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Review

# Consolidation and coating treatments for glass in the cultural heritage field: A review

Stefano Centenaro[a,b], Giulia Franceschin[a,*], Elti Cattaruzza[b], Arianna Traviglia[a]

[a] Center for Cultural Heritage Technologies (CCHT), Istituto Italiano di Tecnologia (IIT), Epsilon building, via Torino 155, 30170 Venezia-Mestre, Italy
[b] Dipartimento di Scienze Molecolari e Nanosistemi (DSMN), Università Ca' Foscari Venezia, Eta Building, via Torino 155, 30170 Venezia-Mestre, Italy

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ABSTRACT

Consolidation and coating treatments are two types of interventions that form part of the active conservation actions developed for historical and archaeological glass over the years. While thermoplastic and thermosetting resins are widely adopted by conservators worldwide, issues related to the toxicity and the material compatibility of these products remains unsolved. To address these issues, efforts have been made to develop new formulations that can functionally replace or exhibit performance advantages with respect to these canonical polymeric materials. In this review, we discuss the main classes of materials applied thus far for protection and consolidation aims in the cultural heritage glass field, starting from the beginning of the 19th century and continuing until present days. We also assess the potential of hybrid organic-inorganic materials and full inorganic materials as alternative solutions to the limitations of organic materials in application. Finally, we provide our perspectives on future directions for the development of consolidation products that meet the specific requirements of the cultural heritage field.

## Introduction

Archaeological and historical glass artefacts are often exposed to various risks that can negatively impact their stability and integrity. Dulling [1], iridescence [2], opalescence [3], pitting [4–7], crizzling [8–10], cracking of the surface [11,12], discoloration and a total loss of glassy nature [13] are the main phenomena that affect those glass artefacts as a result of degradation processes (some examples are reported in Fig. 1). Their occurrence depends on the location of the object and the environmental conditions that surround and interact with it [14,15].

Two different approaches are adopted by conservators to address glass degradation phenomena: preventive actions and remedial interventions [16]. Over the past few decades, the emphasis of conservation efforts has consistently moved from remedial interventions, which are directly applied to the object, to the adoption of preventive conservation strategies, which minimize and prevent future deterioration or loss without interfering in the physical structure of the object [17]. Nowadays, different conservation associations place great emphasis on preventive conservation in their code of ethics and guidelines for practice, stating that it should be a primary objective of the conservation professional that must be considered prior to direct intervention [18–21].

In general, preventive interventions concern the monitoring and control of environmental parameters such as humidity, temperature, air movement, mechanical and thermal shocks, vibrations, lighting and gaseous pollutants [22–24]. However, not all museums have the financial and human resources available to manage all these tasks. Objects for display may be kept in airtight metal cabinets located in air-conditioned spaces, as well as in wooden showcases where volatile organic compounds (VOCs) like acetic acid, formic acid and aldehydes contribute to glass alteration. Even worse, glass artefacts located or held outdoors are exposed to harsh atmospheric agents including rain, UV radiation, and acidifying gases. For this reason, it is also important to rely on innovative active conservation practices with the lowest possible interference on the original artefact, as a complementary strategy for glass conservation.

Since the first attempts in the 19th century, consistent efforts have been made to design appropriate consolidation and coatings treatments to preserve the integrity of cultural heritage items. The aim of consolidation treatments on glass artefacts is to strengthen

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[*] Corresponding author.
*E-mail address:* giulia.franceschin@iit.it (G. Franceschin).

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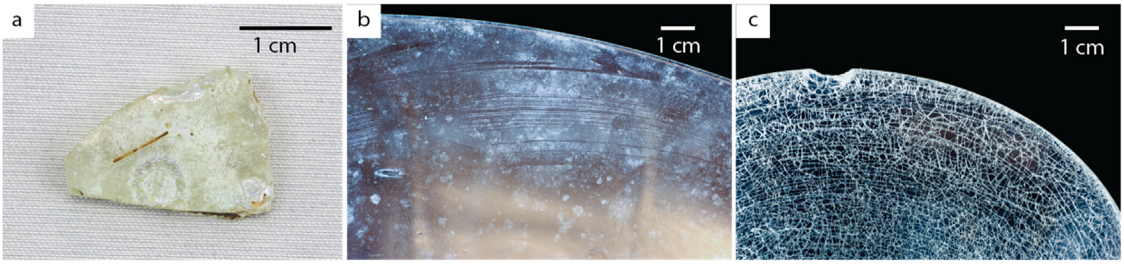

**Fig. 1.** From left to right, examples of iridescence, dulling and crizzling on ancient glass. (a) Fragment of Roman glass retrieved during field walking surveys on the archaeological site of Aquileia, inventory n. 581558, Museo di Aquileia; (b) bell-shaped cup (calyx), Venetian manufacture, end 16th – beg.17th Century, achromatic and fumé blown glass, inventory n. 57, from the Physics Laboratory of the University of Modena –1889, Museo Civico di Modena; (c) glass cup, Venetian manufacture, 18th Century, achromatic glass, inventory n. 70, donated by Luigi Alberto Gandini, Museo Civico di Modena.

and stabilise the glass surface by introducing a small amount of consolidant with a brush or a pipette, allowing it to be drawn in by capillary action [25]. Therefore, the concentration of the resin and the choice of the solvent are fundamental aspects to achieve good penetration into the surface cracks and between flaking layers. If the resin concentration is too low, unfilled spaces may result, whereas if the concentration is too high and the solvent is volatile, resin penetration may be reduced [26]. In the case of coatings, instead, the objective is to protect the artefact from deterioration by applying a surface treatment that shields the artefact from external agents [27]. The materials, as well as the techniques applied, should conform to acknowledged and shared conservation principles, like preservation of the aesthetic and historical aspect of the object, compatibility with the artefact characteristics, ease of application at room temperature, reversibility, non-toxicity, [28,29].

There has been for years an ongoing debate related to the ethics of conservation, especially on the principle of treatment reversibility [30]. This term first appeared in 1968 [31], in response to years of inappropriate interventions that caused significant and permanent harm to numerous valuable artifacts, both in terms of their structural integrity and aesthetic appeal. The conservation community used to agree that all conservation/restoration procedures should be fully reversible, which means that it should always be possible to bring the artefact back to state it was before the treatment, even after several years [32]. However, there is no such thing as a reversible coating or consolidant because no matter how resoluble a material may be, removing it does not return an object to its previous state [33]. For example, the consolidation of flaking layers in glass implies the penetration of the treatment between the layers (and between the layer and the glass object) and its hardening to hold the structure together. In this situation, the removal of the consolidant will inevitably affect the inner structure of the artefact, no matter which material is used. Today, conservators from various disciplines suggest that reversibility is a concept that cannot practically be implemented. Instead, other terms have been introduced with the hope to define a “good” conservation, such as removability or retreatability [34].

This review represents a deep critical analysis of the advances made in the time frame that spans from the first materials and treatments used for consolidation and coating of archaeological and historical glass artefacts –dating back to the 19th century– to the most up-to-date and newly proposed strategies established. Knowing the key milestones in the development of materials and treatments for consolidation and coating is crucial to defining future technological strategies in the field. The aim of this work is to establish the state-of-the-art in terms of materials used and techniques applied and to outline the most promising trends to go beyond the present limits.

In the following paragraphs, the most frequently used coatings and consolidants are presented in chronological order, and their advantages and limitations are discussed. The review is structured accordingly to material type, beginning with organic materials, both natural and synthetic, which were applied from the beginning of the 19th century. It then moves on to inorganic and hybrid organic-inorganic sol-gel treatments, which were introduced at the turn of the 20th century for conservation purpose. Finally, the latest research outcomes in protective coating research are discussed, including the application of zinc salts and the use of atmospheric pressure plasma jet as an alternative deposition system. By providing a historical overview of conservation treatments and highlighting the latest research, this review offers a valuable resource for researchers and practitioners in the field.

## Natural organic materials

Prior to the development of synthetic polymers, natural organic materials were used for archaeological and historical glass consolidation and coating treatments. Among the natural resins utilised, animal glue and shellac were the most frequently employed [35]. Animal glue is essentially the hydrolytic product of collagen, the main protein in animal skins and bones [36]. The viscosity, strength, and overall mechanical behaviour of the glue vary depending on the source of the collagen as well as the extraction and preparation procedures [37]. A variety of different animal glues are available on the market, such as hide and bone glues, fish glues, isinglass, and gelatine. Before choosing animal glue for conservation purposes, it is crucial to have a comprehensive understanding of their individual properties. However, in the past, conservators relied primarily on their empirical experience, rather than scientific knowledge on the material to determine which animal glue to use. One drawback of animal glues for glass conservation is that they tend to shrink upon drying, resulting in high internal stress and tensile forces within the glue matrix [38]. This can lead to significant damage to the substrate. Additionally, animal glue is a nutrient source for many fungi and bacteria [39], which can promote bio-deterioration processes on the glass surface, thus compromising even more the conservation status of the artefact and altering its original visual appearance.

Shellac is an animal resin secreted by an insect (Fig. 2) commonly found in India and Southeast Asia. It consists of a mixture of mono- and polyesters coming from hydroxy aliphatic acids (mostly aleuritic acid) and various cyclic sesquiterpene acids [40]. The chemical composition of shellac, which affects the material’s mechanical and thermal properties, often varies depending on the species of the insects, the host tree and the environmental conditions [41,42]. The yellowish or brownish colour of natural shellac extracts can limit their use in some applications [43], such as glass consolidation. Consequently, a bleaching step is necessary to remove the colour using decolorising agents, which may have a negative impact on the final properties [44]. The main reason why

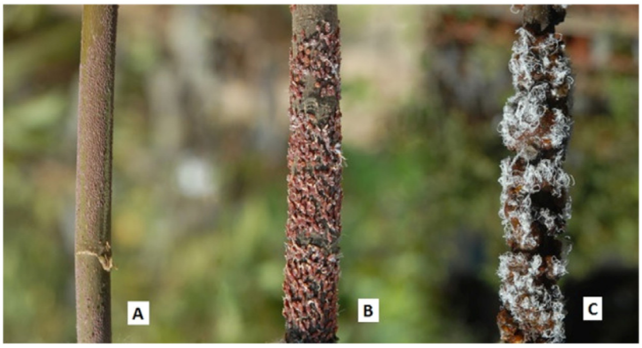

**Fig. 2.** Lac insects growing on a host plant (reprinted from ref. [43], Copyright (2022), with permission from Elsevier).

shellac has been condemned in glass conservation is due to its tendency to become increasingly brittle with age, resulting in stress on the object [45]. Furthermore, it becomes insoluble to alcohol solvents, requiring the use of toxic amines such as pyridine for its removal [46,47].

In the past, animal glue and shellac were utilised for the consolidation of glass due to the lack of alternative solutions. However, their poor physicochemical and mechanical properties, as well as their tendency to detach from the substrate after short periods of time, limited their success. Nowadays, shellac and animal glue are not recommended for any conservation purpose involving glass artefacts: these materials are aesthetically and mechanically incompatible with the underlying glass, which can result in the detachment of surfaces features, in the best-case scenario; to structural failure of the whole glass object, in the worst.

## Synthetic organic materials

Thanks to the advancements in polymer chemistry, more suitable synthetic materials became available for conservation purposes starting from the mid-century. These new products were inspired by the properties of natural organic materials, and achieved improved performances in terms of durability, physicochemical stability, and mechanical properties. Several types of materials belong to this category, including those described below in the following subsections.

### *Cellulose derivatives*

The polynitrate ester of cellulose, or cellulose nitrate, is a semisynthetic polymer from the most abundant natural polysaccharide. It has been utilised as a conservation material since its discovery in the late 19th century (1833) [48], although it is inherently hard and brittle. Therefore, the incorporation of a plasticiser is essential to make it a workable coating material. The type and quantity of these plasticisers significantly affect the mechanical and chemical properties of the resulting material. The earliest commercially available formulation of cellulose derivative consisted of two parts cellulose nitrate to one part camphor. However, camphor was later replaced by triphenyl and tricresyl phosphates and, in the early 1920s, phthalates such as dibutyl phthalate became the primary choice for plasticisers [49].

Cellulose nitrate was one of the first coatings proposed to counter the phenomenon of glass instability, commonly known as crizzling or “glass disease” (Fig.1c) [50]. Compared to previously popular animal glues, cellulose nitrate offered some advantages such as water resistance and resistance to bacteria, insects, and fungi. However, cellulose nitrate is an unstable material that poses threats to museum collections [51]. It is highly susceptible to photochemical degradation, which leads to discoloration (Fig. 3), embrittlement of the material and cracking which, in turn, can lead to the material collapse [52]. Additionally, cellulose nitrate degradation produces nitrogen oxides ($NO_X$) and related products such as nitric acid, highly oxidizing and corrosive. These products act as catalyst for the cellulose nitrate decomposition reaction, resulting in a autocatalytic process [53,54]. As a result, the use of this material is strongly discouraged not only for the risks associated with the integrity and visual appearance of the object, but also due to the hazards posed to human health from the product’s toxicity.

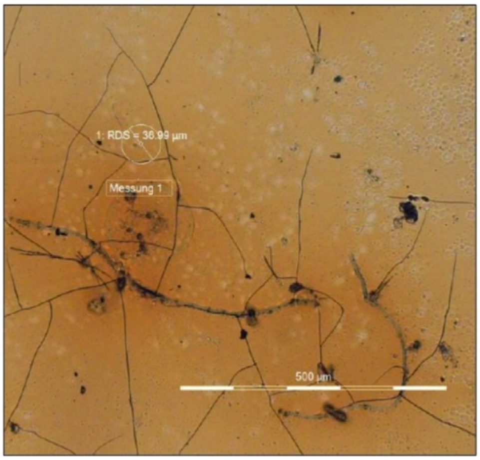

**Fig. 3.** A yellowed cellulose nitrate sample artificially aged observed under an optical microscope (Fig. 4© Elena Gómez-Sánchez et al., CC BY 4.0).

### *Soluble nylon*

Soluble nylon is a chemically modified form of nylon that is created by reacting nylon with formaldehyde and an alcohol or mercaptan in the presence of an acid to substitute alkoxymethyl groups on the nitrogen atom [55]. In 1970, Dowman reported using soluble nylon as a consolidant for flaking glass surfaces [56]. In 1985 and 1986, soluble nylon was used to consolidate the colour layer of 15 paintings on glass [57] during an important conservation and restoration campaign of glass plates of the Goriski and Tolminski Museums (Slovenia).

Soluble nylon was favourably for conservation use because it had the desirable properties such as flexibility, a clear matt appearance, no undue contractile forces, good adhesive properties and [58]. However, there was a lack of extensive ageing tests and background information on the material stability over time [59]. Hydrolysis, with or without crosslinking, is the main cause of soluble nylon’s chemical evolution and adverse effects [60]. This reaction reverses the formation of the modified nylons, resulting in a return to the original unmodified nylon with all its properties, such as insolubility. Unsubstituted nylon is soluble only in corrosive solvents such as m-cresol, phenol, formic acid or concentrated mineral acids, none of which is suitable to conservation. In extreme cases, even these solvents can be ineffective [61], which is concerning in terms of reversibility and environmental sustainability of the treatment. Additionally, degradation phenomena like embrittlement, yellowing, and adhesion failure of the consolidation coating were observed [62], all of which pose a risk to the object aesthetics and stability which can result in irreversible structural damage of the treated artefact. As a result, the use of soluble nylon in conservation is no longer justified or recommended.

### *Vinyl resins*

Polyvinyl acetate (PVAc) is a popular vinyl resin that is commonly used for the consolidation and coating of degraded glass [35]. It is a thermoplastic material that is produced by the polymerisation of vinyl acetate, discovered in Germany by Dr. Fritz Klatte in 1912 [63]. The process of polymerisation used to create PVAc can be adjusted to produce a range of products with different molecular weights. This results in a variety of materials that exhibit different properties, such as viscosity, hardness, melting point, tensile strength, and glass transition temperature ($T_g$, rising as molecular weight increases) [64]. PVAc can be obtained in solid form, such as pellets or beads, or as a dispersion [65]. The nature of the solvent chosen when using PVAc in solid form is crucial as it can affect the mechanical and chemical properties of the material and its behaviour upon ageing [66]. When using PVAc as a dispersion, additives, such as co-monomers, plasticisers, protective colloids, colorants, fillers, and stabilisers, may influence the film degradation by promoting different reactions with the surrounding environment. [67]

PVAc were has been used for consolidation and coating on archaeological and historical glass; for instance, a PVAc emulsion was used to consolidate iridescent layers of broken artefacts recovered from the archaeological site of Sardis (Turkey), [68] while a 5% solution of PVAc (solid) in acetone was used to coat a Roman glass inlaid bronze from Uley, Gloucestershire [69]. In Down's comprehensive study on polyacrylates and polyvinyl acetates from the 1980s, the performance of 27 different PVAc products collected from conservation suppliers and manufacturers was investigated in terms of their response to dark ageing and light ageing. The study examined various factors such as acidity or alkalinity of the material, potential harmful volatile emissions, flexibility and strength of the film and colour change (yellowing) [65,70–74]. The authors noted that most of the pH measurements on the dry film extracts were acidic, and that light ageing tended to increase the acidity of the adhesives more than dark ageing. This is significant as the acidity of coatings and consolidants contribute to the degradation of glass. Additionally, dried films of PVACs released volatile acetic acid in the first three months of ageing and light exposure caused a greater increase in acetic acid emission than dark ageing. These volatile emissions may pose a threat to the treated object, particularly when placed in an enclosed space.

In terms of mechanical properties, PVAc showed strong cohesive strength and stiffness even after ageing, while PVAc with additives exhibited lower cohesive strength but higher flexibility, which, however, was lost after ageing. Generally, rigid substrates such as glass, benefit from the application of flexible coatings or consolidants because they can relax residual stresses upon drying. A PVAc resin without additives inherently has incompatible mechanical properties with the underlying glass, and even with the additives, the same issue may arise since flexibility is not retained over time. Finally, PVAc products showed poor yellowing resistance properties, especially when exposed to light ageing tests. This long-term behaviour poses significant limitations on the integrity of the treated object, requiring conservators to treat the artefact a second time to regain the original visual and optical aspect of the glass object.

### *Epoxy resins*

Epoxy resins are thermosetting resin systems composed of two parts: one containing the epoxide group and the other serving as the hardener that cross-links the molecules by reacting with the epoxide [75]. By changing one or both the components, a wide range of polymers can be produced. The addition of accelerators, diluents, plasticisers, and other additives adds further complexity to the basic formulation [76]. Epoxy resins commonly used in conservation are based on the aromatic diglycidyl ether of Bisphenol A (DGEBA), with the notable exception of Hxtal NYL-1, a cycloaliphatic epoxy resin specifically designed for restoration and conservation [77–79]. While the former suffers from poor weatherability due to the aromatic ether segment of the backbone, the latter are more resistant to yellowing owing to their aliphatic structure [80]. However, aliphatic epoxies require a longer curing time (approximately 1–2 weeks) and are more expensive [81].

Epoxy resins are primarily used as adhesives and gap-filler. They have also been used for the consolidation of deteriorating paint on glass, like in the interior face windows of the Church of St Ann and the Holy Trinity in Brooklyn (New York) [82], and for the consolidation of archaeological glass on site [83]. More recently, three different epoxy formulations were evaluated for their efficacy in consolidating cracks and fissures in *dalle de verre* windows, but the results were quite unsatisfactory due to poor penetration properties [84]. Epoxy resins were valued for their good refractive index properties, which can match those of lead glass and medieval stained glass [85]; they have low shrinkage on curing and they bond firmly to glass thanks to their polar nature [86]. However, epoxies can fail when exposed to moisture, as in the case of stained glass exposed externally, and often exert enough force upon shrinkage to damage the artefact's surface by removing glass flakes [27]. Another disadvantage is that these polymers are thermosetting, which means that they crosslink during the curing process, forming irreversible chemical bonds. Consequently, they are difficult to remove if necessary as they tend to swell when exposed to solvents. Dimethylformamide, tetrahydrofuran, chloroform and methylene chloride were generally more effective in removing epoxies than alcohols and ketones [87]. However, these solvents pose environmental hazards, and their use should be limited as much as possible.

Down investigated the behaviour of several commercially available epoxy resin products under natural dark ageing and high intensity light ageing [88,89]. In terms of intense light ageing tests, although some formulations like Hxtal-NYL 1 are more resistant to UV radiation, yellowing phenomena are usually a marked undesired problem. When epoxies were aged in the dark at room temperature, Down found that the majority of products had an unacceptable level of stability, according to the standards of evaluation proposed by Feller [90]. All these evidences limit the use of epoxies, because exposure to direct sunlight may have extremely detrimental effects on the material. Therefore, the use of epoxy resins can be considered acceptable only in controlled museum environments where UV, humidity and temperature are carefully regulated.

### *Acrylic resins*

Acrylic resins are polymers made from two families of monomers: acrylates and methacrylates [91]. Within this class of materials, Paraloid B-72, also known as Acryloid B-72, is a copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA) that is widely used for glass conservation [92]. Paraloid B-72 is highly regarded due to its relatively high $T_g$ of 40 °C, which is higher than other organic materials like PVAc ($T_g = 28$ °C), which implies a lower tendency to cold flow [93]. Additionally, it has a refractive index (RI) of 1,49 matching the lower end (1.49–1.53) of the refractive indices of ancient glasses, unlike other materials such Polyvinyl acetate (1.46) [85], thereby maintaining the optical properties of the treated glass. Paraloid B-72 has been widely used for various conservation purposes, like the consolidation of glass artefacts affected by crizzling, as in the case of the unique glass radioactive beads adorning a shamanic apron, which is part of the British Museum collection [94]. It has also been used for consolidation treatments of ancient glass retrieved from underwater sites, like in the case of the oldest and largest known collection of glass ingots, recovered from the Uluburun shipwreck [95]. Also in the last decade, Paraloid B-72 kept a central role in the domain of glass consolidation and it has been applied both for the consolidation of flaking paint on stained glass windows [96], and for the consolidation of weathering layers on glass vessels [97].

Although Paraloid B-72 is highly valued in the conservation community [98], it shares with other organic materials used in this field some issues related to vapour permeability and photochemical stability. In the former case, vapours can penetrate the coating, depending on the concentration and solvent type, and trap salt or pollutants beneath, which may attack the glass surface over time [99]. In the latter case, Paraloid B-72 is prone to yellowing phenomena, becoming brittle, and developing an acidic pH upon light ageing [65]. The degree to which Paraloid B-72 is susceptible to these phenomena strongly depends on environmental conditions. Therefore, it is generally agreed that an indoor application, with low UV exposure and controlled humidity and temperature conditions, is far better than outdoor application where weathering agents can give cause of concern over time.

Lastly, it is important to highlight that the formulation of Paraloid B-72 has undergone compositional changes over the years. According to de Witte and coworkers [100], in the 1970s, the composition changed from an EMA/MA molar ratio of 68:32, to an EMA/MA molar ratio of 70:30. In 1996, gas chromatography-mass spectrometry (GC–MS) analysis performed on the commercial product by Chiantore et al. [101], revealed that an additional compound, butyl methacrylate (BMA), was added to the formulation making up 2% of content. These changes in the product may pose challenges for conservators since it becomes difficult to predict the behaviour of the material once applied. For instance, in 2003, the ageing behaviour of Paraloid B-72 and an EMA/MA (70:30) analogue was evaluated after 4000 h of artificial irradiation through the use of a Xenon lamp, and it was observed that the former showed a greater tendency to cross-link, probably due to the difference in composition [102].

## Inorganic sol-gel systems

Sol-gel is a well-established synthetic technique widely used for producing inorganic (glassy or ceramic) and inorganic-organic (hybrid) materials in various shapes, including nanoparticles, coatings, fibers, or monoliths [103]. amongst the different types of sol-gel systems, silicon based sol-gel ones have been extensively studied, as they were the first compounds to be developed by sol-gel chemistry [104]. In particular, the most used precursor of silica thin films is tetraethoxysilane (TEOS) [105].

### *Single-phase sol-gel systems*

In the field of cultural heritage glass, TEOS based sol-gel formulations have been tested for treating glass with different compositions. Various catalysts, like $H^+$ and $Pb^{2+}$, and densification temperatures have been investigated as well. For example, acid catalysed TEOS solutions were found to be effective for depositing protective thin films on unaltered and cleaned soda-lime glass without any heat treatment [106,107]. To simulate the deposition of sol-gel solution with a brush, which is often used for historical stained glass, successive $H^+$ catalysed sol-gel depositions (multidipping) were performed on the same soda-lime glass substrate. The resulting thick coating appeared homogeneous and its adhesion to the surface was effective even after weathering [108]. Tests were also performed on golden leaf glass mosaic replica tiles (*tesserae*) for the protection of the residual golden leaf exposed due to the detachment of the thin layer of blown glass that used to cover it

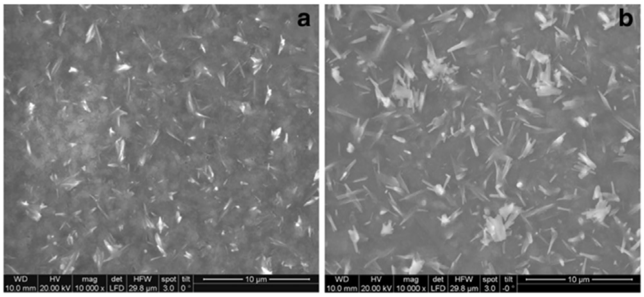

**Fig. 4.** SE image of bare glass weathered at 10 ppm $SO_2$ and 80% RH for one week (a) and four weeks (b) (Adapted from Fig. 3© Monica De Bardi et al., CC BY 4.0).

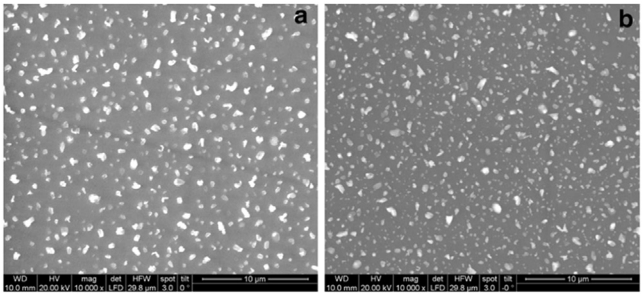

**Fig. 5.** SE image of coated glass weathered at 10 ppm $SO_2$ and 80% RH for one week (a) and four weeks (b) (Adapted from Fig. 4© Monica De Bardi et al., CC BY 4.0).

(‘*cartellina*‘). The samples were obtained under high vacuum conditions, by depositing a thin layer of gold on pristine soda-lime glass through a magnetron sputtering technique. This treatment was found to be effective only when the gold surface shows cracks, as the sol-gel coating can bond with the soda-lime glass underneath [109].

This $H^+$ catalysed formulation was also tested on tailor-made potash-lime-silica ($K_2O$–CaO-$SiO_2$) glass replicas with polished surface. The coating obtained was homogeneous and did not affect the aesthetical appearance of the underlying glass. Leaching tests in aqueous acidic solutions showed that, regardless of the exposure time, the surface remained unaltered, with no cracks and flaking-off phenomena [110]. Accelerated ageing tests were performed exposing glass samples to an atmosphere containing $SO_2$ with a high relative humidity (RH = 80%). The results showed that the protective effect of the coating is remarkable when comparing coated samples with uncoated ones (Fig. 4 and Fig. 5 respectively) [111].

In the case of lead-silicate glass, the $H^+$ catalysed TEOS solutions proved to be inapplicable due to $Pb^{2+}$ diffusion from the substrate to the coating, which caused undesirable colour change and iridescence formation [112]. As a result, $Pb^{2+}$ catalysed TEOS solutions densified at room temperature were investigated, and an optimised formulation was proven effective for the deposition of a stable and optically transparent film on unaltered and cleaned lead-silicate glass replicas. After accelerated ageing tests, performed following the ASTM G26 standard, it was observed that the coating maintained a good appearance, with no flakes or cracks [108]. A product based on this TEOS sol-gel technology has been produced and commercialised by a company founded in 2011, which focuses on designing surface treatments for Cultural Heritage and industry [113]. The company now markets two different products, namely SIOX-5 RE20C as a consolidant for grisailles and archaeological glass, and SIOX-5 RE36 as a protective coating for artistic glass. Compared to the inorganic formulations previously studied, both these products are based on silica alkoxides that are organically modified, allowing for better mechanical properties, such as elasticity of the coating, and a hydrophobic behaviour that is useful for repelling water. SIOX-5 RE20C has been applied between 2019 and 2020 in a restoration campaign of the stained glass window of right transept of Santi Giovanni e Paolo in Venice [114]. However, there are no published results on the effect of the treatment on pre-aged samples and on its performance on the long-term.

Moreover, regarding reversibility, while it has been reported that it is possible to remove the sol-gel treatment using alkaline solutions [115], typically containing sodium hydroxide [116], this method could also cause glass dissolution, presenting a significant risk to the stability and integrity of the glass artefact.

An alternative acid catalysed TEOS formulation for protection of heritage glass in the $K_2O$–CaO-$SiO_2$ system was investigated by Carmona et al. [117] The authors observed that the coating's performance improves as the densification temperature increases, depending also on the coating thickness. A three-layered coating densified up to 250 °C for 1 hour was found to be more protective than a single coating densified up to 400 °C for the same amount of time. These types of results, however, have limited applicability to ancient glass, which is characterised by a fragile nature that could be further damaged by stresses due to heat treatments at high temperatures.

Silica ($SiO_2$) thin films can be obtained using different precursors, including perhydropolysilazane (PHPS). PHPS is an inorganic polymer made up pf Si–N skeletons with Si–H groups that can be converted into silica films using various methods, such as heat treatment in water vapour, exposure to a vaporised ammonia atmosphere, ultraviolet irradiation or oxygen plasma treatment followed by high-pressure water vapour heating [118]. These films have been investigated for various applications, from gas-barrier layers against water and oxygen [119,120] to nanophosphors encapsulation for luminescent materials [121]. Silica thin films obtained from PHPS through exposure to atmospheric moisture were investigated as an alternative to those obtained from TEOS through sol-gel route for the protection of stained glass windows. Palladium and ammonia vapours were used as catalysts and a mild heat treatment (45–50 °C) was applied to facilitate the conversion of PHPS to silica in a reasonable time frame [122]. This protective treatment was performed on replicas of soda-lime glass painted with a paintbrush and on an original glass tile decorated in grisaille from a stained glass window of the Basilica di SS Giovanni e Paolo in Venice (Italy). While the results were promising and could have opened the possibility to design coatings that are homogeneous, transparent, and uncoloured, conversion of PHPS to silica can be less efficient and migration phenomena of mobile ions from the soda-lime glass to the film may show different behaviours, depending on the exposure time to ammonia vapours and on the concentration of ammonia itself. For these reasons, it was not possible to define the best coating parameters [123].

Other inorganic sol-gel treatments based on metal alkoxides, aside from silicon-based ones, were investigated within the European Commission (EC) funded CONSTGLASS project [124]. The pilot product that was developed was later improved in the framework of another EC funded project, NANOMATCH, and is now marketed by the Fraunhofer ISC with the trademark name of Cloisil-A18. Originally named A18, this consolidant is derived from an aluminium-triethanolamine complex (alumatran, $C_6H_{12}NO_3Al$), and is applied to microfissures that are less than 40 µm in size. Upon hydrolysis and condensation reactions, the complex leads to a glass-like network that fills the cracks and stabilises them [125]. However, the original product developed during the first project was moisture-sensitivite, leading to loss of adhesive strength of the formulation. During the NANOMATCH project, the adhesion performance of Cloisil-A18 was improved and optimised for very humid environments [126]. Cloisil-A18 is now a two-component system, consisting of an A-component, which is the aluminium alkoxide complex, and a B-component, which is an epoxy-functional component for accelerated and thorough curing [127].

### *Binary sol-gel systems*

In addition to sol-gel formulations that lead to pure silica coatings, other inorganic sol-gel systems have been evaluated for use in heritage conservation. One example is SZA, a Silicon-Zirconium consolidant based on alkoxides precursors that was developed by the Fraunhofer Institute for Silicate Research (ISC) and has received great attention from the expert community. The idea behind this product is to exploit the long-term stability induced by the inorganic nature of the material to overcome the poor ageing properties of organic polymers [128]. Pilot studies of this product were performed on historic stained glass windows at the Parish Church of St. Andreas (Germany) and the Canterbury cathedral (United Kingdom) since 1990 [129,130]. It was also tested for the consolidation of glass with artificially corroded paint layers. The results showed that SZA is not suitable for fixing paint layers that are already flaking away from the glass beneath, but it is ideal for fixing poorly fired paint layers [131,132]. SZA has excellent optical and penetration properties, but its main drawback is that it is very sensitive to humidity and does not fully hydrolysing unless relative humidity exceeds 50%. Besides, it has a short pot-life [99]. Despite being used in many experimental conservation project over the years, SZA was never marketed by ISC [133].

Other binary inorganic sol-gel treatments evaluated for use in the conservation field are those based on TEOS and zirconium tetrabuthoxide (ZTB). These $ZrO_2$-$SiO_2$ coatings were developed for the protection of soda-lime-silica and potash-lime-silica ancient glass [134]. It was observed that the addition of ZTB in the formulation increased the reflectance of the coating due to the increased refractive index provided by the zirconium oxide. A $10ZrO_2 \cdot 90SiO_2$ (mol%) formulation was proposed as it ensures transparency of the treatment, which does not modify the appearance of the glass substrate. Accelerated ageing tests – based on variation of humidity, temperature and $SO_2$ concentration's – performed on replica glass and pre-aged samples demonstrated that the protective effect increased with the temperature used for densification (from 250 °C to 400 °C), leading to a coating that has less cracks, less crystals formed on the surface, good adherence to the glass and good transparency. However, heat treatments must be undertaken on ancient glass artefacts, which may be why further tests involving ancient glass specimens were not performed and the experimentations were interrupted.

A more recently developed binary inorganic sol-gel system is that based on TEOS and zinc acetate dihydrate [135,136]. These $SiO_2$-ZnO coatings, formulated for the protection of historical glass objects and proved to be chemically resistant during acid corrosion tests performed according to the STAS 598/3–76 standard. Moreover, the introduction of ZnO provided antibacterial activity to the coating, which is important as microbial growth on glass surfaces can produce several types of damage, from bio-pitting to cracks and patina formation [137]. However, these systems require treatments at temperatures between 300 °C to 400 °C, making their applicability less feasible on real cultural heritage samples.

## Hybrid organic-inorganic sol-gel systems

ORMOCER is a type of inorganic-organic hybrid polymers that was developed by the ISC over 30 years ago [138]. The concept behind this material was to combine the properties of organic polymers (such as functionalisation, and easy processing at low tem-

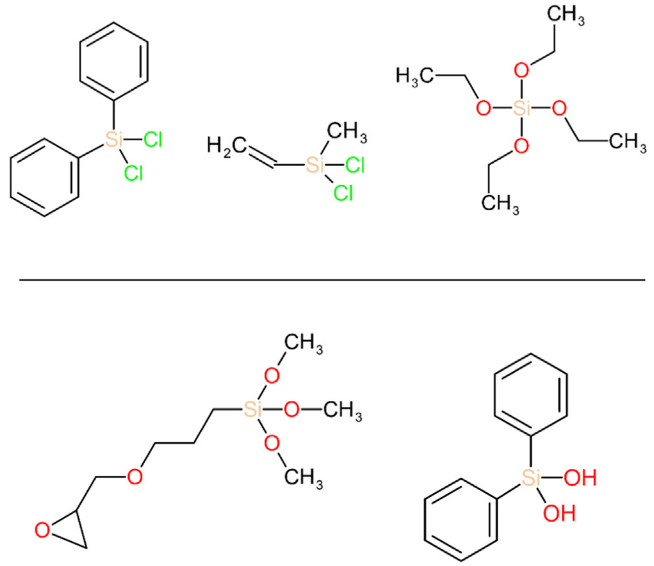

**Fig. 6.** Starting materials for the synthesis of Glasormocer (top) and Bronzeormocer (bottom).

peratures) with properties of glass-like materials (like hardness, chemical and thermal stability), in order to obtain synergetic properties that cannot be achieved by either component alone [139]. ORMOCERs are classified as “class II hybrid”, which means that inorganic and organic moieties are covalently bonded together [140].

These materials can be fine-tuned to suit different application; for example, Glasormocer (OR-G), a hybrid organic-inorganic material characterised by vinyl-functionalised organic substituents in the network, was first used in 1986 as a coating for corrosion protection of historic stained glass windows [141]. Since then, ORMOCER protective systems, some of which are blended with Paraloid B-72, have been utilised for conservation projects on stained glass windows of the Cologne cathedral (Germany), the Parish Church of St. Andreas (Germany) and the Canterbury cathedral (United Kingdom) [129,130,142]. ORMOCER has also been tested in pilot studies for the consolidation and stabilisation of paint layers on glass. In these experiments, tests were carried out on glass with artificially corroded paint layers to simulate real conditions, and it was observed that the performance of ORMOCER varied considerably depending on the type of damage that was simulated. In particular, the best performance was achieved when ORMOCER was applied for fixing loose flakes of paint [131].

In a recent study, the performance of a blend consisting of Glasormocer, Bronzeormocer, which is a hybrid organic-inorganic material characterised by epoxy-functionalised organic substituents (Fig. 6), and Paraloid B-72, applied from 1999 to 2004 for the consolidation and coating of enamels and art objects, was re-evaluated in 2017. Researchers observed that art objects stored in climate cases were better preserved thanks to the controlled atmospheric conditions, whereas replica enamels that were shelved in the laboratory under less favourable conditions exhibited more advanced signs of corrosion [143]. ISC is still conducting research and testing to improve ORMOCER formulations [144].

Several hybrid organic-inorganic treatments have been studied through the sol-gel route, including different organic-inorganic alkyl-alkoxysilane systems. In the industrial field, these systems were investigated for the fabrication of antireflective and hydrophobic coatings on various substrates [145–147]. Carmona et al. [133] found that the combination of TEOS with 3-trimethoxysilyl propyl methacrylate (MEMO) was the best organic-inorganic formulation tested in terms of pot life, penetration ability, adhesion, and chemical resistance for consolidating unstable paint on stained glass windows. However, further research is necessary to test the product on original glass artefacts before its application in restoration workshops can be recommended, as all tests were performed on replicas.

De Ferri et al. [148] investigated several water-repellent hybrid sol-gel coatings for protecting historical window glass characterised by potash-lime-silica composition. TEOS was used in different proportions with other silane precursors: octyltri-ethoxy-silane (OTES), hexadecyl-tri–methoxy-silane (HDTMS), 3-(tri–methoxy-silyl)-propyl-Methacrylate) (TMSPM), tri-methyl-ethoxy-silane (TMES) and methyl-tri-ethoxy-silane (MTES). Only the best performing sols based on the contact angle values and the organic content (5% HDTMS, 20% OTES, and 5% HDTMS + 20% OTES) were applied on potash-lime-silica glass replicas. The results were promising because the coatings were transparent and colourless, water repellent, stable under UV ageing and $SO_2$ corrosion tests [149]. However, the authors did not investigate the optimization of the formulation, and no further results have been published to the best of our knowledge.

## Future perspectives

The chemical action of zinc salts was initially investigated for an industrial application to protect soda-lime silicate glass against atmospheric alteration during transport and storage, or against silicate network dissolution during dishwasher washing. Later, its potential to reduce the chemical and physical degradation of soda, potash and mixed alkali ancient glass exposed to atmospheric conditions of unsatured relative humidity (RH $<$ 100%) was explored [150]. This treatment was sprayed on freshly polished glass replicas and on pre-altered ones and analysed. Accelerated ageing tests were conducted at 40 °C and 80 °C (85% RH) in static mode (that means without cycling temperature or relative humidity during the test), along with ambient atmosphere ageing tests. It was observed that zinc salts sprayed on the surface did not modify the aesthetic appearance of the glass and that, after accelerated ageing tests, there was a reduction in the thickness of the hydration layer, along with reduced salt formation on the surface (Fig. 7). However, the treatment did not show any positive effect after the ageing test at ambient temperature. This is because the most efficient species for glass protection are chemisorbed Zn(II) species and those inserted in the glass structure in the near-surface region. These species are

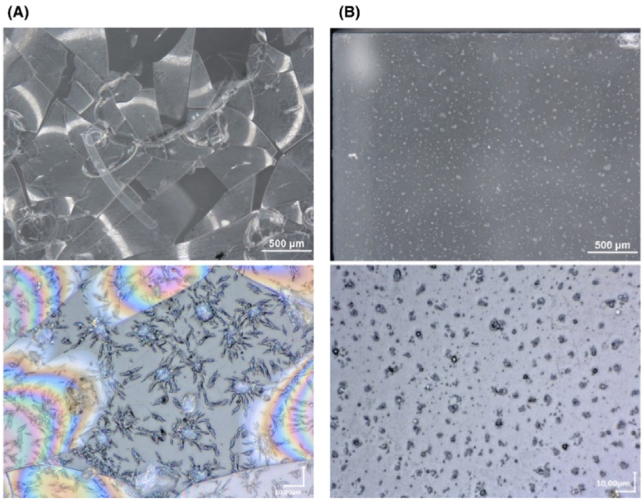

**Fig. 7.** Optical images after accelerated ageing tests (80 °C, 85 RH%, for 3 days) of: (A) the surface of bare glass. (B) the surface of the glass treated with Zinc salts applied by spraying (reprinted from ref. [150], Copyright (2020), with permission from The American Ceramic Society).

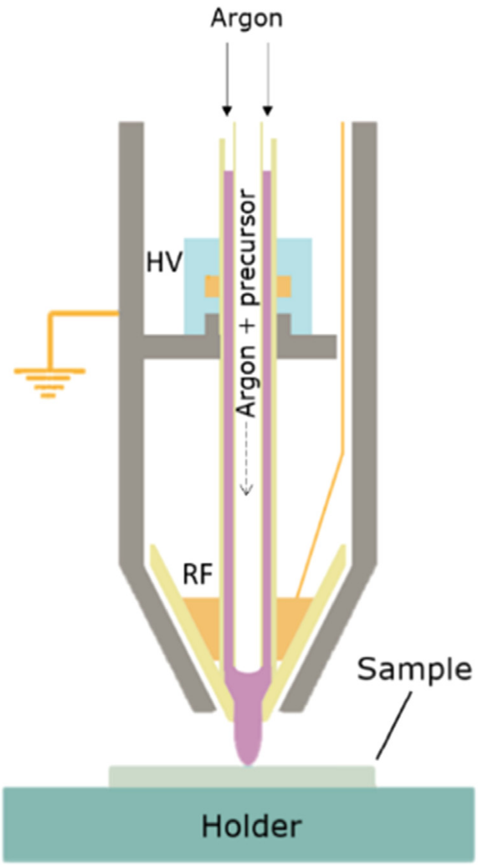

**Fig. 8.** Scheme of the atmospheric plasma jet characterised by its three coaxial gas ducts and the double couple of electrodes RF an HV (Adapted from Fig. 1© Alessandro Patelli et al., CC BY 3.0).

formed by thermal activation, indicating that the protective action of zinc salts manifests at high temperature (80 °C). Hence a moderate heating step seems necessary [151]. Moreover, the treatment applied on pre-altered samples did not slow down the hydration kinetics. Therefore, although the deposition of zinc salts is a promising alternative protection treatment, further experiments are required to improve the treatment protocol before applying it to real ancient glass samples [152].

Atmospheric pressure plasma jets are innovative devices used for surface treatments and have gained attention from the Cultural Heritage conservation community. These devices were first developed in the late 1990s and studied for their ability to etch materials like polyimide, tungsten, tantalum and silicon dioxide [153], and to deposit silicon dioxide films on silicon wafers [154]. They are of great interest because they operate at atmospheric pressure and exhibit similar performances with respect to low-pressure plasma discharges, which are widely used systems for surface treatments [155].

A commercially available APPJ device (Dual Frequency Plasma Jet, Nadir-Plasma and Polymers s.r.l.) was designed specifically to meet conservation and restoration requirements [156]. This device is based on a dielectric barrier discharge (DBD) system that consists of a double couple of electrodes, including a first upstream couple powered with a high voltage (HV) supply in the kilohertz regime (∼ 17 kHz) and a downstream couple in radio frequency (RF) at about 27 MHz (Fig. 8). It has demonstrated that room temperature operation does not generate electrodes deposition on the substrate, has high efficiency rates, is cost-effective for restoration works, is suitable for localised treatment, can be easily stopped by the restorer and can operate *in-situ* [157].

Several other commercial and experimental APPJ systems have already been trialled for a variety of conservation and restoration purposes. Pflugfelder et al. tested the ablation effects of a commercial plasma jet (Plasma-BLASTER MEF, Tigres GmbH) and of a patented plasma jet prototype for removing organic materials used as coatings for mural paintings and architectural surfaces [158]. Similarly, Boselli et al. used another commercial plasma jet source (kINPen 09, Neoplas Tools GmbH) to study the effectiveness of plasma treatment in removing tarnishing products while preventing damage to the surface of deteriorated 19th century daguerreotypes [159]. Yan et al. investigated the use of a different commercial atmospheric pressure plasma jet system (PlasmaTreater AS400 with a PFW10 nozzle, PlasmaTreat GmbH) to plasma polymerise hexamethyldisiloxane (HMDSO) into a protective coating towards water penetration in paper-based relics [160].

These plasma polymerised HMDSO based protective coatings were also applied on (contemporary) glass. Lin and Wang, for example, managed to deposit plasma polymerised HMDSO based hydrophobic coatings that showed great potential for applications as barrier layers against water penetration [161]. Hossain et al. investigated mechanically resistant and stable hydrophobic coatings by plasma polymerisation of (3-aminopropyl)triethoxysilane (APTES) together with HMDSO. The durability of the coating was evaluated through natural and thermal ageing, while scratch tests were performed to evaluate the robustness of the coating [162]. Since water is the primary cause of degradation for archaeological and historical glass artefacts, this technology should be further investigated for its protection as well. Regarding reversibility, it has been shown that plasma can effectively ablate organic coatings, removing layer by layer, therefore preserving underlying paint and decorations. However, in the case of hybrid materials, such as HMDSO-based coatings, the effectiveness of plasma is limited because only the organic groups can be removed, leaving the inorganic backbone fractured due to tensile stresses. Although the coating is not completely removable, retreatability can still be achieved by reapplying another protective coating on top, after the organic features have been removed [163].

## Conclusions

It has become evident that when addressing the conservation of glass artefacts, their original composition and the environmental conditions to which they were exposed must be considered, as they trigger various physical and chemical processes during the natural ageing, leading to different outcomes that can range from lifting flakes of degradation layers to the formation of cracks that can severely compromise their integrity. Today the strong emphasis on preventive conservation has led the conservation community to spend a significant amount of time identifying the conditions that endanger collections. This change in approach has prompted them to take action to address these issues, or at the very least, reduce them to acceptable levels.

Although this trend has decreased the necessity of direct treatments, remedial measures are still valuable in situations where preventive measures are unfeasible. However, consolidation or coating treatments must be customised to the structure and provenance of the glass and its degradation, adding a layer of complexity to the engineering process of new products.

Concurrently, conservation guidelines should always be considered when designing and developing new consolidation or coating treatments for cultural artefacts. In practice, it is often not possible to adhere to all principle when treating ancient or historical objects, and it is frequently necessary to reach a compromise between what is desirable and what is necessary to ensure treatment effectiveness. For example, the first materials used for consolidation and coating purposes, such as organic materials, had more negative aspects than positive ones due to their inherently poor physicochemical properties or because many synthetic organic materials were not originally engineered for cultural heritage artefacts and their specific needs.

Currently, an increased focus on safeguarding and protecting cultural heritage has led to the development of coatings and consolidants that are more compliant with mainstream conservation principles and requirements. In the authors' opinion, this development should not only consider the material type, but also the viscosity and solvent selection to attain optimal performances and adhere to environmental sustainability standards. Moreover, although synthetic organic materials such as acrylic resins are much appreciated and still frequently used for conservation purposes, alternatives should be considered and tested by practitioners.

Sol-gel treatments have demonstrated great potential due to their versatility, enabling the design of formulations including inorganic systems as well as hybrid organic-inorganic ones. From the authors' standpoint, formulations based on organically modified silica alkoxides represent the best commercially available solution at present for both coatings and consolidants, thanks to their transparency, hydrophobicity and stability under ageing and corrosion tests. A promising strategy for future technological developments in this field is represented by the formulation of coatings with antibacterial activity, an aspect often underestimated. Combining the efficiency of silica alkoxides organically modified with the antibacterial behaviour of ZnO could enhance the performance of these protective systems against glass degradation from multiple fronts. The initial attempt made in the case of binary $SiO_2$-ZnO sol-gel systems represents the first steps in this research, but improvements in the effectiveness of these treatments are undoubtedly still necessary, especially for what concerns densification temperatures, which should be limited as much as possible, and tests on pre-aged samples, which should be always carried out in order to verify the quality of the deposition even when the sample is not flat and smooth.

Outside sol-gel processes, other new research trends related to the use of zinc and other elements for the protection of archaeological and historical glass artefacts are emerging. Although the preliminary results appeared promising, further experiments aiming to improve the treatment protocol should be still carried out, such as improving the efficiency of the treatment on pre-aged samples. Finally, in parallel to materials development, new frontiers in deposition technologies such as atmospheric pressure plasma jet show great promise for historical and archaeological glass protection, thanks to devices designed to meet the specific requirements of cultural heritage.

In the current conservation field, a prevailing sense of scepticism surrounds the suitability of employing coatings and consolidants on glass. This apprehension has been forged through years of interventions that regrettably led to a range of health, environmental, and material issues. The formulation of new remedial conservation strategies demands a profound connection to rigorous risk assessment protocols, which become effective when achieved through enhanced cooperation between researchers and conservation practitioners. This collaborative synergy holds promise for both domains, potentially facilitating the emergence of innovative materials and strategies, while concurrently bolstering awareness of the potential risks associated with the adoption of these novel materials.

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## Aknowledgements

The image in Figure 1a reproducing a fragment of archaeological Roman glass (inventory n. 581558) is made available under the concession granted by the Italian Ministry of Culture, Regional Directorate of Museums of Friuli Venezia Giulia, and is subject to specific conditions. Any further reproduction, duplication by any means, as well as downloading and subsequent manipulation, is strictly prohibited.

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