

## Sol-gel process: an outstanding technology for coatings

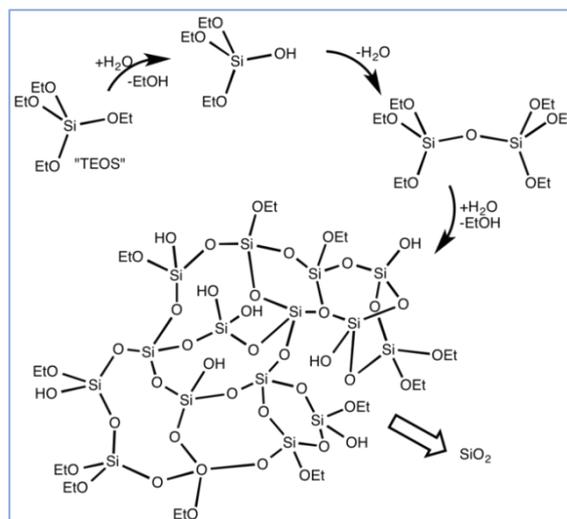
### Sol-gel process

In materials science, the sol-gel process is a method for producing solid materials from small molecules [1]. The polymerisation of the small molecules occurs at room temperature to form glassy and ceramic solid materials contrary to traditional ceramic and glass technology.

The first sol-gel polymerization was carried out in 1845 by a French chemist Ebelmen [2]. Since then, sol-gel process has been deeply studied, developed and used in many industrial applications. Sol gel process, for solution – gelation, consists in hydrolysing, dissociation chemical bonding by water molecules and condensation, (inorganic polymerisation) of precursors which are generally metal alkoxides. The process involves the formation of two consecutive phases of a “sol,” which is a stable of solid particles in a liquid, and a “gel,” which is an inorganic integrated network formed by the sol [3].

The class of precursors most widely used in the sol-gel technology are metal (and metalloid) alkoxides which

are members of the family of *metalorganic* compounds and have an organic ligand attached to a metal or metalloid atom. An *alkoxy* is a ligand formed by removing a proton from the hydroxyl on an alcohol, as in *methoxy* ( $\bullet\text{OCH}_3$ ) or *ethoxy* ( $\bullet\text{OC}_2\text{H}_5$ ) for example. Contrary to *organometallic* compounds, which are defined as having direct metal-carbon bonds, the metal alkoxides  $\text{M}(\text{OR})_z$  (where M is a metal or metalloid and R is a proton or an alkyl group) have metal-oxygen-carbon linkages.



**Figure 1 : Schematic representation of hydrolysis and polymerization of tetraethyl orthosilicate (TEOS) at low temperature [4].**

Metal alkoxides precursors are popular because they react readily with water. In the sol-gel process, the

species formed in the first step is a M-OH bond that is not stable and reacts with other species. This first step is called hydrolysis.

In a second step, the labile M-OH group condenses with other M-OH and M-OR (if alkoxides were the precursors) groups to form M-O-M bonds under the release of water or alcohol. Thus, a three-dimensional network is formed. Generally, the produced species are not fully condensed in this kinetically driven process but still include water or OH-groups [5-7].

Structurally, the hydrolysis and condensation lead first to solid particles that are suspended in the liquid, it is the *sol*. However, the particles are still active due to the chemical groups on their surface leading to crosslinking, transforming thus, the *sol* to a *gel*. These reaction steps can be carried out in water but also in organic solvents with a minimal quantity of water to promote the first reaction step. In essence, the preparation of a sol-gel solution involves the use of inorganic or metal organic compound aqueous organic/alcoholic solvent with the addition of an acid/base conditioner as a catalyst. Additives as tension-actives, organic monomers, etc can be used to modify the final composition or structure or to improve some properties as surface adherence, etc.

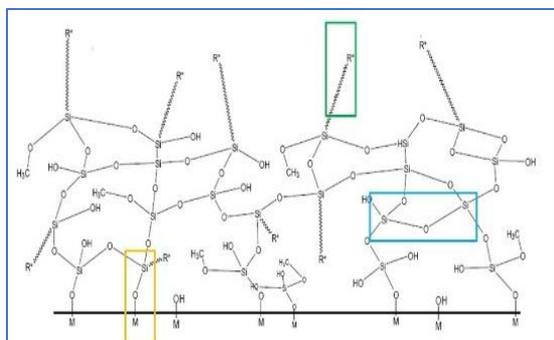
In sol-gel processes, the most common material used is **tetraethyl orthosilicate (TEOS)**. This material,

once hydrolysed with water, allows the production of glasses by polymerisation at low temperature. The chemical reactions are illustrated above in the Figure 1. As the case of TEOS, the silicon-based sol-gel process is the one that has been most investigated. The most widely used metal alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS), (3-Glycidyloxypropyl)-trimethoxysilane (GPTMS), Methyltriethoxysilane (MTES) and 3-(Trimethoxysilyl)propyl methacrylate (MPS). The key feature that makes the silicon-based sol-gel processes predominant in the formation of hybrid materials is the simple incorporation of organic groups using organically modified silanes. Indeed, Si-C bonds have enhanced stability against hydrolysis in the aqueous media usually used, which is not the case for many metal-carbon bonds, so it is possible to easily incorporate a large variety of organic groups in the network formed. Sol-gel reactions of non-silicates compounds are also possible. Other alkoxides such as aluminates, titanates, zirconates, etc are commonly used in the sol-gel process, either alone or in combination with other alkoxides such as TEOS. Metal and transition-metal alkoxides are generally more reactive towards hydrolysis and condensation reactions compared with silicon. In the reference [8], more details on sol-gel technology are reported and discussed.

## Sol gel coatings

The sol is applied on the surface by different application techniques. After solvent evaporation, a xerogel is formed which will undergo further curing (densification). The curing step is generally carried out under heating. However, UV-curable hybrid coatings are currently developed where a mix of -M-O-M- and polymeric chains are formed (epoxy, acrylates, etc).

What makes sol gel coating remarkable compared to classical varnishes is illustrated in the following Figure 2: (i) formation of covalent bonds on most metals (-Si-O-M in the figure when alkoxysilanes are used) which allow strong coating adhesion on the substrates (in yellow); (ii) coating density due to the formation of -Si-O-Si-chains (siloxanes when alkoxysilanes are used, in blue); (iii) coating flexibility thanks to non-hydrolysable functions -Specific functionalities thanks to R\* groups: adhesion with topcoat, hydrophobic character, etc.



**Figure 2: Schematic representation of the different bonds in a coating obtained by sol gel process and applied on a metallic substrate.**

## Application techniques

In terms of application techniques, there are several deposition options such as dip-, spin-, flow-, spray- and roll-coating which can be used to coat a surface with a sol solution. The coated substrate is heat treated or UV cured to form dense coating and complete the polymerisation reactions.

**Dip coating** technique can be described as a process where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined speed under controlled temperature and atmospheric conditions. In this process, the atmosphere controls the evaporation of the solvent and subsequent destabilization of the sols by solvent evaporation leads to the gelation process and the formation of a film with small particle size inside. The coating thickness is defined mainly by the withdrawal speed, the solid content and the viscosity of the liquid. The interesting part of dip coating process is that, by choosing an appropriate viscosity, the thickness of the coating can vary precisely from 20 nm up to 50 nm while maintaining high optical quality.

In the **spin coating** process, the substrate spins around an axis that should be perpendicular to the coating area. This process has been developed for the so-called spin-on glasses in microelectronics and substrates with a rotational symmetry, e.g. optical lenses. There

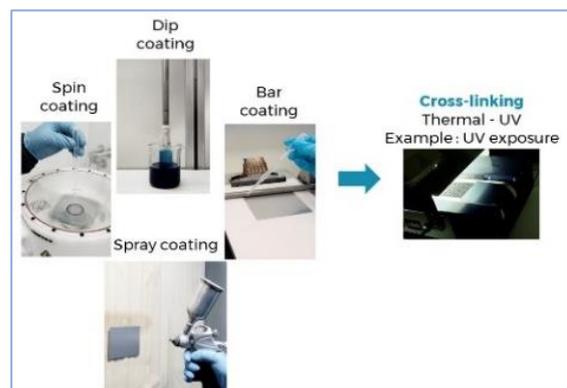
are four stages in this process: the deposition of the sol, spin up, spin off and gelation by solvent evaporation. The spin coating differs from dip coating in that the deposited film becomes thin by the centrifugal draining and tends to be uniform due to the balance between the centrifugal force and the viscous force (friction).

In the **flow coating** process, the liquid is poured over the substrate to be coated. The coating thickness depends on the angle of inclination of the substrate, the coating liquid viscosity and the solvent evaporation rate.

**Spray coating** techniques are widely used in industry for organic lacquers. The preparation of optical coatings by spray technique offers several advantages compared to the dip coating technique, since the so far realized processing speed is 10 times faster, the waste of coating sols is much smaller, coating sols with rather short pot lives can be used and the coating step is suitable for establishing an in-line process.

Finally, the **roll coating** is a process whereby liquid flows into a narrow gap between two rotating cylinders, the surfaces of which move either in the same direction (forward) or opposite directions (reverse). Some of the liquid passes through the gap and splits downstream into two films, each coating one of the rolls. This technique is extensively used in the roll-to-roll painting, photographic and tape-recording, painted metal

industries for covering a large surface area with one or several uniform layers.



**Figure 3 : Application techniques and curing of sol gel coatings.**

## Some examples and properties

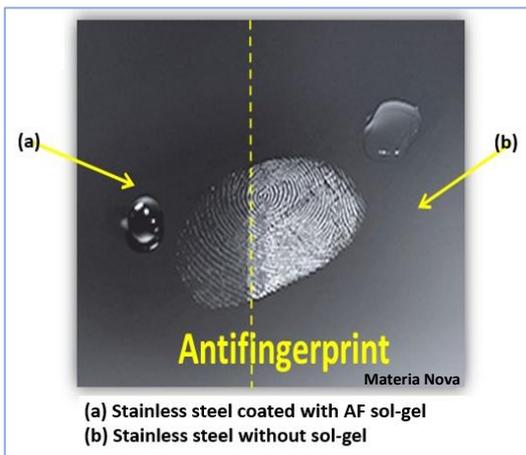
Sol-gel technology is used for different applications and sectors such as biomedical, energy, metallurgy and luxury industries. Sol-gel coatings can be used to target different properties such as aesthetic, anti-fingerprints, hydrophobic, scratch and wear resistance, anti-corrosion, and dielectric properties. Compared to classical organic varnishes, sol gel coatings are applied as thinner layers (typically maximum several microns), show higher thermal resistance and excellent adhesion on a large number of substrate materials.

The main parameters influencing the coatings properties are (i) thickness of the coatings, (ii) thermal treatments (drying and annealing) and (iii) the chemical composition of the dried gel (types of sol-gel precursors, additives, etc).

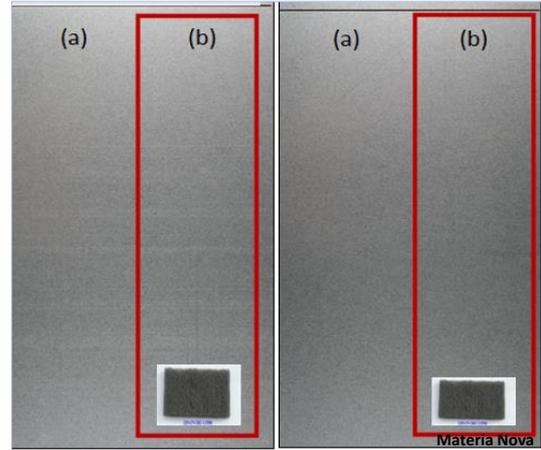
Sol-gel coatings can be tailored by adding different functional groups, organic and inorganic additives such as coloured pigments, anti-fingerprint agents, ceramic hard particles and conductive particles. The images below show some examples of sol gel coatings and their properties deposited by various application techniques on different substrates. The different properties are mentioned for each sample.



**Figure 4 :** Coloured sol-gel coatings obtained by spray coating on stainless steel. The bending test carried out after coating application and curing shows no cracks on the bended part.



**Figure 5 :** Image of anti-fingerprint sol-gel coating obtained by spray coating on stainless steel; (a) coated zone and (b) non coated zone.



**Figure 6 :** Image of anti-scratch sol-gel coating obtained by bar-coater coating on stainless steel; (a) zone without scratch and (b) zone with scratch test.

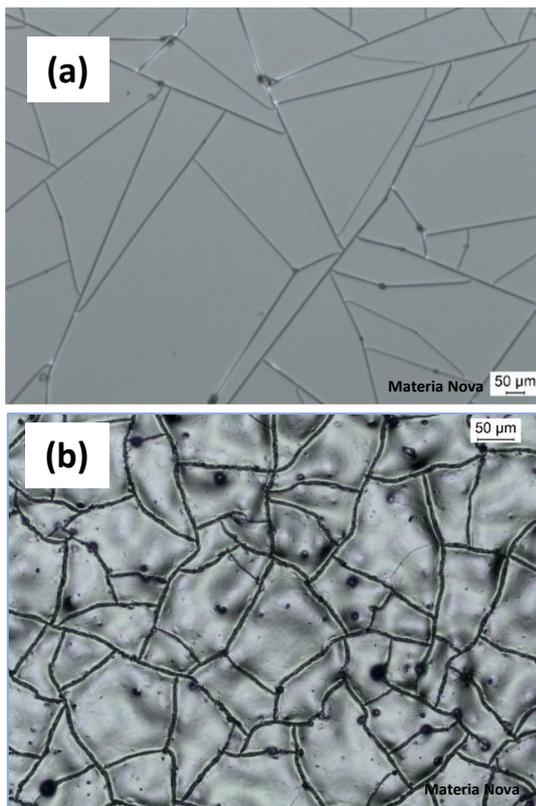
## Sol gel for electrical insulation

Thanks to their dielectrical properties, sol gel coatings can be used for electrical insulation. This property is also linked to the coating thickness. There is indeed a proportionality between breakdown potential and thickness. For example, the dielectric strength of air is 3KV/mm meaning 1 mm thick air can withstand maximum 3KV voltage. However, the ceramic nature of sol gel coatings may limit the thickness and lead to defects and cracks. However, this thickness can be increased under certain conditions as described hereunder.

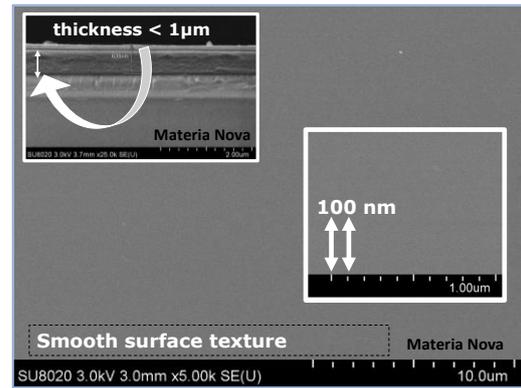
The drying and curing of the sol-gel coatings can lead to cracks on the microstructure if the thickness is not optimized. An example showing the presence of cracks for high thickness ( $\geq 3 \mu\text{m}$  dried thickness) after annealing is given in Figure 7.

To avoid cracks and defects, the thickness of the coating, the annealing, curing and chemical composition of the sol need to be controlled. Figure 8 shows an example of a smooth surface texture and crack free ceramic hard coating deposited on glass substrates with thickness coating below 1  $\mu\text{m}$ . The annealing treatment was carried out using temperature program ramp to prevent cracks and defects.

Increasing the organic fraction of the coatings or adding charges are other manners to increase the thickness.



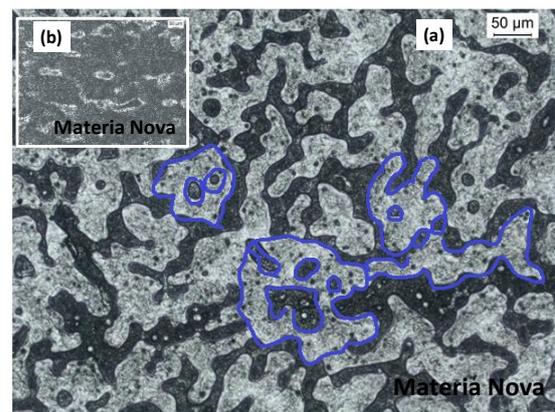
**Figure 7 :** Thick sol-gel coating obtained by bar-coater on (a) glass substrate and (b) painted stainless steel: cracks appear after curing (200°C for 10 minutes; humid thickness 200  $\mu\text{m}$ ).



**Figure 8:** SEM images of sol-gel coatings on glass substrates showing crack free and smooth surface texture. The coating is deposited by bar-coater and dried at 550°C.

The additives such as a wetting agent may also lead to improved homogeneous structures of sol-gel coatings.

An example showing the presence of Halloween monster-like structures for sol-gel coated on glass without wetting agent is presented on Figure 9. When wetting agents are added to the sol-gel formulation, the coatings lead to improved surface texture coating (image b, Figure 9).



**Figure 9<sup>o</sup>:** sol-gel coatings images obtained on glass substrates from silica based solution of (a) Halloween monster-like structures without addition of a wetting agent and (b) with addition of a wetting agent (improvement of the wettability).

## Sol gel in HI-ECOWIRE

Ceramic-like sol gel coatings will be developed in HI-ECOWIRE to promote adhesion of an extruded polymer coating applied on copper wire for electrical insulation at high temperature. The sol gel thin layer will have to guarantee a perfect bonding between the metallic substrate and the polymeric layer while contributing to the electrical

insulation properties of the whole layer system. The new magnet wire will find applications in motor applications for aeronautic, automotive and wind turbine fields. This project will thus lead to innovative application opportunities of the sol gel coating technology.

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## Interested in knowing more on the HI-ECOWIRE project?

**Website:** [www.nweurope.eu/hi-ecowire](http://www.nweurope.eu/hi-ecowire)

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