, to impart durability, water resistance and heat resistance to paints, coatings and adhesives.
Other applications	Used as water scavengers in moisture-sensitive formulations, as blocking agents in antibiotic synthesis, polypropylene catalyst 'donors' and as silicate stabilizers.

The growth of many microorganisms can be reduced on surfaces treated with alkylsilanes of C8 or less substitution, due not only to water resistance but because dry surfaces deprive organisms of metabolic water requirements. In general, the reactivity of hydroxylated surfaces with organofunctional silanes decreases in the following order: Si–NR₂ > Si–Cl > Si–NH–Si > Si–O₂CCH₃ > Si–OCH₃ > Si–OCH₂CH₃. The methoxy and ethoxysilanes are the most widely used organo-functional silanes for surface modification. Reasons for this include the fact that they are easy to handle and the alcohol byproducts are non-corrosive and non-volatile. The methoxysilanes are capable of reacting with substrates under dry, aprotic conditions, while the less reactive ethoxysilanes require catalysis. The low toxicity of ethanol, a byproduct of the reaction, favors the use of ethoxysilanes in many commercial applications (Arkles, 2006).

2.3. Legislation aspects

Research and development in the field of innovative materials is progressing at pace as part of the search to achieve more environmentally-friendly solutions. However, the design of tailor-made materials presents a real challenge. It involves reverse engineering based on industry requirements, not simply on the availability of food-contact surfaces. Novel solutions based on organo-silane components are expected to play a major role here, taking into account all additional safety considerations and filling the current gap in knowledge. The key safety requirement for novel materials in contact with food is to be as inert as possible, i.e., there should be minimal interaction between the food/beverage and the modified surface.

The European and United States regulatory attitudes to food-contact materials differ not only in detail but in approach. In the USA there is a comprehensive body of food contact legislation contained in Chapter 21 of the Code of Federal Regulations (CFR). This has been built up over the years since 1958 to the present day by incorporating food contact substances petitioned to the FDA and probably represents the most extensive system of food contact regulation. However, not everything that can be used is listed in the Regulations. In addition, it is necessary to be aware of prior sanctions, which substances are generally recognized as safe, the basic resin doctrine, the mixture doctrine, the threshold of regulation, the housewares exemption, the no migration exemption and of substances notified since October 1999 using the Food Contact Notification (FCN) programme. Particular substances that can reasonably be expected to migrate to food because of their intended use in the food contact material should be covered by one of the following: a regulation listed in Title 21 CFR, a prior sanction letter meeting the criteria for GRAS status (including but not limited to a GRAS regulation or GRAS notice), a Threshold of Regulation (TOR) exemption request, or an effective FCN programme (FDA, 2013). The European approach starts from the principle that there must be toxicological data on all substances regardless of the level of anticipated exposure. The regulation of such materials in Europe is still evolving. Initially, all European food-contact legislation originated and was applied in individual member states. However, with the formation of the European Union, member states elected to harmonize legislation in order to create a single market and overcome complications and barriers to trade. So far, EU legislation on materials in contact with foodstuffs has protected the health of consumers by ensuring that no material in contact with foodstuffs can bring about a chemical reaction that might change the composition or organoleptic properties of such foodstuffs (i.e., the taste, appearance, texture or even smell). All standard and new materials are subject to all requirements for food-contact materials, including overall migration limits (OMLs) and specific migration limits (SMLs) (Restuccia et al., 2010).

Regulation 1935/2004 on materials and articles intended to come into contact with food already contains general provisions concerning the safety of such materials and sets the framework for the European Food Safety Authority's (EFSA) safety evaluation process (Dainelli, Gontard, Spyropoulos, Zondervan-van den Beuken, & Tobbback, 2008; Restuccia et al., 2010). Based on the outcome of this evaluation process, the Commission (DG SANCO) may grant a petitioner authorization to use submitted compounds, which will be entered into the regulations. For example, European regulations have supported the development and commercial use of alternative anticorrosion treatments to replace chromium VI in plating, coil coating and metal painting. According to the judgment of the EFSA, 3-aminopropyltriethoxysilane can be used as a comonomer in a polysiloxane layer applied to metal substrates which are subsequently given polymer coatings. On the basis of migration and negative genotoxicity tests, however, the substance was limited on SCF List 3 to 0.05 mg/kg food when used for the surface treatment of materials and articles (EFSA, 2005). Directive 2002/72/EC contains lists of monomers and other starting substances and of additives authorized for the manufacture of plastic materials and articles. For monomers, other starting substances and additives the European Union list is now complete, which means that only substances authorized at the EU level may be used. The new Regulation No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food lists the silane components and derivatives polydimethylsiloxane, polyoxyalkyl (C2–C4) dimethylpolysiloxane, vinyltriethoxysilane, vinyltrimethoxysilane, aminopropyltriethoxysilane, methylsilsesquioxane, [3-(methacryloxy)propyl] trimethoxysilane and n-octyltrichlorosilane – all of which may be used as additives for polymer production with special restrictions, specifications and/or with SML values. EU regulations should correspond perfectly with the food safety strategy, involving an improved level of food safety and transparency for consumers.

3. Antimicrobial and antiadhesive properties of active organo-silanes

Bacteria, fungi, algae and other organisms can adhere to solid surfaces and form biofilms. In the food industry, contamination and colonization of microorganisms on surfaces can result in problems as slight as an offensive odor to serious food-borne infections. Controlling or even removing the biofilm after its development is difficult. Therefore, a useful strategy is to control biofilm formation before it starts (Kokare, Chakraborty, Khopade, & Mahadik, 2009). To prevent biofilm formation, control of both the adherence and colonization of the microorganisms on the substrate surface is critical. One of the strategies for preventing biofilm formation is to modify the physicochemical properties of the surface in order to minimize or reduce the attractiveness of the surface to the microorganism, thereby controlling its adherence. Introducing an antimicrobial agent into synthetic material can create microbe resistant, non-porous surfaces. However, careful selection of this agent is essential to ensure the protection of the final product as well as to protect the health of the consumer. The list of available agents is limited by selection criteria including durability, regulatory approval, the spectrum of activity and toxicity to both the manufacturer and the end-user (Monticello, 2010).

A suitable biocide should be selected to provide broad activity against micro-organisms found commonly in the target application area and may be added to polymers during their manufacture. It should be noted that antimicrobial surfaces can prevent cross-contamination between, for example, food and beverage products, but should not replace good hygienic practices in product handling (de Carvalho, 2007).

One of the most established and successful uses for the application of organo-silanes is prevention against biofilm formation. The use of the proper quaternary amine-based organo-silane can provide durable antimicrobial protection against a wide variety of microorganisms (Loontjens, 2013). Quite a large number of international companies have filed patents on different formulations comprising organo-silanes. In particular, organo-silanes with octadecyl as a reactive group have been available on the market for many decades.

There are many ways to modify surfaces so that they are less receptive to the settling, attachment and colonization of microorganisms. These modifications can create treated surfaces on which microorganisms are inhibited or killed or more easily cleaned away. The non-leaching behavior of such reactive surfaces allows for the control of surface microbial contamination without continuous release of toxic components into the environment, which may contribute to the appearance of resistant organisms (Monticello & White, 2010).

In the 1960s, researchers discovered that antimicrobial organo-functional silanes could be chemically bound to receptive substrates by what were believed to be Si–O linkages. The method was described as orienting the organo-functional silane in such a way that hydrolysable groups on the silicon atom were hydrolyzed to silanols and the silanols formed chemical bonds with each other and the substrate (Isquith, Abbott, & Walters, 1972). Physical adsorption on modified substrata was suggested as a way to promote structural rearrangement of the microbial cell surface (Gaboriaud & Dufrene, 2006). The active ingredient monomer, when applied to surfaces and polymerized, provided a mode of antimicrobial activity that physically ruptures the cell membranes of microorganisms by ionic association (microbial cell membranes carry a negative charge) and lipophilic attraction (the C18 associating with the lipoprotein of the membrane) causing disruption and lyses of the microbial cell. The depletion of the cellular electrochemical potential across the membrane and release of cytoplasmic materials leads to the complete destruction of microbial cells (Jothi, 2009) (Fig. 3).

Since the mid-1960s, the antimicrobial activity of [3-(trimethoxysilyl) propyldimethyloctadecyl] ammonium chloride has been studied on a variety of treated surfaces. In these studies, dose-dependent antibacterial activity was demonstrated against both the gramnegative *Escherichia coli* and the grampositive *Staphylococcus aureus* bacteria. These were followed by other studies which measured the broad spectrum of antimicrobial activity against a mixed fungal spore suspension (*Aspergillus niger*, *Aspergillus flavus*, *Aspergillus versicolor*, *Penicillium funiculosum*, *Chaetomium globosum*) or *Algae* (*Chlorophyta*, *Cyanophyta* and *Chrysophyta*) (Isquith & McCollum, 1978).

The use of reactive silane chemistry to attach durable, non-leaching antimicrobials to synthetic material has been established as a way of controlling microbial contamination in a safe and effective manner. Quaternary ammonium salts (QAS) have antibacterial properties, and they are often used as disinfectants in the food

industry. They also provide protection against fungi, amoeba and some viruses. These compounds act by disrupting the cell membrane (Palermo, Lee, Ramamoorthy, & Kuroda, 2011). Gottenbos, der Mei, Klatter, Nieuwenhuis, and Busscher (2002) describe the antibacterial properties of a positively charged organo-silane quaternary ammonium compound, 3-(trimethoxysilyl)-propyldimethyloctadecylammonium chloride, coated on silicone rubber after plasma treatment to obtain hydroxyl groups on the surface. The coating was tested against a variety of different bacterial strains. QAS coating was also investigated for its efficacy against mixed fungal and bacterial biofilms by Oosterhof, Buijssen, Busscher, van der Laan, and van der Mei (2006). This coating was shown to be biocidal, even in the presence of proteins. Gong et al. (2012) used artially hydrolyzed QAS co-polymerized with 2,2-[4(2-hydroxy 3-methacryloxypropoxy)-phenyl] propane has been shown to possess desirable mechanical properties and to kill biofilms of *Streptococcus mutans*, *Actinomyces naeslundii* and *Candida albicans*.

Selected linear polydimethylsiloxanes with 20% siloxane units substituted at silicon by 3(dimethyl-n-octylammonio) propyl chloride or 3(dimethyl-n-hexadecylammonio) propyl chloride and terminated by silanol functions at both chain ends were used in studies conducted by Fortuniak et al. (2011). The organo-silanes were crosslinked and also incorporated by co-crosslinking into an RTV (room temperature vulcanized) silicone elastomer. It is worth noting that a thousand-fold reduction of *S. aureus* was achieved within two minutes of contact with polymer containing n-octylamine (20 wt%).

In studies conducted by Kregiel et al. (2013) modified polyvinyl chloride surfaces were made by coupling silanes with the native material. At the beginning of the modification procedure, the plates were irradiated by radio frequency generated plasma. The modifications were made also to the silicone elastomer by co-crosslinking organo-silane with an RTV material. The most effective antibacterial modification was obtained using 20% of dimethylsiloxane-co-(N,N-dimethyl-N-n-octylammonio)propylchloride)methylsiloxane and (3 glycidoxypropyl)trimethoxysilane, in the modification of gumsil and polyvinyl chloride respectively.

Similar studies by the authors of the present study showed that (3-N,N,N-triethanolaminopropyl) trimethoxysilane and (3-N-n-octylaminopropyl) trimethoxysilane on glass surfaces showed the best adhesiveness and antibacterial properties. The best layers were able to reduce bacterial cell counts by more than three orders of magnitude. On the other hand, the kind of carrier had no significant effect on the viability of free *Aeromonas hydrophila* cells in the culture medium. Therefore, the antibacterial activity of active organo-silanes can be attributed to the modified glass surfaces only (Kregiel, 2013).

Yoshino et al. (2011) studied silane coupling agents with a quaternary ammonium groups with the aim of using these agents to make material surfaces antimicrobial for long periods of time. In studies conducted by Xu, Li, Jia, and Liu (2006) a nano-fumed silica derivative with N, N-dimethyl-n-hexadecylamine was synthesized with γ -chloropropyltrimethoxysilane as the coupling agent, and subsequently treated with N,N-dimethyl-n-hexadecylamine. This polymer strongly inhibited the growth of *E. coli*, *S. aureus* and *C. albicans*

Materials with permanent antimicrobial activity can be obtained not only from silanes with QAS, but from other reactive groups. The alkylation of monoazoles, diazoles, triazoles and tetrazoles with dimethylheptyl(3-iodopropyl) silane produced dimethylheptyl [3-(N-imidazolyl)propyl] silane that demonstrated high fungistatic activity with respect to yeasts in combination with high cytotoxicity (Sturkovich et al., 1989).

Using a parallel plate flow chamber, adhesion of the bacteria *Streptococcus salivarius*, *Staphylococcus epidermidis* and yeast strains *C. albicans* and *Candida tropicalis* to the chemisorbed fluoroalkylsiloxane layers was investigated by Everaert, van der Mei,

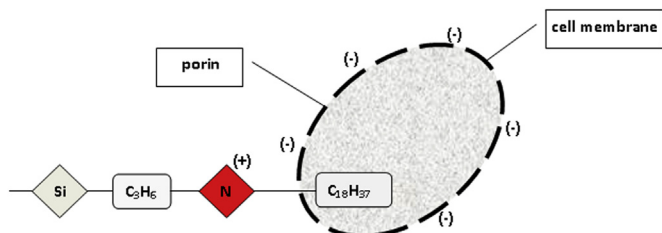


Fig. 3. Disrupting the cell membrane through physical and ionic phenomena.

Table 3
Application of organo-silanes to control of microbial attachment.

Organo-silane	Substrate	Microorganism	References
3-amino-propyl triethoxy silane	Support-films	<i>Bacillus subtilis</i> <i>Escherichia coli</i> , wild-type magnetotactic bacteria	Taylor et al., 2000
3-(trimethoxysilyl)-propyldimethyloctadecylammonium chloride	Silica	<i>Escherichia coli</i> <i>Staphylococcus aureus</i> , <i>Deinococcus geothermalis</i>	Song, Kong, & Jang, 2011
2-[methoxy(polyethylenoxy)propyl]trimethoxysilane Tridecafluoro-1,1,2,2,-tetra-hydrocytl-1-triethoxysilane	Rubber	<i>Candida albicans</i>	Price et al., 2002
1H,1H,2H,2H,2H-Perfluorodecyl trichlorosilane			
2-[methoxy(polyethylenoxy)propyl]trimethoxysilane			
[3-(trimethoxysilyl)propyldimethyloctadecyl] ammonium chloride	Silica	<i>Aspergillus niger</i> , <i>A. flavus</i> , <i>A. versicolor</i> , <i>Penicillium funiculosum</i> , <i>Chaetomium globosum</i>	Isquith & McCollum, 1978
[3-(trimethoxysilyl)propyldimethyloctadecyl] ammonium chloride	Glass	<i>Chlorophyta</i> , <i>Cyanophyta</i> <i>Chrysoophyta</i>	Walters, Abbott, & Isquith, 1973
[3-(trimethoxysilyl)propyldimethyloctadecyl] ammonium chloride	Rubber	<i>Staphylococcus aureus</i> <i>Staphylococcus epidermidis</i>	Gottenbos et al., 2002
[3-(trimethoxysilyl)propyldimethyloctadecyl] ammonium chloride	Rubber	<i>Escherichia coli</i> <i>Pseudomonas aeruginosa</i> Mixed fungal and bacterial biofilms	Oosterhof et al., 2006
2,2-[4(2-hydroxy 3-methacryloxypropoxy)-phenyl]propane	Co-polymerization with 2,2-[4(2-hydroxy 3-methacryloxypropoxy)-phenyl]propane	<i>Streptococcus mutans</i> , <i>Actinomyces naeslundii</i> , <i>Candida albicans</i>	Gong et al., 2012
3(dimethyl-n-hexadecylammonio)propyl chloride	Silicone elastomer	<i>Staphylococcus aureus</i>	Fortuniak et al. 2011
poly [dimethylsiloxane-co-(N,N-dimethyl-N-n-octylammonio)propylchloride) methylsiloxane]	Gumasil	<i>Aeromonas hydrophila</i>	Kregiel et al., 2013
(3-glycidoxypropyl)trimethoxysilane	PVC	<i>Aeromonas hydrophila</i>	Kregiel et al., 2013
(3-N,N,N-triethanolaminopropyl)trimethoxysilane	Glass	<i>Aeromonas hydrophila</i>	Kregiel, 2013
(3-N-n-octylaminopropyl)trimethoxysilane			
N, N-dimethyl-n-hexadecylamine with γ -chloropropyltrimethoxysilane fluoroalkylsiloxane	Silica	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i> , <i>Candida albicans</i>	Xu et al., 2006
	Silicone rubber	<i>Streptococcus salivarius</i> , <i>Staphylococcus epidermidis</i> <i>Candida albicans</i> , <i>Candida tropicalis</i>	Everaert et al., 1998
heparin with octadecyltrichlorosilane	Silicone	<i>Staphylococcus epidermidis</i>	Tang et al., 2006
3-(3-amino-2-hydroxy-1-propoxy)propyldimethoxysilane	Chamotte	<i>Saccharomyces cerevisiae</i> <i>Saccharomyces pastorianus</i>	Berlowaska, Kregiel, & Ambroziak, 2013
3-(N, N-dimethyl-N-2-hydroxyethyl) ammonium propyldimethoxysilane			

and Busscher (1998). The modified surfaces showed significantly reduced microbial adhesion as compared to native silicone rubber, both with respect to initial deposition rates and adhesion in a stationary end-point.

Silane surface treatment inhibits the adherence of the yeast *Candida* spp., possibly through the formation of a barrier between the surface of the material and the yeast (Price, Waters, Williams, Lewis, & Stickler, 2002). Sambhy, Peterson, and Sen (2008) demonstrated a versatile methodology combining both covalent surface anchoring and polymer cross-linking that is capable of forming long-lasting coatings on reactive and nonreactive surfaces. Polymers containing reactive methoxysilane groups form strong Si–O–Si links to oxide surfaces, thereby anchoring the polymer chains at multiple points. The interchain cross-linking of the methoxysilane groups provides additional durability to the coating and makes the coatings highly resistant to solvents. Finally, antibacterial agents, such as silver bromide nanoparticles and triiodide ions were introduced into these functional polymers to generate long-lasting and renewable antiseptic coatings on glass, metals, and textiles.

In other studies, a polycationic lipopeptide polymyxin B was selected as the bioactive agent for covalent immobilization on the surface. First, by using sol–gel technology the inert glass substrate was functionalized by applying a silane coating with epoxide rings to which the peptide was coupled by means of a catalyst. The material obtained showed antimicrobial properties indicating that in spite of immobilization the peptide retained its bioactivity. The coated surface was able to reduce bacterial cell counts of the gramnegative bacteria *E. coli* by more than five orders of magnitude after 24 h of incubation, without leaching into the environment (Mohorčić et al., 2010).

Examples of functional organo-silanes used to control microbial attachment and biofilms are given in Table 3.

4. Pro-adhesive properties of active organo-silanes

Various methods are available for attaching proteins to solid surfaces. Most rely on nonspecific adsorption, or on the reaction of the chemical groups which make up cell wall proteins (mainly, amino and carboxylic acid groups) with surfaces containing

complementary reactive groups. In each case the protein is attached to the surface in random orientations (Camarero, 2008; Katsikogianni & Missirlis, 2010). Covalent attachment to a solid support requires two unique and mutually reactive groups on the protein and the support surface. The reaction between these two groups should be highly chemoselective, behaving like a molecular velcro. Moreover, the reaction should work under physiological conditions (i.e., in aqueous buffers around pH 7) in order to avoid denaturation of the protein during the coupling step (Camarero, 2008).

Microbial immobilization on solid surfaces is a relatively simple, inexpensive, quick and therefore popular process. Covalent attachment requires the linking of a reactive group on the cell, such as an amine or carboxyl group, to a reactive group on the surface. Organo-functional silanes have been employed for the covalent attachment of different biomolecules to various materials such as glass, silica, or quartz (Carré, Birch, & Lacarriére, 2007; Li & Ho, 2008; Saal et al., 2006; Seo, Shin, Mukundan, & Revzin, 2012; Shriver-Lake, Charles, & Taitt, 2008; Yamaguchi et al., 2011). The immobilization of biomolecules in silicate glass formed by the sol–gel method has been employed in a number of works. The resultant sol–gel is an interconnected rigid network with pores of sub-micrometer dimensions and polymeric chains of which the average length is more than a micrometer (Kandimalla, Tripathi, & Ju, 2006). By attaching to an inert support material, bioactive molecules can be rendered insoluble, retaining catalytic activity, thereby extending their useful life. These techniques can be used in biotechnology (fermentation processes, bioremediation) as well as in fundamental studies, chemotherapeutic drugs or in biosensor applications (Arakaki, Nakazawa, Nemoto, Mori, & Matsunaga, 2008; Beringer et al., 2009; Chevalier et al., 2010).

Shriver-Lake, Gammeter, Bang, and Pazirandeh (2002) present results of studies on immobilization of bacterial *E. coli* cells on porous glass beads employing 2.5% aminopropyltrimethoxy silane and 2.5% glutaraldehyde as cross-linkers. Scanning electron micrographs showed an even distribution of cells over most areas, but there were areas where the cells clumped together. Deleting glutaraldehyde or aminosilane from the immobilization protocol resulted in at least a 10-fold decrease in the number of attached cells. The density of cells per bead was determined as approximately 3.0×10^8 cells per bead, and the viability of bacterial cells decreased by 70% following immobilization.

A systematic study of the effect of surface modification of silicone on *S. epidermidis* adhesion and colonization was conducted by Tang et al. (2006). Silicone was modified with different biopolymers and silanes. The heparin coated octadecyltrichlorosilane/silicone showed significant increases in bacterial adhesion. These results indicate that the nature of the organo-functional group determines the level of bacterial adhesion and colonization. It was also noted that the hydrophobicity of the surface did not appear to play a determining role in bacterial adhesion and colonization.

The adhesion of microorganisms is inherent in immobilized cell technology with immobilized yeast systems, which has useful applications in the fermentation industry (Kourkoutas, Bekatorou, Koutinas, Banat, & Marchant, 2004; Verbelen, De Shutter, Delvaux, Verstrepen, & Delvaux, 2006). Immobilized yeast systems have been used in ethanolic fermentations with successful adhesion of *Saccharomyces cerevisiae* to diverse solid carriers (Baptista et al., 2006; Demuyakor & Ohta, 1992; Dragone, Mussatto, & Silva, 2008; Mariam, Manzoor, Ali, & Haq, 2009; Tata et al., 1999; White, Yohannan, & Walker, 2008). The application of immobilized microorganisms in biotechnology has been the subject of many studies conducted over the last 30 years, and continues to be an area of great interest for scientists and technologists.

The adhesion of yeasts to surfaces is the first step in immobilization and results from complex physicochemical interactions between the cell, the surface and the liquid phase. It depends on physicochemical properties of the support and cells (surface charge, hydrophobicity, functional groups, electron donor-electron acceptor properties and support porosity and roughness) and on the environmental conditions (ionic strength, temperature and contact time) (White & Walker, 2011).

The application of immobilized cells is a technically difficult process. The continuous systems used in the industry require a large immobilized biomass, good access to the culture medium, a simple immobilization procedure, high surface area to volume ratio, mechanical stability (resistance to shear and abrasion), the chemical stability of the carriers, rapid immobilization of cells and media separation and effective control of infections.

Support materials should be approved for food contact and suitable for sterilization and regeneration. Meeting these requirements results, however, in a number of advantages. For example, in beer production continuous processes allow for a significant reduction in the time it takes for wort fermentation and maturation, minimizing the time associated with inter-process activities, and allowing for better plant operation and facilitation of both pH and temperature control, as well as for full automation and computerization of the process. Reducing the number and size of fermenters, the space required and the workload results in a significant lowering of production costs. Current research on the application of immobilized yeast cells in brewing technology focuses on three main continuous systems: the production of alcohol-free beer, conducting the main fermentation, and green beer maturation (Berlowska et al., 2013).

The influence of the physicochemical properties of biomaterials on microbial cell adhesion is well known. The extent of adhesion depends on hydrophobicity, surface charge, the specific functional groups and acid-base properties. White and Walker (2011) compare the adhesion of three industrially relevant strains of *S. cerevisiae* strains, used in the production of Scotch whisky, ale and lager beer, to the biomaterial hydroxylapatite [$\text{Ca}_5(\text{PO}_4)_3\text{OH}$]. The adhesion of the whisky yeast was greatest, followed by that of the ale strain, while the adhesion of the lager strain was approximately 10-times less. A MATS analysis revealed the ale strain to be hydrophobic while the whisky and lager strains were moderately hydrophilic. There was a linear correlation between adhesion to HAP and the overall surface free energy of the yeasts. Adhesion to hydroxylapatite carriers was reversible and better results were observed in the case of another ceramic carrier-chamotte [Al_2O_3 (36%); SiO_2 (58%); Fe_2O_3 (2.6%)]. In studies conducted by Kregiel, Berlowska, and Ambroziak (2012), the number of immobilized cells was measured as around 10^6 – 10^7 per carrier and cell adhesion was stable during the whole fermentation process. Additionally, a comparison of the volatile products formed during fermentation did not show any significant qualitative or quantitative difference between the free and immobilized cells.

Yeast cell surface is for the most part negatively charged, due to the presence of carboxyl, phosphoryl and hydroxyl groups (White & Walker, 2011). Strong attachment can be achieved either by pre-treating the substrate with polycations (Schaer-Zammaratti & Ubbink, 2003) or by exploiting the ability of microorganisms to attach to solid substrates by means of extracellular polymeric substances (Beech, 1996). Therefore, specific adhesion can be induced by such chemical-support modifications as coating with the proper organo-silane and silane derivatives.

Organo-silanes with amine groups and high positive surface charge may be an interesting option in the modification of native surfaces to improve the adhesion process (Metwalli, Haines, Becker, Conzone, & Pantano, 2006). When trying to attach cells to surfaces,

the most common surfaces employed are silicon based (e.g., glass slides or Si/SiO₂ wafers) or metals (mainly Au and Ag). The most widely used agent for organo-silane based surfaces is (γ -amino-propyl)trialkoxysilane which is relatively cheap and easy to handle. The presence of the amine group enables a variety of subsequent chemical transformations that can produce the desired complementary chemical moieties, and which react with the appropriately modified cell surface protein. In aqueous solvents the amino group rapidly catalyzes the hydrolysis of alkoxy groups (Camarero, 2008).

A study conducted by Berłowska et al. (2013) continues previous studies on the application of porous chamotte carriers in biotechnological processes (Kregiel et al., 2012). Chamotte modification was shown to enhance the efficiency of yeast cell adhesion. Chamotte porous surfaces modified using different organo-silanes were tested for proadhesive properties using industrial brewery yeast strains. Eight brewing strains belonging to bottom-fermenting *Saccharomyces pastorianus* and top-fermenting *S. cerevisiae* were tested. Modification of chamotte carriers by 3-(3-amino-2-hydroxy-1-propoxy) propyldimethoxysilane and 3-(N,N-dimethyl-N-2-hydroxyethyl) ammonium propyldimethoxysilane groups increased yeast biomass loaded on the supports. The spatial distribution of immobilized microorganisms on modified carriers was imaged using a scanning electron microscope. This analysis confirmed the placement of the cells in deep crevices and pores. There was no multilayer three-dimensional structure, as is characteristic of many biofilms, although dense cell clusters were observed. It is significant that immobilized cells appear to have similar CO₂ productivity to free cells, producing (depending on the strain) between 15 and 45 g L⁻¹ of ethanol, with better productivity for ale strains. It is also worth noting that the immobilized yeasts exhibited greater fermentation activity in comparison to the free cells.

5. Conclusion

This paper has given an overview of the most widely used research on the controlled attachment of microbes to surface cells modified by organo-silanes, and a summary of the latest developments in this area. The ability of organo-silanes to attach to different solid supports plays a critical role in cell biology and biophysics and is a powerful tool in many applications, including the control of microbial adhesion. Organo-silane surface treatment has possible uses in the control of the food production chain as well as in the maintenance of accuracy of process parameters in the fermentation industry. However, specific organo-silanes have to be developed for different applications in the food and beverage industry, and the regulations concerning materials which come into contact with food must be observed.

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