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Hydrogel Green Gellan/γ-valero lactone for the Removal of Paraloid B72: Rheological Design and Applications in Conservation of Cultural Heritage

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Abstract

This doctoral thesis is situated within the broader framework of the green transition in cultural heritage conservation, which calls for a reduction of the environmental impact and health risks associated with conservation materials and processes, without compromising their technical effectiveness or compatibility with artworks. In this context, the controlled removal of aged Paraloid B72, an acrylic copolymer widely used as consolidant and protective varnish, represents a critical challenge, as long-term ageing leads to reduced solubility, partial reversibility and the need for aggressive, difficult-to-control solvent mixtures.

The research investigates the development of “green” hydrogels based on gellan gum, a natural-origin biopolymer, loaded with the bio-based solvent γ-valerolactone (GVL) for the controlled removal of aged Paraloid B72 from substrates relevant to cultural heritage. The main objective is to quantitatively correlate the formulation and rheological/chemorheological properties of these hydrogels with their solvent release behaviour, cleaning efficacy and penetration into the substrate, in line with the principles of green chemistry and preventive conservation. After reviewing the literature on synthetic polymers used in conservation (including B72 ageing and removal methods as well as biopolymer hydrogels and green solvents) a series of gellan/GVL hydrogels were prepared by varying polymer concentration, solvent content and gelation conditions. The formulations were characterised using shear oscillatory and rotational rheology, chemorheology and rheology-based 3D printing to map sol–gel transitions, structural stability and “easy peelability” as a function of composition.

The cleaning performance was evaluated on laboratory specimens coated with aged Paraloid B72 through controlled protocols and a multi-technique diagnostic approach, which include microscopy, spectroscopy, colour measurements and wettability tests. The solvent mass transfer was studied by diffusion cells, low-field

NMR and complementary methods to quantify GVL penetration and retention. The results show that suitably designed gellan/GVL hydrogels exhibit favourable viscoelastic properties for application and peelable removal and are capable of effectively softening and removing the superficial B72 layer. This can be performed with a reduced use of free solvents, limited colour changes and substrate alterations. Diffusion data indicate a significant reduction in solvent penetration depth compared to non-gelled systems, highlighting an improved balance between acrylic film solubilisation and control of solvent action.

Overall, the thesis demonstrates the feasibility of a rheology-driven and green chemistry-oriented design strategy for gellan-based hydrogels aimed at the removal of aged acrylic coatings and provides conceptual and practical guidelines for the development of more controlled and sustainable cleaning systems in conservation.

Contents

I. INTRODUCTION

The conservation and restoration of cultural heritage are increasingly framed within a broad vision that interweaves identity, social, economic and environmental dimensions. Cultural heritage, understood as the ensemble of tangible and intangible assets, constitutes a reservoir of memories, knowledge and values that significantly contributes to the construction of collective identities and to the intergenerational transmission of skills and practices. Numerous studies have highlighted how the state of preservation of heritage affects the quality of life of communities, strengthening their sense of belonging to places, fostering social participation and supporting processes of cohesion, especially in contexts characterised by high cultural diversity.

From a socio-economic perspective, cultural heritage is recognised as a strategic resource for local development, particularly through cultural and creative tourism. The presence of well-preserved historical and artistic assets enhances the attractiveness of territories, generates employment and income, and triggers entrepreneurial initiatives in the cultural, craft and service sectors, provided that enhancement strategies are compatible with the carrying capacity of sites and with the protection of their authenticity. In this framework, preventive and planned conservation plays a central role in ensuring the long-term continuity of the benefits associated with heritage, reducing the need for invasive interventions and the related economic, social and environmental costs.

European policies on ecological transition and circular economy have progressively included conservation and restoration among the sectors where it is necessary to reduce the environmental impact of processes, promote the use of safer and more sustainable materials, and critically re-evaluate the use of hazardous substances. Policy instruments such as the European Green Deal, the Circular Economy Action Plan, the REACH framework and specific regulations on volatile organic compounds

(VOCs) encourage a revision of established practices, pushing towards the replacement of high-impact solvents and formulations with alternatives that exhibit lower toxicological and ecotoxicological risk. As a result, conservation is no longer only a question of technical effectiveness, but also a testing ground for green chemistry and “safe and sustainable by design” approaches, in which the choice of treatment systems must reconcile compatibility with the artefact, operator safety and environmental sustainability over the entire life cycle.

In response to the complexity of degradation processes and the growing attention to risks and impacts, research in conservation science has progressively adopted a paradigm inspired by medicine, in which the artefact is regarded as a “patient” to be diagnosed, treated and monitored over time. Within this paradigm, analytical and diagnostic phases assume a structural role: the development of non-invasive or micro-destructive in situ techniques, including spectroscopy in different spectral regions, multispectral and hyperspectral imaging, thermography, scattering methods, geophysical investigations and advanced morphological analysis, allows high-resolution stratigraphic and compositional information to be obtained while minimising sampling. The combination of several techniques in multimodal approaches, supported by dedicated data management and analysis platforms, makes it possible to reconstruct the conservation state of objects and sites more accurately, to identify degradation phenomena at an early stage and to support intervention decisions based on measurable evidence.

Within this diagnostic and prognostic framework, the operational phases of restoration, and cleaning in particular, are crucial, as they directly affect visual legibility, chemical and physical balance and, ultimately, the aesthetic and cultural usability of the work. Traditionally, cleaning has relied on free solvents, hydroalcoholic mixtures, surfactants and poultices, sometimes combined with more or less controlled mechanical methods. Although these approaches have enabled the

removal of oxidised varnishes, surface deposits and non-original layers, they show well-documented limitations, including poor selectivity of action, limited spatial control, uncontrolled penetration into porous substrates, risk of extraction of original components and significant impacts on operator health and the environment.

In the last few decades, colloid and materials science has provided a new repertoire of soft-matter systems, such as micelles, microemulsions, nanostructured fluids and functional gels, specifically designed for cleaning tasks. Oil-in-water microemulsions, micellar solutions and nanostructured fluids have proved able to increase selectivity and effectiveness in removing aged synthetic paints, adhesives and greasy dirt, while reducing the amount of free solvent and the impact on original binders. More recent developments combine these fluids with gelled and polymeric matrices capable of confining the cleaning agents, modulating water or solvent release and limiting penetration into porous materials, in line with internationally promoted criteria of safety and sustainability.

Within this context, gels and hydrogels have become key tools for controlled cleaning of painted and stone surfaces, due to the possibility of designing three-dimensional networks with tailored rheological properties, retention capacity and release dynamics. The recent literature reports a wide range of systems based on synthetic polymers, biopolymers and interpenetrating networks. able to host microemulsions, chelating agents, enzymes and other active ingredients, thus allowing for the selective removal of different classes of contaminants with a single design framework. At the same time, the growing focus on green chemistry has fostered the development of nanostructured gels and fluids formulated with bio-based solvents, biodegradable surfactants and polymers of natural origin, which aim to reduce the overall toxicity and improve the environmental profile of cleaning systems without sacrificing performance.

Among the materials introduced in restoration practice, synthetic polymers, used as consolidants, adhesives and protective coatings, play a particularly critical role. Since the 1960s, acrylics, epoxy resins and fluoropolymers have progressively replaced traditional materials such as animal glues, waxes and natural resins, as they appeared more stable, reproducible and easy to apply. However, the extensive use of these polymers on wall paintings, canvases, stone sculptures, archaeological wood, ceramics and other substrates, has revealed relevant limitations related to ageing, additive migration, removal difficulties after decades of in situ placement, and complexity of their chemical-physical and biological degradation mechanisms.

Synthetic polymers employed in conservation undergo multiple degradation pathways that act simultaneously or sequentially, progressively altering both molecular structure and macroscopic properties. Some of the most significant processes are photo-oxidation induced by UV radiation, thermal oxidation, hydrolysis of functional groups (especially esters), main-chain scission, cross-linking, migration and volatilisation of additives (plasticisers, biocides, flame retardants) and biodegradation mediated by micro-organisms. In the early stages of ageing, chain-scission processes usually predominate, lowering the average molecular weight and often leading to initial softening; as degradation advances, the formation of cross-links results in increased stiffness and brittleness, micro and macro cracking, changes in glass transition temperature and loss of adhesion.

Within this synthetic polymers family, Paraloid B72 has assumed a paradigmatic role in conservation, and is often regarded as a “standard” consolidant and protective varnish. Paraloid B72 is a thermoplastic acrylic resin consisting of an ethyl methacrylate/methyl methacrylate copolymer, amorphous and not strongly cross-linked, with intermediate glass transition temperature and good transparency. The balance between more polar and less polar units affords solubility in a wide range of organic solvents, in particular ketones, esters and suitably formulated

alcohol mixtures, together with effective adhesion to both inorganic and organic substrates and limited short-term yellowing. These features have favoured its widespread use as a consolidant for stone, painted plasters and archaeological artefacts, as an adhesive for pictorial fragments and as a final varnish on oil paintings, modern artworks and polychrome surfaces.

Natural and accelerated ageing studies have nonetheless shown that, although Paraloid B72 generally maintains acceptable colour stability, it undergoes oxidation, chain scission and cross-linking processes that modify its rigidity, glass transition temperature. The increase in polarity along the polymer chain, the formation of oxidised groups and possible cross-links progressively reduce the effectiveness of traditional solvent mixtures, making more aggressive solvents (and longer contact times) necessary. In addition, deep penetration of B72 into porous materials such as stone and plaster often makes complete removal impossible without compromising cohesion: in many cases, “reversibility” must be understood as a partial modulation of the surface layer only, while internal residues continue to influence the behaviour of the system in the long term.

Current removal methodologies for Paraloid B72 represent a critical issue from both theoretical and practical standpoints. Conventional approaches based on free organic solvents (e.g. acetone, ethanol or tailored solvent blends) may be effective on relatively fresh or thin films, but suffer from poor selectivity, potential extraction of original components, uncontrolled penetration and high volatility, with associated health and environmental risks. More advanced gels and hydrogel systems, including those based on PVA–borax and PVA-B/agarose blends, have improved spatial and temporal control of solvent action, reducing penetration and enabling peeling removal. Yet they still raise questions regarding optimisation of formulations, residue management and compatibility with highly sensitive surfaces.

In parallel, the broader green transition has brought increasing attention to biopolymers, “green” hydrogels and bio-based or biomass-derived solvents as alternatives to conventional systems. Gellan gum has emerged as a particularly promising biopolymer for preparing hydrogels and microgels for cleaning paper, painted surfaces and porous materials, thanks to its natural origin, its ability to form stable and tunable three-dimensional networks and its generally good compatibility with heritage materials. Recent studies have shown that gellan-based hydrogels and microgels, when properly designed from a rheological standpoint, can provide high cleaning efficiency with short contact times, limited release of water or solvent into the substrate and negligible residues after removal. In the same vein, bio-based solvents such as γ-valerolactone (GVL), derived from biomass and characterised by a favourable toxicological profile, have been proposed as alternatives to conventional mixtures for the removal of acrylic resins and synthetic varnishes, showing good ability to solubilise Paraloid B72 and other polymers, with potential advantages in terms of sustainability and safety.

Despite these advances, a significant gap remains concerning the integrated design of “green” gelled systems specifically tailored for the controlled removal of aged Paraloid B72. On the one hand, many studies have separately investigated biopolymer-based hydrogels, bio-based solvents and nanostructured fluids; on the other hand, there is still a lack of contributions that quantitatively link the rheological and chemorheological behaviour of gels to solvent release, removal efficiency and penetration into the substrate, in a framework consistent with green transition requirements. Moreover, most existing works focus on qualitative or semi-quantitative cleaning tests, whereas fewer studies integrate advanced rheological characterisation, solvent diffusion measurements and multimodal diagnostics of polymer residues and possible substrate alterations.

This doctoral thesis is situated precisely in this research space and proposes the development and characterisation of "green" hydrogels based on gellan gum loaded with γ-valerolactone for the controlled removal of aged Paraloid B72 from surfaces relevant to cultural heritage. The overarching aim is to demonstrate that a design strategy grounded in a thorough understanding of the viscoelastic and chemorheological behaviour of the gel–solvent system can yield highly effective, selective and more sustainable cleaning materials, reducing the impact on both substrates and operators.

More specifically, the thesis pursues the following objectives: to design and prepare gellan-based hydrogels with different γ-valerolactone contents, exploring the effects of composition, polymer concentration and gelation conditions on key rheological properties (elastic and viscous moduli, yield behaviour, "easy peelability"); to employ chemorheology and rheology-based 3D printing methods to monitor in situ gel formation, sol–gel transitions and structural stability as a function of temperature, time and composition, and to correlate rheological maps with expected operational performance; to assess the cleaning efficacy of gellan/GVL hydrogels on samples coated with aged Paraloid B72 through controlled experimental protocols and a set of diagnostic techniques (microscopy, spectroscopy, colour and wettability measurements), quantifying both acrylic film removal and possible residues or substrate alterations; finally, to investigate solvent penetration and release using diffusion cells, low-field NMR and complementary methods, in order to elucidate transport dynamics and optimise formulations in terms of selectivity and safety.

To address these aims, the thesis is organised as follows. Chapter II presents an extensive state of the art, covering the regulatory and conceptual framework of the green transition in conservation, the degradation mechanisms of synthetic polymers and Paraloid B72 in particular, existing removal methodologies, the role of biopolymers and "green" hydrogels, and recent developments in bio-based and

biomass-derived solvents for cleaning. Chapter III describes in detail the materials and methods used, including the preparation of gellan/GVL hydrogels, rheological and chemorheological protocols, rheology-based 3D printing, preparation of B72-coated samples and the diagnostic techniques employed to evaluate cleaning performance, solvent penetration and possible substrate changes. Chapters IV-VI presents and discusses the experimental results, relating rheological and gel-formation properties to operational performance in terms of B72 removal, solvent release control and compatibility with original materials. The last Chapter draws together the main conclusions of the work, discusses its limitations and outlines possible future developments in the field of gellan-based hydrogels and green solvents for the conservation of cultural heritage.

II. State of art

2.1. Introduction on the importance of cultural heritage conservation

The importance of preserving and restoring cultural heritage must be today understood within a vision that integrates identity, social, economic and environmental aspects. Cultural heritage, seen as a set of tangible and intangible assets, represents a resource of memories, knowledge and values that contributes to the construction of collective identity and the transmission of knowledge between generations. Numerous studies highlight how the proper conservation of cultural heritage has a positive impact on the quality of life of communities, strengthening ties with the local area, social participation and cohesion, especially in contexts characterised by high cultural diversity. From this perspective, the protection of heritage is not only an ethical and regulatory duty, but also a central element for human development and the resilience of contemporary societies (1–4).

From a socio-economic perspective, cultural heritage is recognised as a strategic resource for local development, particularly through cultural and creative tourism (5,6). Recent studies show a significant relationship between the presence of cultural heritage, the attractiveness of territories and the ability to generate employment and income, while highlighting the need to balance economic growth and the protection of the authenticity of places (1–3,6–8). In this context, sustainable tourism policies that integrate heritage with other local resources are considered effective tools for promoting local prosperity, provided they are accompanied by adequate strategies for protection, participatory management and impact control. Preventive and planned conservation of cultural heritage therefore plays a fundamental role in ensuring the continuity of these benefits in the long term (9).

However, the deterioration of works and sites of historical and artistic interest poses a constant threat to these symbolic and socio-economic functions. The deterioration

processes are the result of a complex combination of environmental (temperature, humidity, light radiation, atmospheric pollutants), biological, mechanical and anthropogenic factors, augmented by the accelerating effects of climate change and extreme events. Added to these are the risks associated to obsolete restoration work or work carried out with incompatible materials, which can trigger chemical and physical instability, optical alterations and mechanical stress in the medium to long term. In response to this scenario, scientific research has gradually adopted a paradigm inspired by medicine, in which works are treated as “patients” to be diagnosed, prognosed, treated and monitored, with the aim of containing risk factors and prolonging the life of the artefact while respecting its material and historical integrity (10–12).

Within this paradigm, diagnostics play a structural role. Non-invasive and micro-destructive in situ techniques, including spectroscopy in different regions of the spectrum, multispectral and hyperspectral imaging, thermographic methods, scattering techniques, geophysical methods and advanced morphological analysis tools, allow for the acquisition of high-resolution stratigraphic and compositional information, thus minimising the need for physical sampling (10–14). Recent reviews show how the integration of multiple techniques into multi-method approaches, supported by dedicated data management and analysis platforms, makes it possible to reconstruct the state of conservation of objects and sites, identify degradation pathologies at an early stage, and support intervention decisions based on measurable evidence. At the same time, the spread of portable devices, advanced sensors and remote monitoring systems paves the way for preventive and predictive conservation practices, in which continuous monitoring of microclimatic and structural conditions allows for targeted intervention before damage becomes irreversible (15–18).

In this diagnostic and prognostic context, the operational phases of restoration, and in particular cleaning, take on decisive importance, as they directly affect visual legibility, chemical and physical balance and, consequently, the aesthetic and cultural usability of the work. Traditionally, cleaning has been based on the use of free-form solvents, hydroalcoholic mixtures, surfactants and compresses, accompanied by more or less controlled mechanical methods. These approaches have made it possible to remove oxidised varnishes, surface deposits and incongruous layers, but they have well-documented limitations: poor selectivity of action, difficulty of spatial control, uncontrolled penetration into porous substrates, risk of extraction of original components and significant impacts on the health of operators and the environment. The literature also highlights how the repeated application of solvents and compresses can alter the mechanical and optical properties of the original materials, generating over time phenomena such as embrittlement, yellowing or changes in gloss and colour saturation (9,12,19).

To address these critical issues, colloid and materials science has introduced a new repertoire of “soft matter” systems for restoration, in which micelles, microemulsions, nanostructured fluids and functionalised gels are designed ad hoc for specific cleaning problems (12,19). In particular, oil-in-water microemulsions, micellar solutions and nanostructured fluid complexes have been shown to significantly increase selectivity and effectiveness in removing aged synthetic paints, adhesives and greasy dirt, while reducing the free solvent content and impact on the original binders [Fig. 1] (12,19–21).

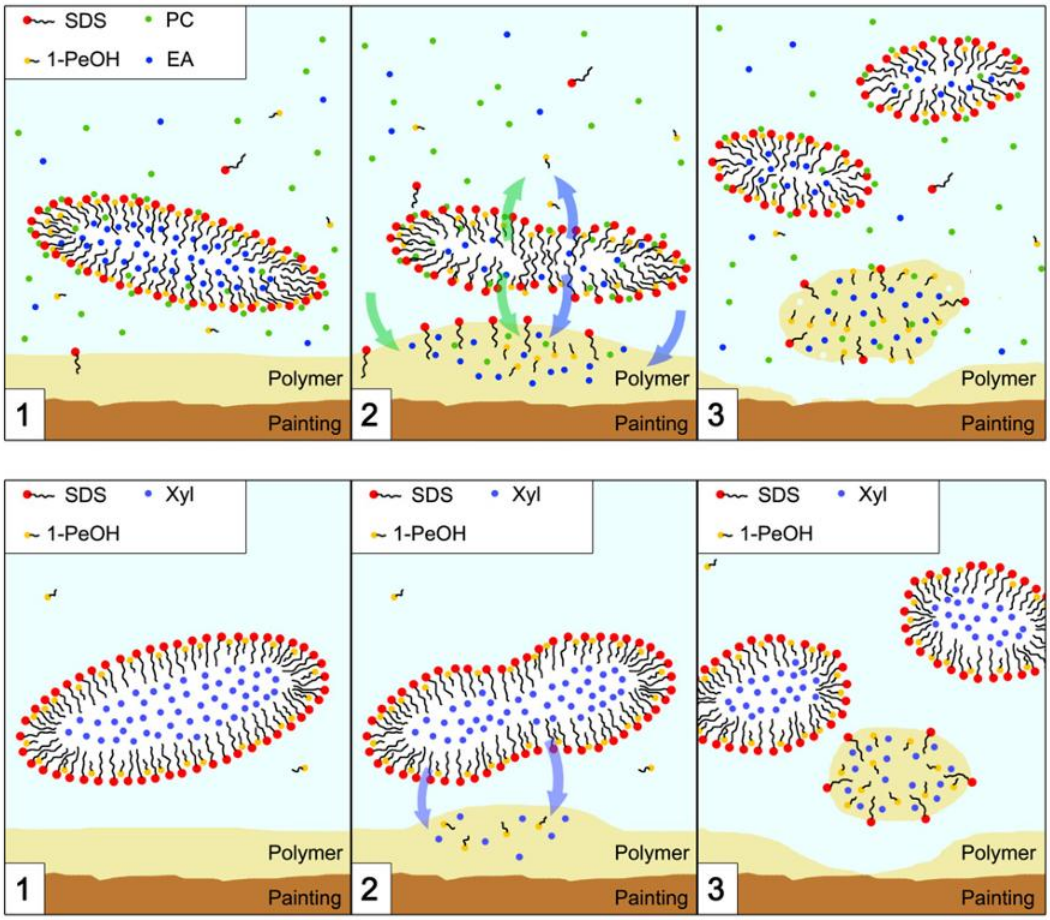

Figure 1. Schematic representationof the interaction mechanism between detergent nanostructured systems (top: EAPC; bottom: XYL) and the polymer coating. From Baglioni et al., 2014. (19)

The most recent developments see these systems combined with gelatinous and polymeric matrices, capable of confining the cleaning fluid, modulating the release of water or solvent and limiting penetration into porous materials, in line with internationally promoted safety and sustainability criteria (22).

Gels and hydrogels, in particular, have established themselves as key tools for the controlled cleaning of painted and stone surfaces, thanks to the possibility of designing three-dimensional networks with appropriately calibrated rheological properties, retention capacity and release dynamics (12,22–24). Recent literature

describes a wide range of systems based on synthetic polymers, biopolymers and interpenetrating networks, capable of hosting microemulsions, chelating agents, enzymes and other active ingredients, making it possible to selectively remove different classes of contaminants with a single design tool. At the same time, the focus on “green” chemistry has encouraged the development of nanostructured gels and fluids formulated with bio-based solvents, biodegradable surfactants and polymers of natural origin, which reduce the overall toxicity of the system and improve its environmental profile without sacrificing performance (12,19,25). These innovations place soft matter technologies at the centre of a new restoration paradigm, in which cleaning is no longer an empirical operation, but a process designed and validated experimentally, supported by advanced diagnostics and risk assessment protocols.

The importance of cultural heritage conservation and restoration emerges as the result of a convergence between cultural, social and scientific demands. On a cultural level, the preservation of heritage ensures the transmission of the aesthetic, symbolic and ethical values that have shaped different traditions, contributing to intercultural dialogue and the construction of non-exclusive identities. On a social and economic level, the presence of a well-preserved heritage supports production chains, responsible tourism and social innovation processes, provided that enhancement strategies are compatible with the carrying capacity of the sites and with long-term sustainability objectives (1–9). Finally, from a technical and scientific point of view, the transition from traditional methods with little control to advanced technologies based on non-invasive diagnosis, soft matter and “green” approaches makes it clear that every decision regarding heritage is both a cultural and ethical choice, which must balance the protection of materials, responsibility towards future generations and the reduction of environmental impact (12,19–23). In this context, reflection on cleaning and innovative conservation materials plays a paradigmatic role in

understanding the evolutionary trajectories of contemporary restoration and its contribution to the protection of heritage as a global common good.

2.2. Restoration materials and degradation mechanisms, synthetic polymers used in conservation

Restoration materials, particularly synthetic polymers, now play a central role in the preventive conservation and restoration of works of art, historical artefacts, archaeological finds and cultural heritage of various kinds (26). Since the 1960s, the search for materials with superior physical and chemical properties compared to traditional natural consolidants (animal glues, waxes, natural resins) has led to a gradual shift towards the use of synthetic polymers such as acrylics, epoxy resins and fluoropolymers (27–29). However, the extensive use of synthetics in very different contexts such as wall paintings, canvases, stone sculptures, archaeological wood, ceramics and others has gradually revealed significant limitations related to accelerated ageing, plasticiser migration, difficulties in removal after decades of permanence and, above all, to the complex chemical-physical and biological degradation mechanisms to which these materials are subject (30–33).

Synthetic polymers used in preservation are subject to multiple degradation mechanisms, operating simultaneously or sequentially, which progressively modify both the molecular structure and the macroscopic properties of the material. These mechanisms include photo-oxidation induced by UV radiation, thermal oxidation, hydrolysis of functional groups (especially esters), cleavage of the main polymer chain, cross-linking, migration and volatilisation of additives (plasticisers, biocides, flame retardants), and biodegradation processes mediated by microorganisms (27,34–36).

Photodegradation is one of the most critical processes for polymers used in conservation, as most cultural heritage items are exposed, at least periodically, to

natural (sunlight) or artificial (museum lighting systems) light radiation. The absorption of photons in the UV regions of the spectrum (wavelengths between 300 and 400 nm) induces the breaking of chemical bonds in the polymer chain, generating free radicals and reactive radical species [Fig. 2] (30,34,36). These radicals initiate propagation reactions, leading to a cascade of chemical transformations that include the introduction of oxidised groups (carbonyls, hydroxyls, peroxides), the cleavage of C-C and C-O bonds, and the formation of conjugated double bonds responsible for colour changes (yellowing, brownish colouring) (34,37). The speed of this process depends on the intensity of UV radiation, the duration of exposure, temperature, relative humidity, and the chemical composition of the polymer.

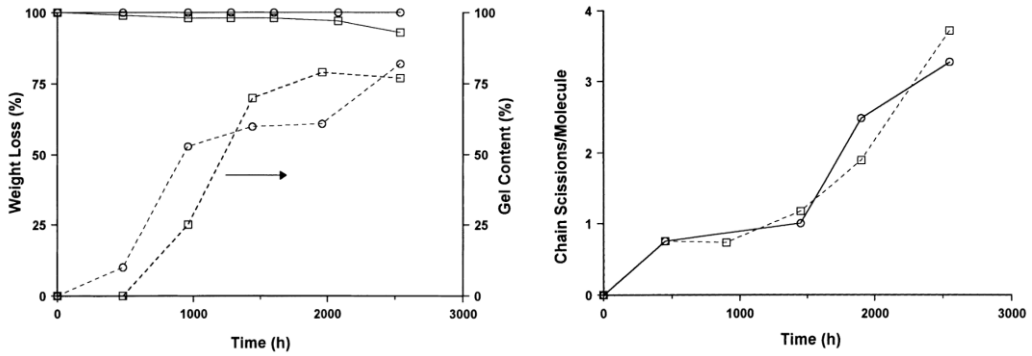

Figure 2. Weight loss and gel content of Paraloid B66 (W) and Paraloid B67 (A) as a function of treatment time (plot on the left). Scissions per initial molecule of Paraloid B72 (W) and Paraloid B82 (A) as a function of treatment time (plot on the right). From Chiantore O, et al., 2001(36)

Thermal oxidation is particularly relevant in contexts of prolonged exposure to high temperatures or repeated thermal cycles, as it occurs in many indoor environments that are not climate-controlled (warehouses, churches or museums without air conditioning). The increase in temperature accelerates the diffusion of oxygen molecules within the polymer matrix and speeds up the oxidation reactions of the polymer chains (27,34). At temperatures above 50°C and in the presence of high

relative humidity (>80-90%), degradation intensifies significantly. Experimental data show that degradation kinetics can increase by 30-50% compared to normal environmental conditions (34–36). Thermal oxidation produces the same oxidised functional groups as photodegradation (carbonyls, destroyed esters, hydroxyl groups), but through direct thermochemical mechanisms.

Hydrolysis is the process by which water molecules break chemical bonds, particularly ester bonds present in acrylic and vinyl polymers. For polymers containing ester groups, such as Paraloid B72, based on ethyl methacrylate (EMA) and methyl methacrylate (MMA), hydrolysis is a critical mechanism of degradation (29,34–38). Atmospheric humidity, the presence of liquid water (from leaks, condensation, or very humid environments), and acidic or basic conditions significantly accelerate hydrolysis. Rising temperatures also increase the kinetics of the process, according to Arrhenius kinetic relationships. Under extreme conditions (temperature >50°C, humidity >90%), hydrolysis can accelerate by 30-50% compared to standard conditions (37–41).

During ageing, competition between chain scission and cross-linking determines the evolution over time of critical properties such as glass transition temperature (T_g), hardness, brittleness, solubility, and the ability to penetrate porous substrates (27,34,42,43). In the early stages of degradation, chain scission processes caused by oxidation and hydrolysis tend to prevail, reducing the average molecular weight. This leads to an initial softening of the polymer but, as degradation progresses, the formation of cross-links between the degraded fragments can lead to progressive cross-linking, resulting in increased hardness and brittleness (40–43).

Commercial synthetic polymers contain numerous chemical additives, including plasticisers, biocides, flame retardants, antioxidants, and polymerisation catalyst residues. These additives are often weakly bound to the polymer matrix and tend to migrate to the surface and volatilise over time, especially when exposed to high

temperatures, humidity, and UV radiation. The loss of plasticisers leads to embrittlement of the polymer (loss of flexibility) and increased mechanical fragility, resulting in the formation of micro and macro cracks. The volatilisation of biocides reduces the ability to inhibit microbial colonisation, increasing the biosusceptibility (biological susceptibility) of the material over time(27,30–34,36,44–46).

2.3. Paraloid B72 use and ageing

Paraloid B72 is a thermoplastic acrylic resin consisting of a copolymer of ethyl methacrylate and methyl methacrylate, originally developed as an industrial coating and subsequently adopted in conservation due to its good optical and mechanical properties. From a structural point of view, it is an amorphous polymer with relatively rigid but not strongly cross-linked chains, which results in an intermediate glass transition temperature (between 40 and 45°C) and a certain flexibility of the film at room temperature. The composition of the copolymer is balanced in terms of more polar (ethyl methacrylate) and less polar (methyl methacrylate) units, giving the material solubility in various organic solvents, in particular ketones, esters and suitably formulated alcohol mixtures [Fig.3] (47–50).

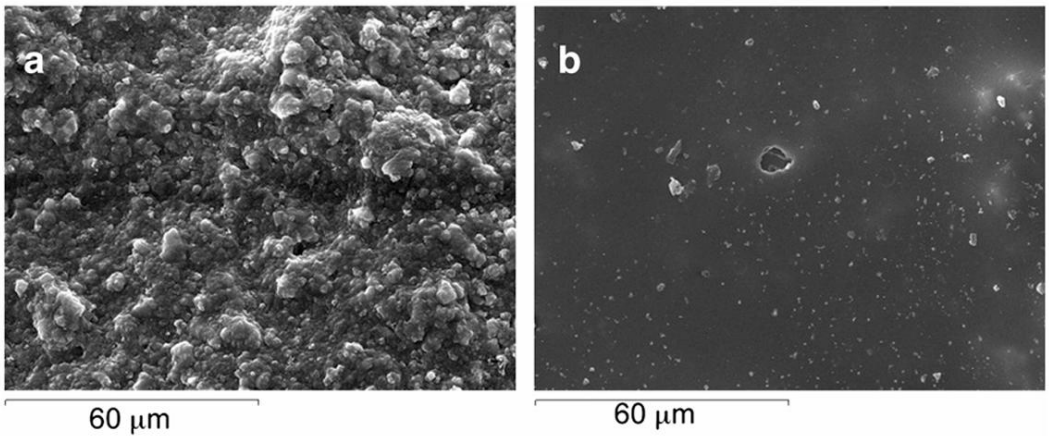

Figure 3. SEM micrographs of the sample reproducing a wall painted with the fresco technique. SEM images show the appearance of a wall painting model sample before (a) and after (b) the application of a Paraloid B72 coating. From Baglioni et al., 2014 (19)

The chemical and physical properties of Paraloid B72, such as transparency, limited tendency to yellowing, and good adhesion to various inorganic and organic substrates, have contributed to its rapid spread as a consolidant and protective varnish. Natural and accelerated ageing studies have shown that the material maintains reasonable colour stability, but undergoes oxidation and chain scission or cross-linking, resulting in increased rigidity, variation in T_g and progressive reduction in solubility in the solvents originally used. Photo-oxidative ageing can generate more polar groups along the polymer chain, altering interactions with the substrate and cleaning systems, while exposure to fluctuating environmental conditions (humidity, temperature) affects microcracking and film deformation (34,47,49,51).

From the point of view of wettability and interface with historical materials, Paraloid B72 forms continuous films with low water vapour permeability and moderate surface tension, which promotes the wetting of stone substrates and mortars but can also hinder their long-term transpiration. Studies on porous substrates, such as limestone and plaster, have shown that the penetration of B72 can be significant,

with the formation of consolidation zones distributed along the capillary network, especially when the polymer is applied at high concentrations or in solvents with low surface tension. On the one hand, these characteristics improve the internal cohesion of decohesive materials; on the other hand, they complicate the reversibility of the treatment, since the resin does not just form a surface film that is easily accessible to solvents, but is distributed in depth (47–51).

The systematic introduction of Paraloid B72 in the field of restoration dates back to the second half of the 20th century, coinciding with the gradual replacement of natural materials (waxes, animal glues, natural resins) with synthetic polymers that were more reproducible and controllable. Paraloid B72 has been used as a consolidant for natural stone, painted plaster, archaeological finds in wood and ceramics, as well as an adhesive for pictorial fragments and as a final varnish on oil paintings, modern works and polychrome surfaces (47,52–55). Its versatility derives from the possibility of modulating concentration, viscosity and carrier solvent, obtaining formulations suitable for both deep consolidation and simple low-thickness protective coatings. Furthermore, its high transparency and limited chromatic impact on the substrate have long made it preferable to natural varnishes, which are more prone to yellowing and oxidation (56,57).

Numerous experimental studies have evaluated the behaviour of B72 under simulated ageing conditions on different substrates, confirming good mechanical resistance and reasonable colour stability, but also susceptibility to microcracking and loss of adhesion in the presence of marked thermo-hygrometric variations (34–36,38).

Research on Paraloid B72 nanocomposites enriched with nanoparticles (e.g. ZnO or TiO_2) shows improvements on barrier properties, UV resistance and hydrophobic characteristics, but raises questions about colour compatibility and long-term reversibility (55,58–65)]. The widespread use of B72 on archaeological finds and

architectural surfaces has also highlighted critical issues related to excess consolidant, unwanted glossiness and the difficulty of removing or modulating layers applied in previous interventions (66–68).

Paraloid B72 has also been used as an intermediate or insulating layer between different materials, for example between a mineral consolidant and an organic varnish, or as a temporary barrier in selective cleaning procedures. In such cases, the treatment design requires careful prediction of the interactions between the different polymer layers and the possible cumulative effects of ageing, since the overlapping of acrylic resins, organic consolidants and protective coatings can make any subsequent removal extremely complex (49).

The principle of reversibility is traditionally considered one of the main arguments in favour of using Paraloid B72, as the copolymer is soluble in a relatively wide range of organic solvents compatible with restoration practices. However, technical literature and field experience have shown that this reversibility is often only partial and strongly influenced by the ageing state of the resin, the nature of the substrate and the original application methods. Photochemical and thermal ageing leads to changes in the distribution of molecular weights and functional groups, with the possible formation of cross-links or more polarised regions, which reduce the effectiveness of the solvents initially used (35,36,39,47).

Studies correlating natural and accelerated ageing of B72 have shown a progressive increase in Tg and film rigidity, accompanied by a decrease in solubility in weaker solvents and a greater need for complex or more aggressive mixtures to achieve the same degree of dissolution. In operational terms, this translates into longer contact times, higher solvent concentrations and a potential increase in risk to the original materials, particularly sensitive paint layers, natural binders and porous supports (36,38,49,69,70). Furthermore, the deep penetration of B72 into the pores of stone and plaster makes complete removal virtually impossible without compromising the

integrity of the substrate: in these cases, reversibility should be understood rather as the possibility of modulating or reducing the surface layer, while maintaining an internal consolidating residue that is still functional (51,71–74).

The concept of ‘compatibility’ must also be reinterpreted in light of these results. Although B72 interacts relatively little with many inorganic matrices, it can interfere with the wettability and breathability of stone and masonry substrates, altering moisture flows and salt distribution over time. The selective removal of the consolidant, especially decades after application, carries the risk of exposing the material to mechanically critical conditions or triggering decohesion phenomena if the residual consolidation is weakened beyond a certain threshold (38,47,69,74,75).

2.4. Methodologies for the removal of Paraloid B72

The removal of Paraloid B72 from historical surfaces and artefacts is a particularly delicate phase of conservation and restoration work, as it directly involves the principle of reversibility and requires careful control of the interactions between the polymeric material, the original substrate and the removal methods used. Although Paraloid B72 has long been considered an easily removable material due to its solubility in various organic solvents, practical experience and recent studies have shown that this reversibility is often only theoretical, especially when a relatively long time has elapedafter application and in the presence of ageing phenomena (36,69,71). The removal methods currently used can be broadly divided into approaches based on the direct use of solvents, gelling systems and, more rarely, assisted physical or mechanical techniques, each of which has specific advantages but also significant limitations.

The most traditional approach to removing Paraloid B72 is based on the direct application in free form of organic solvents, such as acetone, ethanol, toluene or mixtures composed on the basis of solubility parameters such as Hansen parameters

(38,69,76). Under favourable conditions, such as relatively fresh films, limited thicknesses, or low-porosity substrates, this method allows rapid dissolution of the acrylic film, which is then removed by buffing or micro-suction. The action is based on the diffusion of the solvent into the polymer, causing the film to swell, breaking the cohesive interactions and solubilising the chains(47,77,78).

This strategy has numerous limitations. The poor selectivity of the solvent can lead to the extraction of original components, in particular organic binders, natural resins and low molecular weight substances present in the paint layers or finishing materials (37,79,80). The high volatility of many solvents used makes it difficult to control contact times and can lead to uncontrolled penetration into the pores, with possible migration of the dissolved Paraloid towards the inside of the support rather than towards the outside. Furthermore, prolonged exposure to organic solvents poses significant risks to the health of the operator and the environment, especially in large-scale or repeated interventions over time (81,82).

In cases of severely aged Paraloid, the solvents traditionally used during application may be ineffective or require a very long time, leading to the use of more aggressive mixtures (e.g. with a high proportion of aromatic solvents or esters with high solubilising power), which in turn increases the risk of damage to the substrate. Contemporary practice, therefore, tends to reduce the use of free solvents, favouring systems that limit their mobility and uncontrolled diffusion (83).

To overcome some of the critical issues associated with the use of liquid solvents, gel-based removal systems have been developed and progressively adopted in recent decades, with the aim of confining the solvent action and improving control of the intervention (81,84,85). Traditional gels, often based on synthetic polymers such as carboxymethylcellulose, poly(acrylates) or other gelling agents, reduce the lateral and in depth diffusion of the solvent, prolonging its contact time with the polymer

film to be removed. The application of solvents in gel form has been shown to offer greater selectivity than free solvents and to limit, at least in part, the migration of Paraloid B72 within the substrate (23,81,86,87).

Between the late 1990s and early 2000s, Solvent Surfactant Gels became widespread. These are a class of gelled systems designed for the extremely controlled cleaning of sensitive surfaces, in particular polychrome artefacts and layered works of art, where the main requirement is to selectively remove dirt, altered paints or overlaid layers while minimising the penetration of solvents into the original layers. In these systems, a mixture of organic solvents and water is immobilised in a polymer matrix, often consisting of thickening polyacrylates in combination with basic surfactants, to obtain a viscoelastic material that adheres to the surface without dripping, allowing longer contact times and precise control of the treated area (88,89). The presence of surfactants gives the gel a dual function: on the one hand, it acts as an emulsifying and cleansing agent, facilitating the removal of greasy dirt, oxidised resins or aged films; on the other hand, it contributes to the structure of the gel itself through acid-base interactions with the polymer, stabilising the microstructure and modulating the system's ability to incorporate and release solvent molecules (90,91). It is precisely this combination of high solvent power, surfactant action and the ability to “carry” solvents in a targeted manner that makes these gels very effective but also potentially risky tools because, if poorly formulated or applied without adequate preliminary testing, they can solubilise not only dirt or non-original layers, but also paint binders, old varnishes or historical retouches, causing irreversible loss of material (92). Added to this is the issue of operator safety: although the solvent mixtures used are partially “trapped” in the gel, they remain volatile and can pose risks if inhaled or if they come into contact with the skin or eyes, requiring the systematic use of personal protective equipment, good ventilation and codified working protocols. Finally, a critical aspect often highlighted in the conservation field is the management of residues: if the gel is not completely

removed and adequately rinsed, traces of polymer or surfactant may remain inside or on the surface of the paint film, altering its wettability, gloss, attraction of dust or response to subsequent interventions. for this reason, the use of Solvent Surfactant Gels is generally reserved for trained operators who are familiar with both the chemical-physical behaviour of these systems and the characteristics of the original materials to be treated, and who are able to calibrate each variable (formulation, application time, removal method) according to the objective of maximum effectiveness with minimum risk to the work (93–96).

Over the last two decades, gels and hydrogels have established themselves as key tools for the controlled removal of acrylic resins and Paraloid B72 in particular (97,98). These materials, based on hydrophilic or hybrid polymer networks, allow organic solvents, hydroalcoholic mixtures, chelating agents or microemulsions to be confined, drastically reducing the free diffusion of the liquid and allowing precise control of contact time and depth of action (96,99,100). Traditional hydrogels based on agar, agarose or pectins have been widely used for cleaning stone and painted surfaces, offering a good compromise between water retention, adaptability to the surface and ease of removal. However, their highly hydrophilic nature limits their ability to incorporate and retain non-polar or low-polarity organic solvents, making them ineffective in solubilising and removing layers of paint and hydrophobic polymeric materials (86).

A particularly important role is played by hydrogels based on polyvinyl alcohol (PVA) cross-linked with borax (PVA B), which behave as elastic materials on short time scales and as viscous fluids on longer scales, ensuring high malleability, controlled adhesion and removal by peeling without macroscopic residues. Rheological studies have shown that formulations with approximately 3% PVA and 0.6% borax have elastic moduli suitable for maintaining the gel structure during application and allowing continuous detachment from the surface, even on porous

substrates, and are capable of retaining up to 30% organic solvents, thus improving their effectiveness in solubilising layers of paint and hydrophobic polymeric materials (101–103). Cleaning tests on limestone samples treated with Paraloid B72 have shown that these gels are able to effectively remove the acrylic film without leaving visible residues and largely restoring the substrate's water absorption capacity (104,105).

Specific experiments on PVA borax hydrogels loaded with solvent mixtures (e.g., acetone ethanol) confirmed their effectiveness in removing aged B72 from wooden and stone substrates, both in laboratory conditions and on actual archaeological artefacts. In these studies, the action of the gel was optimised by modulating the contact times (from a few tens of seconds to a few minutes) and evaluating its effectiveness through microscopic observations and spectroscopic analyses of the polymer residue, showing a good compromise between extraction capacity and limited penetration of the solvent into the substrate [Fig. 4] (106).

Further research on PVA B blends with agarose (PVA B/AG) indicates that combining different polymer networks improves mechanical properties and the retention of solvents or nanostructured fluids, expanding the field of application to antique wall paints (107,108).

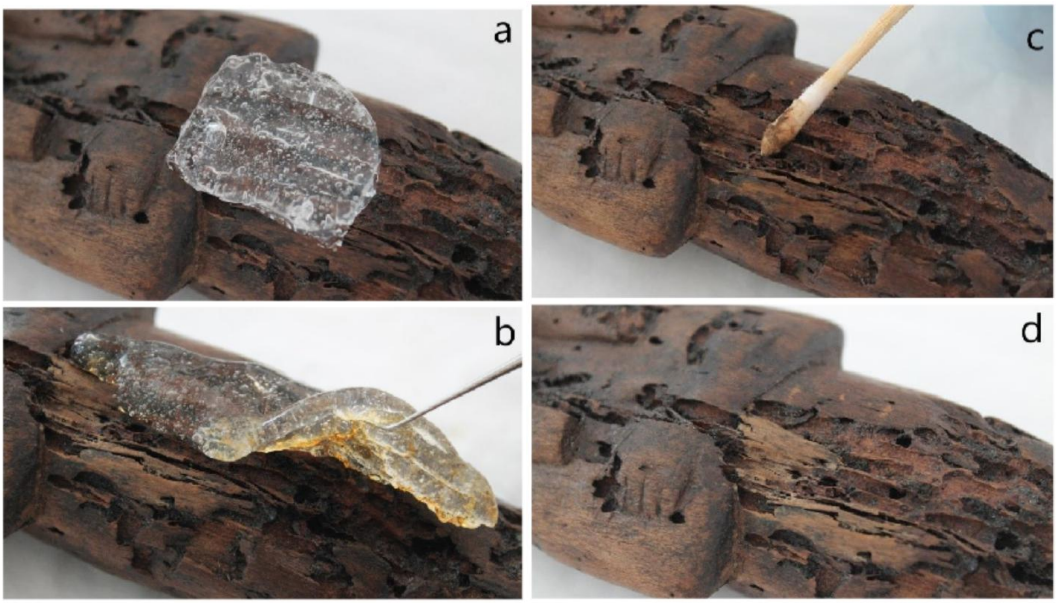

Figure 4. Cleaning treatment of wooden artifact using PVA-Borax hydrogel loaded with 20% Acetone and Ethanol 1:1. Application of the gel for 120 seconds (a); removal of the gel (b); removal of residual Paraloid B72 by dry swabbing (c); area of the surface after cleaning treatment (d). From Altobelli et al., 2023 (106)

Colloid science has made a decisive contribution to the design of advanced cleaning systems, introducing micelles, microemulsions and nanostructured fluids as selective vehicles for the removal of aged polymer coatings. Oil-in-water microemulsions, composed of water, one or more organic solvents and surfactants, create nanometric domains in which the solvents are confined, allowing for fine modulation of the solubilisation of acrylic resins such as Paraloid B72 and reducing the use of free solvents. Starting from the pioneering work of Ferroni and Baglioni, these formulations have been applied to the cleaning of stone surfaces, wall paintings and modern works, demonstrating high effectiveness in removing greasy dirt, oxidised paints and polymer films, with a relatively low impact on the original materials.

The integration of nanostructured fluids into high-retention gel matrices, for example, PVA B hydrogel or cross-linked polymer gels, has further improved the spatial and temporal control of the cleaning action. In these combined systems, the

microemulsion or micellar fluid is trapped in the gel network, which limits its diffusion and allows it to maintain close and uniform contact with the surface, reducing the risk of deep penetration into porous substrates. Studies on wall paints and contemporary painted surfaces have shown that hydrogels loaded with low VOC microemulsions can soften and solubilise aged Paraloid B72, minimising colour changes and preserving the microstructure of the substrate.

Despite these advantages, gelled systems have also significant limitations. Firstly, complete removal of the gel from the treated surface is not always easy, with the risk of leaving residues that can interact with the substrate over time or alter its appearance. Furthermore, the effectiveness of the gel depends heavily on the formulation, solvent concentration and application conditions, requiring a preliminary optimisation phase that is often long and complex. In cases of heavily aged Paraloid B72 or where it has penetrated deeply into porous materials, even gels may be insufficient, requiring prolonged contact times or repeated applications that increase the risk of undesirable side effects

Alongside traditional gels, removal strategies based on physical or mechanical approaches have also been explored, such as the use of compresses, micro-suction or controlled abrasion. The use of lasers, especially in controlled pulse mode, can allow selective ablation of organic coatings by differentiating between film and substrate absorption, but requires extremely precise calibration of energy parameters to avoid colour changes, microcracks or surface melting (109–111). Although these methods may be effective in specific situations, they are highly invasive and pose a significant risk of damaging the original surfaces, especially in the presence of fragile paint layers or highly porous materials. For this reason, their use is generally limited to extreme cases or combined with other more selective chemical approaches.

Overall, a critical analysis of Paraloid B72 removal methods shows that none of the currently available strategies is without limitations. The difficulty of controlling the

solvent action, the loss of polymer solubility due to ageing, the risks to the substrate and the environmental impact of organic solvents are recurring problems that motivate the search for alternative solutions. In this scenario, there is a strong need to develop more controlled, selective and sustainable removal systems that can act effectively on Paraloid B72 while minimising interaction with the original artefact. These requirements constitute the scientific and operational context within which the development of innovative hydrogels with reduced environmental impact is taking place. They are designed to better control the solvent release and the overall safety of the intervention, and represent the natural transition point to the next chapter of this research work

The green transition in cultural heritage restoration is part of a broader transformation of European policies on sustainable chemistry, the circular economy and the reduction of the environmental impact from production and service activities, which fully includes conservation sites (112,113). Starting with the European Green Deal and the new Circular Economy Action Plan, EU institutions have set a series of targets calling for the gradual replacement of substances that pose a high risk to health and the environment, the reduction of volatile organic compound (VOC) emissions, and the promotion of safer and more sustainable materials and processes throughout their entire life cycle (83,114–118).

In this scenario, the conservation-restoration sector is called upon to re-evaluate the traditional use of organic solvents, synthetic polymers and high-impact formulations, gradually integrating “green” materials and approaches based on the principles of green chemistry without compromising the long-term protection of the works (25,115,119).

European regulations on chemicals, in particular the REACH framework and the CLP Regulation, have had a significant impact on substances commonly used in restoration worksites, leading to restrictions or reclassifications of various solvents

and monomers, and making the use of formulations with high toxicity, persistence or bioaccumulation more complex(120–122).

Added to this are the directives and regulations on VOCs in paint and similar products, which, although not specifically designed for restoration, affect the commercial availability of many raw materials and encourage the use of low-solvent or water-based products. This regulatory framework, combined with growing awareness for operator health and the environmental impact of construction sites, has led to the spread of guidelines and recommendations that encourage the selection of less hazardous materials, the reduction of quantities used and the adoption of "low-impact" methodologies, in which gelled systems, biopolymers and solvents from renewable sources play an increasingly central role (12).

At the same time, the scientific community involved in conservation science has begun to apply the principles of green chemistry to the specific context of cultural heritage, highlighting how concepts such as waste prevention, the use of safer solvents, design for degradability and maximisation of process efficiency can be translated into operational criteria for the choice of materials and procedures (123,124). In this sense, attention has shifted from a mere assessment of the 'technical effectiveness' of the material (e.g., its ability to remove a layer of dirt or consolidate a substrate) to a more complex assessment that includes toxicological and ecotoxicological parameters, life cycle impacts, and potential long-term effects on the artefact (125). This integrated approach has fostered the development of European projects and interdisciplinary collaborations in which chemists, conservators, toxicologists and environmental engineers work together to design intervention materials that meet both compatibility and reversibility requirements and sustainability and safety criteria (126,127).

One of the critical aspects highlighted by several authors concerns the risk that the "green shift" will be interpreted solely in terms of the replacement of one hazardous

substance with another considered safer, without addressing the issue of the overall design of the intervention system. For example, replacing traditional solvents with mixtures based on “bio-based” or low-toxicity components does not in itself guarantee a lower overall impact if these formulations require longer contact times, larger quantities or generate residues that are difficult to remove and manage (128). Consequently, recent efforts have focused on a methodological approach in which “green” assessment considers the entire cycle of the intervention (selection, application, removal, waste management, long-term effects on the asset), including through tools borrowed from life cycle assessment (LCA) and risk assessment (23,78,81,103,129).

In the European regulatory context, a further boost to the green transition comes from the package of initiatives on sustainable chemicals, which aims to promote ‘safe and sustainable by design chemistry’ and also influences the development of new polymers, thickeners and solvents for specialist sectors such as restoration (98,127,128). This approach encourages the design of intervention materials that combine low hazard requirements, renewable sources, reduced persistence in the environment and compatibility with cultural heritage needs from the outset, rather than adapting products designed for other sectors ex post. The most recent literature highlights how this “by design” vision is beginning to translate into the development of functionalised biopolymers, hydrogels and organogels based on natural or bio-derived components, and new-generation solvents (including deep eutectic mixtures and biomass-derived solvents), which are candidates as alternatives to traditional high-impact materials (86,98,119,122,128).

The state of the art in green transition in cultural heritage restoration shows a gradual convergence between heritage protection requirements and European objectives in terms of environmental sustainability and chemical safety. On the one hand, the EU regulatory framework and policies are moving towards a systematic reduction in the

use of problematic substances and encouraging the adoption of materials and processes with a lower impact. On the other hand, research in the field of conservation science is developing critical tools and technological solutions capable of translating these guidelines into operational practices, with a particular focus on biopolymers, gel systems (hydrogels and organogels) and “green” solvents, which will be discussed in detail in the following sections.

2.5. Green biopolymers in the restoration of cultural heritage

The adoption of biopolymers and “green” hydrogels in the restoration of cultural heritage is one of the most concrete responses to the scientific and regulatory demand to reduce the toxicological and environmental impact of the materials used on construction sites, while maintaining high standards of effectiveness, selectivity and compatibility with the works. Compared to synthetic polymers traditionally used as thickeners or gel supports (e.g. polyacrylates and polyurethanes), naturally occurring biopolymers, such as polysaccharides (cellulose derivatives, alginates, gellan gum, agar, carrageenans), proteins (gelatin, casein) and their derivatives, offer the advantage of greater biodegradability, lower persistence in the environment and, often, lower toxicity, in line with the principles of green chemistry and European policies on material sustainability. From a conceptual point of view, these materials allow the design of hydrogels and gelled systems in which the “supporting structure” of the gel is provided by renewable macromolecules, often already known in other sectors (food, pharmaceutical, biomedical), whose safety is more widely documented than many synthetic polymers developed in the past for conservative use (23,81,99,115,130).

One of the main reasons why conservation science research is converging towards natural biopolymers is the possibility of obtaining hydrogels with modifiable rheological properties (viscoelasticity, water retention capacity, controlled adhesion)

that allow for highly selective cleaning, reducing both penetration into porous substrates and the migration of components within the paint layers. Systematic studies on polysaccharide-based hydrogels (e.g. agar, gellan, Xanthan, Alginate) have shown that by varying the concentration, degree of ionic cross-linking, gelation temperature and presence of co-thickening agents, it is possible to "design" gels with different rigidities and capacities for releasing aqueous solutions, which can carry buffers, delicate surfactants, chelating agents or, in some cases, small fractions of water-miscible solvents (86,131–134). This fine control is essential for treating polychrome surfaces, wall paintings, paper and water-sensitive substrates, where excessive wetting or uncontrolled diffusion of liquids can cause swelling, salt migration, mobilisation of binders and other forms of degradation [Fig. 5]

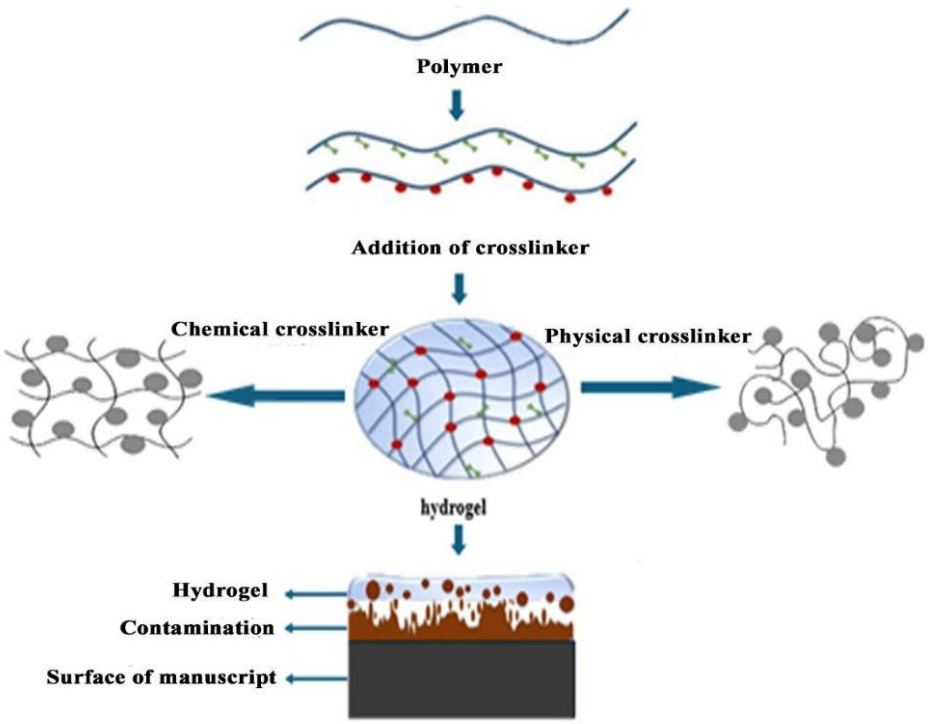

Figure 5. Suggested mechanism of hydrogel cleaning, namely the entrapment of impurities in the gel's porous structure. From Awad et al., 2025 (131)

From the point of view of compatibility with the original materials, the use of biopolymers offers some significant advantages (115,135). Firstly, many of these polysaccharides have relatively “mild” chemistry, with ionic charges and functional groups (hydroxyls, carboxylates) that interact mainly through hydrogen bonds and weak electrostatic interactions, reducing the risk of irreversible reactions with the organic components of paint films or paper materials. Furthermore, their ability to form highly hydrated three-dimensional networks allows for good surface adhesion without the need to add potentially more problematic plasticisers or co-solvents. Experimental literature shows that, in many formulations, biopolymer gels can be removed cohesively (in a “single piece” or in large fragments), limiting the amount of residue left on the surface compared to certain low-cohesion synthetic gels or traditional “wrap-around” systems.

A series of studies has shown that agar and agarose-based hydrogels, introduced into restoration in the 2000s, represent a key step towards the systematic use of biopolymers in cleaning processes (86,136–138). These thermoreversible gels, derived from red algae, have demonstrated a favourable combination of rigidity, ease of preparation, low cost and good controlled release capacity of aqueous solutions, quickly becoming a standard for cleaning polychrome surfaces and paper (86,104,136,138). However, their thermogelifying nature and certain limitations in modulating their structure (e.g. difficulty in widely varying the gelation temperature window or porosity) have stimulated research into more “designable” polysaccharides, such as alginates, xanthan and, above all, gellan gum, which allow for greater engineering of rheological and release properties.

Studies on hydrogels based on sodium alginate, an anionic polysaccharide extracted from brown algae, have demonstrated the possibility of exploiting ionic cross-linking (e.g. with calcium ions) to obtain gels with a stiffness gradient that can be modulated to improve surface adhesion and limit water diffusion into the substrate. Such

systems have shown promise for cleaning sensitive paper, metals and wall paintings, where the use of liquid solutions or less structured gels would pose a significant risk of over-wetting (139–142). Similarly, xanthan hydrogels and xanthan/gellan blends have been studied for cleaning complex surfaces, thanks to their marked pseudoplasticity (high viscosity at rest, reduction in viscosity under stress), which facilitates application and mechanical removal without dripping.

The choice of natural biopolymers is also linked to operator safety considerations. Numerous studies emphasise that the use of polysaccharide-based hydrogels significantly reduces the use of volatile organic solvents and concentrated formulations, as water becomes the main phase of the system (81,135,143). This does not eliminate the use of solvents or more aggressive chemicals, when necessary, but it reduces their quantity, controls their spread and, in many cases, allows solvent-free interventions to be replaced with cleaning procedures that use only water or low levels of additives. For operators, this translates into lower inhalation and skin exposure to hazardous substances. For the environment, in potentially less impactful construction sites in terms of liquid waste management (19,22,115).

Biopolymers also lend themselves to “green functionalisation” strategies, in which relatively benign functional groups or co-components are incorporated into gel networks to confer specific functionalities (e.g. chelating capacity, mild biocidal action, greater affinity to certain types of dirt) (99,135,144,145). Some studies have explored, for example, the combination of biopolymers with inorganic nanomaterials (nanocalcium, nanosilicates) or with more sustainable surfactants to create composite hydrogels capable of removing aged paint or stubborn deposits while maintaining a low hazard profile. Other studies have evaluated the inclusion of small percentages of “green” solvents in biopolymer hydrogels to broaden the spectrum of action towards hydrophobic materials, without sacrificing the advantages of the polysaccharide matrix (146,147).

The use of biopolymers in restoration is not without challenges and requires careful assessment of any residues. Although these materials are generally more biodegradable than many synthetic polymers, their residual presence on hectares of painted surfaces or paper supports can affect wettability, dust attraction, microbiological susceptibility and response to future interventions, especially in microclimatic conditions favourable to biological growth. Accelerated ageing studies and post-treatment analyses are gradually providing data on the behaviour over time of traces of agar, gellan, alginates and other polysaccharides left on artefacts, highlightingthe tendency for relatively effective removal with controlled rinsing, as well asthe need for precise application and cleaning protocols to minimise any unwanted accumulation (104,135,136).

2.6. Green solvents in Cultural Heritage conservation

The use of 'green' and eco-sustainable solvents for the removal of acrylic resins in the restoration of cultural heritage stems from the need to overcome the limitations of traditional organic solvents (ketones, aromatics, halogenated compounds), which are often effective but characterised by high toxicity, volatility and environmental impact (148). Acrylics used as protective coatings, consolidants or paint binders exhibit complex solubility behaviour linked to their copolymer composition, degree of cross-linking and ageing. For this reason, replacing traditional solvents with bio-based or "green" alternatives requires careful planning, taking into account both the polymer's "solubility window" and the safety constraints imposed by regulations and site practice(22,124,149). In recent years, a growing body of literature has focused on the identification and evaluation of biomass-derived solvents, lactic solvents, "green" esters and deep eutectic solvents (DES/NADES), studying their ability to remove aged acrylic films and polymeric coatings from painted and stone surfaces, with a reduced risk profile compared to conventional systems (12,83,97).

One of the best-known proposals in this area is the development of “triads” or sets of bio-based solvents as alternatives to the traditional combinations used in solubility tests and cleaning mixtures (e.g. acetone/ethanol/hydrocarbon-based triads) (119,150). Melchiorre et al., 2023, Discuss the use of green (γ-valerolactone, solketal, ethyl lactate or fatty acid esters) as components of alternative triads, capable of covering a polarity range useful for the solubilisation of many acrylics, while reducing volatility and acute hazard compared to traditional solvents [Fig. 6]. These bio-based solvents generally have lower vapour pressure, higher flash points and superior biodegradability, with potential benefits not only for operator health but also for waste management and the overall environmental impact of the construction site. Solubility studies and practical tests on acrylic paint films and protective resins have shown that these solvents, individually or in blends, can match or in some cases exceed the effectiveness of traditional systems, especially when combined with controlled application strategies (gels, wraps, emulsions) (119,146).

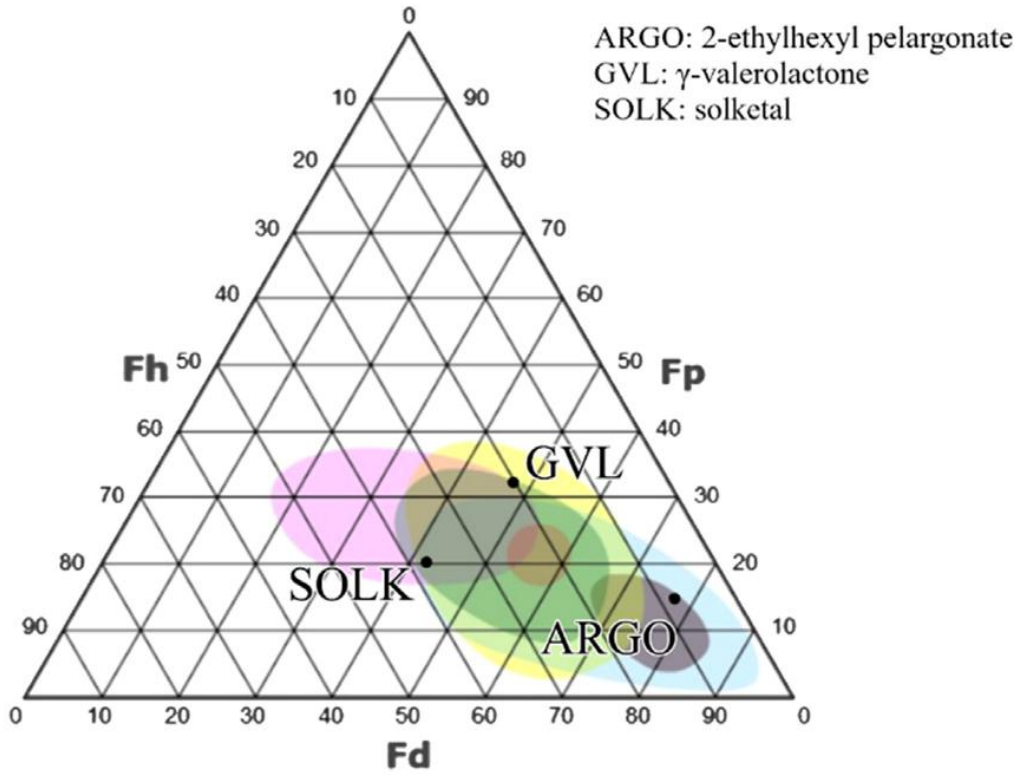

Figure 6. Teas plot with biobased solvent trio (ARGO, GVL, SOLK) and solubilities areas: pink – proteins and polysaccharides; green – natural varnishes; yellow – synthetic varnishes; brown – aged oil paint layers; cyano – fresh oil paint layers; purple – waxes. From Melchiorre et al., 2023 (119)

Attention has also turned to deep eutectic solvents (DES), binary or ternary systems formed by combinations of a hydrogen bond donor and acceptor (e.g. choline chloride with organic acids or urea) which, at certain compositions, generate low-melting-point liquids with modifiable solvent properties (78,129,145,151). Some hydrophilic and hydrophobic DESs have been tested as more sustainable alternatives for removing waxes, polymer coatings and aged paints from wall surfaces and other substrates, often integrating them into polysaccharide gels ('DES-based green gels') to improve penetration control and localised application. A particularly significant study describes a DES-based gel for removing polymer coatings from wall paints, highlighting its effectiveness in solubilising the film and reducing risks compared to

traditional solvents, thanks to its lower volatility, higher viscosity and ability to contain the solvent phase within the gel network (145).

Other studies evaluate the use of DES as dispersion systems or “carriers” for pigments and paint components, suggesting a potential role in the formulation of new selective removal protocols.

However, “green” solvents should not be considered universally safe or free from critical issues. Several methodological reviews emphasise that the classification of a solvent as “green” must consider multiple parameters, renewable origin, toxicity, ecotoxicity, degradability, bioaccumulation potential, energy required for production, recyclability, and that not all bio-based solvents automatically meet these criteria. For example, some biomass-derived solvents may present risks of sensitisation or chronic toxicity or require energy-intensive industrial processes for their purified synthesis, reducing the overall advantage in terms of environmental impact.

For this reason, the most recent studies propose structured methodologies for testing and selecting “greener” solvents, combining sustainable chemistry tools, “greenness” indices (such as GSK or CHEM21 metrics) and specific tests on materials of conservation interest, to avoid “cosmetic” substitutions and aiming at actual improvements in the risk/benefit profile.

The integration of green solvents into gelling matrices, in particular biopolymers such as gellan gum, alginates, agar, xanthan, represents an area of strong growth and great interest for the conservation of surfaces treated with acrylic resins. In these systems, small or moderate fractions of bio-based solvents or DES are dispersed/emulsified in the aqueous phase and then trapped in the gel network, which limits their mobility and deep penetration, improving control of the intervention and reducing the operator's direct exposure to the solvent. Available studies indicate that these “green gels” can effectively remove aged acrylic films and other synthetic

coatings, with minimal damage to the original layers and a significant reduction in toxicological and environmental impact compared to traditional solvent-free strategies. However, research topics remain open regarding the systematic evaluation of residues, the long-term effects of bio-based solvents on original materials, and the definition of shared operational guidelines, all of which will be crucial for consolidating the use of green and eco-sustainable solvents in the removal of acrylic resins as standard practice in contemporary conservation.

2.7. Gamma Valero Lactone

γ-Valerolactone (GVL) is a cyclic lactone derived from lignocellulosic biomass (e.g. through hydrogenation of levulinic acid). It has emerged in recent years as one of the most promising bio-based solvents in the field of sustainable chemistry, thanks to its combination of good solvent capacity, low volatility, relatively favourable toxicological profile and potential production from renewable sources (152–155). In the conservation field, GVL has been proposed as a component of "green" mixtures for the removal of synthetic paints and resins, including some acrylic resins, often as a partial or total replacement for traditional solvents such as ketones and aromatics, with an eye to reducing exposure to high-impact compounds and aligning cleaning practices with the principles of green chemistry (119). Its solubility parameters (intermediate polar Hansen values, high dielectric constant compared to hydrocarbons but lower than water and short alcohols) enable it to interact effectively with moderately polar polymer matrices such as many acrylics, while maintaining a high boiling point and low vapour pressure, characteristics that help to limit evaporation during on-site work (156).

From a chemical-physical point of view, γ-valerolactone has a five-membered structure with a carbonyl group and a cyclic ether that give it a mixture of polarity and the ability to form hydrogen bonds, although it is not completely miscible with all organic matrices. This combination allows the solvent strength to be modulated

by mixing it with other bio-based solvents (e.g. ethyl lactate, solketal) or with aqueous fractions, obtaining systems capable of swelling and solubilising aged polymer films in a controlled manner. Studies conducted on acrylic paint films and protective coatings have shown that mixtures containing GVL can achieve performances comparable to traditional combinations in terms of swelling and removal capacity, particularly when applied through gelled systems (polysaccharide wraps, organogels) that limit its penetration into the original layer. This has led to GVL being proposed as a component of "green triads" for solubility testing and cleaning protocol design, in which a set of 2-3 bio-based solvents covers a polarity range similar to classic triads but with a lower overall environmental impact (115,119,146,147).

A particularly interesting aspect of γ-valerolactone in the context of cultural heritage concerns the possibility of integrating it into gelled or emulsified systems, further reducing exposure risks and improving the selectivity of the action. The inclusion of small or moderate fractions of GVL in biopolymer-based hydrogels or organogels allows its solvent power to be exploited on acrylic coatings and polymer films, maintaining high spatial and temporal control thanks to the gelling matrix, which slows down the diffusion of the solvent towards the underlying layers (99,115,146,153,157). In these formulations, GVL can act as a co-solvent or dispersed phase within water-in-oil or oil-in-water emulsions trapped in the gel, allowing for fine modulation of the interaction energy with the acrylic film and preventing the complete dissolution of sensitive layers or deep interpenetration in porous substrates. At the same time, the lower volatility and greater thermal stability of GVL compared to many traditional solvents reduce the formation of vapours on site, helping to improve operator safety. However, it is still necessary to use appropriate protective equipment and to assess toxicity and compatibility with the original materials on a case-by-case basis, in line with the methodological recommendations on green solvents.

2.8. Conclusion

The conservation of cultural heritage is now at the centre of a paradigm that integrates cultural, social, economic and environmental issues, requiring increasingly selective, reversible and sustainable interventions. In this context, synthetic acrylic polymers, and Paraloid B72 in particular, have played a crucial role as consolidants, adhesives and protective agents, but their ageing, loss of solubility and difficulty in removal have highlighted the need to rethink their use in light of the principles of compatibility, reversibility and risk management.

Traditional removal techniques based on free-form solvents are often effective but difficult to control and have a high impact on operators, the environment and original substrates, prompting research into the development of gelled systems, advanced hydrogels and nanostructured fluids capable of confining the solvent action and improving selectivity. At the same time, the green transition and the European regulatory framework have promoted the introduction of biopolymers, bio-based solvents and DES, paving the way for cleaning strategies with a lower impact but still in need of systematic validation and shared protocols.

Within this context, gellan gum is a particularly promising biopolymer for the design of "tailor-made" hydrogels, thanks to its combination of high gelling performance, good mechanical cohesion, compatibility with sensitive surfaces and the possibility of integration with green additives. γ-valerolactone, for its part, is a bio-based solvent with solubility parameters suitable for interaction with acrylic resins and a more favourable toxicological and environmental profile than many traditional solvents. The convergence of these two fronts, namely gelling biopolymers and green solvents, identifies a high-potential area of research for the controlled removal of aged Paraloid B72. The experimental study developed in this thesis aims to explore, such an area, contributing to the definition of more effective and sustainable operational tools for contemporary restoration.

III. Materials and Experiments

3.1. Materials

PVA (CTS Conservation, 87.7% hydrolysis, Mw = 6.7 × 104 g/mol), sodium tetraborate (borax) (CTS Conservation, Mw = 381.37 g/mol), sodium alginate (Sigma Aldrich, Mw = 8.4 × 104 g/mol), calcium chloride (Sigma Aldrich, Mw = 110.98 g/mol), Pluronic F68 (Sigma Aldrich, Mw = 8,350 g/mol), calibration fluid (Cannon, Instrument Company, viscosity = 96,090mPas at 25°C), Gamma-Valero Lactone GVL (Sigma Aldrich, stated purity +99%), Kelcogel F Gellan Gum (CP Kelco), Paraloid B72 (AN.T.A.RES), Acetone (Sigma Aldrich), Calcium sulfate dihydrate (CTS Conservation), Animal skin glue (Laverdure), Cobalt blue, dark greenish pigment 45701 (Kremer Pigment Inc.), bidistilled water (Sigma Aldrich) are used as received.

3.2. Experimentals

a) Validation of the experimental system, rheological protocol

Rheological measurements were performed on a stress controlled rotational rheometer MCR 702 (Anton Paar, Graz, Austria) equipped with a Peltier unit for temperature control. Tests were performed in the linear viscoelastic regime using the custom-made parallel plate geometry, as illustrated below. A gap of 1 mm between plates was always used for all experiments. To prevent sample evaporation of the aqueous solutions during the measurement, a solvent trap consisting of a low-viscosity silicon oil sealing (ηoil = 0.1 Pa s at 25°C) was poured around the rim of the PLA plate. Oscillatory shear isothermal tests were conducted on the PVA-borax and the alginate-CaCl2 systems at a temperature of 25°C to monitor the sol-to-gel transition as a function of time. Tests included a pre-mixing phase that was made possible by the specially designed set-up of the tools. The Pluronic F68 solution was instead tested at 40°C by monitoring the inverse, gel-to-sol transition upon dilution of the Pluronic solution, whose microstructure changed from soft body centred cubic

(BCC) crystals to a micellar solution [44–47]. In all cases, measurements were performed under an oscillatory frequency of 1 rad/s and a deformation of 3%. Measurements of the PVA-borax and alginate-CaCl2 systems were performed in the same way as follows: an oscillatory time sweep test started with the 1 mm plate gap empty. Then, the two solutions were simultaneously injected inside the plate through the inlet of each channel. The amount of materials to be injected was specifically calculated to exactly fill the gap between the two plates and the cavities inside the 3D-printed plate while achieving a specific final composition. A movie of the procedure is reported in the SI. For the Pluronic F68 solution, due to its high viscosity, it was decided to use a different protocol: the measurement started after loading the aqueous solution of Pluronic. Later, a predetermined amount of water, which guarantees a change in Pluronic F68 concentration such as to produce a transition from a BCC phase to a micellar solution, was injected from both holes.

b) Rheological Characterization of the hydrogels

Rheological properties were measured with a stress-controlled rheometer (Discovery HR-2, TA Instruments, Newcastle, DE, USA) using parallel plates (gap 1000 μm, diameter 40 mm). The control in temperature was ensured by a Peltier system. The edge of the samples was covered with silicon oil to prevent moisture evaporation during measurements. Before each test, the samples are kept at 60°C for 30 minutes to minimize the effects of thermal history. The linear viscoelastic regime was determined by strain sweep test in the strain range 0,01-100 % at the angular frequency of 10 rad/s. Temperature sweep tests were, then, conducted in the range 50-10°C at several cooling/heating rates (5°C/min, 3°C/min, 1°C/min and 0,5°C/min) setting the oscillation frequency at 10 rad/s and the strain at 0,1% (or anyway within the limits of the linear viscoelastic region). Then, some reversed ramp tests have been carried out at 0,5°C/min, to verify the gel thermo-reversibility. Based on the previous experimental results, dynamic frequency sweep tests are performed at a fixed linear strain, within the range 0.1-100 rad/s, at a temperature of

10°C. Finally, to observe the relaxation of the material, a long creep experiment can be performed, and the results of compliance converted in G' and G''. The test was carried out at different stress values within the linear range for 1 hour.

c) Cleaning efficiency evaluation

Hydrogel pads were applied first to slides treated with Paraloid B72 for 60 minutes and their effectiveness during application was observed using an Axioskop 2 plus Zeiss microscope, equipped with a digital camera (Optika C-P12), which made it possible to collect real-time videos and images during hydrogel application on the Paraloid film. Subsequently, hydrogel samples were tested on mockups created in the laboratory for an application time of 10 minutes. The surface of the mockups was analyzed before and after the hydrogel application, using FT-IR spectroscopy performed with a Bruker INVENIO spectrometer in attenuated total reflection (ATR) (spectral range from 15 to 28000 cm^{-1}, spectral resolution 0.085 cm^{-1} and Optical Photothermal IR spectroscopy (O-PTIR) with a quantum cascade laser (QCL). This technique combines optical imaging with high spatial resolution IR spectroscopy (≈ 1 μm) enabling the Paraloid B72 mapping distribution in tiny areas of the sample. The resulting IR maps clearly indicate regions with and without resin and can be overlaid with optical images, providing integrated information on both morphology and chemical composition without direct contact with the sample, O-PTIR probes optically the photothermal effect with a Raman-type green laser of 532 nm wavelength focused on the sample surface through a Schwarzschild objective. The laser is reflected by the sample, the intensity of the reflected light and the one scattered by the sample is detected during the acquisition(158). The angular distribution of the incoming scattered light is determined by the refraction index, which will be modified by the heat change of the photothermal effect, generating a variation in the distribution of the reflected and scattered light. Consquently, the green probe monitors the refraction index change, and allows to retrace the IR absorption. As the probe green laser has a shorter wavelength compared to the IR

spectral domain, this setup allows to increase the lateral resolution by one order of magnitude better than the resolution reached with a classic µ-FTIR system. The system used in this study is a mIRage IR microscope from Photothermal corp. (Santa Barbara) operating in reflection mode, 2 cm^{-1} spectral resolution, with a top-down illumination and a 532 nm visible laser probe that is co-focused with the IR laser source. Measurements were performed using an IR laser power at 6%, a repetition rate at 200 kHz, a pulse width at 200 ns,a green laser probe power at 0.09% detected using an APD detector. The hyperspectral acquisitions were obtained by averaging 4 spectra per point with a step size of 500 nm between each point.

d) Solvent penetration in the substrate, NMR-Mouse

To analyze the interaction between the solvent and the layer of Paraloid B72 to be removed in greater depth, an NMR campaign was conducted to investigate the diffusion times of the solvent in the Paraloid B72 layer. NMR relaxometry measurements were performed with PM2 NMR- MOUSE (Magritek) connected to a Kea2 console (Magritek) and operating at a 27.63 MHz proton frequency with a static gradient of 1.63 MHz/mm allowing a maximum spatial resolution of the order of 20 µm. A high precision mechanical lift makes it possible to scan the sample by 20 µm steps to determine the profile of NMR properties in the depth of the sample.

IV. 3D printed tool to study chemorheology

The system composed of polyvinyl alcohol (PVA) and borax is one of the most extensively studied examples in the literature of hydrogels physically crosslinked through reversible dynamic interactions, based on the continuous formation and breakage of borate–diol complexes along the polymer chains. Its linear and non-linear viscoelastic properties, as well as their dependence on the concentration of the components, on pH (which governs borate speciation), temperature and ionic strength, have been widely investigated, making this system a consolidated benchmark both for the fundamental study of gelled materials and for the comparison between different formulations designed for conservation. PVA–borax hydrogels for the cleaning of historic and artistic surfaces have in fact been the subject of intensive rheological characterization, which has made it possible to finely correlate formulation, microstructure and application performance: oscillatory rheology in the linear regime (mechanical spectra G′ and G″ as a function of frequency) shows a behaviour typical of viscoelastic soft solids, with G′ dominant in the frequency range relevant to handling and application, and a dependence on PVA/borate concentration consistent with the chemorheological framework developed for transiently crosslinked gels (1–4). In this context, PVA–borax is regarded as a particularly effective benchmark because, from an experimental standpoint, PVA and borax are readily available, inexpensive and water-soluble, they allow reproducible preparations over a wide concentration window, and they exhibit gelation that can be controlled via pH, temperature and stoichiometric ratio, without requiring extreme conditions; at the same time, the rheological response covers several phenomena of interest, such as shear thickening at critical shear rates, a relatively narrow distribution of relaxation times in the linear regime, G″ maxima at characteristic frequencies, pronounced non-linearities at high deformations and, in dual cross-link systems, self-healing properties and validity of time–temperature superposition (163). On the application side in cultural heritage restoration, these hydrogels are

supported by a broad body of tests on painted surfaces, paper-based materials and porous substrates, in which PVA–borate formulations in water or hydro/cosolvent systems have been evaluated in terms of cleaning effectiveness, selectivity, substrate safety and residue presence: it has been shown that the system is able to confine and release solvents, chelating agents and other cleaning agents in a controlled way, enabling targeted action and "film-like" removal with low mechanical stress, reduced penetration into the substrate and limited release of polymer residues when the formulation is properly optimised (106,115). Overall, PVA–borax hydrogels, either simple or double-network (when mixed with agarose or PEO), thus fall within the family of physically crosslinked gels with dynamic bonds, for which the rheological response, from linear viscoelasticity to non-linear strain-hardening, becomes a key tool for designing formulations with mechanical and release properties tailored to specific cleaning scenarios in the field of cultural heritage (105–107,163,164); at the same time, the extensive literature available makes them both a scientific and an operational reference for assessing the behaviour of new fast-gelling "green" hydrogels, whose gelation, in this thesis, is investigated from the very first instants thanks to the development of an innovative rheometric geometry, designed and fabricated via 3D printing to monitor in real time the evolution of G′ and G″ immediately after contact between the gel precursors.

4.1. Sample Preparation

a) PVA/Borax

The PVA solution was prepared dissolving 8%wt of PVA in bi-distilled water at 80°C by magnetic stirring at 200 rpm for 8 hours. The solution was then stored for 2 days at room temperature before use. A 4%wt solution of Borax was made by dissolving the salt in bi-distilled water at room temperature by magnetic stirring at 100 rpm for 2 hours until full dissolution. The PVA solution was used in combination with the borax solution in a 4:1 proportion for the gelation in situ experiment.

b) Alginate/$CaCl_2$

Sodium alginate was solubilized in water in a concentration of 2%wt at room temperature and magnetic stirring for 24 hours at 200 rpm. In the same way, a 75 mM solution of Calcium Chloride was prepared. The alginate solution was mixed with the $CaCl_2$ solution in a 5:1 proportion for the gelation in situ experiment, following Besiri et al. (165).

c) Pluronic F68

The Pluronic F68 solution at 45%wt was prepared by dispersing the polymer in cold water at 5°C. The solution was stored at 5°C for five days, and periodically subjected to magnetic stirring at 300 rpm to allow for complete dissolution. The Pluronic F68 solution was mixed with bi-distilled water in a 1:1 proportion for the gelation in situ experiment.

For the PVA-Borax and Alginate-$CaCl_2$ systems, a somewhat rapid increase in moduli is expected due to the formation of chemical networks (166) while for the third system, the reverse trend, that is, a lowering of moduli, is expected for the occurring change in phase transition (167–169).

4.2. Custom-Made 3d Printed Plate

To make in situ rheological measurements, and to obtain information on the early stages of phase transition, a 3D-printed plate was created. The CAD of the plate was developed using the open-source software Fusion 360 [Fig. 7]. The goal was to monitor the kinetics of phase transitions for those two-component systems where two different solutions react when in contact, from the earliest instants.

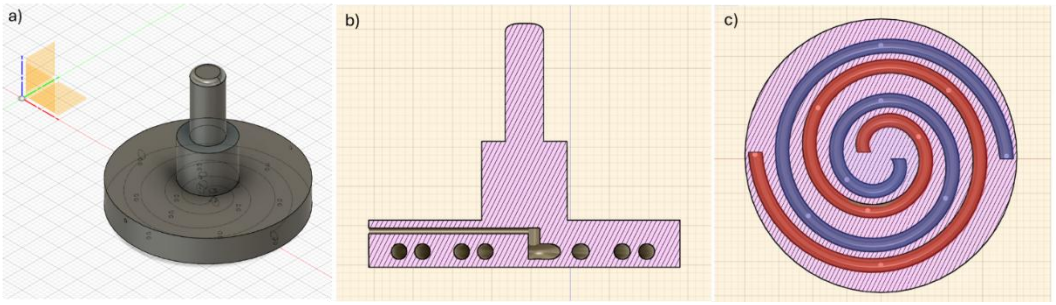

Figure 7. CAD design of the parallel plate, adaptable to the Anton Paar rheometer via the disposable attachment. The drawing shows: a) the whole plate setup with the double internal spirals; b) the middle transversal section of the plate showing the syringe input hole and some exit holes of the spirals; c) the different spirals, coloured in red and blue.

The plate is characterized by a diameter of 40 mm and a thickness of 6 mm, and hosts two small holes on the rim, with a diameter of 0.5 mm. The latter are used to independently feed two fluids, to be brought in contact immediately before the start of the test, upon injection into the channels (diameter 1 mm) by means of syringes. The needles of the syringes (2 cm length) are allocated in a straight channel as shown in Figure 7b), that reaches the plate centre, where the separate spirals receive the two solutions. Along each of the two spiral-like channels there are six equally spaced exit holes (diameter 0.5 mm) for the two solutions. The holes of the six couples are adjacent to each other, so as to guarantee the best local mixing conditions. The spiral shape, in turn, aims at guaranteeing the most homogeneous mixing conditions around the plate surface. It must be stressed that mixing of the fluids occurs only outside the spiral channels, once the rheology test is started.

Following CAD optimization, the next step involved 3D printing of the tool. The printing was done with a Raise 3D E2 printer (Raise 3D Technologies, Inc., Irvine, California), using polylactic acid (PLA). Figure 8 shows microscopic images of the 3D printed tool, obtained with Axioskop 2 plus, Zeiss, equipped with a digital camera (Optika C-P12). The images, analysed with the ImageJ software, show PLA printed

on a single surface (in a and b) and the roughness of the printed layer, measured to be roughly 150 microns.

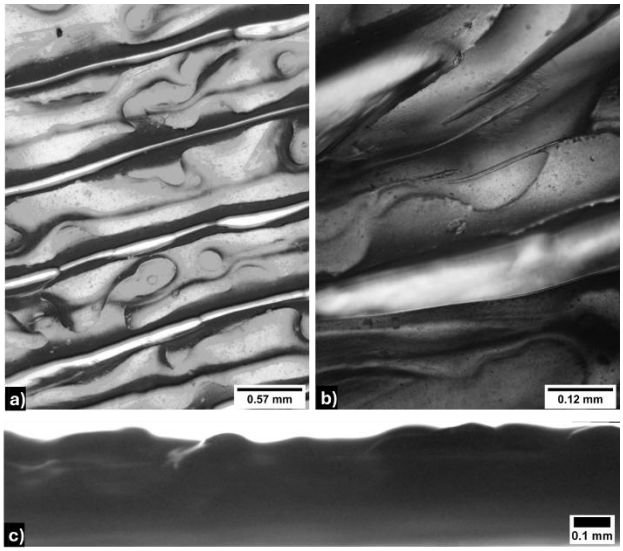

Figure 8. Microscope pictures of the PLA printed layer, captured with a) 3x magnification, b) 10x magnification and c) 3x magnification.

Once the plate was printed, it was mounted on the Anton Paar rheometer using the shaft for disposable measuring tools. Some pictures of the measuring system are shown in Figure 9.

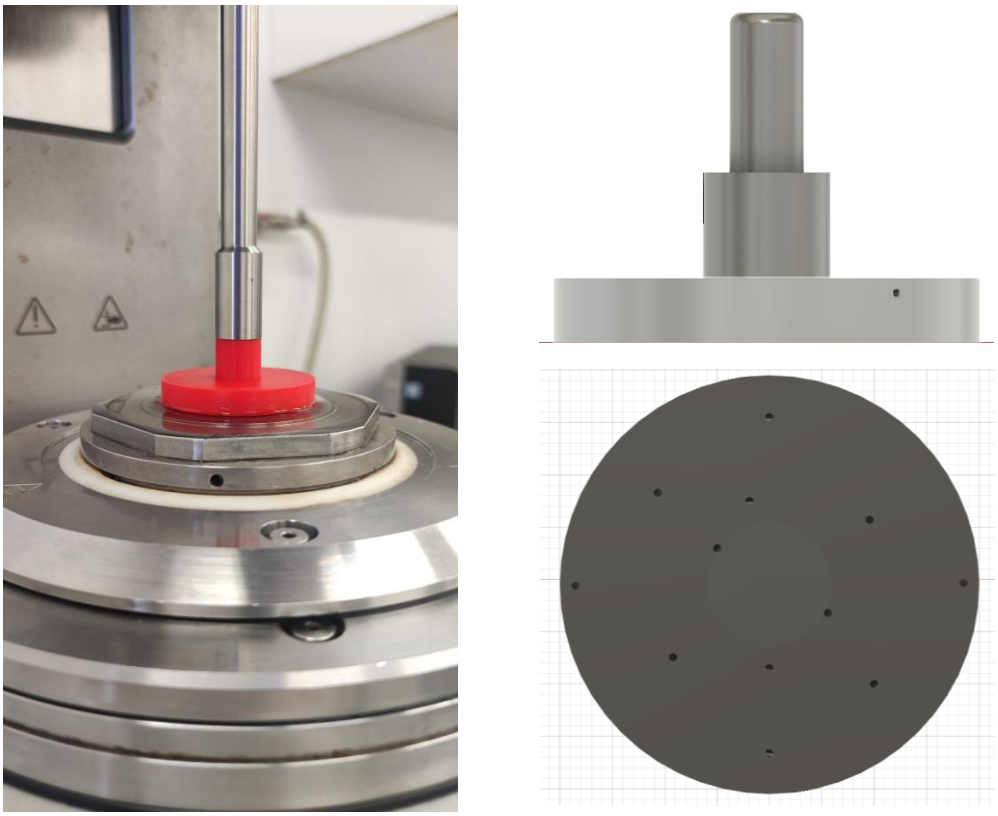

Figure 9. Setup for rheological measurements with 3D printed PLA plate

The new tool underwent all the required steps to be used with the rheometer, including registration of the new geometry, setting of the measuring parameter window, and motor adjustment for inertia correction. As reported below, a calibration fluid was used to compare the performance of the plate with that of the standard tools provided by the manufacturer.

4.3. Rheological Protocols and Measurements

Rheological measurements were performed on a stress controlled rotational rheometer MCR 702 (Anton Paar, Graz, Austria) equipped with a Peltier unit for temperature control. Tests were performed in the linear viscoelastic regime, using the custom-made parallel plate geometry, as illustrated below. A gap of 1mm between plates was always used for all experiments. To prevent sample evaporation of the

aqueous solutions during the measurement, a solvent trap consisting of a low viscosity silicon oil sealing, (η_{oil} = 0.1 Pa·s at 25 °C) was poured around the rim of the PLA plate. Oscillatory shear isothermal tests were conducted on the PVA-Borax and the Alginate-$CaCl_2$ systems at a temperature of 25°C, to monitor the sol-to-gel transition as a function of time. Tests included a pre-mixing phase that was made possible by the specially designed setup of the tools. The Pluronic F68 solution was instead tested at 40°C, by monitoring the inverse, gel-to-sol transition upon dilution of the Pluronic solution, whose microstructure changed from soft body-centered cubic (BCC) crystals to a micellar solution (11,168–170). In all cases, measurements were performed under an oscillatory frequency of 1 rad/s and a deformation of 3%.

Measurements of the PVA-Borax and Alginate-$CaCl_2$ systems were performed in the same way as follows: an oscillatory time sweep test started with the 1mm plate gap completely empty. Then, the two solutions were simultaneously injected inside the plate through the inlet of each channel. The amount of materials to be injected were specifically calculated to exactly fill the gap between the two plates and the cavities inside the 3D printed plate, while achieving a specific final composition. For the Pluronic F68 solution, due to its high viscosity, it was decided to use a different protocol: the measurement started after loading the aqueous solution of Pluronic. Later, a predetermined amount of water, which guarantees a change in Pluronic F68 concentration such as to produce a transition from a BCC phase to a micellar solution, was injected from both holes.

4.4. Results

In order to validate the new tool, the calibration fluid was first used to perform a frequency sweep test, shown in Figure 10. The measurements were compared with those obtained with a standard 40mm, stainless steel plate. Up to frequencies of about 100 rad/s the measurements are essentially coincident, while at higher frequencies some discrepancies are observed. In particular, a spurious cross-over at the highest

frequency can be seen, not expected from the calibration certificate of the fluid and not present in the standard tool data. As a consequence, in the subsequent measurements, frequencies above 100 rad/s were never used.

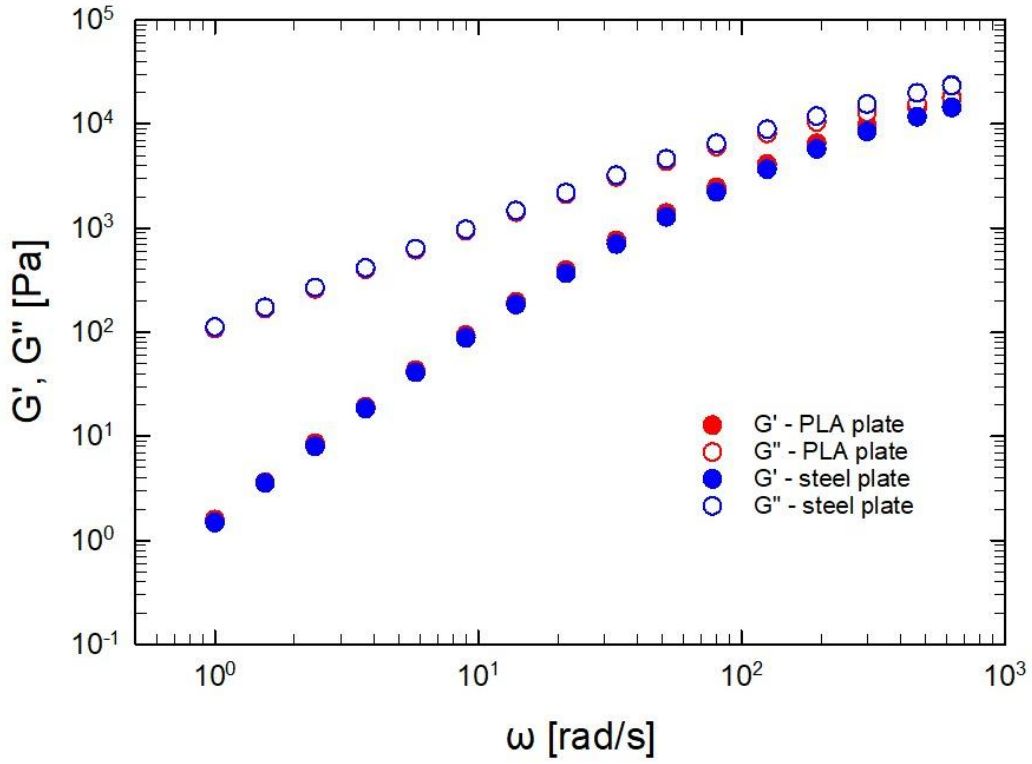

Figure 10. Frequency sweep test carried out on the calibration fluid at 25°C and 1% of strain, with the 40 mm PLA plate (red symbols) and a regular 40 mm steel plate (blue symbols).

The positive results obtained from the calibration fluid measurement allowed us to use the novel setup to make in situ phase transition measurements of different systems. The first system considered is the one formed by sodium alginate and $CaCl_2$. Alginate is a polysaccharide derived from seaweed in the form of a Sodium salt. In aqueous solution, long polymer chains are freely dispersed in water. When $CaCl_2$ is added, calcium ions (Ca^{2+}) replace sodium ions (Na^{+}) on the alginate chain, forming

a water trapping, egg-shaped Alginate-$CaCl_2$, thus transforming the solution into a gel (171).

The gel formation is a rapid process that can be controlled by varying the concentration of both sodium alginate and calcium chloride, as well as temperature. In our case, tests were carried out by injecting 0.9 ml of 2%w/w alginate and 0.2 ml of 75mM $CaCl_2$ aqueous solutions into the two lateral holes of the plate. These concentrations allow to work on a stochiometric excess of alginate in comparison to the Calcium Chloride. The optimal *"merging"* of the systems is guaranteed by the fact that both systems fall between the measuring plates at the same time, and are spatially distributed thanks to the design of the plate. Systematic time sweep measurements were performed to verify alginate gelation. Figure 11 shows the increase in moduli as a function of time, after sample mixing, along with the initial value of the viscoelasticity of the solution before the mixing procedure. The increase of the viscoelastic moduli marks the onset of the gelation due to the presence of $CaCl_2$. The viscoelastic moduli sharply increase up to a final value, characteristic of the gel strength at 25°C.

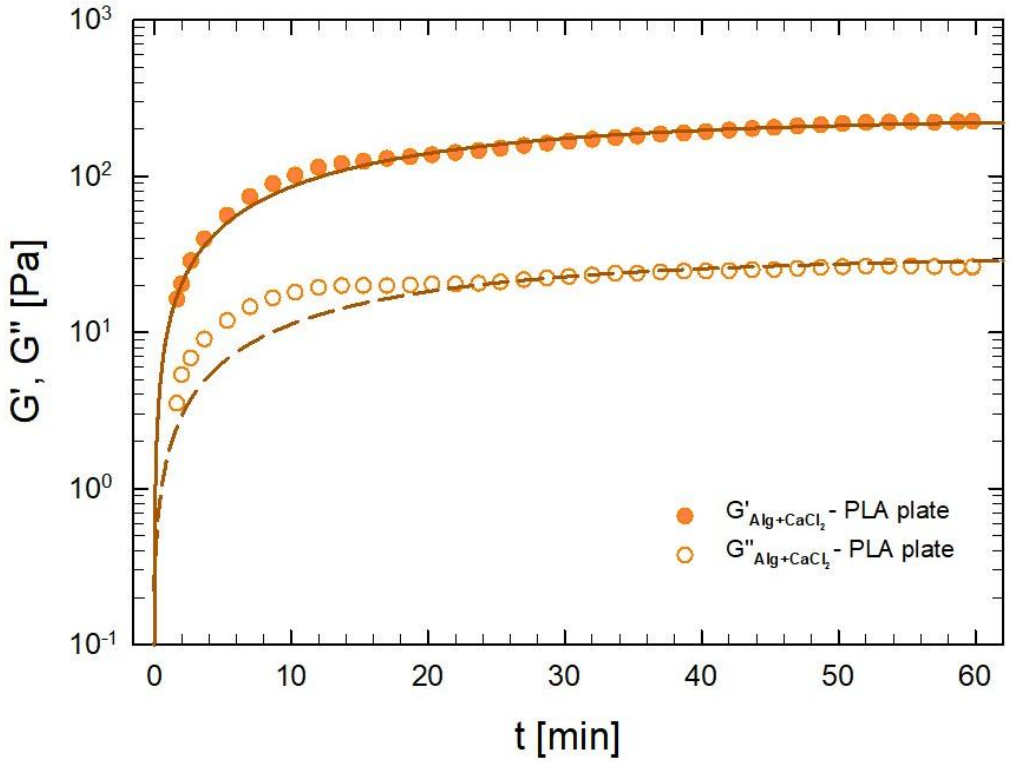

Figure 11. Small amplitude oscillatory shear measurements at 25°C and 3% strain and an angular frequency of 1 rad/s on alginate and $CaCl_2$ samples.

As previously discussed, the blue symbols in Figure 11 are the moduli values of the alginate solution at the final concentration, in the absence of Calcium Chloride. It is evident that the interaction kinetics are quite fast, and the very early stages of gelation are difficult to be caught.

Inspired by the pioneering work of Scott Blair et al. (172) the gelation process can be described by a first-order kinetic reaction in the concentration of the limiting reactant, which determines the final number of chemical bonds in the formed gel (173). The elastic modulus (G') can be, then, considered as an approximate measure of the number of bonds; the most likely kinetic situation in the early gelation stages would be that the rate of increase of G' at any time is proportional to the number of bonds already formed. Later, however, at long times, there should be a deceleration

process as number of bonds diminishes. Hence, the kinetics of gelation can be fitted through the three-parameters exponential raise to maximum equation, as follows:

$$G = G_0 + (G_\infty - G_0) \cdot \left[1 - \exp\left(-\frac{t}{\tau}\right)\right] \quad [1]$$

where G_∞ represents the value of the viscoelastic moduli at time infinite, G_0 is the value of the viscoelastic moduli at time zero (unfitted), τ is the characteristic time of the gelation process and t is the experimental time. This type of fit has been used for the experimental data on G', and the fitted characteristic time τ has been, then, fixed to fit G'' too. The best fit through the data is obtained with the parameters shown in Table 1, and the relative curves are reported in Figure 5 with lines (continuous for G' and dashed for G'').

G	G_0 [Pa]	$(G\infty - G_0)$ [Pa]	τ [min]
G'	0,0007	235,8 ± 4,3	22,17
G''	0,0177	31,0 ± 0,2	22,17

Table 1. Parameters obtained by the fits on the experimental data reported in Figure 4.

It is possible from the parameters presented in Table 1 to evaluate the onset of the gelation process, by measuring the time at which G' equals G''. This time is 0,13 seconds, suggesting that the sol-gel transition is fast.

The results shown in Figure 11 are in line with those already found in the literature. Besiri et al. (174), to monitor in situ the gelation of sodium alginate solutions combined with Calcium Chloride solutions, designed a system similar to the one presented in this paper, where a certain amount of $CaCl_2$ was gradually added to the alginate solution, the last already kept between the two plates. The addition was done from the bottom plate, through two holes, making difficult the mixing efficiency and the temperature control. From the comparison made between the results achieved here and those presented in several papers published by the same group (174,175), similarities were found in terms of the trend of the moduli over time. Unfortunately,

the tests conducted here and those carried out by Besiri and co-workers cannot be directly compared, due to the different type of alginate used.

The same type of test was carried out on the PVA-Borax system. The formation of the gel network in solutions of PVA and Borax is an example of chemical cross-linking that transforms the liquid solution into a viscoelastic gel (176). This process occurs through the formation of hydrogen bonds and chemical interactions between PVA and borax molecules (172). The PVA solution is characterized by the presence of long linear molecules; when borax is added, the latter dissolves in water by dissociating into borate and sodium ions. In the same way, as with alginate and $CaCl_2$ solution, borate ions form complexes via hydrogen bonds with the hydroxyl groups (-OH) present along the chains of PVA. In parallel, the incoming boric acid, that forms when sodium tetraborate is added to an aqueous solution, can also react with the hydroxyl groups of PVA to form boron-ester complexes, producing covalent bonds between the different chains of PVA (177). The combination of hydrogen bonds and boron-ester bonds between the PVA chains creates a three-dimensional structure (178), within which water is trapped, transforming the solution into a viscoelastic gel. As in the previous case, this system shows very fast early stages gelation kinetics, followed by a slower evolution at longer times.

Tests were carried out by injecting 0.9 ml of 8% w/w PVA solution on one side and 0.2 ml of a 4% w/w aqueous borax solution on the other side into the perforated plate. These concentrations allow to work on a stochiometric excess of PVA in comparison to borax. As in the previous case, the rapid increase of the moduli during the first instants of the test marks the onset of the gelation and is followed by a slower kinetics at longer times [Fig.12]. Measurements were also conducted on PVA samples at the same PVA concentration, but in absence of Borax to get an initial value of the moduli before gelation, reported with red circles in Figure 12.

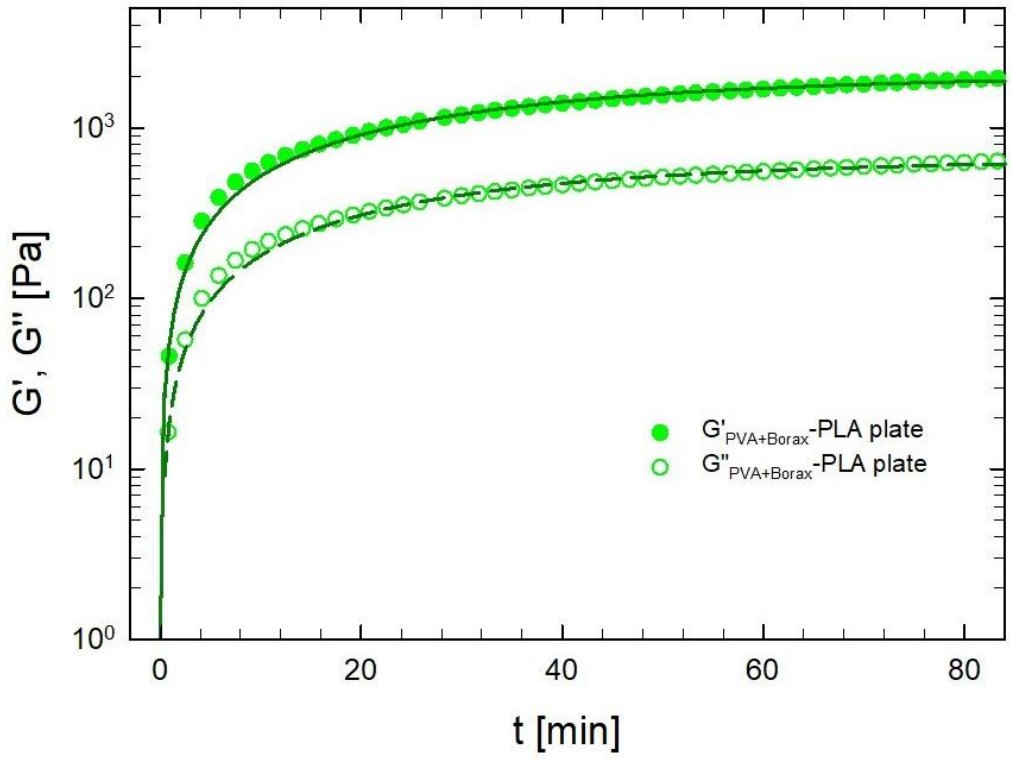

Figure 12. Small amplitude oscillatory shear measurements at 3% strain and an angular frequency of 10 rad/s on PVA and Borax samples.

The test provides several pieces of microstructural information about the hydrogel that has formed: during the first few minutes of the test the rise of the moduli is rapid, as the two solutions in contact begin to react and gel. At later times the gelation slows down due to the decrease in available bonds. The kinetics of the gel formation can be followed, again, by fitting the rheological data with Equation 1, as previously explained. The best fits through the data are obtained with the parameters shown in Table 2. Fitted lines are also reported in Figure 6 along with the experimental data.

G	G_0 [Pa]	$(G_\infty - G_0)$ [Pa]	τ [min]
G’	0,003	2008,6 ± 21,7	32,00
G’’	0,294	661,8 ± 7,2	32,00

Table 2. Parameters obtained by the fits on the experimental data reported in Figure 5.

The characteristic time of the gelation for the system PVA-Borax lasts roughly 30 minutes, with a characteristic time for the sol-gel transition of roughly 0.41 seconds.

A completely different proof of the successful functionality of the novel setup was obtained from the measurement of the aqueous dilution of Pluronic F68 in water. According to the phase diagram of Pluronic F68 (167) at fixed temperature different phases are present. In particular, at 40°C the system undergoes a phase transition from a Body Centered Cubic (BCC) crystalline structure to a spherical micelle homogeneous suspension when the Pluronic F68 concentration decreases. It was decided to carry out an oscillatory time sweep experiment, where water was gradually added through the lateral holes of the plate to the Pluronic solution (to dilute it), thus *"pushing"* the phase transition from a BCC structure to a micellar suspension. To perform the test, the temperature was set at 40°C. 1 g of the 45% Pluronic solution is already present between the two plates, and it is characterized by a solid-like high modulus, due to a BCC phase at these concentration and temperature. Keeping the temperature constant, 1 ml of water was injected (Figure 7), in a way that the Pluronic F68 concentration could reach a final concentration of 22,5%w/w. According to the phase diagram reported elsewhere (167,168), at this concentration the system presents spherical micelles disposed randomly in water, such as characterized only by a viscous modulus. The test was performed for about 14 hours while keeping the temperature constant.

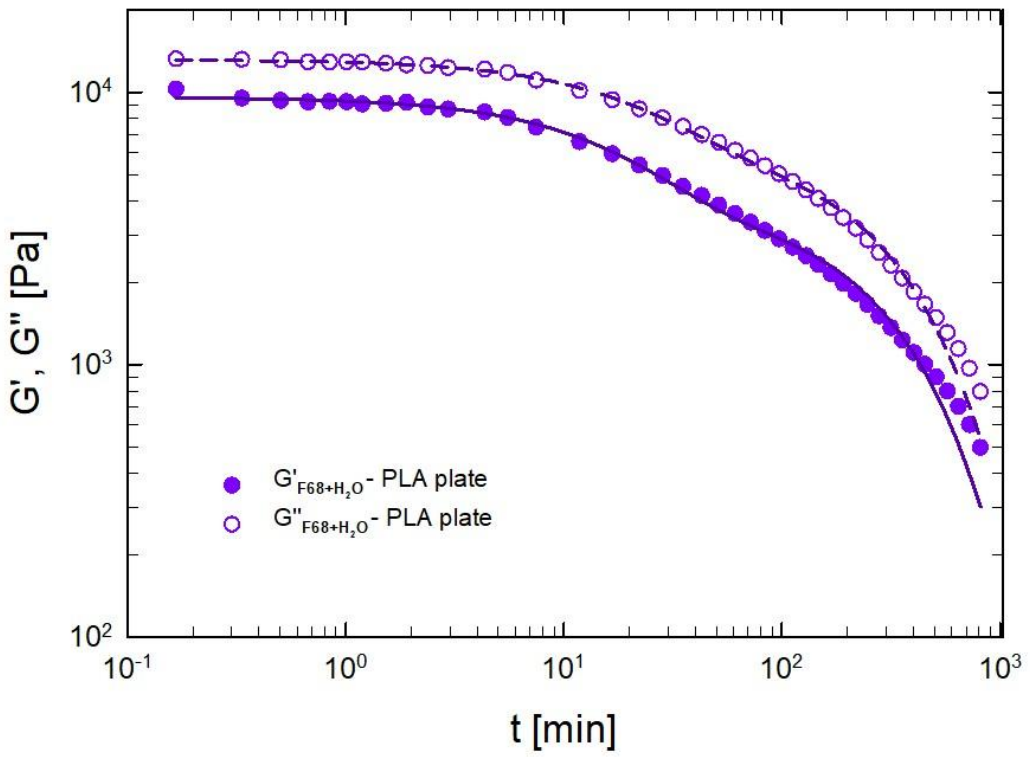

Figure 13. Small amplitude oscillatory shear measurements at 3% strain and an angular frequency of 1 rad/s on Pluronic F68 samples.

Figure 13 shows a completely different trend if compared to the previous two cases. The moduli, indeed, remain stable for roughly 10 minutes, and then drop because of the water diffusion in the BCC structure, and the consequent break of the crystal morphology (culminating in the formation of spherical micelles at very long times). In this case, the kinetics are marked by two characteristic times, as clearly identified by the double exponential decay equation used to properly fit the data:

$$G = G_{\infty} + G_{0,1} \cdot \exp\left(-\frac{t}{\tau_1}\right) + G_{0,2} \cdot \exp\left(-\frac{t}{\tau_2}\right) \quad [2]$$

where G_{∞} (unfitted) represents the value of the viscoelastic moduli at time infinite (i.e. evaluated on the sample with F68 Pluronic concentration of 22,5%w/w), G_{∞} +

$G_{0,1} + G_{0,2}$ represents the value of the viscoelastic moduli at time zero (although G_∞ *is* negligible), τ_1 and τ_2 are the two characteristic times of the process. This type of fit has been used for the experimental data on both the viscous and the elastic moduli (*G* can be *G'* or *G"*). The best fit through the data is obtained with the parameters shown in Table 3, and the relative curves are reported in Figure 7 with lines.

G	G_0 [Pa]	$G_{0,1}$ [Pa]	τ_1 [min]	$G_{0,1}$ [Pa]	τ_2 [min]
G"	0,023	6672,15 ± 138,40	24,33	6508,84 ± 141,12	322,58
G'	0,001	5678,75 ± 143,10	18,86	3909,36 ± 144,00	312,50

Table 3. Parameters obtained by the fits on the experimental data reported in Figure 7.

The presence of two characteristic times, which differ of one order of magnitude, suggests, as previously mentioned, that the dissolution process is probably double step. We speculate that the first characteristic time relates to the diffusion of water within the sample, while the second characteristic time represents the breaking time needed by the BCC structure to transform in randomly distributed spherical micelles. The τ_1 value of *G"* can be used to estimate the diffusion coefficient of water within the gap containing the solution of Pluronic F68. By considering the sample measurement gap, *h*, as the characteristic length of the system, the effective diffusion coefficient (i.e. the diffusion coefficient of water in a Pluronic network characterized by a specific microstructure) can be evaluated as $D_{eff} = h^2/\tau_1$, which brings to a value of $4 \cdot 10^{-8}$ m^2/s.

4.5. Conclusions

This study presents an experimental validation on a new tool, designed, engineered and produced in a way to monitor in situ phase transitions of different materials. One of the advantages of using this tool is the ability to obtain in situ information on the kinetics of fast phase transitions, being them gelation or dilution. With this tool, an attempt has been made to overcome the limitations of the instruments currently used

to carry out measurements of this type, by ensuring optimal merging of two different solutions directly in the measuring system. The main advantage of this new tool is its modularity; since it is 3D printed and designed, it is possible to change the size of the plate, as well as the geometry of the feeding channels, to adapt to different experimental conditions and protocols and to be mounted on any commercial rheometer. Moreover, it is possible to avoid problems such as sample slippage, since the printed surface has a “natural” roughness, typical of surfaces that are obtained by overlapping filament-printed layers.

We validated the use of this tool with two systems undergoing gelation and one system facing a phase transition. The possibility of obtaining information about the early stages of the mixing procedures allows to fit the experimental data and obtain the characteristic times of the processes. The results obtained are consistent with those found in literature, which are in any case limited to the properties of the final product. Nevertheless, there may be some limitations related to the use of this tool, such as the application of high temperatures, that could affect the polylactic acid. This, indeed, softens at temperatures close to 70°C, and could deform in nonlinear regime. A way to overcome these limitations could be to consider the same tool printed with other polymers, for example thermosetting resins (179). We are already working on this option, and on the way to implement for fast in-situ analysis (eg. chirp methodology (180)) by using other rheometers.

V. Rheological Characterization of GVL-Gellan Hydrogel

After the characterization of the benchmark systems (PVA-Borax) presented in the previous chapters, the second phase of the experimental work was dedicated to the design, selection, and characterization of a new formulation capable of simultaneously meeting requirements of functional effectiveness, safety of use, and environmental sustainability. The objective of this phase was not only to identify a material effective in removing acrylic resin, but also to develop a controlled cleaning system that was safe and compatible with the conservation criteria specific to cultural heritage. The starting point for the experimental activity was the identification of the main application objective: the selective removal of Paraloid B72 from artistic surfaces. The choice of this material as a reference is motivated by its widespread use in recent decades as a consolidating and protective agent, as well as by the documented difficulty in removing it, especially in aged forms, characterized by reduced solubility and greater adhesion to substrates. The bibliographic analysis highlighted that, among solvents of natural origin or with low environmental impact, γ-valerolactone (GVL) represents one of the most promising options for the solubilization of Paraloid B72, thanks to its combination of good solvent capacity, favourable toxicological profile, and renewable origin. However, the use of solvents as they are presents known critical issues in the cleaning of artistic surfaces. The use of free solvents can in fact lead to uncontrolled penetration into the stratigraphy of the artifact, an unselective action that can also involve layers not intended for removal, swelling or mobilization of sensitive materials, and a general lack of reproducibility of the intervention. These aspects make the direct application of solvents incompatible with the requirements of safety, selectivity, and reversibility inherent in conservation practice. In light of these considerations, the objective of the research was redefined as the development of a system capable of confining the

solvent within a stable gel matrix, limiting its mobility and modulating its release, allowing for a predominantly contact action and reducing penetration into the underlying layers. In this way, it would have been possible to maintain the chemical effectiveness of GVL against acrylic resin, but in a physically controlled and safer form for complex and sensitive surfaces. For solvent confinement, various gelling agents already used in the field of cultural heritage restoration were considered, including κ-carrageenan, agarose, and xanthan gum, chosen for their proven compatibility and safety. Mixtures containing these gelling agents and GVL were studied using a trial-and-error approach, evaluating their ability to incorporate and retain the solvent, the stability of the gel formed, and the qualitative mechanical response of the system. This preliminary screening phase revealed that the most suitable gelling agent for providing a stable and coherent network is low acylated gellan gum, particularly in its commercial formulation Kelcogel F. Once the most promising matrix had been identified, rheological characterization was used as the main tool for understanding the mechanical behavior of the gel and its stability as a function of solvent concentration. More specifically, this characterization was designed for practical purposes: to verify that the system had physical and rheological properties compatible with use on artistic surfaces, including predominantly elastic behavior, low adhesiveness, sufficient internal cohesion to prevent fragmentation or residue, and stability sufficient to allow controlled release of the solvent. Rheological characterization is therefore a key step in this research, as it allows the chemical composition of the system to be correlated with its functional performance. By analyzing the viscoelastic response of the gel, it was possible to assess how the presence of the solvent affects the structure of the polymer network and to what extent the compromise between solvent efficacy and mechanical stability can be optimized. This chapter therefore illustrates the results of this characterization, relating them to the design objectives of the material and providing the basis for subsequent verification of its effectiveness on model systems.

The objective is to define a range of formulations for which these systems form stable, homogeneous, and mechanically robust gels, distinguishing them from regions of instability or failure to gel. The analysis focuses in particular on identifying the gellan/GVL/water composition window in which the gelled network is well structured, then quantifying the combined effect of polymer concentration and green solvent fraction on viscoelastic moduli and yield stress, studying the frequency and creep/relaxation response, and finally evaluating the influence of composition on the sol-gel transition and thermo-reversibility of the final system.

5.1. Sample Preparation

The system studied consists of gellan gum (KELCOGEL F®) as a gelling agent, γ valerolactone as a green organic solvent, and double-distilled water as a continuous phase. GVL was used in mass fractions between 10 and 40% by weight, while gellan was used at concentrations between 1.0 and 2.0% w/v, to construct a matrix of formulations covering the range of interest for network formation. The three-component solutions were prepared by dissolving gellan in water, then adding GVL and heating to 80 °C under stirring to ensure complete solubilization of the polymer and homogenization of the gel; the samples were then kept at 60 °C until measurement to minimize thermal history effects. Rheological characterization was performed with a stress-controlled rheometer, parallel plate geometry (diameter 40 mm, gap 1 mm), and temperature control using a Peltier system.

5.2. Results

a) Gel formation and dependence on composition

By combining different concentrations of gellan (1.0–2.0% w/v) and γ-valerolactone (0–40% by weight), it was possible to describe how the composition influences gel formation and quality. Within the range explored, three distinct behaviors were observed: systems that remain in a solution state (sol), systems that

give rise to metastable gel structures, and systems in which a macroscopically homogeneous and stable gel forms over time.

Formulations with gellan between 1 and 1.5% w/v and GVL between 20 and 30% by weight lead to the formation of well-structured gels, transparent or only slightly opalescent, without obvious phenomena of syneresis or macroscopic segregation. As the GVL fraction increases further, the response of the system changes markedly: the samples become progressively more turbid [Fig. 14], insolubilized polymer domains appear, and as the GVL content approaches or exceeds 50% by weight, the formation of a continuous gel network is no longer observed.

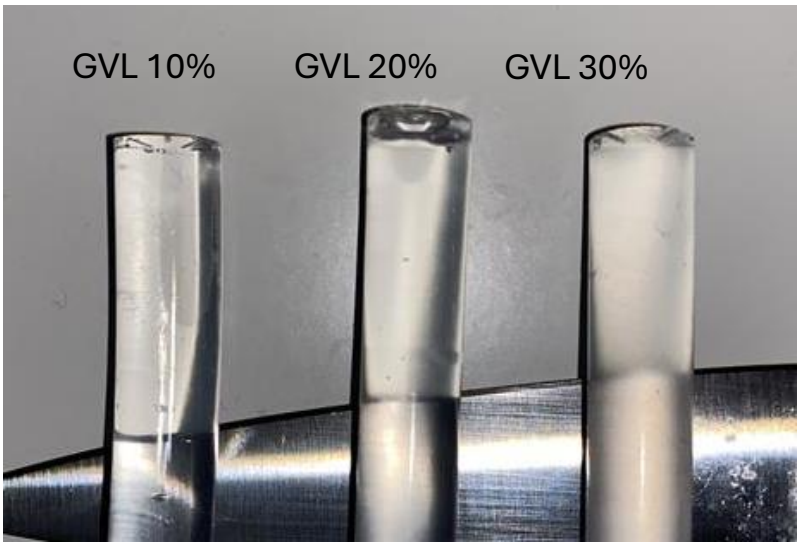

Figure 14. Trasparency of samples with 1,3% of gellan gum and 10%, 20%, and 30% of GVL

These behaviors depend on composition and highlight the structural role of the green solvent: GVL is not simply a “vehicle” added to the aqueous phase, but a component that profoundly modifies the conditions in which the gellan network can form and remain stable. Figure 15 shows, indeed, the presence of insolubilized polymer domains and a highly heterogeneous microstructure for samples

containing high concentration of GVL, in fact, when the percentage of solvent is above the 40% it's possible to see the metastable nature of the system and the loss of homogeneity of the gelled network.

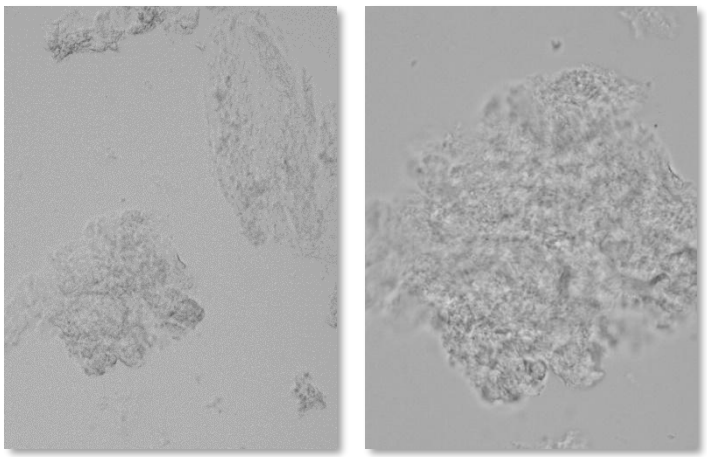

Figure 15. Optical images (10X magnification on the left and 20X magnification on the right) of a sample with 1.4% w/w gellan and 50% w/w γ-valerolactone.

The purpose of this characterization was to determine the range of concentrations, both of solvent and polymer, which would produce transparent gels, when combined, that are stable over time and do not exhibit phase separation. For this reason, several formulations containing increasing concentrations of both gellan gum and GVL were prepared. These were observed over time to assess their stability. Formulations that showed phase separation were excluded from the characterization, as the instability of the system made it difficult to repeat the rheological measurements. Figure 16 lists, highlighted in green, the formulations for which complete characterization was obtained.

		GVL concentration				
		0%	**10%**	**20%**	**30%**	**40%**
Gellan Gum concentration	**1%**					
	1,3%					
	1,5%					
	2%					

Figure 16. Graphical rappresentation of the characterized samples (in green) and the samples where the phase separation was too fast to allow a coherent characterization (in red).

b) Linear response and thermoreversibility

As a reference, gels composed only of water and gellan gum, without GVL were investigated to isolate the effect of polymer concentration on the mechanical properties of the system.

The effect of gellan gum concentration in water was therefore investigated. Gellan is a polysaccharide obtained from the fermentation of *Sphingomonas elodea* bacteria. The polymer chains form a double helix and gel when cooled. It is completely natural and is also used in the food industry as a stabilizing and thickening additive, but also in the field of restoration, at high concentrations (≥ 1%) to create controlled-release gels for the surface cleaning of delicate substrates such as paper.

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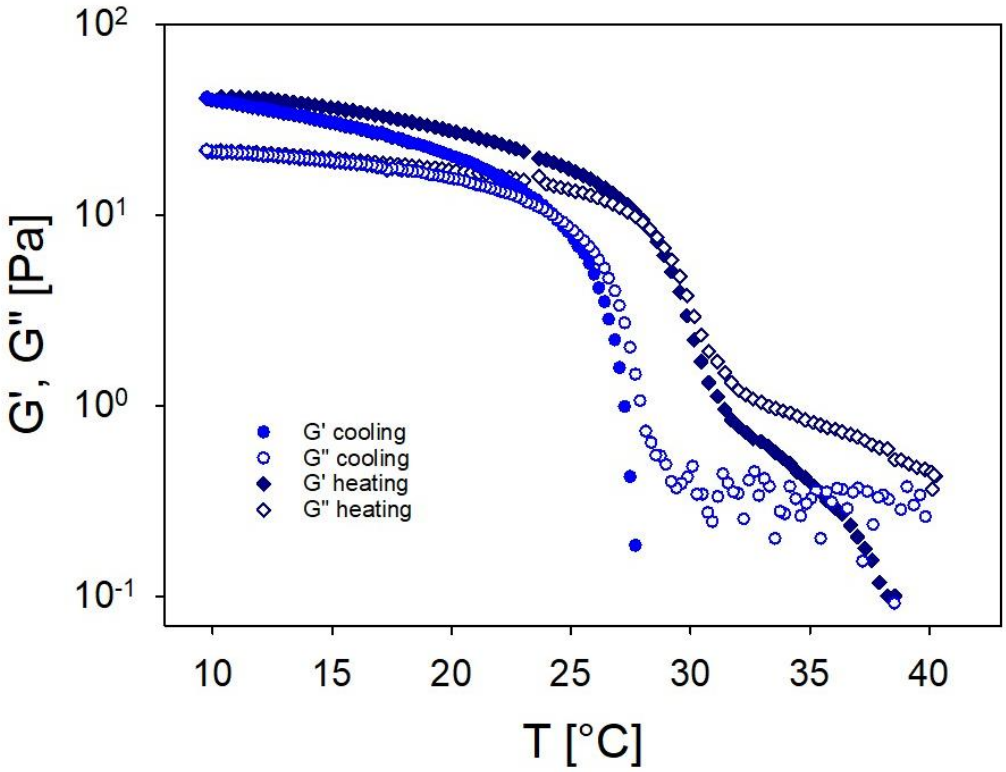

Figure 17. Storage (G') and loss (G") moduli as a function of temperature during cooling and heating ramps at 3°C/min for sample containing $1\%_{w/w}$ of Gellan Gum in water.

Gellan alone in water is thermo-reversible (181), as shown in Figure 17. At high temperatures, the measured G' and G" moduli describe the gellan gel as being in liquid form. In fact, the viscous modulus (G") is greater than the elastic modulus (G'), which is lower than the minimum sensitivity of the instrument used for the rheological measurement of the system. During cooling, a rapid increase in the elastic modulus can be observed, with a consequent crossover of the modules indicating a sol-gel transition. During the heating cycle, on the other hand, we can observe the opposite behavior, i.e., the modules that cross show a gel-sol transition

until reaching high temperatures where the system returns to liquid form with the value of G" returning to be greater than G'.

The effect of adding GVL is immediately evident in Figure 18, which shows two temperature ramps for two different systems containing increasing concentrations of GVL but the same concentration of Gellan Gum (1% w/w) as in the previous figure. In this case, a slowdown in the reverse transition is evident, while the cooling ramps show behaviour similar to the system without the addition of GVL, also showing an evident sol-gel transition. This cannot be seen in the heating ramps, during which the system is stabilized in gel form, showing no transition even at higher temperatures. Comparing the two systems in Figure 18, it can be said that the presence of GVL in the water/gellan system stabilizes its gel form, and this stabilization is even more pronounced as the concentration of the added solvent increases.

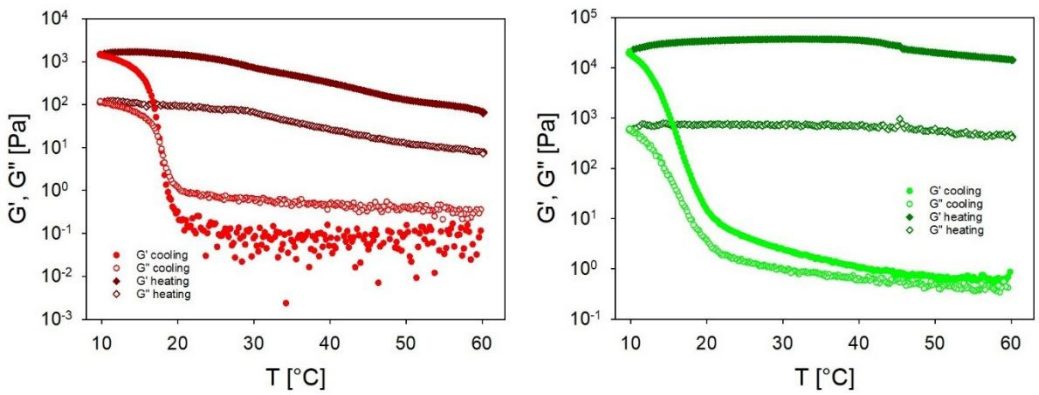

Figure 18. Storage (G') and loss (G") moduli as a function of temperature during cooling and heating ramps at 3°C/min for sample containing 1%$_{w/w}$ of Gellan Gum in water and 10%$_{w/w}$ of GVL (red plot) and 30%$_{w/w}$ of GVL (green plot).

The effect of solvent concentration, as well as that of gellan, is also visible when analyzing the sol-gel transition temperature ($T_{sol-gel}$) value and the intrinsic value of the modules measured for the different systems with increasing concentrations of gellan and GVL.

Figure 19 shows the methodology used to collect the $T_{sol\text{-}gel}$ value for each concentration. Starting from the representation of G* for each sample, the derivative of G* was plotted with respect to temperature. The minimum peak is the temperature at which the transition from sol to gel occurs.

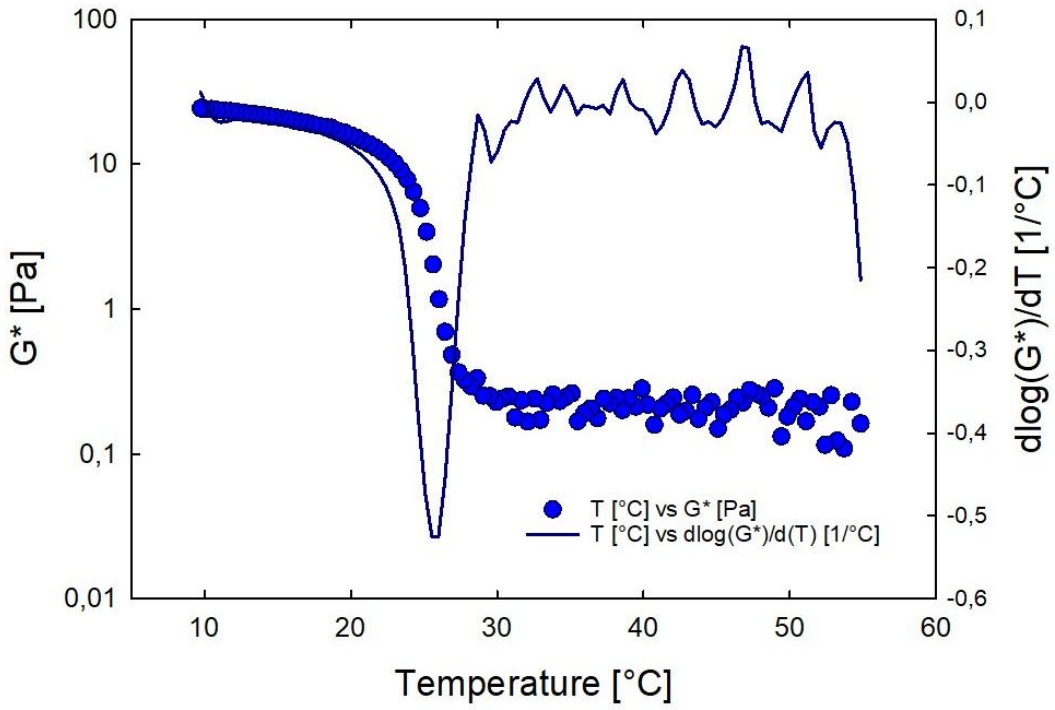

Figure 19. Complex modulus (G*) as a function of temperature during cooling ramp at 3°C/min for sample of $1\%_{w/w}$ of Gellan Gum in water. The derivative curve (dlog(G*)/dT) highlights the transition region with a pronounced peak, reflecting the $T_{sol\text{-}gel}$ of the system.

The graph in Figure 20 shows the trend of the complex modulus G* as a function of temperature for two formulations being compared, both containing 1% w/w gellan and different concentrations of GVL. Specifically, the red graph relates to a concentration of 10%w/w GVL, while the green graph relates to 30% w/w GVL. From the comparison of the plots, it is clear that at low temperatures, the 30%w/w solvent formulation shows a higher complex modulus; this behavior could be interpreted as a more rigid gel structure compared to the formulation with 10%w/w

GVL. Observation of the graph suggests that the presence of GVL may somehow modulate the polymer network formed by GG, influencing the thermal stability and mechanical strength of the gelled solutions.

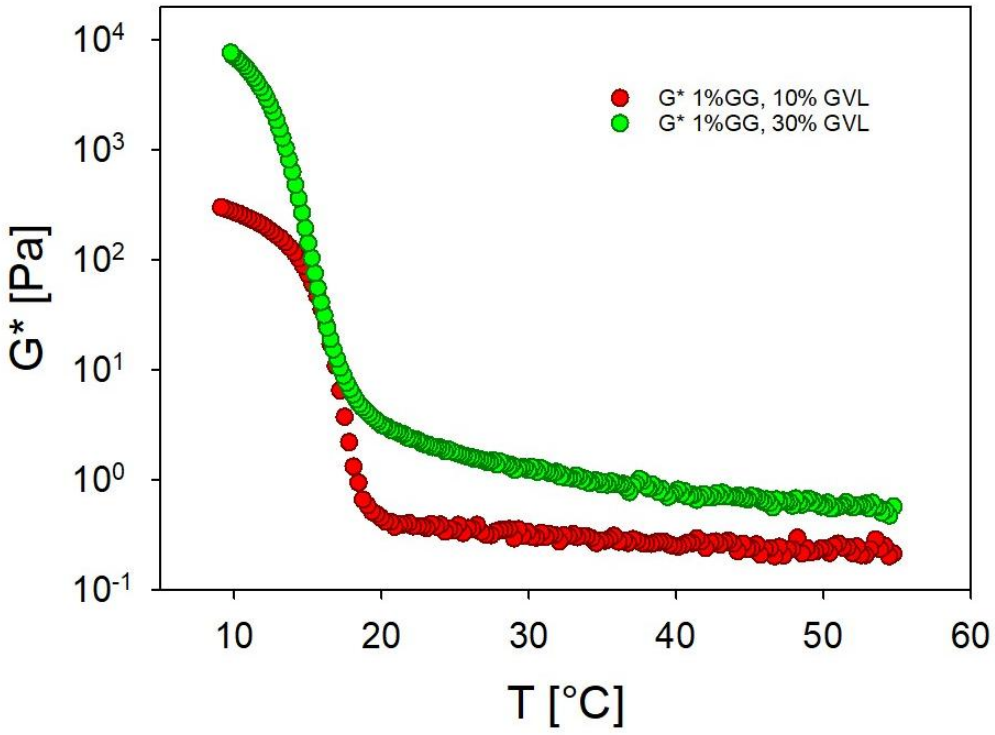

Figure 20. Complex modulus (G*) as a function of temperature during cooling ramp at 3°C/min for samples of 1%$_{w/w}$ of Gellan Gum in water and 10%$_{w/w}$ of GVL (red plot) and 30%$_{w/w}$ of GVL (green plot).

A complete picture of the effect of the solvent on the transition temperature is shown in Figure 21, which compares the sol-gel temperature values as a function of the percentage of GVL for four concentrations of Gellan Gum (1, 1.3, 1.5, and 2% w/w).

The graph shows that for all concentrations, the presence of GVL initially (for low concentrations) leads to a reduction in the sol-gel transition temperature,

suggesting a probable interference of the solvent with the intermolecular interactions of gellan with water or intramolecular interactions between gellan molecules. At the same solvent concentration, a higher concentration of gellan leads to a transition at higher temperatures, indicating a more robust gel network that requires, as we have seen previously, more thermal energy to transition to the sol state.

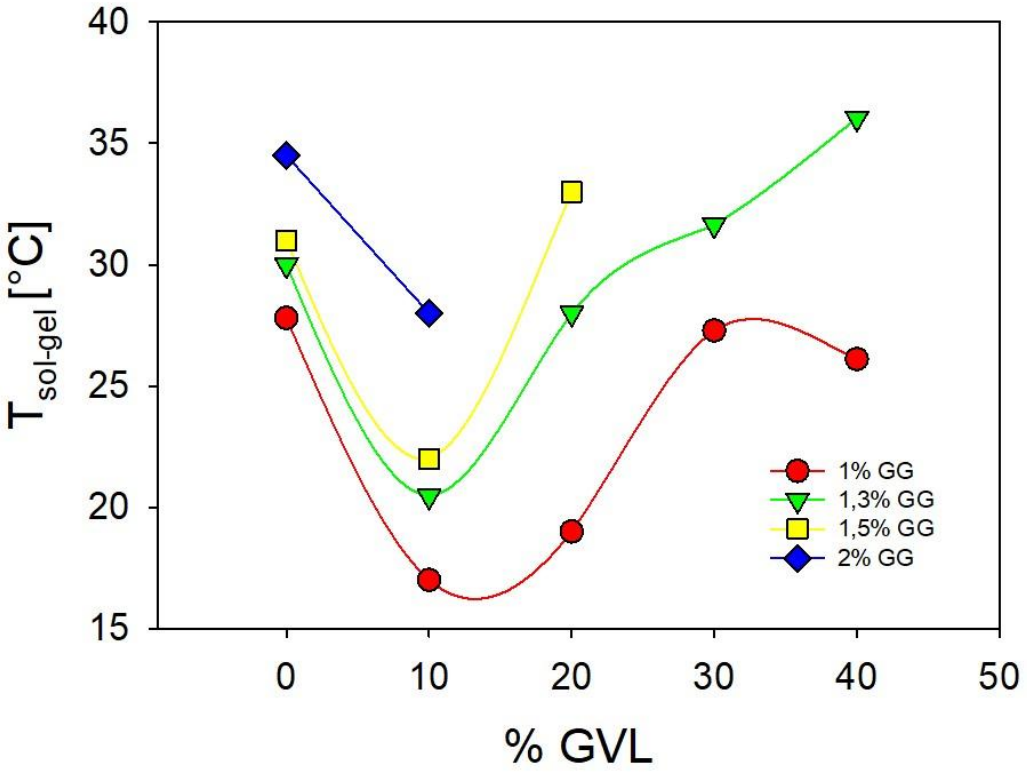

Figure 21. $T_{sol-gel}$ as a function of %GVL, parameterised with % of gellan gum.

Figure 22 shows how the elastic modulus G' varies as the concentration of added solvent increases for the four gellan concentrations analyzed. At the same solvent concentration, an increase in gellan concentration leads to a significant increase in the value of G', indicating a denser and more structured gel network. For all gellan

concentrations, an increase in GVL concentration within 20% w/w tends to raise the G' value, showing a significant increase in gel rigidity compared to gels that do not contain GVL. However, starting at 30% w/w GVL, the observable trend is reversed, the modulus value begins to decrease, suggesting possible interference of the solvent with the formation of the gel network, disrupting intermolecular interactions.

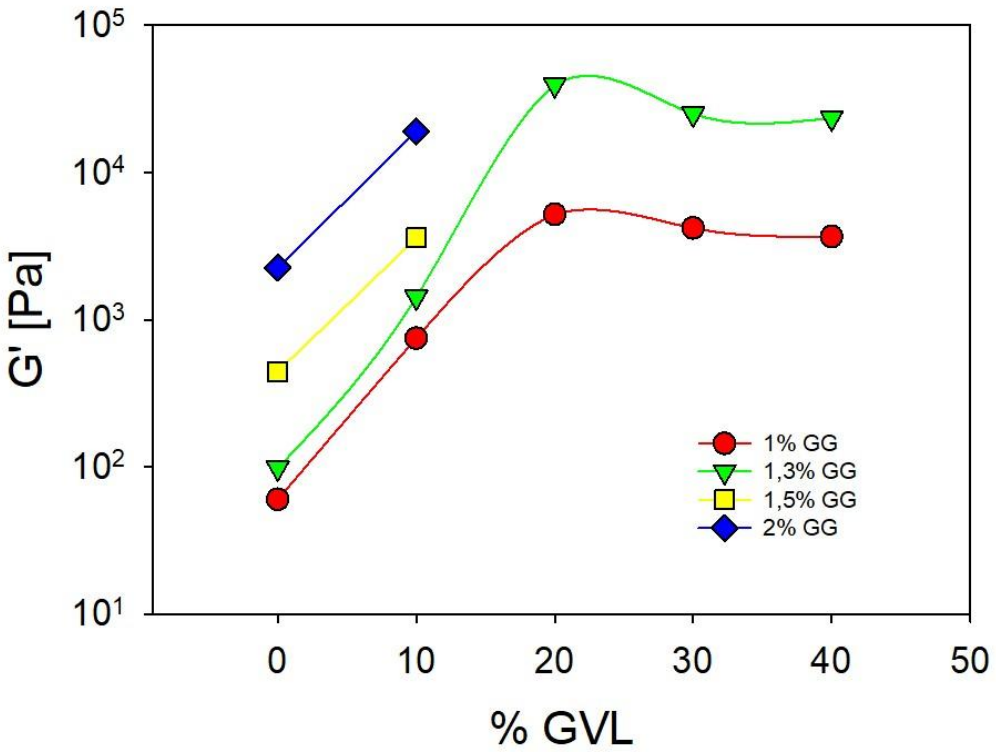

Figure 22. G' as a function of %GVL, parameterised with % of gellan gum.

These data demonstrate how the thermal and mechanical behavior of the GG-GVL system can be finely modulated by adjusting two key parameters: the concentration of the polymer and that of the GVL solvent. An increase in the percentage of gellan gives the system greater thermal stability and more rigid and stable structures, while the addition of GVL lowers the gelation threshold, increasing temperature

sensitivity and modulating the rigidity of the gel. In this way, it is possible to obtain materials with customizable mechanical properties, from more rigid systems to softer and more flexible gels, suitable for applications that require thermal adaptability or controlled release.

c) Non-linear response

Non-linear properties are particularly important for gels used in the restoration of cultural heritage. Gels that break easily, when used on uneven and porous surfaces, can leave active residues on the surfaces to which they are applied and damage them over time. Amplitude sweep tests were therefore carried out on all the gel formulations under examination to understand the behavior of the gel in relation to the amount of solvent and polymer present in it (182). As shown in Figure 23 on the left, the values of G' and G" were plotted as a function of oscillation stress (σ), and the 'break' point of the gel (σ_{yield}) was identified at the crossover point of the modules. Similarly, the strain values were collected from the plots of G' and G" as a function of strain (Figure 23 on the right).

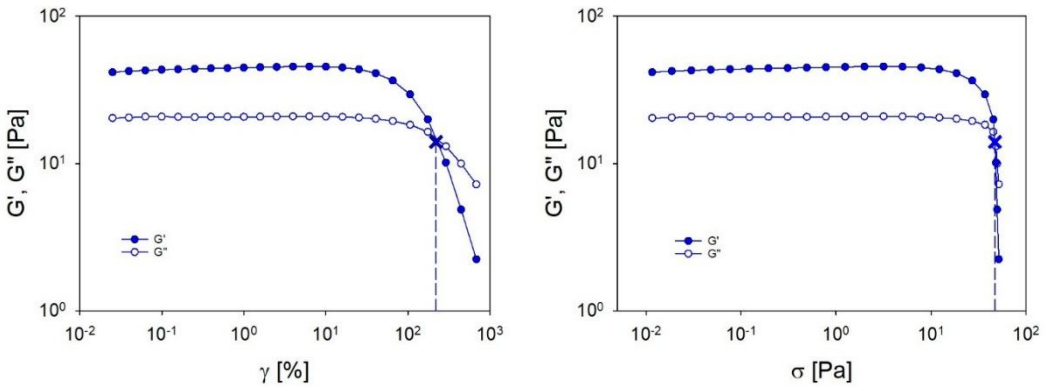

Figure 23. Storage modulus (G') and Loss modulus (G") as a function of strain (on the left) and as a function of the stress (on the right) for sample containing $1\%_{w/w}$ of Gellan Gum in water.

The σ_{yield} values and the the strain values at which the system collapse are reported in Figure 24.

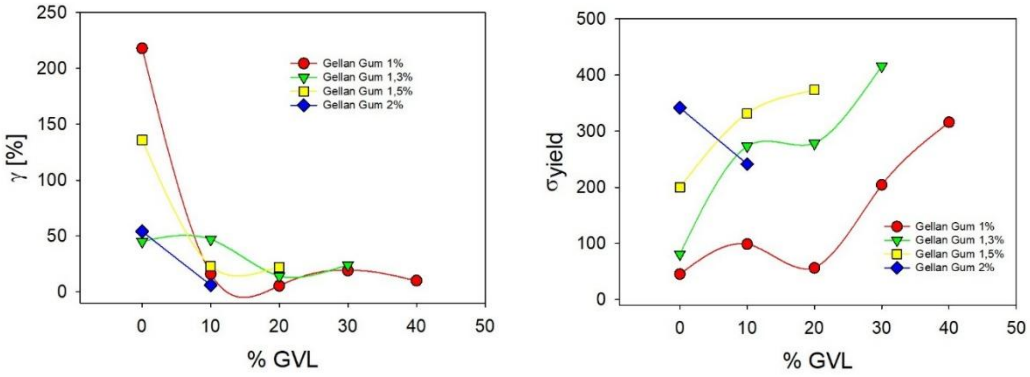

Figure 24. γ (graph on the left) and σ_{yield} (graph on the right) as a function of %GVL, parameterised with % of gellan gum.

The joint analysis of critical deformation and yield stress at the crossover point between the G' and G" modules allows us to clearly outline the combined effect of Gellan Gum concentration and GVL percentage on the mechanical stability of gels. Critical deformation shows that an increase in GVL tends to reduce the material's ability to withstand large deformations before failure, with a particularly marked effect in formulations with low gellan concentration, where the sparser polymer network is more vulnerable to the destabilizing action of the solvent. At the same time, the yield stress trend shows a decrease in the mechanical strength required to trigger structural failure, although with more complex behavior in formulations with higher gellan gum, where the effect of GVL appears to be mitigated or non-linear. Taken together, the two parameters indicate that GVL progressively weakens the gel network, reducing both deformability and stress resistance, but the extent of this effect strongly depends on the polymer network: more concentrated gels maintain greater mechanical strength, while showing a lower capacity for deformation before failure. These results suggest a complex interaction between gellan and GVL, in which the modulation of the composition allows materials with differentiated mechanical profiles to be obtained that are potentially adaptable to specific applications.

5.3. Conclusions

The rheological characterization of the hydrogel system based on gellan gum (Kelcogel F) and γ-valerolactone (GVL) represented a crucial step in the development of an innovative material for the restoration of cultural heritage, aimed at the selective removal of Paraloid B72 acrylic resin from artistic surfaces. Rheological analysis has made it possible to systematically clarify how composition influences the transition from polymer solutions to stable and mechanically robust gels.

From the point of view of linear response, thermal ramp tests confirmed the thermoreversible nature of pure gellan in water, with well-defined sol-gel transitions during cooling and heating, identified by the crossover between the elastic modulus G′ and the viscous modulus G″. The introduction of GVL profoundly modulates this behaviour: the sol-gel transition during cooling remains observable, while the reverse transition during heating is attenuated or suppressed in a dose-dependent manner, stabilizing the gel form. The transition temperature ($T_{sol-gel}$), determined by the derivative of the complex modulus G*, initially decreases at low GVL fractions, probably due to interference with gellan-water interactions, but increases with higher polymer concentrations, reflecting the formation of a more robust network. In parallel, the elastic modulus G′ increases significantly with increasing gellan concentration up to about 20/30% w/w GVL, indicating a strengthening of the network, before decreasing at higher organic solvent fractions due to progressive disruption of the polymer structure. These results highlight the dual role of GVL: at low and intermediate contents (10/20% w/w), it improves network cohesion, increasing storage moduli and expanding the linear viscoelastic region, while at higher concentrations it induces structural heterogeneity and instability, imposing a central constraint on material design.

The nonlinear response, investigated using amplitude sweep tests, allowed us to quantify the linear viscoelastic region and yield parameters, which are fundamental for practical application in the field of conservation. The crossover point defines the yield stress and critical strain, parameters that are crucial for ensuring residue-free gel removal on irregular or porous surfaces. The increase in GVL content systematically reduces γ, making the network more susceptible to deformation failure, especially at low gellan concentrations, while σ_{yield} shows an overall decreasing trend, mitigated, however, by denser networks at high polymer concentrations. The central formulations of the compositional window therefore represent the best compromise between internal cohesion, low adhesiveness, and resistance to fragmentation. Overall, rheological characterization has made it possible to directly correlate the chemical composition with the functional performance of the material, demonstrating that the gellan/GVL system meets the requirements of predominant elasticity, improved thermal stability, and mechanical robustness. Compared to PVA-borax reference systems, this "green" formulation, based on a renewable solvent with a favourable toxicological profile, offers greater safety and control, overcoming the limitations of free solvents such as uncontrolled penetration and poor reproducibility.

Based on this evidence, a system containing 1% w/w gellan and 30% w/w GVL was selected for cleaning artistic surfaces and removing acrylic resins, as it allows a high quantity of solvent to be retained while maintaining an adequate degree of rheological stability. This formulation was then tested on samples that reproduced real paintings in order to verify its cleaning effectiveness and compatibility with the substrates.

VI. Cleaning efficiency

To consider a material truly suitable for restoration applications, its validation must not be limited to physical-chemical and rheological characterization alone but must also include functional testing under conditions that reproduce, as far as possible, the complexity of real systems. This is the context for this chapter, which represents the transition from the characterization of the material to the evaluation of its effectiveness in application, i.e., its ability to selectively remove aged acrylic resin from painted surfaces without altering their constituent materials.

The main purpose of this chapter is to evaluate the effectiveness of the hydrogel developed in removing Paraloid B72 applied with a brush and subjected to artificial aging through exposure to controlled light and temperature. To this end, pictorial mock-ups were created consisting of a linen canvas support, a preparation based on chalk and animal glue, a pictorial layer obtained with cobalt blue pigment dispersed in animal glue, and a surface varnish of Paraloid B72. This stratigraphy was chosen to reproduce in a controlled manner a type of painting system representative of real artifacts and to allow the study of the interaction between the formulation and materials of different nature and sensitivity. The effectiveness and safety of the treatment were assessed using a combination of complementary analytical techniques, including optical observations, FTIR and O-PTIR spectroscopy to monitor resin removal and the possible presence of residues, and portable NMR to study solvent penetration into the paint layer and underlying layers and its evolution over time. This multi-technique approach not only allows verification of whether the resin is actually removed, but also assessment of the extent to which the cleaning system is controllable, selective, and compatible with the original materials of the work.

In the overall context of the thesis, this chapter therefore represents the synthesis between design, characterization, and application. While the previous chapters answered questions relating to the nature and behavior of hydrogel as a material, this chapter addresses the central issue of its functionality as a conservative intervention tool. Attention is focused not only on the effectiveness of removal, but also on the controllability of the process (in terms of penetration and contact times) and the sustainability of the formulation, in line with the growing need to develop restoration methods that are safer for the operator, the work, and the environment. The results presented in this chapter therefore allow us to critically discuss the potential and limitations of the proposed formulation and to evaluate its contribution to the development of innovative, selective, and green cleaning strategies for removing aged acrylic paints from painted surfaces.

6.1. Sample Preparation

a) Hydrogel

Different three-component hydrogel formulations were prepared: Gellan gum concentration was fixed at 1% w/w and GVL concentration was varied at 20, 30 and 40% w/w.

The gellan powder was completely hydrated in water, and, only after, the needed percentage of GVL was added. The systems were placed on a magnetic stirring plate at room temperature for about 2 hours to homogenize the sample. The solution was then heated to 80°C for another 2 hours to achieve complete dissolution. Finally, the hydrogel was poured into preformed molds, cooled, and stored at 4°C for 24 hours. Once solid, the hydrogel blocks were brought to room temperature and stored for about 2 hours before being used for cleaning tests and then applied to the mockups.

To evaluate their cleaning action, hydrogel pads were applied to slides treated with Paraloid B72 for 60 minutes. Hydrogels were also tested on the mockups with an application time of 10 minutes.

b) Mock-ups

Two different kinds of samples were prepared to perform different analysis. On the one hand, a solution of Paraloid B72 was prepared by dissolving 20% w/w of resin in Acetone, and 5 g. of it were applied dropwise onto glass slides and let it dry. In the other hand, some mockups were prepared as described below: a linen canvas was prepared with 3 layers of gesso composed of 60 wt% calcium sulfate powder and mixed with 40 wt% animal glue. The animal glue was prepared by dissolving glue granules in water at a 1:8 ratio (glue:water). Each gesso layer was applied by brush and allowed to dry for 3h before the application of the subsequent layer. After the deposition of the third layer, the sample were left to dry completely for 48h, after which a paint film was applied. The latter was made with animal glue as the binder and Cobalt blue (cobalt aluminate, $CoAl_2O_4$) as the pigment, mixed at a 1:1 weight ratio. Once dried, the paint film was covered with a layer containing 20 wt% of Paraloid B72 in Acetone, to simulate the protective varnish.

All samples and mockups were aged for 2 weeks with a xenon lamp (SUNTEST XLS+, Atlas Material Testing Technology LLC, USA) with the daylight option (without filter). The intensity of the lamp is 50 mW/cm^2, the wavelengths range from 300 nm to 800 nm.

6.2. Cleaning Efficiency Evaluation

a) Optical microscopy

The observation of the Paraloid B72 film under the action of the hydrogel was recorded for 60 minutes, and a series of images were captured during this period. A small amount of hydrogel loaded with different percentages of solvent was applied on a glass slide on which a flake of Paraloid B72 had been applied. A series of images

was therefore collected during its application to monitor and record in real time the softening of the acrylic resin upon contact with the solvent gradually released by the system. Figure 25 shows the effect of three different hydrogels prepared at three solvent concentrations (20, 30, and 40%), applied to Paraloid B72 film. The comparison clearly shows that the solvent concentration affects the softening time of the resin to which the hydrogel is applied. Lower solvent concentrations generate smaller changes in shape than higher concentrations for the same application times.

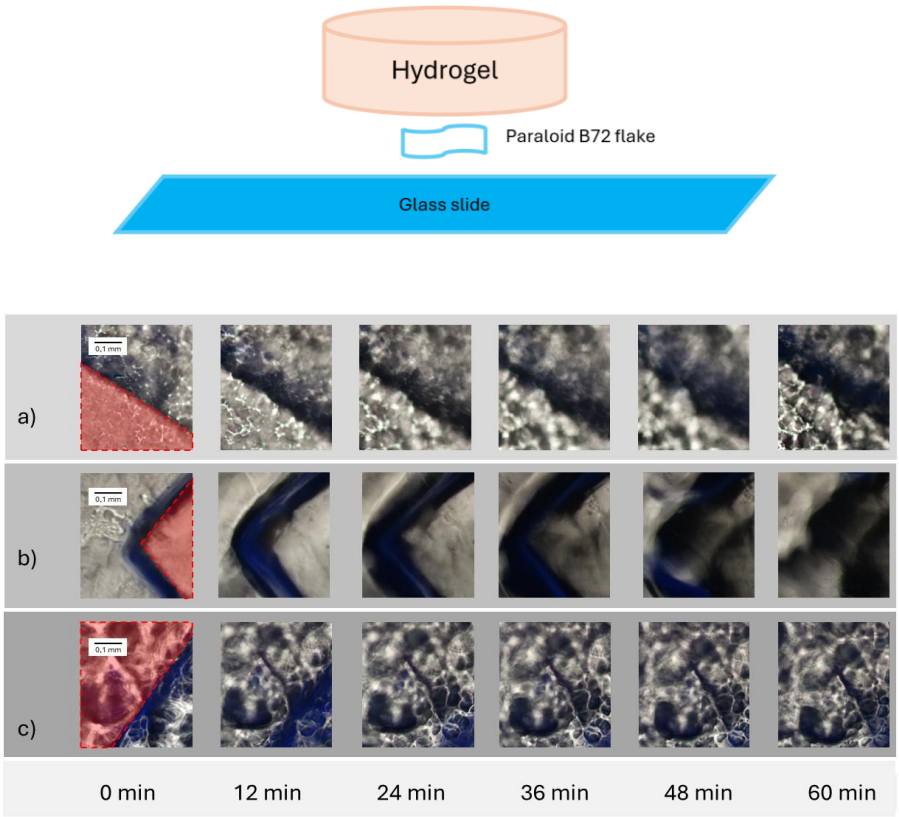

Figure 25. Scheme representing the setup (on the top) and Images of a flake of Paraloid B72 (boundaries outlined in red in the image at time 0) (on the bottom) during the application of hydrogels made by three different percentage of γ-valerolactone. a) application of the hydrogel with 20% GVL. b) application of the hydrogel with 30% GVL. c) application of the hydrogel with 40% GVL.

b) Ft-Ir

To verify the cleaning efficiency of the system under examination, the FT-IR spectra collected from mockups reproducing real samples of paintings on canvas were compared. Spectra were collected from the surface of the painting (glue + cobalt blue) coated with Paraloid both before and after the application of the hydrogel containing 30% GVL. Cleaning tests were carried out by applying a hydrogel pad - obtained by cutting a cylindrical disk with a diameter of 1 cm and a height of 0.5 cm - onto the surface of the sample, leaving it on the surface for a variable time between 10 and 30 minutes [l1](depending on the thickness of the polymer film) and finally lifting it off. The surface was then analysed [l2]using FT-IR to verify the presence of Paraloid B72 surface residues.

The spectrum in figure [26a] was collected on a sample not yet treated with hydrogel. The presence of Paraloid B72 is marked by the band at 1730 cm^{-1}, attributable to the stretching vibration of the carboxyl groups present in the polymer molecule. Comparing this spectrum with the one in figure [26b], collected after the application of the hydrogel, the absence of the Paraloid band is evident, while the fingerprint of cobalt blue, the pigment present in the paint layer, is clearly visible at roughly 450 cm^{-1}. The zoom in the 1000-3000 cm-1 region indicates bands which can be assigned to the glue binder, as well as bands probably coming from residues of Paraloid, still present in the paint porosity.

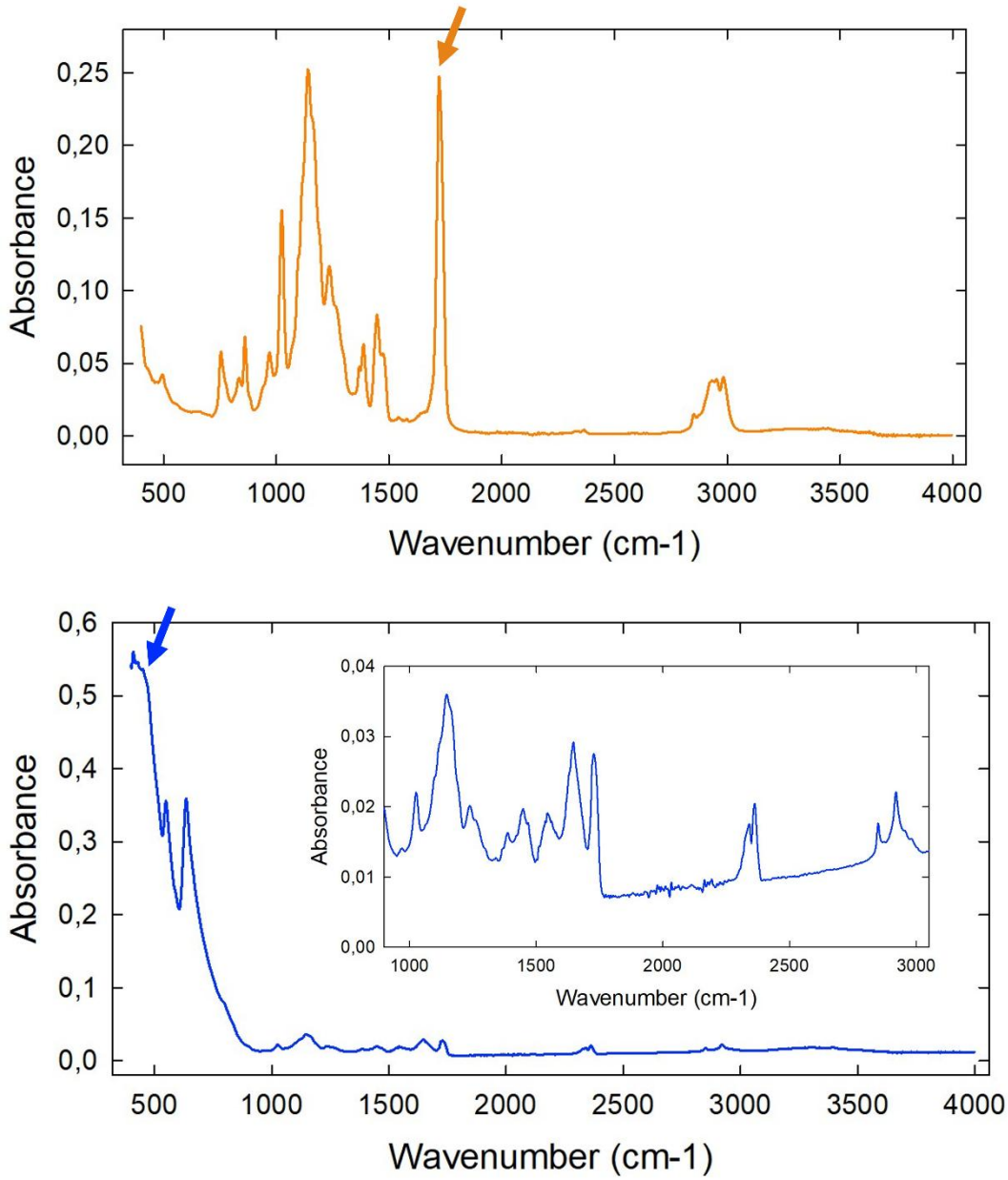

Figure 26. FT-IR spectra comparison between a (graph on the top, in orange) not yet treated area of painting covered with Paraloid B72 and a (graph on the bottom, in blue) treated area with a piece of hydrogel 30% GVL kept on the surface for 15 minutes.

c) O-Ptir

O-PTIR spectroscopy was used to investigate the presence or absence of Paraloid B72 on the treated surfaces of the mockups. The area investigated was selected at the edge of a cleaning test, in a way to include both the cleaned and uncleaned zones. A map showing the intensity of a pre-selected IR band is shown in Figure 27. Again, the stretching vibration band of the carboxyl group typical of the Paraloid resin is visible. The investigation revealed a low intensity of this band in the area subjected to the cleaning treatment, confirming the efficiency of the GVL based hydrogel in removing the polymeric layer.

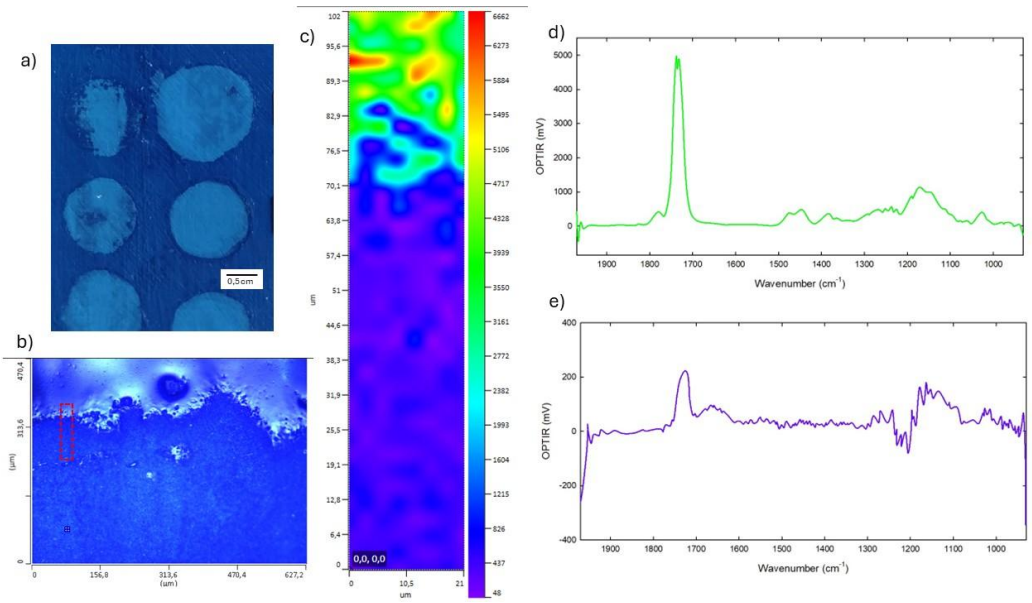

Figure 27. a) Macroscopic image of the analyzed area; b) Microscopic image, highlighting the section analyzed in OPTIR, delimited by a red dotted rectangle; c) Hyperspectral map of the distribution of the reference IR peak of the carboxyl group, at 1730 cm-1, in the area highlighted in (b); d) IR spectrum collected in the area not subjected to cleaning, colored green in the hyperspectral map; e) IR spectrum collected in the area subjected to cleaning, colored blue-purple in the hyperspectral map. Cleaning performed with hydrogel composed of 30% GVL and 1% Kelcogel applied for 15 minutes to the surface to be treated.

6.3. Solvent penetration

a) Single-side NMR Spectroscopy

The diffusion of the green solvent in the Paraloid B72 film and its swelling were studied by collecting NMR profiles from the resin samples deposited on the glass slides. They were treated with drops of water/GVL mixtures, and NMR scans were made at different times after application. Scans were performed from top to bottom, that is, from the outer surface of the sample (the side exposed to the solution), to just above the glass surface of the supporting slide, one single scan last 4 minutes. Different solvent concentrations, namely, 20, 30, and 40%wt, were used.

Figure 28 shows graphs comparing the application of three different free solutions containing increasing concentrations of solvent. Each line within the same graph shows a series of scans of the sample taken approximately three minutes apart. Between the first and the last scan, taken after approximately 60 minutes, a shift of the signal towards the Paraloid sample can be observed, which increases in speed as the solvent concentration increases.

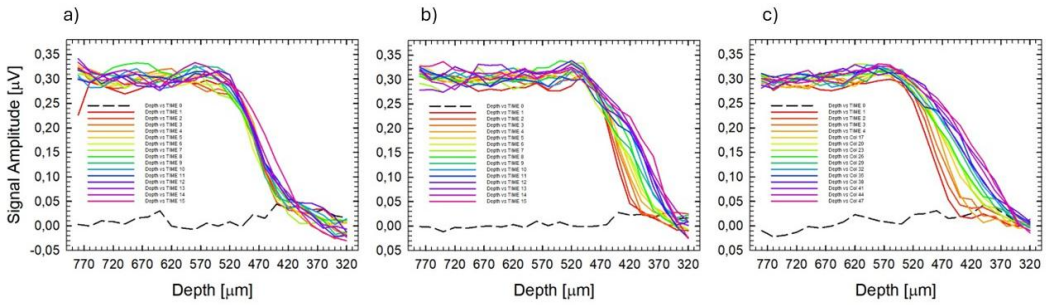

Figure 28. NMR signal amplitude profiles as a function of sample depth for the application of a free solvent (a) 20% GVL, (b) 30% GVL and (c) 40% GVL on a glass slide covered with Paraloid B72

Figure 29 reports the results for the case where the GVL-containing hydrogel is applied onto the sample. Also in this case higher concentrations of solvent accelerate

penetration. GVL penetration, however, is modulated by the gel confinement effect, which clearly slows down the penetration process with respect to the free solvent in water[13] case.

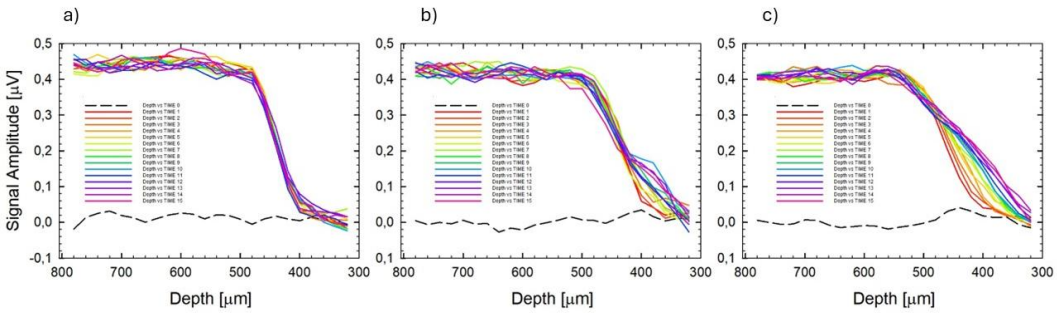

Figure 29. NMR signal amplitude profiles as a function of sample depth for the application of am hydrogel with (a) 20% GVL, (b) 30% GVL and (c) 40% GVL on a glass slide covered with Paraloid B72.

Figure 30 compares the normalized profiles of Paraloid B72 during the application of a 30% GVL solution and that of the same solution confined in the hydrogel. I/I_0 was calculated by dividing the intensity at a given depth by the intensity measured at a depth of 800 nm. The value of I/I_0 at a fixed depth of $\delta = 0.25$ µm—selected because it lies within the Paraloid layer confined between δ_1 and δ_0—was then considered. This ratio at $\delta = 0.25$ µm was further normalized to its value at time zero, ensuring that both curves start from unity, and subsequently plotted as a function of time in Figure 31.

The resulting plot clearly indicates that the presence of the hydrogel slows down the solvent penetration kinetics. In other words, the hydrogel releases the solvent in a more controlled manner, promoting a more uniform diffusion of the solvent into the polymer layer.

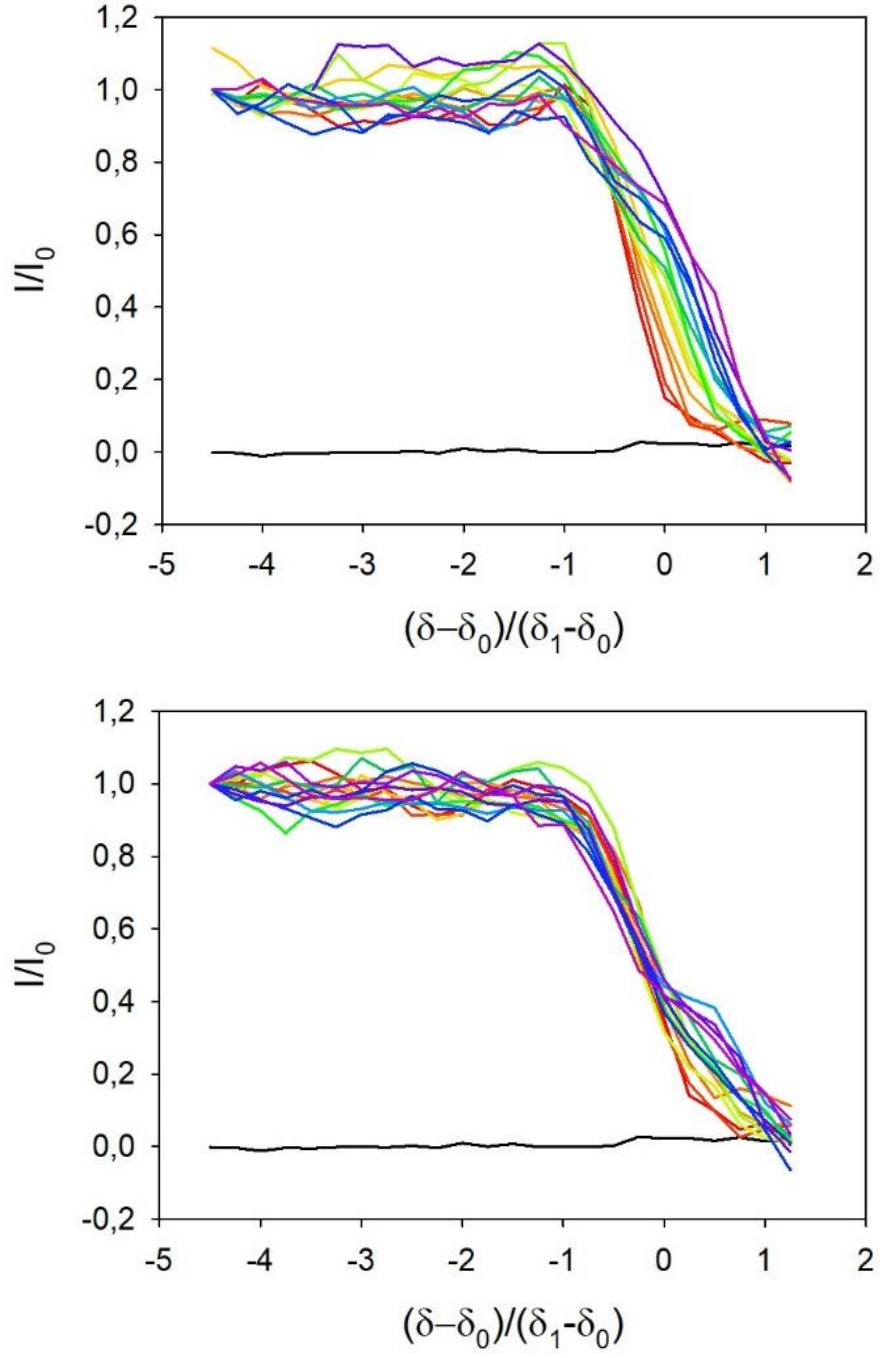

Figure 30. Normalized NMR signal amplitude profiles as a function of sample depth for the application of GVL on a glass slide covered with Paraloid B72 in the case of (a) 30% GVL in water and (b) 30% GVL in the gellan hydrogel.[l4]

b)

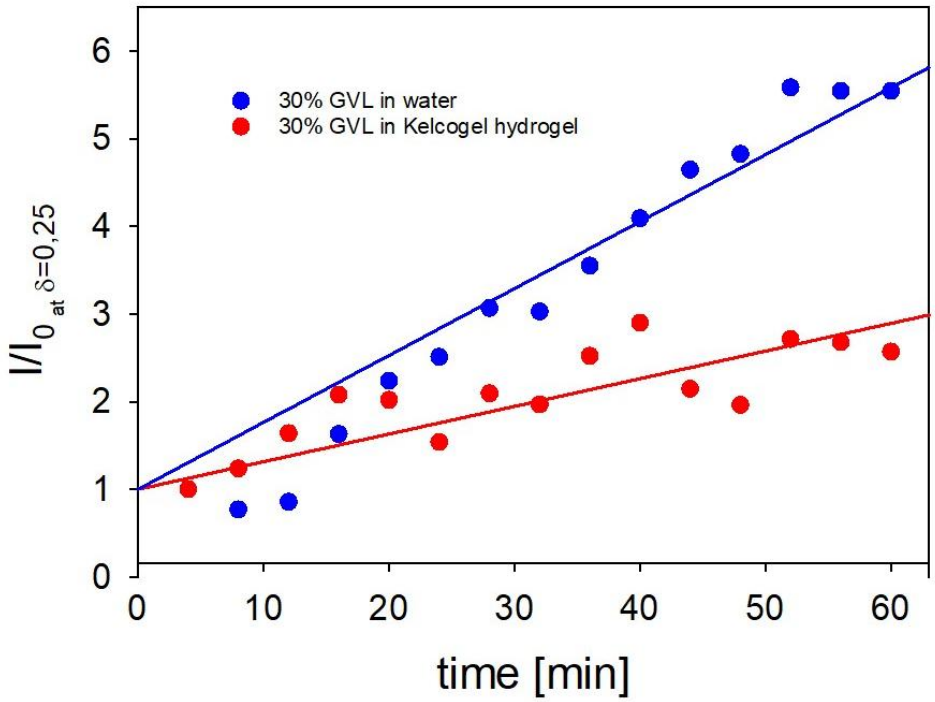

Figure 31. Time evolution of the ratio I/I_0 measured at $\delta = 0.25$ [l5]for a 30% GVL solution in water (blue symbols and line) and for a 30% GVL solution in Kelcogel hydrogel (red symbols and line). Solid lines represent linear fits to the experimental data, with slopes of 9.48×10^{-3} $\text{min}^{-1}$for the blue line and 3.53×10^{-3} min^{-1} for the red line.

6.4. Conclusions

The results of this study confirm that the use of hydrogels loaded with green solvents is an effective and controlled strategy for removing protective layers of Paraloid B72 from glass supports and painted mockups. Direct observation using optical microscopy showed that the concentration of the solvent significantly influences the behavior of the resin: higher concentrations promote faster and more pronounced softening of the surface, while lower concentrations allow for a more gradual and controlled action, reducing the risk of alterations to the support or the underlying paint film. Chemical analysis, conducted using FT-IR and O-PTIR, confirmed the

efficiency of the removal, showing that the areas treated with the hydrogels were rid of Paraloid B72. In particular, the O-PTIR maps made it possible to correlate the chemical distribution of the resin with the morphological characteristics of the surface, providing integrated information on the homogeneity of the removal and any residual areas.

NMR relaxometry investigations provided insight into the processes of solvent penetration into the resin, highlighting that the hydrogel matrix regulates solvent transfer in a more uniform and localized manner than free solutions. This control slows down diffusion, limiting the action of the solvent to the surface layer and reducing potential damage to the substrate or paint film. Analysis of the diffusion profiles also showed that, even when the solvent concentration is increased, penetration into the resin remains modulated by the presence of the gel, confirming the importance of solvent confinement in achieving targeted and safe action.

In summary, the approach based on solvent-loaded hydrogels proved to be a versatile, effective, and controllable method for cleaning painting surfaces protected with Paraloid B72. The combination of microscopic observations, high-resolution chemical mapping, and NMR analysis has provided a first assessment of the cleaning efficiency and solvent penetration, offering a solid basis for the optimization of conservation and restoration protocols that require precision and safety. The results obtained suggest that this approach can also be successfully applied to other acrylic resin systems and artistic supports, opening new perspectives for controlled cleaning interventions on paintings and, more in general, on delicate artistic materials.

VII. Conclusions

This doctoral research is framed within the broader context of the green transition in cultural heritage conservation, where the need to safeguard the material integrity of artworks must be reconciled with the reduction of environmental impact and health risks associated with the materials and processes used. Within this framework, the thesis has addressed the scientific and operational challenge of the controlled removal of aged Paraloid B72 from sensitive substrates, proposing the development of "green" hydrogels based on gellan gum loaded with γ-valerolactone (GVL) as an alternative to traditional methodologies relying on free solvents or incompletely optimised gel systems.

A critical analysis of the literature has shown that, while Paraloid B72 has long been valued for its versatility and apparent stability as a consolidant and protective varnish, its extensive use has also generated significant issues related to ageing, loss of solubility in originally employed solvents and the consequent difficulty of selective removal after long residence times. Conventional solvent-based cleaning methods suffer from limited control over solvent action, risks of extracting original components, uncontrolled penetration into porous substrates and non-negligible impacts on operator health and the environment, whereas existing gel and hydrogel systems, though representing a substantial improvement, do not always meet in an integrated way the requirements of efficacy, selectivity, easy peelability, reduced penetration and improved sustainability now expected in conservation practice.

Against this background, the thesis set out to design, characterise and test gellan/GVL hydrogels, establishing quantitative links between their rheological and chemorheological behaviour, their solvent release dynamics, their cleaning performance on aged Paraloid B72 and their interaction with the substrate. The experimental strategy combined a systematic study of gel formation, sol–gel transitions and viscoelastic responses as a function of composition and gelation

conditions with controlled cleaning tests on B72-coated specimens, complemented by diffusion measurements and multi-technique diagnostics to assess possible substrate alterations.

Rheological and chemorheological investigations demonstrated that gellan/GVL hydrogels can be tuned to exhibit highly controllable mechanical behaviour, in which the balance between elastic and viscous components, the yield threshold and the adhesion/detachment characteristics can be adjusted by varying polymer concentration, solvent content and preparation parameters. Rheological maps made it possible to identify compositional domains in which the gels show sufficient structural stability during application, good conformability to complex surfaces and easy peelability upon removal, with limited formation of macroscopic residues and reduced need for post-cleaning refinement. The integration of oscillatory tests, flow measurements and in situ observation of gelation processes allowed robust correlations to be drawn between preparation conditions, gel microstructure and the ability of the network to retain and release the solvent in a controlled manner over time.

Cleaning tests on samples coated with aged Paraloid B72 indicated that suitably formulated gellan/GVL hydrogels are capable of softening and removing the acrylic film with a good degree of effectiveness, while reducing the use of free solvents compared with conventional protocols. Microscopic and spectroscopic observations, together with colour and wettability measurements, revealed a satisfactory recovery of surface legibility, with colour changes kept within acceptable ranges and no macroscopic evidence of substrate damage under the investigated conditions. The analyses pointed to a significant removal of the superficial B72 layer, with residual polymer predominantly confined to deeper regions of the porous matrix, consistent with the original penetration behaviour of the consolidant.

A particularly relevant contribution of the work lies in the study of solvent penetration conducted through diffusion cells, low-field NMR and complementary techniques, which enabled quantification of GVL transport from the gel to the substrate and comparison with non-gelled systems. The results indicate that, under optimised operational conditions, gellan/GVL hydrogels substantially limit solvent penetration beyond the upper layers of the substrate while still ensuring sufficient contact to solubilise and mobilise the Paraloid B72 film at the surface, thus achieving a more favourable compromise between removal efficiency and preservation of the support.

Taken together, these findings allow several contributions to be attributed to this work. On the scientific side, the thesis offers an in-depth characterisation of the rheological and chemorheological behaviour of gellan-based hydrogels loaded with a bio-based solvent such as γ-valerolactone and proposes an interpretative framework that systematically relates microstructure, mechanical properties, retention and release capability and cleaning performance. On the applied side, it demonstrates the feasibility of a cleaning system that integrates a natural-origin biopolymer, a biomass-derived solvent with a promising sustainability profile, a rheology-driven design approach and a multi-criteria experimental evaluation encompassing efficacy, compatibility and diffusion control. In this sense, the research brings the developed system closer to the "safe and sustainable by design" paradigm in the cultural heritage domain, showing that compatibility with the artefact, technical effectiveness and reduced environmental impact can be combined within a single operational tool.

The study nonetheless has limitations that define the scope of its conclusions and suggest future directions. Cleaning tests were carried out on a finite set of substrates and ageing conditions for Paraloid B72, chosen to represent realistic but not exhaustive scenarios; the response of the gel–substrate system may vary with

substrate nature, porosity, coating thickness and application history, and will require further case-by-case validation before broad generalisation. Moreover, experiments were performed primarily under controlled laboratory conditions, which, while ensuring high reproducibility, do not fully reproduce the complexity of restoration sites, where surface geometry, accessibility, microclimatic variability and operational constraints strongly influence application procedures. In situ testing, conducted in collaboration with conservators and heritage institutions, will therefore be essential to validate and refine both formulations and protocols under real working conditions.

Another area that demands further work is the comprehensive assessment of sustainability through life cycle assessment and risk assessment approaches, covering production, use, waste management and possible long-term effects on operators and the environment. Although the profiles of GVL and gellan gum are promising, a full qualification of the system as a "green" option calls for the integration of additional data and modelling efforts.

Despite these limitations, the results of this thesis open several promising research avenues. One concerns the extension of the approach to other substrates and protective polymers, exploring whether gellan/GVL formulations can be adapted to the removal of different acrylic resins, modern varnishes or more complex multilayer systems. A second direction involves the development of multicomponent formulations that combine gellan gum with other biopolymers or functionalised networks and incorporate low-VOC microemulsions, biodegradable surfactants or chelating agents, thereby broadening the range of removable contaminants while retaining the advantages in terms of control and sustainability. Finally, a third perspective relates to the definition of operational protocols and guidelines for the use of gellan/GVL hydrogels on site, prepared in close collaboration with

conservation professionals and supported by pilot studies on real case studies, so as to translate laboratory findings into practically usable tools.

In this perspective, the research carried out not only advances scientific understanding of gellan-based hydrogels and green solvents for heritage cleaning, but also lays the groundwork for more controlled, informed and sustainable restoration practices, consistent with the shared responsibility towards cultural heritage as a common good and towards future generations.

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