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Sol-Gel Nanocoatings to Functionalize Fibers and Textiles: A Critical Perspective

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Two decades after their commercial introduction, environmentally friendly and easily applied silica-based sol-gel nanocoatings are used by selected textile companies to produce high performance textile fabrics endowed with new functional properties. Reports on their industrial utilization, however, are conflicting. Collecting updated information from leading industry's practitioners, this study identifies the main technical and economic reasons that will drive widespread application of hybrid sol-gel coatings in the textile industry.

1. Introduction

Textile fibers and fabrics can be easily functionalized with silica nanosols.[1] Several reviews and book chapters have been published on the functionalisation of textiles with silica[1] and organically modified silica[2] nanosols. In general, organic or metal dopant species are often added to the nanosol to further endow the sol-gel glassy coating with new functionalities such as antibacterial, oil-repellent and flame-retardant properties.[3] For example antimicrobial ceramified textiles are generally based on sol-gel entrapped silver nanoparticles.[4]

Pioneered since the late 1990s by several teams, especially based in Germany, the technology for textile fibers functionalization with silica-based sol-gel coatings was first comprehensively described in a seminal book published in 2008.[5]

Though the authors emphasized how "due to the manifold different types of modification of textile materials gained by nanosol finishing, there is a tremendously high number of potential applications",[5] the "Applications" chapter concluding the latter book did not include any coating already commercialized.

Two years later, scholars in Slovenia underlined how the utilization sol-gel process to functionalize textiles "is of great commercial importance in the production of woven fabric, knitwear and unwoven textiles for protective work clothing, textiles for sport and recreation, textiles for the home and the public sector, medical textiles, sanitary materials and technical textiles".[6]

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Similarly, in a review devoted to sol-gel coatings for fabric finishing published in 2016 in the journal of the International Sol-Gel Society one could read that "sol-gel technology has become one of the most important innovative finishing technologies in the fabric industries to impart the demanded functional properties and to cope with the need for revolutionary fabrics to face the great challenges in the global market without adversely affecting the environment".[7]

However, the authors of a recent (2018) review on progress in textile surface modification underlined that "sol-gel coating have not yet been industrialized, therefore, further effort is needed to prepare and introduce these technologies into large scale production".[8]

In general, scientific publications dealing with sol-gel functionalized textiles either report specific advances concerning certain coatings and specific fabrics, or review recent advances.

Aimed at both researchers and industry practitioners engaged with textile functionalization technology, this study addresses this controversy in the literature and offers a forward looking perspective based on selected key technical and economic aspects.

2. Silica-based nanosols and textiles

In 1951, a chemical company in Japan (Nissan Chemical) started production of colloidal silica for the treatment of textiles. Tradenamed *Snowtex*, the silica nanosol was quickly adopted by other industries such as paper, steel and refractory.[9] It was known since 1948 that deposited as a micrometric, flexible layer on fabrics fibers, silica enhances the tensile strength of yarns formed from such fibers.[10]

Decades later, silicon alkoxides chiefly produced for manufacturing sol-gel coating became available at affordable cost and on industrial scale. Hence, for example, Nissan Chemical launched the hybrid (inorganic-organic) version of colloidal silica.[9] Dubbed "Organosilicasol" the hybrid coating expands the coating possibilities of customers in several industrial segments.

We briefly remind that hybrid organosilica coatings are obtained under very mild conditions in liquid phase via the hydrolytic polycondensation of silicon alkoxides of general formula Si(OR)4 or R'nSi(OR)4-n affording an ORMOSIL (organically modified silicate).[11]

In 1999, Böttcher and co-workers reported the preparation and thermal-releasing behavior of silica sol-gel glasses functionalized with high loads of organic liquids.[12] Provided that the boiling points of the hydrophobic oil (the organic liquid) and the solvent (ethanol in most cases) differ sufficiently, and that the sol has a low water content, widely different organic liquids can be easily be incorporated in sol-gel silica by adding the hydrophobic oil to the completely hydrolyzed silica nanosol. Eventually, upon mild drying a silica xerogel with an entrapped liquid content up to 50 wt% (and typically between 15% and 32%) is obtained.[12]

The team extensively pioneered the application of the continuous coating of textile fibres, paper and medical products clearly establishing that textiles with water, oil and soil repellency and with antimicrobial properties could now be easily produced.[1]

The rapid and effective deposition of the nanosol coating (finishing) typically comprised of a liquid dispersion of oligomeric silica or organosilica nanoparticles smaller than 50–60 nm (often containing dissolved organic or metal species) over the textiles is usually made via dip coating or via 2-roll or 3-roll foulards commonly used by the textile industry for dyeing, impregnation, and squeezing.[5]

In other words, the use of silica-based waterborne liquid nanosols makes them immediately applicable onto widely different fibres and fabrics using existing finishing application techniques such as foulard, dip coating or spray methods already present in textile manufacturing plants. In this way, the sol-gel technology with its silica-based nanosol deposition, drying and curing steps acts as a "drop-in" solution, which requires minimal or no capital expenditure for new deposition systems.

The nanosol can be used to functionalize both natural and synthetic fibers. Usually stabilized against thermodynamically favored aggregation by the addition of alcohol or other co-solvents such as diethylene glycol, it is easily deposited on fabrics forming a lyogel (from the Greek "lyo" for solvent) which dries at relatively low temperature to form a porous, thin (micrometric) homogeneous and dense xerogel film comprised of polymeric organosilica tightly bound to the substrate.[11,5]

Sol-gel nanosols, furthermore, are amid the few textile nanotechnology treatments that, besides to fabrics, can be easily applied to fibres by simply running the fibre yarn through a coating bath, followed by quick drying and curing at relatively low temperature.

3. Selected commercial coatings

In the early 2000s, shortly afterwards the papers from Böttcher and co-workers, a company based in Germany (CHT R. Beitlich) launched a colloidal dispersion of silver chloride particles (iSys

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AG) in a partly hydrolyzed sol-gel silane binder (iSys MSX) to produce antibacterial textiles (Figure 1).[13]

Available as concentrated (30 wt%) nanosol dispersed in diethylene glycol, the latter binder prior to use is diluted with water affording an aqueous finishing low in volatile organic compounds (VOCs).[14] A fabric functionalized with iSys AG + iSys MSX could be certified to retain its antibacterial activity for 50 washing cycles at 60 °C as early as 2006.[15]

The SEM images of modal fibers (high breaking strength regenerated cellulose fibers produced by using viscose rayon) optimally treated with 1 wt% iSys AG and 1 wt% iSys MSX followed by curing for 20 min at 120 °C, clearly show formation of a thin and homogeneous coating with porous morphology formed on the surface of fibers.[16]

Leaching of silver occurs at each washing cycle but as long as the silver content on fibres remains above 60 ppm, the fibers retain excellent antimicrobial activity.[16]

In the subsequent years, a number of new silica and hybrid silica-based nanosol coatings have been successfully commercialized. Examples include fluoroalkylfunctional waterborne oligosiloxane "Dynasylan F 8815" (Evonik, Germany) for the functionalization of natural fibers like cotton into water- and oil-repellent, easy-to-clean textiles;[17] and the waterborne sol-gel formulation "NewPro Nano Textile 4 NC" (NewPro, Germany) forming an invisible and hydrophobic/oleophobic coating on widely different fabrics which are thereby protected from water, dirt, oil and widely different staining substances.[31] Industrially applied using a standard high-volume, low-pressure (HVLP) spray system on both clothing articles and home textiles (upholstered furniture, curtains, mattresses, carpets, and so on), the organosilica coating requires 24 h hardening at room temperature, after which a stable easy-clean effect is imparted to the functionalized fabrics.[18]

Three key advantages over other functional coatings used in the textile industry are emphasized by the company: *i*) longevity equal to the lifetime of the coated fabric due to high stability against of the coating to UV photons present in solar irradiation, *ii*) resistance to abrasion due to the chemical bonding of silanes with the fibers, and *iii*) high chemical stability to washing agents present in washing formulations.

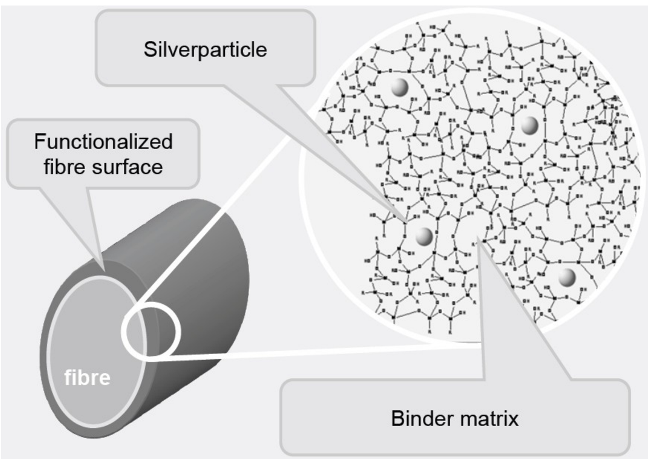

Figure 1. Fibre functionalized with a silver-baed antibacterial finish incorporating a binder to enhance binding and make the fibres washable. [Reproduced from Ref.14, with kind permission of CHT R. Beitlich].

Another waterborne silica-based sol-gel coating commercially available is "Nano4-Textile" (Nano4Life Europe, Greece). Similarly, the product is a water-based nanosol product easily applied to virtually all commercial textile fibers requiring 24 h curing to form a micrometric thin layer of organosilica providing fabrics with "invisible protection" against water, dirt and stains. In case of accidental formation of wet stain due for example to contact of protected clothes with wine or coffee, it is enough to dab the temporary stain with an absorbent cleaning cloth and the fabric goes back to its original state.[19]

The company emphasizes two major aspects of organosilica-based sol-gel technology: namely the breathability of the coated textile, and complete safety for skin contact. Accordingly, the company's product is certified according to the demanding Oeko-Tex 100 standard,[20] that indicates that the product is applicable to textile products used also for producing baby clothes.

Rather than presenting a comprehensive list of sol-gel textile coating formulations and their manufacturers which would rapidly become obsolete, we emphasize how next to large specialty chemical companies several small and medium enterprises emerged in the course of the last decade which manufacture an increasing number of said coatings targeting the huge textile industry.

This, we argument in the following section, has been made possible by powerful trends concerning the silane industry which are eventually making possible the development of the sol-gel product industry.

4. Technical and economic aspects

Writing in 2007 on textiles functionalized with sol-gel coatings in the specialized journal of the sol-gel materials, Böttcher underlined how, when compared to the application of an ointment, the use of sol-gel coated textiles offered "a more continuous and prolonged release of the embedded bioactive liquids"[21] being also "more convenient".[21]

Professor Böttcher's team in Dresden worked for many years with textile companies trying to transfer the sol-gel technology. Asked to comment for the present study, his insight sheds new light on a issue so far widely unkown also amid researchers in sol-gel materials science and technology:

«We have been working together with many textile companies and textile institutes for almost 20 years. In this time functional sol-gel coatings were developed, which meet all the requirements of users, but were still not produced.

«Why?

«All coatings based on TEOS and alkoxysilanes contain, due to the preparation, alcohol. There is no textile company in Germany that has (i) explosion-proof coating equipments and (ii) a plant for burning the solvent.

«If the alcohol is removed (distilled, blown out) from the coating solution, the coating solution becomes unstable and gels quickly.

«If commercial aqueous SiO_2 products are used, they are difficult to functionalize, often do not form smooth transparent layers and adhere poorly. We have carried out long and intensive work to solve the problem of adhesion and wash resistance of aqueous nanosols on textiles employed and found that polymeric adhesion promoters with reactive terminal epoxy groups solve the issue.»[22]

Accordingly, the authors of a recent market intelligence report note that the $ 2.26 billion rapidly growing global market for sol-gel coatings in 2018 comprised *i*) automotive glass, *ii*) healthcare, *iii*) marine, *iv*) construction, *v*) mobile device screens, and *vi*) solar panels.[23] The textile industry was mentioned as a niche target market for sol-gel coatings, with the same reputed market intelligence company underlining how "the high cost associated with the precursors used for manufacturing sol-gel coatings is likely to affect market growth".[23]

Replacing flammable ethanol in the nanosol precursor with water so as to obtain a waterborne formulation today can be easily done, such as in the case of the aforementioned waterborne coatings "Nano4-Textile" or "NewPro Nano Textile 4 NC".

Cost reduction of the silanes precursors of the xerogel coating is the key requirement that, once met, will drive the widespread uptake of sol-gel nanocoatings in the textile industry. Produced via the hydrolytic polycondensation of Si alkoxides, the manufacturing cost of said coatings chiefly depends on the cost of the latter silicon alkoxides.

The launch of several silica-based products since the mid 2010s has also been due to the end of an old industrial oligopoly for which the price of TEOS (tetraethylorthosilicate) has now significantly decreased from over $20/kg of 1990.[24] Today, not only TEOS production mostly takes place in China but the market has become "highly fragmented",[25] with multiple manufacturers competing to supply customers of a diversified market.

A further significant reduction in the price of TEOS is likely to originate from its new synthesis from different natural sources of SiO_2 as reported by Japanese scholars in 2017.[26] Rather than starting from much more expensive (and toxic) $SiCl_4$, the new synthesis of TEOS starts directly from silica obtained from virtually unlimited and inexpensive rice hull ash (a by-product of rice production) and ethanol at 260 °C in the presence of 3 Å molecular sieves as dehydrating agents and 10 mol% KOH as base catalyst (Eq.1):

$$SiO_2 + 4EtOH \rightleftharpoons Si(OEt)_4 + 2H_2O \tag{1}$$

TEOS is obtained in 70% yield whereas, further lowering the process cost, a simple treatment under vacuum at 300 °C of used molecular sieves makes them available for reuse in a subsequent synthetic run.[26]

Similarly, organosilicon compounds such as organotrialkoxysilane needed to produce the ORMOSIL coatings, can now be produced in a reactive distillation continuous process in which the organoalkylsilane obtained by the esterification of the organochlorosilane with an alcohol is withdrawn as a bottom product and volatile HCl co-product of the reaction is withdrawn from the top of the column.[27]

5. Conclusions

Environmentally friendly sol-gel silica coatings to functionalize textiles will soon no longer be limited to selected textile companies producing technical textiles for high-end applications.

In other words, sol-gel finishings will become routinely used by the textile industry to produce a variety of regular clothing products functionalized with durable, safe and high-performance functional coatings.

Said increasing uptake will be driven by recently achieved economic viability of these coatings. A first significant cost reduction occurred thanks to expanded production of TEOS. Another may follow by adopting the new synthetic route to TEOS starting from low cost natural sources of SiO_2 such as that developed in 2017.[26]

As a result, for instance, in place of expensive fluorinated compounds, textile companies will be able to use low cost ORMOSIL coatings such as a TEOS-based nanosol modified with *n*-octyltriethoxysilane to functionalize cotton fibers enhancing hydrophobicity and washing efficiency.[28]

Reduction of the environmental impact of the textile industry, indeed, also requires to reduce resource consumption, including the amount of water, detergents and heat required to properly wash garments and fabrics.[29]

Textiles functionalized with silica-based sol-gel coatings are part of the larger set of textiles that utilize nanotechnology during their fabrication process. The latter $5.1 billion market (in 2019) is expected to triple to $14.8 billion by 2024, at a compound annual growth rate of 23.6% for the period of 2019–2024.[30]

Amid nanochemistry-based technologies, non toxic silica-based waterborne nanosols used to produce thin and durable ORMOSIL coatings share uniquely excellent health and safety profile for which, for example, they have a number of biomedical applications.[31]

In view of the necessity to develop personal protective clothing to prevent community spread of hazardous infections (like COVID-19, for example) antimicrobial textiles and fabrics realised through functionalized sol-gel coatings assume enhanced global relevance.

As the uptake of sol-gel textile coatings increases, a number of new sol-gel coatings will likely emerge including, for example, the SilverSil antimicrobial xerogel embedding Ag nanoparticles (and not silver salt microparticles) in an ORMOSIL releasing few ppm only of Ag during each washing cycle.[32]

Several other formulations are possible and will be shortly developed, including those including essential oils pioneered by Böttcher and co-workers in the early 2000s.[21,12,1] Technical advances in the formulation of waterborne silica-based nanosols and dramatically lowered production costs suggest that eventually sol-gel functionalized textiles will become ubiquitous. Clarifying a number of issues, including controversy in the literature concerning the real application of said coatings, this study will hopefully accelerate said progress.

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Conflict of Interest

The authors declare no conflict of interest.

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