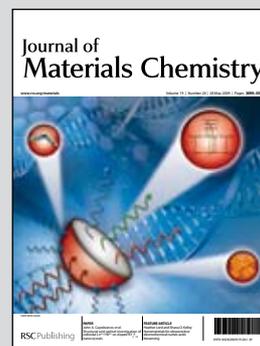


Showcasing research from the collaborative efforts of chemists and marine archaeologists at Palermo's CNR Institute of Nanostructured Materials, Sicily's Superintendency of the Sea and University of New York at Buffalo.

Title: Silica-Based Hybrid Coatings

Painting an undoped ORMOSIL on the metal surface supporting the camera that monitors an archaeological site 30m deep in the waters of Pantelleria prevents costly biofouling. These and similar hybrid coatings provide truly tailorable multifunctional alteration of the surface properties, and are rapidly finding commercial applications. Photo courtesy of Pietro Selvaggio.

As featured in:



See Mario Pagliaro, Rosaria Ciriminna and Giovanni Palmisano, *J. Mater. Chem.*, 2009, **19**, 3116–3126.

Silica-based hybrid coatings

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Organosilica coatings obtained by the versatile sol–gel process are finding applications of great environmental and economic impact, such as in the case of new antifouling and anticorrosive paints entirely devoid of harmful effects. Whether as undoped ORMOSIL (organic modified silicates) or as doped silica/polymer composites, potent nanomaterials are obtained in which chemical and physical protection of the coated surfaces often accompany other functions. We investigate the principles behind this remarkable field of nanochemistry.

1. Background and introduction

Acting as physical and chemical protection agents and providing a number of brand new properties to the coated substrate, functional coatings are immensely important to industry and society in general. Accordingly, a multibillion dollar industry exists that has historically relied upon organic polymers, and also—to a far lesser extent—upon the employment of inorganic polymers such as silica or alumina.¹

Organosilica hybrids, especially in the form of water-based formulations which abate the VOC-content of traditional coating paints, have emerged in the last few years as a broad class of new covering materials capable of serving both traditional requirements of the industry, namely the versatility of organic polymers and the strength and durability typical of inorganic polymers. For instance, the façade of a building painted with one of these new paints containing the sol–gel hybrid formulation (Fig. 1) recently commercialized by BASF will now retain its fresh aspect for years.

Indeed there is purpose in using silica-based hybrid coatings as *multifunctional* coatings that are finding applications in fields ranging from cultural heritage to aircraft protection. These coatings are of special interest since their properties, intermediate

between those of polymers and glasses, can deliver specific and unique requirements not afforded by organic polymers and glasses alone. Alternative coating methods such as chemical vapor deposition (CVD, especially used for barrier coatings) are generally energy- and capital-intensive requiring the use of dedicated plants and deposition processes. Silica and



Fig. 1 The new nanobinder Col.9 combines in one product the different advantages of conventional coating types in terms of low dirt pick-up, chalking and rack resistance, and color retention. (Reproduced from www.col9.com, with permission.)

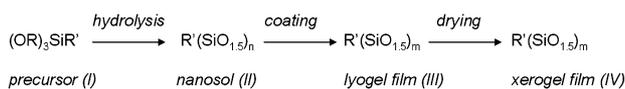
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Scheme 1 Preparation of sol–gel nanocoatings (adapted from ref. 31, with permission).

organosilica coatings, instead, are obtained under very mild conditions in liquid phase by the most prominent *chimie douce* methodology, namely the inorganic chemistry sol–gel process.² Along with the very mild synthetic conditions offered by the sol–gel process, the use of metallo-organic precursors explored at large since the early 1980s allows the mixing of inorganic and organic components at the nanometric scale, yielding highly versatile functional materials at the interface of the organic and inorganic realms, whose chemical and physical properties can be tailored to meet the demanding requirements of widely different chemical applications.³

In general, two approaches to the synthesis of hybrid organic–inorganic coatings are pursued. In the first, and more recently explored, silicon alkoxides of general formula $\text{Si}(\text{OR})_4$ or $\text{R}'_m\text{Si}(\text{OR})_{4-m}$, where the non-reactive organofunctional groups R' act as network modifiers, are used in a hydrolytic polycondensation resulting in the formation of highly porous, reactive organosilica nanocomposites (ORMOSIL) whose applications bridge many traditional domains of chemistry (Scheme 1).

The process allows precise control of the hydrolysis and condensation rate of organosilicon and other metal alkoxides (such as those of aluminium, titanium and zirconium). In general, amorphous hybrid networks are thereby obtained, whereas the use of bridged precursors such as silsesquioxanes $\text{OR}_3\text{Si}-\text{R}'-\text{SiOR}_3$ (R' is an organic spacer) results in the formation of homogeneous hybrid thin films that have a periodically organised porosity.⁴

Coating using the nanosol can either be performed using the alcogel resulting from the hydrolysis step or, even better from an environmental viewpoint, by employing the hydrogel that is easily produced by passing air through the alcogel and simultaneously substituting water.⁵ In general, the coating process is

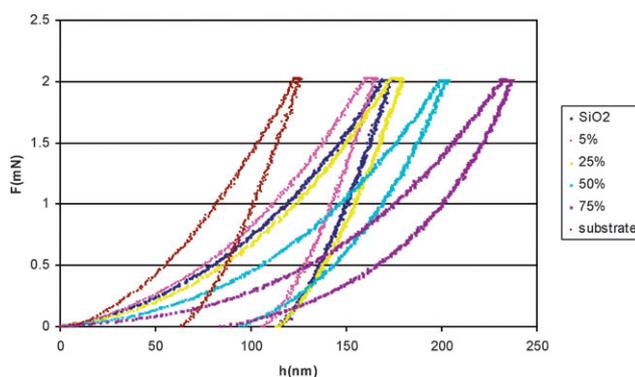


Fig. 2 Loading curves for ORMOSIL thin films with varying degrees of alkylation of the silica matrix. (Reproduced from ref. 6, with permission.)

realized by a simple deposition technique among the many available (spraying, dip- or spin-coating, etc.) which in many practical applications consists simply in brushing a prehydrolyzed solution.

As mentioned above, the physical and chemical properties of the coating can be widely tailored by changing the non-hydrolyzable moiety. For example, the mechanical properties—hardness and elastic modulus—of an ORMOSIL thin film can be tuned by varying the degree of alkylation, opening the way to the fine tuneability of parameters of great practical importance (Fig. 2).⁶

In the complementary approach (Scheme 2) R' reacts with itself or with additional components (R' contains vinyl, methacryl or epoxy groups, for example), resulting in the formation of a flexible network of inorganic oxide covalently bonded to organic polymers, namely a hybrid nanocomposite lacking interface imperfections whose properties intermediate between those of polymers and glasses can deliver unique requirements including thermal, mechanical and corrosion resistance.

Both processes (in which the organic groups R' are either introduced as network modifiers or as network formers) have been exploited for manufacturing organically modified ceramic materials (ORMOCER, a registered trademark of Germany's Fraunhofer Gesellschaft) that have been commercialized as protective hard coatings for transparent plastics since the late 1980s.⁷

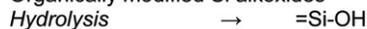
In general, at small film thickness, sol–gel coatings feature excellent scratch, scrub and weathering resistance along with superior thermal stability. Thorough reviews have been published on mesostructured hybrid thin films,⁴ and the general principles behind sol–gel films have been elucidated.⁸ Now, focusing on selected recent examples of hybrid coatings, we aim



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1st step: Formation of the inorganic network

Organically modified Si alkoxides



2nd step: Formation of the organic network



Crosslinking reactions of monomers R' bound to Si alkoxides

Scheme 2 General process of ORMOCER production.

to show how concepts from sol-gel nanochemistry are being used to address practical problems, resulting in a new ubiquitous class of materials for a multiplicity of usages.

2. Protective and antirefractive optical coatings

One of the most important drawbacks of classical and new advanced functional materials for outdoor applications, namely in environments with high ultraviolet (UV) irradiation, is the light induced damage that reduces drastically their effective operational lifetime or durability. UV light, either natural or artificial, causes organic compounds to decompose and degrade, because the energy of the photons in UV light is high enough to break chemical bonds.

UV light is the main factor responsible for the degradation of wooden furniture, plastic parts used in the car industry and artwork in museums, which are all exposed to natural or artificial lighting for long periods of time. Polymers exposed to UV light can lose mechanical strength and integrity, while UV light causes the cellulose and lignin in wood to degrade, discolouring the wood and eventually causing fractures and cracking. The dyes in paintings and photographs progressively fade under UV light and paper becomes yellowed and brittle. All this makes protecting light sensitive materials against UV irradiation an important technological demand nowadays in almost every industrial field. ORMOSIL-based coatings made of *large* amounts of organic UV absorber molecules entrapped in modified silica matrices are capable of reducing drastically the UV light reaching the substrate (Fig. 3), and hence its photodegradation upon prolonged exposition to UV sources.⁹

For example, a thin film of phenylsilica doped with rhodamine dye obtained from a precursor solution consisting of mixtures of TEOS and PhTES (phenyltriethoxysilane) and ethanol in a 0.7:0.3:1 molar ratio, reduces the UV light reaching the substrate to less than seven per cent of the incident light (Fig. 4), whereas the degradation of 20% of the dye molecules is 14 times slower in coated samples, making such a protective coating very attractive for commercial applications.¹⁰

Fig. 4 shows the results of exposing coated and uncoated samples to intense UV radiation, and the intensity of the absorption maximum as a function of the irradiation time. The photodegradation of the dye molecules in the coated samples was much slower compared to the uncoated samples at 25 °C. The UV absorbing molecules are mainly responsible for the

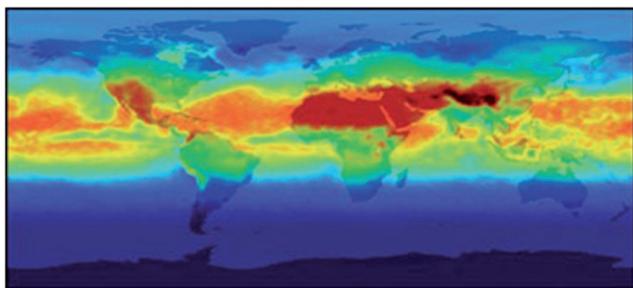


Fig. 3 Solar UV levels vary across the globe, and depend on time of day and season. The highest levels are shown in dark red. (Reproduced from ref. 9, with permission.)

absorption in the UV range as the degradation curve of a fluorescent Rh-101 film coated with an ORMOSIL film with the same composition of protective coating *without* the UV absorber molecules is only slightly slower (due to the reflection of light on the surface of the protective coating) than that of the uncoated Rh-101 film. Coatings just 1 μ thick are highly stable upon prolonged exposure to UV light and are fully transparent in the visible region of the spectrum. This means they can be used to coat a wide range of materials, without affecting the way they look.

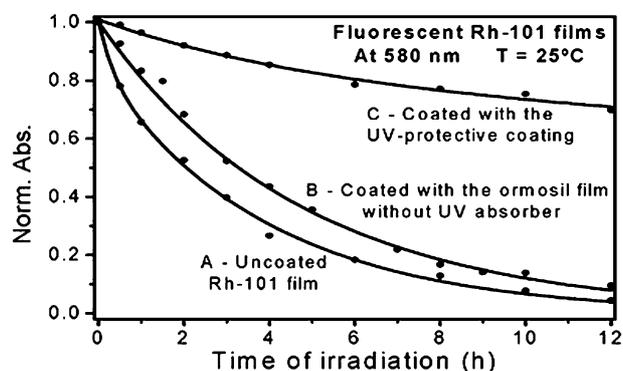


Fig. 4 Photodegradation of the rhodamine films: (a) uncoated; (b) coated with an ORMOSIL coating without UV absorber; (c) coated with a UV protective ORMOSIL coating. (Reproduced from ref. 10, with permission.)

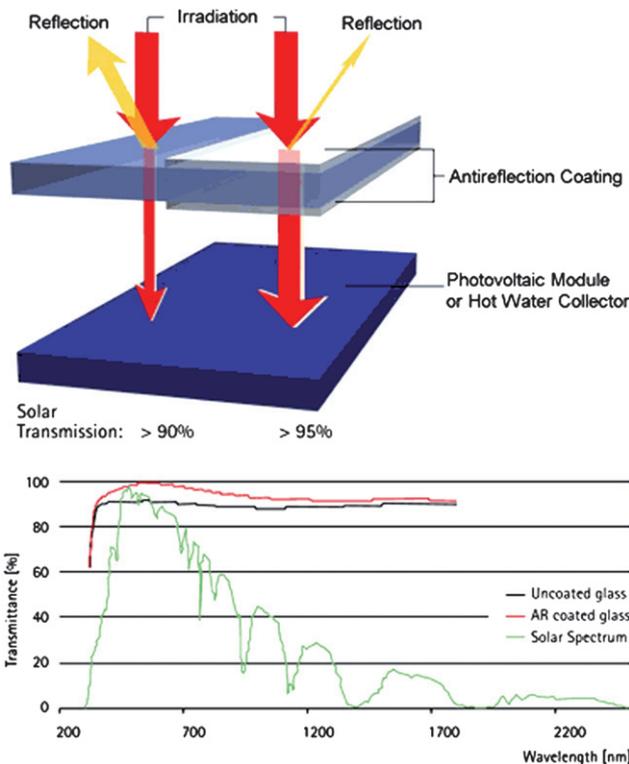


Fig. 5 The solar transmittance of a glass sheet coated with a sol-gel porous SiO₂ antireflective layer increases from 90% to 95%, resulting in an overall 3.5% increase in the PV conversion efficiency. (Image courtesy of Merck.com.)

Similarly, in the crucially important field of photovoltaics (PV), a single-layer, low-refractive and cost-efficient antireflective coating based on SiO_2 serves as an optimal alternative to common multilayer compositions employed as cover sheets for photovoltaic modules (Fig. 5).¹¹

Applied on glass using common wet coating techniques (dip-coating, spin-coating, etc.) the resulting coating exhibits up to 50% porosity. In accordance, the obtained refractive index is between 1.25 and 1.3, which corresponds to a transmission maximum of up to 99% and a solar transmission (weighted average of transmission over total solar range) of >95%; resulting in an overall Watt-peak plus of 3.5% of the original performance. Beyond solar applications (glass and hot water collectors), special high transmittance glass is highly requested for architectural glazing which requires antireflective glass, and large companies such as Merck commercialize several sol-gel silica-based formulations for low-refractive coatings.

3. Antifouling coatings

New, potent antifouling coatings are simply based on the hydrophobicity imparted to the immersed surface by an ORMOSIL coating. In particular, reduced *Ulva* (*syn. Enteromorpha*) zoospore settlement, increased removal of zoospores, increased removal of *Ulva* biomass, and fouling release of

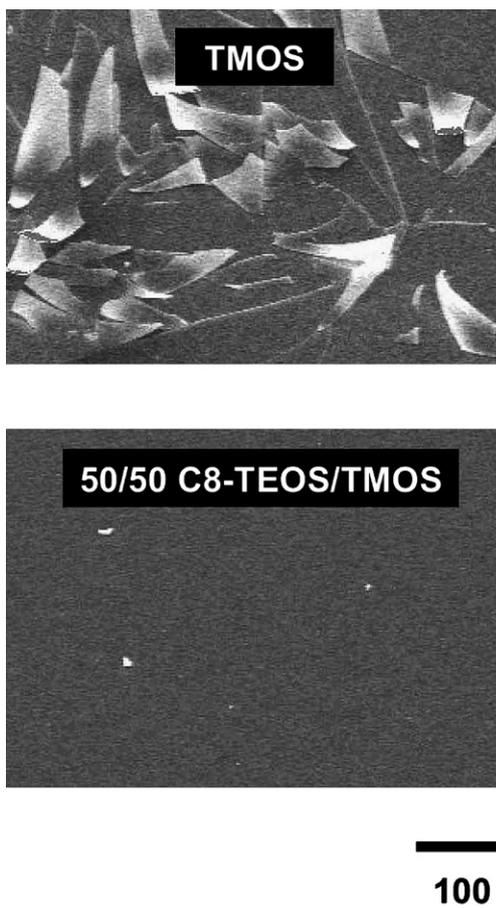


Fig. 6 SEM images of TMOS and 50/50 C8-TEOS/TMOS xerogel films. (Reproduced from ref. 12, with permission.)

juvenile barnacles of *Balanus amphitrite* have been achieved with xerogel surfaces of low wettability and low critical surface tension.¹² Hence, hybrid sol-gel-derived xerogel films prepared from 50/50 *n*-octyltriethoxysilane/tetramethylorthosilicate (C8-TEOS/TMOS) with low critical surface tension inhibit the settlement of zoospores of marine fouling algae as well as of juveniles of tropical barnacles.

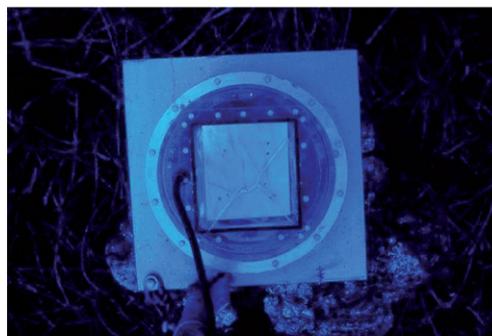
X-ray photoelectron spectroscopy data indicates that the alkyl residues of the C8-TEOS xerogel are located on the surface of the xerogel, which contributes to the film's hydrophobicity. The incorporation of the organic functional groups in the hybrid xerogels reduces the available crosslinking in the silicate structure from $\text{Si}(\text{OSi})_4$ in the pure TMOS or TEOS to $\text{RSi}(\text{OSi})_3$ in the hybrid xerogels leading to a more flexible, less friable surface. Accordingly, whereas the pure TMOS film was highly cracked and poorly adherent, the hybrid xerogel film surface was uniform and uncracked (Fig. 6).

The xerogel films can be tuned to provide surfaces of different wettability and critical surface tension, and the approach has been patented,¹³ developing a commercial product (AquaFast) commercialized in early 2008. The product's usefulness and versatility is shown, for instance, by its employment in protecting the inox steel supporting one of the video cameras 30 m underwater in the sea off the island of Pantelleria (Italy).¹⁴ Painted with a normal brush (Fig. 7a) AquaFast successfully protected the device from fouling over the August–December 2007 period as shown by a picture taken several months after its immersion clearly showing that no vegetation had been deposited on the support (Fig. 7b).

Previously on the unprotected support vegetation growth had been so rapid that the device, used by Sicily's Superintendence of



(a)



(b)

Fig. 7 AquaFast has been successfully used (a) to protect from fouling the camera devices in the marine environment of Pantelleria's island (Italy) used to monitor the nautical archaeological site of Cala Gadir (b).

the Sea to monitor the archaeological site of Cala Gadir, had to be cleaned every month.

The same approach of using a low-surface energy sol-gel paint is at basis of the BioFlow SAFE paint developed by Safe Marine Nanotechnologies.¹⁵ Again, this paint avoids the adhesion of vegetation on a ship's hull without releasing poisonous chemicals into the water. The formulation is mostly made of epoxy-silica hybrids containing small amounts of a silane-functionalized perfluoroether oligomer which reduces considerably the surface energy of the coating due to the fluoroligomer species at the external surface.¹⁶ Application of the paint is easy as it does not differ from the any of the traditional epoxies, whereas the (multifunctional) paint also reduces the vessel's friction in water.

4. Anticorrosive coatings

In spite of its toxicity carcinogenic Cr(VI) unfortunately remains an essential ingredient in the metal finishing industry for corrosion control.¹⁷ Thus its replacement with doped hybrid sol-gel coatings also offers an enormous environmental benefit. Epoxy-silica hybrids are well known for their abrasion resistance and low thermal expansion due to the presence of nanostructured bi-continuous domains.¹⁸ Most recently Safe Marine Nanotechnologies started commercialization of these self-healing anti-corrosives for yachts and for large metal vessels. In general, the silicon alkoxides adhere to steel surfaces by chemical binding to iron surface hydroxyls (Fe-OH) formed upon iron oxidation in water (corrosion) resulting in strong adhesion to a ballast paint.

Typically, these paints are epoxy-silica hybrids doped with molybdate ions which, taking part in the sol-gel condensation reactions, become part of the inorganic network (Fig. 8), to be later slowly released as a corrosion inhibitor. Typically, to

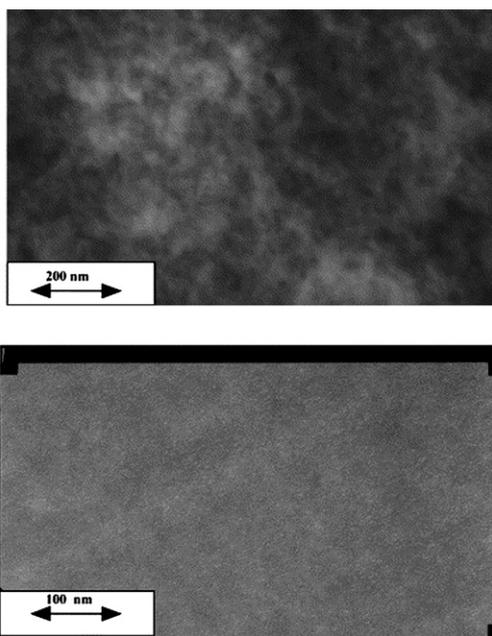


Fig. 8 TEM micrographs of (top) epoxy-silica hybrid (15%, w/w SiO₂) and (bottom) the corresponding molybdenum-doped hybrid. (Reproduced from ref. 16, with permission.)

facilitate the formation of finely dispersed bi-continuous phases the resin is functionalized with alkoxy-silane groups. Then the two components—silica and the epoxy resin—behave synergically in the hybrid, with the inorganic component enhancing the network density by imposing strong constraints on the molecular relaxation of the organic network. The result is a group of nanomaterials with unique characteristics: high solids content (up to 98%), solventless, good mechanical and chemical resistance, high adhesion (>25 MPa) and high gloss (>90).

In general, the application of sol-gels as a means of corrosion inhibition is based on two complementary functions: the physical barrier of the polymeric matrix as well as the specific corrosion inhibition of the non-hydrolyzable moiety R in the ORMOSIL. Magnesium, for example, has high electrical and thermal conductivity, is abundant and easily recycled, and its high strength to weight ratio makes it a valuable asset in the transportation and aviation industries. Yet, its utilization has not reached full capacity because of its high chemical reactivity and tendency to corrode. The very negative standard potential of Mg ($E^{\circ} = -2.37$ V vs. NHE) makes it unstable with respect to water which results in the formation of a protecting oxide layer. Yet, the native oxide layer does not prevent its pitting corrosion, facilitated mostly by halides, which results in destructive effects.

Thin sol-gel ORMOSIL/zirconia films successfully inhibit Mg corrosion (Fig. 9). The combined film obtained by using sol-gel monomers phenyltrimethoxysilane (PTMOS) and zirconium(IV)tetra-1-propoxide (ZrTPO) exhibits superior corrosion inhibition to other films.¹⁹ The sol-gel coatings are prepared by the acid or base-catalyzed hydrolysis and condensation, depositing first a PTMOS film followed by a ZrTPO based film.

An important factor in film quality concerns its adhesion to the substrate, namely the Mg chip. Good adhesion of the layer is necessary, but not sufficient, to inhibit corrosion. Indeed, all the three films show high adhesion to the surface (the films were scratched to visualize the removal effect, and to increase the visibility of the pictures Rhodamine B was added to the deposition solutions), which cannot account for the difference in terms of corrosion inhibition between the coatings.

In another approach, ZrO₂ nanoparticles are used as a reservoir for the storage and prolonged release of a corrosion inhibitor for aluminium alloys such as cerium ions. The resulting nanostructured doped sol-gel material can be proposed as a potential candidate for substitution of the chromate pre-treatments for aluminium alloy AA2024-T3.²⁰ The films are made from TEOS and GPTMS (3-glycidoxypropyltrimethoxysilane) precursors, doping the hybrid nanosol with ZrO₂ nanoparticles and cerium nitrate as the corrosion inhibitor. The AFM scan (Fig. 10) shows that the nanosized particles are incorporated into the film matrix with uniform distribution.

The nanoparticles not only reinforce the hybrid matrix but also absorb inhibitor ions releasing them during contact with moisture, offering effective self-healing properties. The prolonged release of inhibitor provides long term corrosion protection. The hybrid ORMOSIL films in fact lose activity when the coating is partially destroyed.

Indeed, the evolution of the polarization resistance during the immersion tests for the different hybrid sol-gel coatings (Fig. 11)

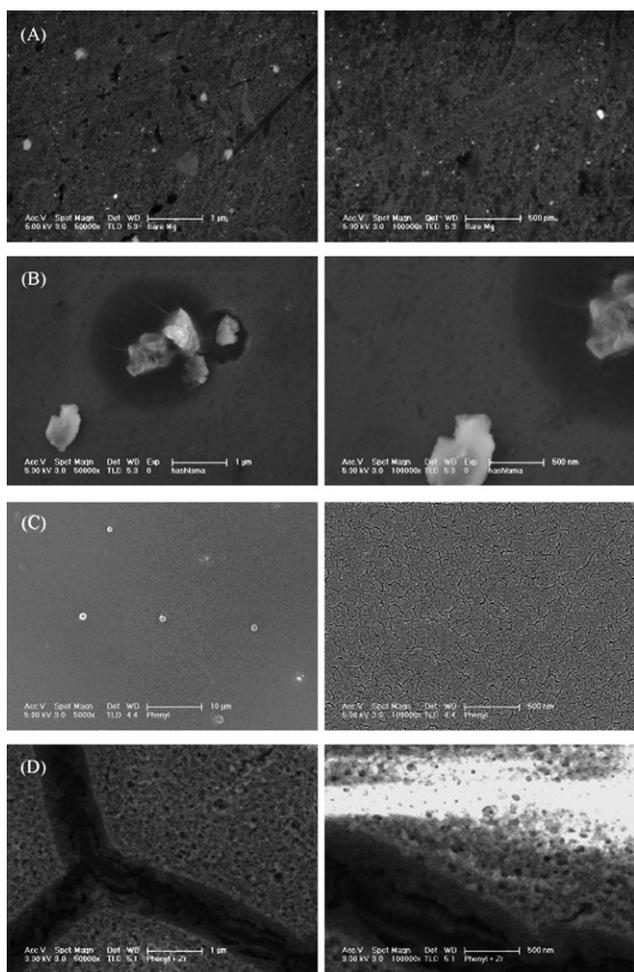


Fig. 9 Low and high magnification SEM images of Mg chips: (A) bare, and coated with (B) ZTPO film, (C) PTMOS film, and (D) combined film. (Reproduced from ref. 19, with permission.)

highlights that AA2024-T3 coated with coating A (with cerium-doped zirconia nanoparticles) shows the first signs of corrosion processes only at the final stage of the immersion tests, namely after 275 h of immersion: one order of magnitude later than in the case of the other coatings (coating B: cerium-doped organosiloxane matrix; coating D and E: cerium-free).

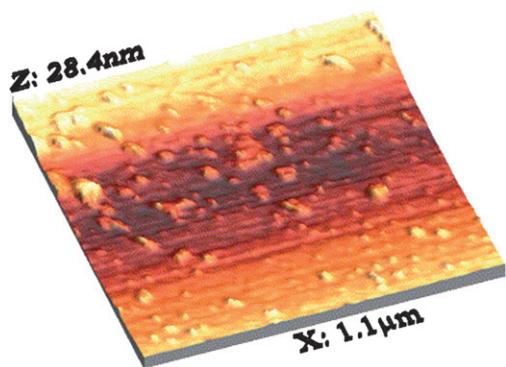


Fig. 10 AFM topography of the sol-gel coated aluminium alloy substrate shows that nanosized particles are incorporated into the film matrix.

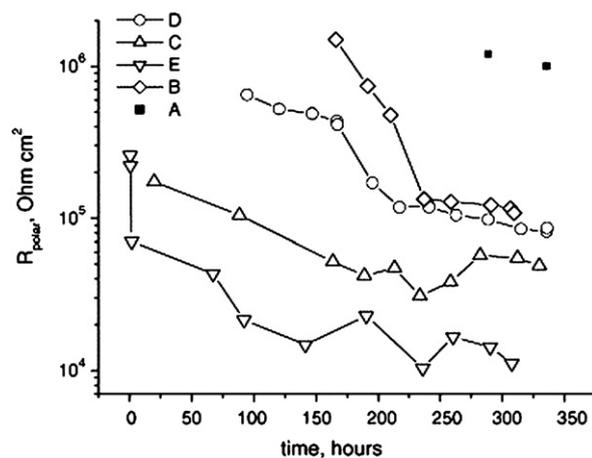


Fig. 11 Evolution of polarization resistance for different coatings during immersion. (Reproduced from ref. 20, with permission.)

5. Scratch-resistant and anti-aging coatings

Numerous ORMOSIL-based coating materials are commercially employed for protecting glasses against scratch and abrasion for sensitive surfaces. Mechanically ORMOSILs alone are not sufficiently strong. Therefore, commercial protective materials are based on (epoxy) alkoxy silanes polycondensed with limited amounts of Al, Ti or Zr compounds used to reinforce the final structure. Once the polycondensed material is prepared, it is diluted in a specific solvent and deposited on the sensitive substrate followed by UV and/or thermal curing. Dyes, pigments and fillers may also be added for specific applications, leading to smart multifunctional hybrid coatings.

Coating formulations are generally clear, transparent, low viscosity, solvent-free liquids that are stable with a shelf life of several months and are supplied by a large number of companies worldwide, such as for instance TOP in Germany and Hybrid Glass Technologies in the US. More recently, a new line of organofunctional- and alkylsilane water-based sol-gel products (Dynasytan) has entered the market.²¹

They provide good corrosion and abrasion protection for valuable metal and also provide excellent adhesion of coatings, without the use of chromium(VI). The improvements in practical applications are based on multiple benefits (functions) offered by silanes. Forming permanent chemical bonds between substrates and organic polymers or resins, the addition of silanes in coating formulations results in excellent adhesion to challenging substrates such as glass, aluminium, steel, or concrete. In challenging environments (bridges, ships, and other installations that are particularly susceptible to corrosion), aminosilanes crosslink silicone-based epoxy resins with the formation of very hard and weathering resistant coating films. Finally, silane-modified inorganic pigments can be easily incorporated into coating formulations allowing, for example, hydrophilic pigments to be hydrophobized. The improved compatibility of the hydrophobized pigments helps to achieve higher levels of filler content, lower viscosities, longer shelf lives, better sedimentation resistance, improved mechanical properties of the cured coating, and increased UV stability.

Applied in a thin layer, these coatings are especially important to the aerospace industry, where weight issues are an important factor, and can be used as primers or protective coatings for coil and sheet coatings, powder coatings, fasteners, automotive parts, steel furniture, appliances and other industries.

Similarly, the first ORMOSIL-based facade coating on the market (trademarked Col.9 by BASF) is a formulation whose half content is a dispersion of organic plastic polymer particles in which nanoscale particles of silica are incorporated and evenly distributed. Thanks to this combination of elastic organic material and hard mineral, coatings based on this novel nanobinder combine in one product the different advantages of conventional coating types in terms of low dirt pick-up, chalking and crack resistance, and color retention (Fig. 12).²²

The inorganic nanoparticles are homogeneously embedded in larger acrylate polymer particles. After drying and curing at room temperature, dirt repellent nanostructures form on the surface of the coating reinforcing the hydrophilic properties of the facade.

The molecular composite nature of the particles ensures that the nanoparticles will remain homogeneously fixed instead of agglomerating when the liquid coating is formulated with water and color pigments; and this enables the formation of a stable three-dimensional network of nanoparticles on the surface which covers the entire film. Because of its high silica content, however, the nanocomposite of Col.9 does not have thermoplastic

tackiness. At the same time, the mineral particles provide the coating with a hydrophilic attracting surface on which rain drops are immediately dispersed. As regards cleanliness, this offers dual benefits: in heavy rain, particles of dirt are washed off extensively from the facade surface, and also the thin film of water remaining when rain has stopped dries extremely quickly, which prevents mold formation. In contrast, the rain rolling off unevenly in thick droplets from water-repellent surfaces of fully synthetic resin coatings often leaves behind unattractive streaks of dirt. Finally, permanently incorporating the mineral nanoparticles in the much larger acrylate polymer particles, means that the color tone remains stable and there is no surface chalking even after years of exposure to weather.

6. Decorative coatings and barrier systems

Decorative hybrid coatings are increasingly used on glass, mineral and metal surface sheets. For example, a series of industrial coatings (SC from Hybrid Glass Technologies) are based on ethanol solutions of various silica or alumino-silica based formulations, made available as clear liquids or colored formulations. Spin-, dip- or flow-coating techniques are then used to apply these formulations to flat windows or sandblasted glass substrates (Fig. 13) to achieve hard 1–10 μm protective coatings for glass that exhibit superior protective anti-staining properties and water repellency when compared to several existing commercial products. Indeed, they form strong chemical bonding with the glass surfaces and protect against staining or water corrosion.

Thin-film coatings made of dye-doped ORMOSILs are increasingly employed in industry as color decorative materials for glasses and plastics. There are more than 7000 types of organic dyes; all readily available, they have several advantages over pigments when they are used in colored thin-films because of their higher intensity of light absorption and transparency, non scattering and high solubility.

Homogeneity of dispersion and the homogeneous nature of the hybrid ORMOSIL result in intensely colored films even at low thickness. Compared to organic polymers, the colored hybrid films have enhanced mechanical properties like higher hardness and stronger abrasion resistance. With respect to inorganic sol-gel films, hybrid films also provide several

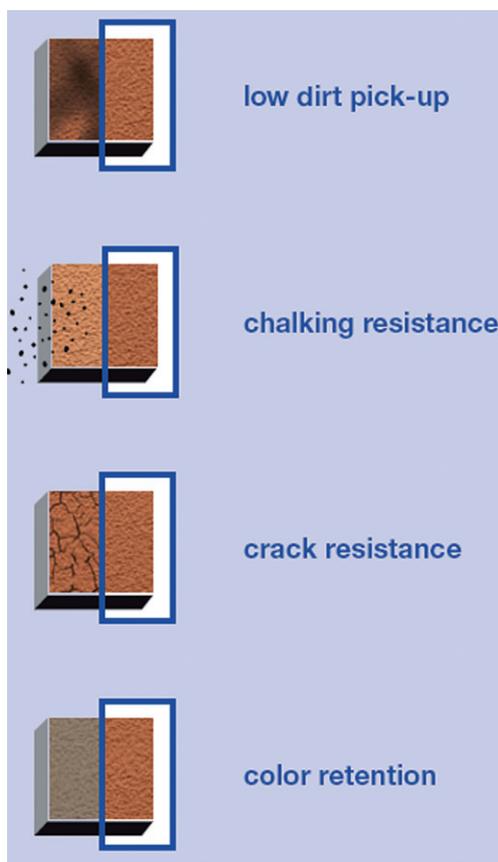


Fig. 12 Multifunctional properties of surfaces treated with the nanobinder Col.9. (Reproduced from www.col9.com, with permission.)



Fig. 13 Decorative hybrid coatings are increasingly used on glass surface sheets. (Reproduced from www.hybridglass.com, with permission.)

advantages such as much better adhesion, transparency, flexibility, reduced surface roughness, and better refractive index matching.

Films made of hybrid polymethylmethacrylate-silica (PMMA-SiO₂) doped with red, blue and green organic dyes and further coated on glass substrates provide a clear example of the versatility of the sol-gel ORMOSIL technology.²³ Smooth polycondensation of a precursor solution made of TEOS:TMSPM:MMA (1:0.5:1 molar ratio of reactants, MMA = methyl methacrylate; TMSPM = 3-(trimethoxysilyl) propyl methacrylate) followed by radical polymerization of MMA ensures the formation of homogeneous and hard films having a smooth surface with very little roughness. Hardness as measured by the modulus of all the hybrid films is at least 9H showing that the inorganic component in the hybrid films reinforces the organic component, producing harder films with more abrasion resistance as compared with pure PMMA films.

The optical transparency of such hybrid films is another indication of their homogeneous composition of both organic and inorganic phases. Finally, the transparent colored hybrid films have very good optical quality, reflected in the interference oscillations (Fig. 14), with color intensity depending on the amount of organic dye in the films.

Hydrophobic silane formulations such as those of the water-based organosilanes line are good surface protection agents for wood (Fig. 15) as the resulting coating repels both oil (dirt) and water, protects the surface from the effects of weathering, and reduces the growth of microorganisms.

The silane formulation does not affect the expansion and contraction behavior of the wood and is therefore particularly suitable for outdoor objects without ground contact. The resulting coating features many relevant properties. The mechanical properties of wood are improved and at the same time the modified silica coating imparts flame retardant, water repellent and antimicrobial properties.²⁴

The properties of silane-based wood coatings are based on covalent chemical reactions between the silanes and the hydroxyl groups at the wood surface (Fig. 16). For the reaction to occur under mild outdoor conditions, the silica has to be modified by

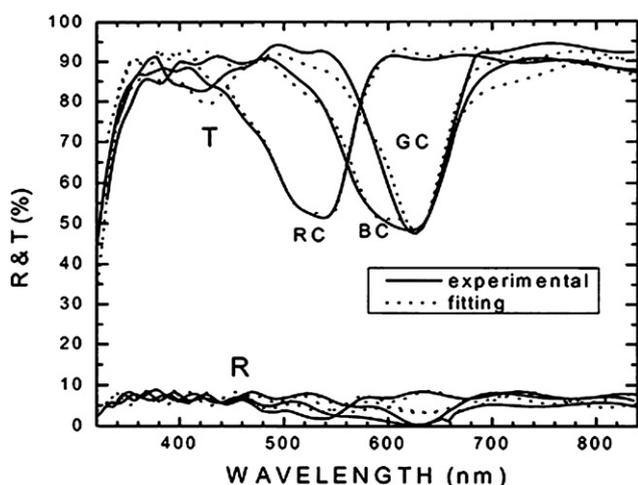


Fig. 14 Transmittance and reflectance spectra of the three colored hybrid films. (Reproduced from ref. 23, with permission.)

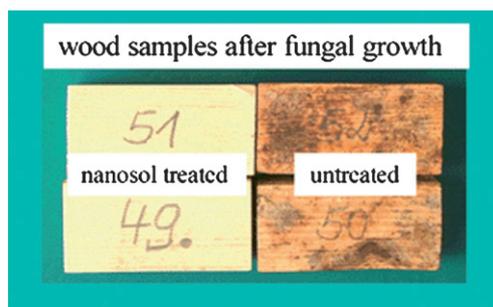


Fig. 15 Organosilane-based coatings form an almost invisible protective layer on untreated wood surfaces and on weathered and varnished wood surfaces. Dynasylan SIVO 121 produces a strong hydrophobic and oleophobic effect (bottom). (Reproduced from ref. 21, with permission.)

using reactive organic groups like epoxysilanes. Indeed, this is what the company has achieved and the formulation with its ORMOSIL precursor is kept undisclosed.

In general, long, alkyl groups stable against UV-induced degradation ensure durability and provide hydrophobicity, whereas oleophobicity is due to the siloxane backbone structure. Finally, for application on wood there is a further product named Sebosil (Kallies Feinchemie, Germany) which is a 70–80% ethanol-based nanosol of SiO₂ (5–20%) that is successfully employed as a wood reinforcement based on penetration of the wood's pores by the nanoparticles.

With careful selection of the combination of starting alkoxides and appropriate synthesis conditions, the sol-gel technology is now widely applied to the conservation of art objects and cultural heritage. For example, a hybrid silica coating now protects the 14th century mosaic situated above the gates of

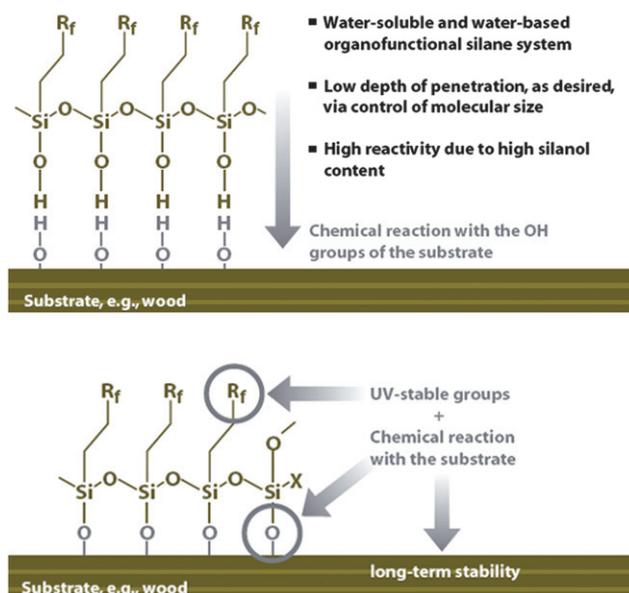


Fig. 16 Covalent bonding of silanes to the wood's surface ensures durable protectability for all wood surfaces. Optimal treatment of 1 m² requires 0.1 L Dynasylan, ensuring 3 years protection. (Reproduced from www.specialchem4coatings.com, with permission.)

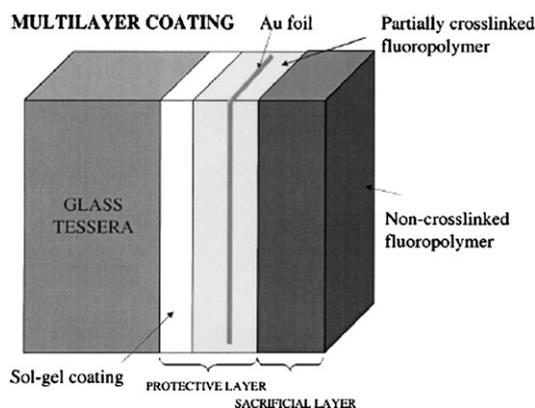


Fig. 17 Schematic cross section of the multi-layer coating used in the long-term protection of the mosaic. The mosaic was originally gilded; therefore, a tiny gold foil is inserted into each tessera. (Reproduced from ref. 25, with permission.)

St. Vitus cathedral, in the center of Prague Castle.²⁵ The coating selected for treatment of the entire mosaic is a multi-layer system in which an organic-inorganic sol-gel layer is placed between the glass substrate and a fluoropolymer coating (Fig. 17). It consists of a protective coating (one sol-gel layer derived from epoxy silanes and methyl silanes, coated with a partially crosslinked functionalized fluoropolymer) and a sacrificial, removable coating consisting of the same fluoropolymer, non-crosslinked, which is removed and re-applied periodically.

The sol-gel layers underneath the top polymer layer are estimated to last for 25 years. Beyond the long term stability under severe ageing conditions, the advantage of such materials compared to polymers lies in their ability to adhere to many substrates, the possibility of making thicker coatings than with purely inorganic sol-gel systems, and their ease of application using a brush (by hand in order to avoid coating the interstitial spaces between tesserae) followed by curing at 90 °C for two hours using large infrared lamps. All organic polymers used in previous protection attempts have failed to stop the corrosion, because of their poor durability, poor adhesion to the glass, and large diffusion coefficients for SO₂ and water. The mosaic indeed is a large outdoor panel 13 meters wide and 10 meters high, made of about 1 million pieces of multicolored, high-potassium glass embedded in a mortar. The glass is chemically unstable as it is exposed to harsh weather conditions (high sulfur dioxide levels, rain, and temperature varying between -30 °C and +65 °C), in which the alkali reacts with the atmosphere and water to form salt deposits.

Similarly, a solution of prehydrolyzed 3-glycidoxypropyl-trimethoxysilane (GPTMS)/MTMS hybrid doped with colloidal silica particles (improving the mechanical properties while maintaining good optical transparency), brushed over art metal objects such as those in brass or bronze, effectively delays corrosion on metal or glass substrates, and imparts good resistance to UV.²⁶

Fig. 18 shows the clear corrosion inhibition due to the sol-gel layer in the plate (right) coated with a sol-gel/fluoropolymer multilayer coating which does not show any degradation even after two years of exposure to a corrosive *milieu*.

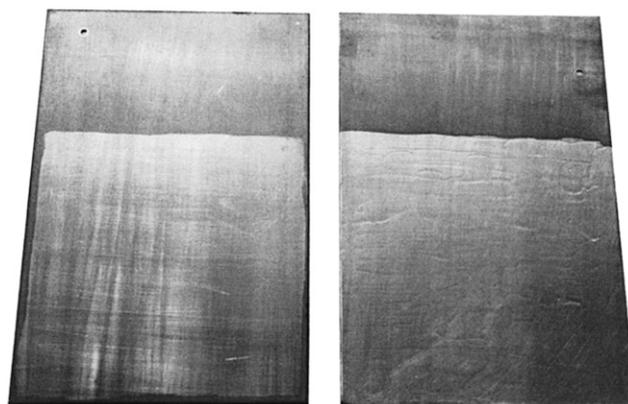


Fig. 18 Brass samples after 2 years exposure to a high sulfur, high humidity environment. *Left:* plate coated with GPTMS/MTMS. *Right:* plate further coated with a Lumiflon polymer. (Reproduced from ref. 26, with permission.)

Finally, polycondensates of some percentage of Al alkoxides with phenyl- and epoxy-functionalised alkoxy silanes (at Fraunhofer ISC),²⁷ or Zr alkoxides with 3-glycidoxypropyl-trimethoxysilane (GTMS, at Boeing),²⁸ are excellent barrier coatings for the coating film for solar cells integrated into modules. Easily deposited by spraying followed by curing at relatively low temperatures (70–80 °C), the latter sol-gel coatings provide improved resistance to radiation damage. In the latter case, the lightweight, durable sol-gel coating reduces the manufacturing steps and overall weight of the traditional Si-based solar cell array because the hybrid sol-gel layer replaces the heavy, fragile glass coverings normally applied to the surfaces of the solar cells.

In the former case, the *flexible* nature of the encapsulants results in an optimized encapsulation process which was specially developed for the manufacturing of flexible thin film solar cells whose lower cost (compared to traditional Si-based cells) and low material demand is crucial for the future dissemination of PV. A low final cost of the solar modules indeed requires the extremely high productivity typical of roll-to-roll manufacturing, whereas flexible modules are suited for non-planar surfaces as

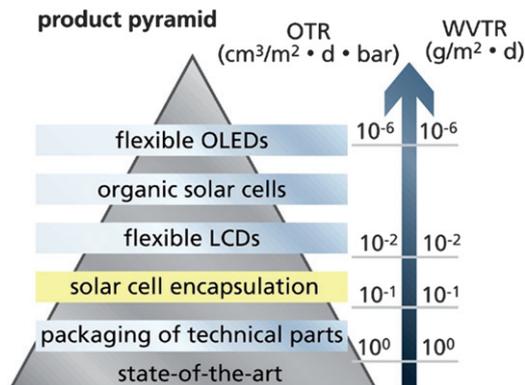


Fig. 19 Especially for high value added applications like encapsulation of solar modules, the requirements for oxygen and water vapor barriers are orders of magnitude higher than today's state of the art polymer technology. (Image courtesy of the Fraunhofer ISC.)

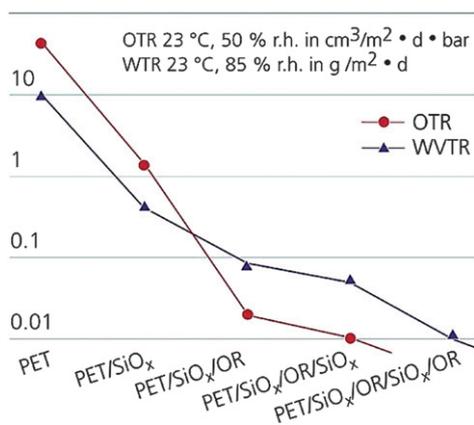


Fig. 20 Barrier properties of the protective systems produced by roll-to-roll processes (OR: ORMOCER. Image courtesy of the Fraunhofer ISC).

well as for wide application in the building industry where such flexible PV cells will soon become a standard integrated part of construction components.²⁹

The new “one component encapsulant” developed is capable of protecting the solar cell from water vapor in the atmosphere, with the necessary very high barrier properties (Fig. 19).

A combination of barrier layers enabled the achievement of high and ultra-high barrier properties. SiO_x and ORMOCER barrier layers were applied on a PET film (36 μm) optimized for vacuum coating, with the four-layered barrier system giving the required oxygen (OTR) and water vapor (WVTR) values (Fig. 20).

Currently, the composite encapsulating materials are being used for the roll-to-roll production of the first test modules at companies in Germany and in France.³⁰

7 Functionalization of textiles by sol-gel coatings

The maintenance and improvement of current performance and the creation of new material properties are the important reasons for the functionalisation of textiles with sol-gel organosilica coatings with particle diameters smaller than 50 nm (nanosols).³¹ Within today's global textile market worth more than \$400 billion high-grade textiles rapidly grow as functional textiles improve applications (enhanced comfort, easier care, better health and hygiene) and extend their range of utilisation (ensuring protection against mechanical, thermal, chemical and biological attacks) affording technical textiles, with numerous usages in automotive, railroad and aviation engineering, in construction and for home textiles.

New products that are being developed include textiles with water, oil and soil repellency and with antimicrobial properties. The nanoparticulate size of the sol particles promotes excellent adhesion to the textile fibres, which can be further enhanced by subsequent thermal treatment (Fig. 21). For example, sol-gel immobilised bioactive liquids such as cineol, camphor, menthol, evening primrose and perilla oil used to functionalize textiles afford either skin-friendly textiles with antimicrobial and anti-allergic effects due to immobilised natural oils; or textiles for therapeutic treatment of the respiratory tract by means of

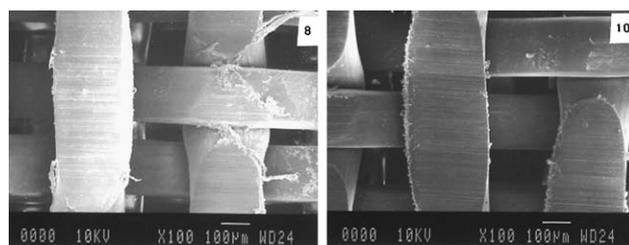


Fig. 21 SEM pictures of polyester sieves after abrasion without (*left*) and with nanosol coating (*right*). (Reproduced from ref. 31, with permission.)

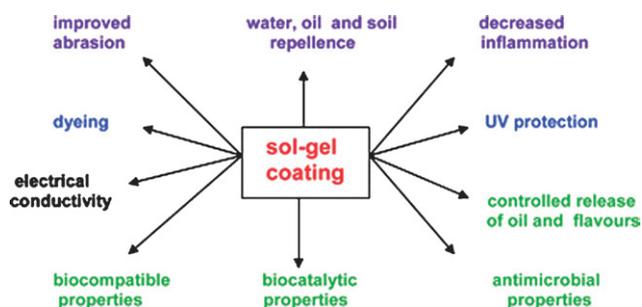
immobilised mixtures of highly volatile natural agents such as eucalyptol, camphor and menthol.³²

Due to the very low layer thickness (below 1 μm) the consumption of coating solutions is also very low, whereas the use of coated textiles offers a more continuous and prolonged release of the embedded liquid, which is also more convenient. The first optimized commercial sol-gel products for textile refinement are manufactured by the company CHT (Tübingen, Germany) which sells a number of water-based (and not inflammable) sols for application onto textiles, resulting for example in the increased stiffness of textiles.³³

8. Outlook and conclusions

Depositing a sol-gel silica-based coating on a piece of substrate is easy and economically attractive as it changes and largely enhances the physical and chemical properties of the coated substrate while consuming limited amounts of valued organosilanes. Methods include spin-coating or dip-coating, spraying, brushing, electrophoresis, inkjet printing or roll coating. Silanes can be easily combined with other species, either using the doping methodology or directly with organic resins or metal oxide sols, to create coatings for an unprecedented large range of applications. The sol-gel coating thus enables the manifold alteration of the physico-mechanical, optical, electrical and biological properties of a material's interface (Scheme 3).

Traditional limitations of sol-gel coatings, namely weak bonding, low wear-resistance, high permeability, and difficult controlling of porosity, are being addressed to arrive at their full industrial potential. For example, the very substrate-dependent nature of the sol-gel technique reflected in the thermal expansion



Scheme 3 Some possibilities of surface functionalisation by modified nanosols. (Reproduced from ref. 31, with permission.)

mismatch limits, is being resolved by developing multicomponent coatings with the required thermal properties.

Another major advancement is provided by the development of sol–gel formulations that no longer require curing at elevated temperatures (typically between 100 °C and 200 °C) but, instead, are capable of effectively curing at room temperature. For instance, researchers in the UK have recently developed flexible, thicker (up to 0.015 mm) hybrid coatings for high volume in-line applications which, depending on the inorganic/organic ratio, can be cured at relatively low temperatures at times as low as tens of seconds, eventually replacing the current commercial system of primer and pre-treatment with a sol–gel layer directly coated with a top coat.³⁴ The team has developed a solvent-free (100% water-based) aqueous variant of their sol–gel coating which has the added environmental benefit that no volatile organic compounds are released during the curing process. Indeed, along with unique performance, hybrid coatings offer enormous advantages in terms of sustainability. As the nanotechnology and “green chemistry” scientific communities will eventually unify their efforts,³⁵ we argue that this area of research will rapidly expand, driven by the urgent and ubiquitous demand for high-performance, low-cost and green protective coatings for use in industry as well as in everyday life.

The current scarcity of commercial applications for hybrid coatings has been due, as we have discussed elsewhere,³⁶ to the prolonged reluctance of many large chemical companies to enter the sol–gel science and technology field. However surprising it may be, most successful sol–gel silica-based products of the last decade have been commercialized by start-up companies that developed the products and eventually rapidly grew. All this suddenly changed with the recent launch of hybrid coatings by large companies such as BASF, Degussa (Evonik) and Merck. Very soon, hybrid silica-based coatings will become ubiquitous nanomaterials with a multiplicity of applications. Due to the versatility of sol–gel chemistry, chemical ingenuity will clearly be greatly needed to conceive and develop such multi-functional coatings. It is the aim of this article to contribute to this progress by highlighting the principles behind selected applications.

Acknowledgements

This article is dedicated to Paolo Carrara on the occasion of his 40th birthday and for the many gifts received, including Stuart Mill’s memorable book on liberty donated to one of us (M.P.).

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