Progress in Organic Coatings 210 (2026) 109730

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Polyvinyl butyral organogels for cleaning of artworks

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ARTICLE INFO

Keywords:
Polyvinyl butyral (PVB) organogels
Cultural heritage conservation
Green solvents
Surface cleaning

ABSTRACT

Novel polyvinyl butyral (PVB)-based organogels have been tailored for the safe cleaning of artworks. The gels were synthesized by cross-linking PVB polymer chains with a polyisocyanate in non-protic organic solvents under mild conditions. High gel fraction values were obtained, and the resulting gels are transparent and elastic, with high cohesion and porosity. Physicochemical and rheological characterizations, including FT-IR, SEM, and oscillatory shear tests, confirmed the formation of stable polyurethane networks and porous structures, suitable for solvent absorption. Solvent loading and release experiments demonstrated high affinity and controlled release for green solvents such as MEK, 2-propanol, and DMC. Cleaning trials on mock-ups coated with a terpenic varnish and a hydrophobic and protective fluorinated oligomer layer showed effective removal with minimal surface alteration, highlighting their potential for treating sensitive Cultural Heritage surfaces. These PVB-based organogels offer an environmentally friendly alternative to traditional cleaning methods in conservation science.

1. Introduction

Artworks undergo natural aging over time, resulting in the degradation of their constituent materials [1,2]. The surface, being the most exposed, often undergoes significant chemical and structural alterations that affect aesthetic appearance and compromise the integrity and readability of the work. Artefacts surfaces act as solid-gas interfaces, with micro-heterogeneous structures both on the surface and in depth. This makes the solid surface, for instance the outermost layer on paintings, wood panels, frescos, ceramics and sculptures, whether protected by a coating or not, especially vulnerable to deterioration due to direct contact with external agents [3–7]. Cleaning is essential to restore the surface aesthetic and prevent irreversible damage to underlying layers. Typically, cleaning targets accumulated dirt, pollutants, aging residues, and deteriorated protective coatings, such as yellowed or insoluble paints or protective agents degraded by oxidation and cross-linking processes [8].

Traditional cleaning methods often employ volatile organic solvents or water-based systems depending on the characteristics of the compounds to be removed or the underlying materials [9–11]. However, the complexity of stratigraphic structure in the substrate, including its porosity and chemical composition, demands highly selective techniques to minimize interaction with the painted layers beneath. The use of free organic liquids is frequently discouraged due to the challenges in controlling solvent action, which can lead to the solubilization and diffusion of removed substances into porous substrates.

Recent advancements have improved traditional cleaning techniques through the development of micellar solutions, microemulsions, and, most notably, gel-based systems [12–16]. The use of gels in conservation brings several key advantages. First, they control the rate of organic solvent evaporation and prevent the solution from spreading to unintended areas or deeper layers, confining the solubilized product inside the gel. Second, gels allow for precise control over the duration of the cleaning process. Finally, the use of gelled systems reduces the risk of exposure to harmful organic solvents, safeguarding both the artwork and the conservator [17].

Traditional thickeners used in restoration such as cellulose derivatives [18–20] and viscous dispersions of poly(acrylic acid) [21,22], often lack adequate retention, exhibit poor mechanical properties, and tend to leave unwanted residues on treated surfaces. To address this issue, chemical gels with stronger covalent networks have been explored, offering improved mechanical properties and reduced risks of residue loss. In the last decade, chemical hydrogels, i.e. gels able to absorb and retain water, have been proposed as optimal matrices to confine fluids for the safe cleaning of works of art. Synthetic hydrogels, made from polymers like polyvinyl alcohol (PVA) [23,24],

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https://doi.org/10.1016/j.porgcoat.2025.109730
Received 5 August 2025; Received in revised form 10 October 2025; Accepted 10 October 2025
Available online 17 October 2025

polyacrylamide (PAAm) [25,26], p(HEMA) [27,28], and PEG [29], offer greater control over key properties, such as mechanical strength, swelling, and porosity. Although hydrogels present many benefits in art conservation, some challenges remain, particularly in developing systems which allow using organic solvents instead of aqueous systems.

Chemical organogels, in which the confined liquid phase consists of organic solvents rather than water, represent a valuable tool in conservation treatments. They exhibit enhanced retentiveness and mechanical integrity, and they enable controlled application of medium- to low-polarity solvents. This expands the range of gel-based cleaning systems to effectively address the removal of coatings and dirt from artifact surfaces. Examples of promising gel systems include gels based on methyl methacrylate (MMA) cross-linked with a dimethacrylate [30,31], and ethyl methacrylate (EMA) polymerized in presence of polyethylene glycol (PEG) and polyvinyl acetate (PVAc) as plasticizers [32,33]. These gels have demonstrated the ability to effectively incorporate low- to medium-polarity organic solvents, such as ketones and alcohols. More recently, castor oil (CO)-based polyurethane gels [34], made by using a polyisocyanate as cross-linker, have emerged as a more sustainable alternative within the organogel family. Each of the organogel systems discussed exhibits advantageous properties, but their formulations often involve multiple components, such as the inclusion of appropriate oligoester chains [35] or plasticizers [33], to achieve desirable rheological characteristics.. Moreover, in all of the above-mentioned systems, a thermal treatment is required to complete the gelling reaction. Simplifying the complexity of the formulation and gelation step represents a relevant advantage in terms of industrial scalability of the process.

In light of these considerations, this study introduces a novel type of organogel with an additive-free formulation and a simple synthesis protocol achievable in mild conditions, yielding gels with adequate transparency, cohesion, elasticity and organic solvents retention/release. The goal was to develop gel formulations able to remove both traditional materials (natural and synthetic finishes) and advanced protective agents. In particular, the removal of protective agents is very interesting, especially when these may present problems due to their dispersion in the environment. In fact, in recent decades, various fluorinated compounds have been employed for the protection, due to their exceptional water and oil repellency as well as their resistance to thermal and chemical degradation [36–39]. However, their environmental persistence and tendency to bioaccumulate have raised significant concerns [40,41]. Given the growing regulatory and ecological pressures, the replacement of fluorinated materials with alternatives free of carbon–fluorine (C—F) bonds is anticipated in the near future. In this context, it is essential to develop removal strategies that enable the controlled containment and safe disposal of fluorinated coatings, minimizing their release into the environment. Gel-based systems loaded with appropriately selected solvents represent a promising and effective solution.

New gels were synthesized using a polyvinyl butyral (PVB), a commercial synthetic resin made by reacting polyvinyl alcohol with butyraldehyde, known for its adhesive, flexible, and tough properties, as well as good transparency and impact resistance, cross-linked with a low toxicity polyisocyanate. Characterization included measurements of Gel Fraction (G%), Equilibrium Water Content (EWC), and FT-IR analysis.

The selection of the solvents covered by the study took into consideration three different criteria: the first concerned the compatibility of the solvents with the chemical structure of the gel on which the rheological/structural properties of the gel itself and retentivity depend. The second concerned the relevance of the selected solvents in the context of conservation, obviously considering the area of solubility as defined by the Hansen parameters (see SI section). MEK, ethanol and 2-propanol are medium polarity solvents widely used by restorers; to this list dimethyl carbonate was added, whose chemical-physical characteristics make it particularly interesting for dealing with medium-low polarity materials to be removed. Finally, DMSO was considered since it is the solvent where synthesis reaction takes place, acting as a porogen agent. The third concerned CHEM21 due to the relevance that the topic of green chemistry and sustainability has assumed in recent years [42]. The evaporation kinetics of the confined solvent, the viscoelastic properties and porosity of the gels were also investigated. Finally, to evaluate the effectiveness of the new PVB-based gels, applicative tests were carried out on a painting mock-up coated with traditional natural resin (Dammar resin) and on a wooden mock-up coated with a novel fluorinated coating [43].

2. Experimental section

2.1. Materials

For the preparation of the gels dimethyl sulfoxide (DMSO) (purity 99.5 %) and 2-butanone (MEK) (purity 99 %) were purchased from Sigma-Aldrich (St. Louis, MO, USA), EASAQUA™ M 502 (EAS), an oligomeric derivative of the hexamethylene diisocyanate (HDI) was provided by Vencorex Chemicals (Grenoble, France), MOWITAL® B 30 T (MOW B30 T) and MOWITAL® B 30 HH (MOW B 30 HH) were provided by Kuraray (Tokyo, Japan). For the loading tests ethanol (purity 95 %), 2-propanol (purity 99 %) and dimethyl carbonate (DMC) (purity 99 %) were purchased from Sigma Aldrich. All the chemicals were used as received. Water was purified by using a Millipore MilliRO-6 Milli-Q gradient system (resistance >18 MΩ·cm).

2.2. PVB organogel production

PVB-based gels were obtained using organic solvents, optimizing reaction conditions and resulting gel properties with small-scale dimensions (2 cm diameter, ~0.4 cm thickness) prepared in glass jars before preparing gel with suitable size for cleaning trials.

Five gel formulations (G1-G5) were developed by modifying the MOW type, MOW/EAS ratio, solvent and temperature as detailed in Table 1.

In the scale up of the most interesting formulations, gels with a 5 cm diameter and 0.4 cm thickness were prepared using Petri dishes as molds, ensuring proper handling for application tests.

As an example, the procedure used for the formulation G2 is reported.

G2 preparation: Gels with a diameter of 2 cm were prepared by solubilizing MOWITAL® B 30 T (50 mg) in DMSO (2 mL) and adding EASAQUA™ M 502 (100 mg). After homogenization the mixture was left to gel in a closed environment at room temperature (RT). Gels with a 5 cm diameter (G5) were prepared following the same procedure with 200 mg of MOWITAL® B 30 T, 8 mL of DMSO and 400 mg of EASAQUA™ M 502. (For **G5 preparation** jars were kept in a MEK-saturated atmosphere to prevent solvent evaporation).

After gelation, the synthesis solvent could be exchanged with other solvents by repeated washing. The complete substitution of the DMSO was confirmed through ^{1}H NMR analysis of the washing liquid. ^{1}H NMR spectra were recorded with a Varian Mercury plus 400 or a Varian INOVA spectrophotometer (both operating at 399.921 MHz), dissolving

Table 1
Gelation factors of the formulations G1-G5.

Formulation	MOW	MOW/EAS ratio	Solvent system	Gelation temperature (°C)
G1	B 30 T	1:1	DMSO	20[a]
G2	B 30 T	1:2	DMSO	20[a]
G3	B 30 T/B 30 HH (70:30)	1:2	DMSO	20[a]
G4	B 30 T	1:2	DMSO	38
G5	B 30 T	1:2	MEK/DMSO (92:8)	20[a]

[a] Room temperature (RT).

the samples in $CDCl_3$. All spectra are reported in ppm and referred to tetramethyl silane as an external standard. The spectra were processed using the MestReNova v6.0.2–5475 software.

2.3. Physicochemical characterization of gels

The Gel Fraction (G%) was determined gravimetrically through the formula (1)

$$G\% = \left(\frac{W_d}{W_0}\right) \times 100 \quad (1)$$

where W_d is the dry sample weight after solvent replacement with demineralized water via serial washings, followed by drying at 120 °C for 4 h. Since DMSO low volatility prevents direct dry weight measurement, W_0, which typically refers to the weight of a dry sample obtained after drying at 120 °C for 4 h without washing, is estimated as the total weight of MOW and EAS used in synthesis, assuming no loss of volatile by-products.

Equilibrium Water Content (EWC) measures the percentage of water retained by a gel when its moisture stabilizes under specific conditions (20 °C, 80 % RH). It is calculated using the formula (2)

$$EWC = \left[\frac{(W_w - W_d)}{W_w}\right] \times 100 \quad (2)$$

where W_w is the gel wet weight after solvent replacement with demineralized water via serial washings, and W_d is its dry weight after the same washing process, followed by drying at 120 °C for 4 h.

Chemical composition of the gels was analyzed through FT-IR spectroscopy. FT-IR spectra were recorded with a Shimadzu FT-IR model IR Affinity-1S and processed with the Lab Solution IR v. 2.16 program. The spectra of solid samples obtained from dried gels were recorded in transmittance mode with KBr pellets. The spectra were collected from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} and 45 scans.

Morphology was observed via SEM. Before performing the electron microscopy analysis, the gel was dehydrated by freeze-drying. After a preliminary immersion in liquid nitrogen for a few minutes and after freezing, each sample was kept at extremely low temperature and pressure (−50 °C, <200 mTorr) for two days. Subsequently, the samples were made conductive through the surface metallization process with a thin layer of gold. SEM images were acquired with a FEG-SEM ∑IGMA (Carl Zeiss) with an acceleration potential of 10 kV and a working distance (WD) of 4.8 mm.

Oscillatory shear measurements were performed on a Discovery HR-3 rheometer operating under controlled shear stress, featuring a plate-plate geometry with a 20 mm diameter plate. The dependencies of the moduli G' and G" on the oscillation frequency were obtained from the phase delay between the applied shear stress and the correlated flow and the ratio of the imposed oscillation amplitudes to the gel response. G' and G" were measured in the frequency range of 0.001–5 s^{-1}. The stress amplitude values were checked by an amplitude sweep test to ensure that all measurements were performed within the linear viscoelastic region. After loading, all samples were equilibrated for 3 s at 25 °C before conducting the experiments. All measurements were performed at a temperature of 25 °C.

2.4. Gel retention and release capacity

Gels underwent a washing cycle with selected solvents, replacing the synthesis solvent. Solvent affinity is evaluated by calculating the absorption percentage (Abs%) using the formula (3)

$$Abs\% = \left[\frac{(W_s - W_d)}{W_s}\right] \times 100 \quad (3)$$

where W_s is the gel weight after washing, and W_d is its weight after drying in a desiccator for at least three days. Affinity was tested with common solvents and mixtures used in conservation for applying and removing protective products. The selection was based on their compatibility with both the PVB-based gel scaffold and the target coating, all within the medium polarity range: MEK, 2-propanol, ethanol, water/ethanol (30:70) and DMC (Hansen solubility parameters reported in Table S2).

In addition, to better clarify the role of the gel in the cleaning process and the active role of the selected solvent it would have been relevant a direct comparison with the behavior of PVB gel swollen with water or the direct application of gel without solvent, but both these experiments were not achievable since the loading of water into the gel quickly change the structure because of polyurea formation, with a significant loss of the gel mechanical properties. On the other hand, the application of gel without solvent is not possible because, upon drying, the consistency of the system changes completely, taking the form of a plastic film.

To quantify the release capacity of the new systems, the solvent-loaded gels were gently dabbed to remove excess solvent from the surface and placed on a layer of 28 sheets of Whatman paper (3 × 3 cm). To prevent solvent evaporation, the gel in contact with the paper was covered with a transparent film. The amount of solvent released onto the paper was determined gravimetrically, normalized by the contact area. The paper weight was measured initially (time 0), at 30 min, 1 h, and hourly until a constant weight was achieved. The release rate was calculated using the formula (4)

$$Release\left(\frac{g}{m^2}\right) = \frac{(W_f - W_i)}{A} \quad (4)$$

where W_f is the weight of the paper after absorption, W_i is the weight before absorption, and A is the contact area of the gel with the paper, calculated from the gel diameter.

To assess the evaporation rate of the solvent present inside the gel, evaporation tests were performed on PVB-based gels. The evaporation rate was compared to that of the same solvent in its free form. The solvent content within the gel network was determined by subtracting the weight of the reagents used in synthesis from the total gel weight, then normalizing with respect to the gel G% value. The same quantity of free solvent was also weighed. Both the loaded gel and the free solvent were placed in identical containers. By weighing both containers at regular intervals, a graph was constructed to show the decrease in solvent content over time.

2.5. Cleaning procedure

Cleaning tests were performed on a paint layer with a Dammar film and a wooden surface treated with C6 fluorinated diethylenetriamine (DF6) [43]. For Dammar varnish, the cleaning trials followed existing protocols, with preliminary tests to verify solvent selection. A new tailored protocol was designed to evaluate the cleaning efficiency of the gel for the fluorinated protective products.

Cleaning tests on canvas covered with a layer of Dammar resin, which gives UV fluorescence, were performed on a quarter of G2 gels loaded with one of the following solvents: MEK, 2-propanol, DMC, and DMSO. The cleaning tests involved applying the gel for 15 min. Cleaning efficiency was assessed by observing the surface under UV and Vis light before and after treatment. UV images were obtained using a Spectroline ENF-260C/FE lamp with an emission in UV-A range at wavelength of 365 nm.

The PVB gels ability to remove DF6 coating from beech wood was evaluated using G2 gels loaded with MEK or 2-propanol, solvents suitable for the fluorinated compound solubilization. A quarter of the gel was placed on the DF6-coated wood, and cleaning efficacy was assessed through Water Contact Angle (WCA) measurements and colorimetric analysis before and after treatment. Based on solvent release and

evaporation data, the gel was applied in consecutive 1 h treatments, with drying for 18 h between each, followed by WCA measurements. The tests concluded after a total of 4 h of gel application, at which point color measurements were conducted.

The colorimetric analyses were performed using a portable X-Rite SP60 spectrophotometer according to the UNI-EN 15886:2010 standard [44]. The results were processed and reported in the standard CIEL*a*b* color space. The analyses were performed on beech wood samples (45 × 50 × 20 mm) treated with fluorinated derivatives before and after the cleaning tests. The color alterations (ΔE*) were expressed as Eq. (5):

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (5)$$

where L* indicates lightness, and a* and b* are the color axes. ΔL*, Δa*, and Δb* were calculated as X_a-X_b where X_a and X_b are the L*, a*, or b* values after and before the cleaning, respectively.

Water contact angles (WCA) of wood samples before and after cleaning tests were measured using a 5 μL drop of distilled water. The shape of the drop was recorded via video using a DJI Osmo pocket camera. The contact angle was calculated from the height and base of the drop obtained by computer processing of the images with the GIMP 2.10.28 program.

3. Results and discussion

3.1. Polymer and cross-linker selection

PVB is a derivative of polyvinyl alcohol (PVA) that finds application in various commercial sectors, and it is synthesized through the reaction of butyraldehyde with PVA with different degrees of hydrolysis and different molecular weight, obtaining the corresponding polyvinyl butyral with various degrees of acetalization (Fig. 1). Consequently, there are different types of PVB on the market with different polarity characteristics and capable of providing solutions with different rheological properties. Among the products present on the market MOWITAL® B 30 T (MOW B 30 T) and MOWITAL® B 30 HH (MOW B 30 HH) from Kuraray have been selected to obtain new chemical organogels. In particular, MOW B 30 T, with higher hydroxyl content, was chosen as the primary component for its better cross-linking potential. A 30 % incorporation of MOW B 30 HH was also explored for its potential to enhance solvent absorption despite forming softer gels (Table 2).

Structural stability requires a cross-linker that creates covalent bonds between polymer chains, forming a three-dimensional network. For this purpose EAS (EASAQUA™ M 502), an aliphatic polyisocyanate marketed by Vencorex Chemicals, was chosen. It is a hexamethylene diisocyanate (HDI) trimer derivative with additives that make the formulation more hydrophilic and with high affinity for polar polymers (Fig. 1, Table S1). The oligomeric structure of the aliphatic polyisocyanate reduces the hazardousness of these reagents making them interesting for numerous applications. In the same commercial line of products, there are also polyisocyanates derived from renewable sources

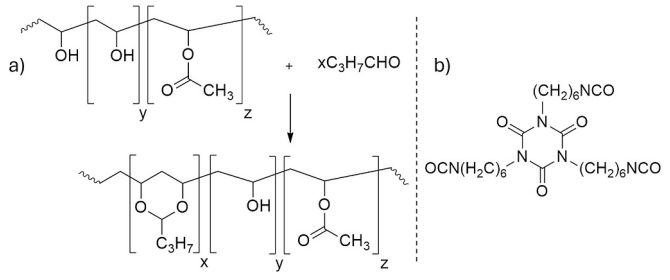

Fig. 1. a) Synthesis of polyvinyl butyral (PVB), with x = units of vinyl butyral, y = units of vinyl alcohol and z = units of vinyl acetate; b) Structure of the trimer of hexamethylene diisocyanate (HDI).

Table 2
Properties of MOWITAL® B 30 T and MOWITAL® B 30 HH (commercial product data as reported by the manufacturer).

MOW	Non-volatile content[a] (wt-%)	PVA content (wt-%)	PVAc content (wt-%)	Dynamic viscosity[b] in ethanol[c] solution 10 % (mPa•s)
B 30 T	≥97.5	24–27	1–4	30–55
B 30 HH	≥97.5	11–14	1–4	35–60

[a] According to DIN 53216.
[b] According to DIN 53015.
[c] Containing 5 % of water.

and more eco-friendly, even if more expensive, not used in this preliminary study but selectable for future developments of more eco-friendly products.

3.2. Gels: composition and properties

Small-scale PVB-based gels (2 cm diameter, ~0.4 cm thickness) were prepared to assess the chemical, physical and mechanical properties of the new formulations.

The copolymer/cross-linker ratio and the reaction conditions selected for different synthesis were optimized to modulate gel porosity, network strength, solvent release and retention properties. Various gels (formulations G1–G5, Table 1) were then prepared by modifying the MOW type, MOW/EAS ratio, solvent and temperature. Preparation at room temperature was preferred for better homogeneity of the resulting gels but the gel preparation time can be reduced by increasing the temperature. DMSO, a polar aprotic solvent, was initially used for its stability with the isocyanate reagent and its hygroscopicity, aiding cross-linking. MEK was also tested as solvent, added with 8 % DMSO to ensure MOW B 30 T solubility. Generally, gels were formed in sealed jars to reduce water vapor interference with the PVB-polyisocyanate reaction. In fact, while excess humidity in the reaction environment accelerates the reaction, it can favor the competitive formation of polyureas, causing opacity and fragility of the gel obtained. G2, G3 and G4, prepared in closed setup with, MOW/EAS ratio 1:2, formed homogeneous, transparent, colorless gels with good elasticity, high compactness, and no volumetric shrinkage. The gel maintains its properties even when scaled up to 5 cm (Fig. 2). By contrast, G1 with less cross-linker remained liquid; after 12 days the jar was uncapped to let in moisture and promote gelation. The resulting gel was opaque white, rigid, and brittle, likely due to excessive polyurea formation. A last, MEK/DMSO formulations (G5) showed lower cohesion than the DMSO ones, but still suitable for cleaning applications. All the formulations lead to high Gel Fraction (G%) values, as reported in Table 3. However, the incorporation of MOW B 30 HH into the G3 gel formulation reduces the degree of cross-linking, which consequently lowers the Gel Fraction and a softer

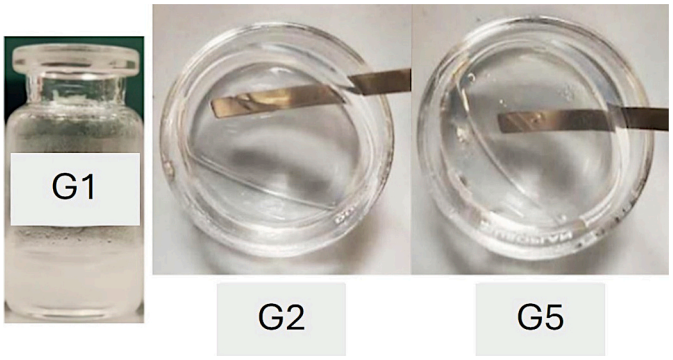

Fig. 2. Macroscopic aspect of 2 cm gel obtained with formulation G1 (left) and 5 cm gels obtained with formulation G2 (center) and G5 (right).

Table 3
Gel Fraction (G%) and Equilibrium Water Content (EWC) values for the gels formulations G1-G5.

Gel	Description	G%	EWC
G1	MOW B 30 T/EAS 1:1 – DMSO – RT	94.7 ± 1.0	90.0 ± 0.7
G2	MOW B 30 T/EAS1:2 – DMSO – RT	93.7 ± 0.5	79.3 ± 0.6
G3	MOW B 30 T/B 30 HH (70:30)/EAS 1:2 – DMSO – RT	84.7 ± 0.6	91.4 ± 0.6
G4	MOW B 30 T/EAS 1:2 – DMSO – 38 °C	91.1 ± 0.4	89.3 ± 0.7
G5	MOW B 30 T/EAS 1:2 – MEK/DMSO (92:8) – RT	89.6 ± 0.9	73.9 ± 0.7

and less coherent gel structure.

Increasing the synthesis temperature, as in the case of G4, accelerates gel formation while preserving a relatively high Gel Fraction and high macroscopic homogeneity, indicating a favorable balance between gelation speed and structural integrity. Higher temperatures were avoided due to the resulting loss of gel homogeneity. Using MEK as solvent instead of DMSO slightly decreases the Gel Fraction. However, this reduction remains within an acceptable range, demonstrating that MEK is a viable alternative solvent for the chemical preparation of the gel, as seen in G5.

In terms of EWC values (Table 3), G3 gel exhibits the highest water content, followed by G1, which is slightly less. This difference in water affinity arises from variations in formulation components and preparation conditions. The inclusion in G3 of MOW B 30 HH reduces cross-linking and structural compactness, increasing water absorption. For G1 the lower amount of EAS reduces cross-linking between MOW chains, leaving more -OH groups free in the chain, resulting in a more hydrophilic behavior, i.e., a higher EWC. Gels formulated with MOW B 30 T/EAS in a 1:2 ratio, both in DMSO (G2) and MEK/DMSO (92:8) (G5), exhibit greater structural compactness, resulting in lower water content and more hydrophobic behavior. Notably, the gel prepared with heating (G4) absorbs more water than its counterpart prepared at room temperature (G2). This is likely due to the faster cross-linking process at higher temperatures, which reduces regularity and compactness in the network structure. G2, with high cohesion and hydrophobicity, proved the most promising formulation.

FT-IR analyses were conducted on powders obtained from all gels after loading them with MEK and dried. The absence of the characteristic isocyanate band at 2270 cm^{-1} in all spectra confirms the complete conversion of EAS. The FT-IR spectra are shown in Fig. 3. The band at 3750 cm^{-1} is consistent with the presence of isolated O—H or N—H stretching while the band at 3450 cm^{-1} is attributable to hydrogen-bonded O—H and N—H stretching. The bands between 2800 and 2900 cm^{-1} are attributable to C—H stretching while the bands at 1650 cm^{-1} (C═O stretching), 1520 cm^{-1} (N—H bending), 1450 cm^{-1} (C—N bending), and 1250–1100 cm^{-1} (C–O–C and C—N stretching) are in agreement with the presence of polyurethane probably with the simultaneous formation of polyurea. Differentiation between the two isocyanate derivatives is challenging due to overlapping bands, and the presence of C–O–C in MOW limits its use as a marker for polyurethanes. For MOW B 30 T/EAS 1:2 composition, gels produced in DMSO at room temperature (G2), 38 °C (G4), and in MEK/DMSO (G5) show similar profiles. The G3 spectrum (MOW B 30 T/B 30 HH) displays a stronger 1250 cm^{-1} band, consistent with the presence of increased acetalization. G1 (1:1 ratio, obtained in the open container) exhibits prominent bands at 3495 cm^{-1} and 1690–1645 cm^{-1}, indicating residual humidity, despite MEK washing and evaporation. Similar but weaker bands are present in other gels, overlapping with polyurea and polyurethane signals.

The area where the peak associated with the isocyanate would be is highlighted in purple.

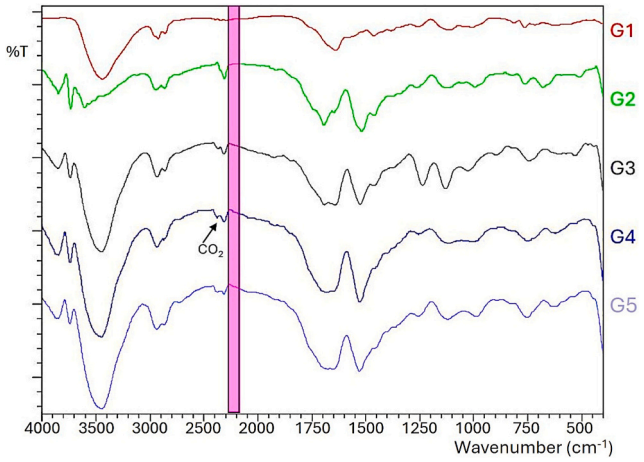

Fig. 3. FT-IR spectra of gels prepared with the following formulations (from the top):
- G1) MOW B 30 T/EAS 1:1 in DMSO at RT
- G2) MOW B 30 T/EAS1:2 in DMSO at RT
- G3) MOW B 30 T/B 30 HH (70:30)/EAS 1:2 in DMSO at RT
- G4) MOW B 30 T/EAS 1:2 in DMSO at 38 °C
- G5) MOW B 30 T/EAS 1:2 in MEK/DMSO (92:8) at RT

Rheological tests were performed on the most promising gel types: G2, G2 loaded with MEK, and G5. After determining the linear viscoelastic region (LVR), the elastic modulus (G'), viscous modulus (G"), and complex viscosity (η*) were measured. Fig. 4 illustrates G' and G" across a frequency range of 100–0.005 Hz for G2 gel. G' dominates G", with a phase angle (δ) below 45°, confirming the viscoelastic solid nature of the material.

Complex viscosity (η*) increases as frequency decreases, showing no Newtonian plateau. This shear-thinning behavior, or pseudoplastic flow, indicates decreasing viscosity with increasing shear. Both the G2 gel loaded with MEK and the G5 gel exhibit phase angles below 45° (Figs. S1 and S2), which decrease with increasing frequency. This indicates a predominantly elastic behavior, more pronounced than that of G2. Notably, the gel containing pure MEK approaches the characteristics of an ideally elastic solid. This may be attributed to the absence of DMSO, which, at higher frequencies, tends to impart a more viscous behavior to the gel.

The morphology and porosity of the G2 gel were analyzed using scanning electron microscopy (SEM). SEM images at varying magnifications (Fig. 5) reveal a dense network of polymer filaments (~10 nm thick) with homogeneous porosity and an average pore size of 77 nm while the pore distribution is reported in Fig. S3. The pores are not continuous channels but part of an interconnected, bi-continuous system with visible polymer filaments and cavities, enabling the gel to absorb large amounts of water or solvents, as confirmed by EWC and solvent absorption tests (see Section 3.3).

3.3. *Affinity of the gels with organic solvents*

The affinity of the gels for organic solvents was evaluated as the percentage absorption (Abs%) and the values obtained for the different gels are reported in Table 4. DMSO and MEK were used as solvents for gel preparation but other solvents, including MEK, were loaded by washing the gels obtained in DMSO as described in the experimental part. All gel types showed a high value of Abs% for each selected solvent, making them suitable as a cleaning system for various materials. After solvent loading, all MOW/EAS-based gels prepared in a 1:2 ratio (G2–G5) showed no significant macroscopic differences when exposed to the same solvent. When water was included in the solvent mixture, all gels became opaque and white, showing increased rigidity and fragility. This effect is likely due to the formation of polyurea within the network,

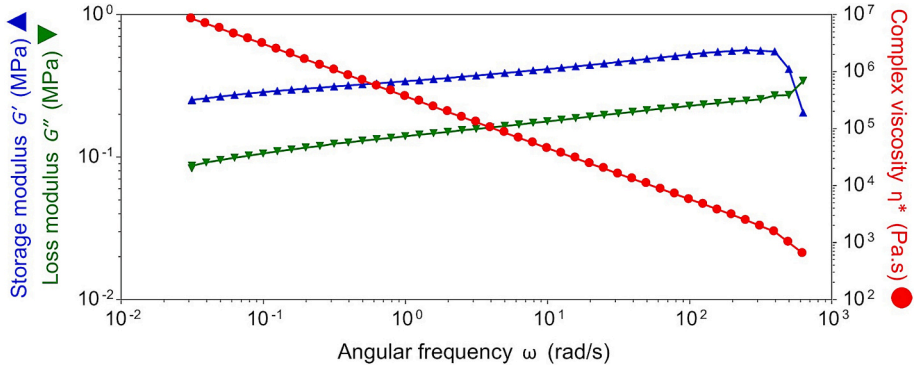

Fig. 4. Frequency Sweep Test done on G2 gel as such.

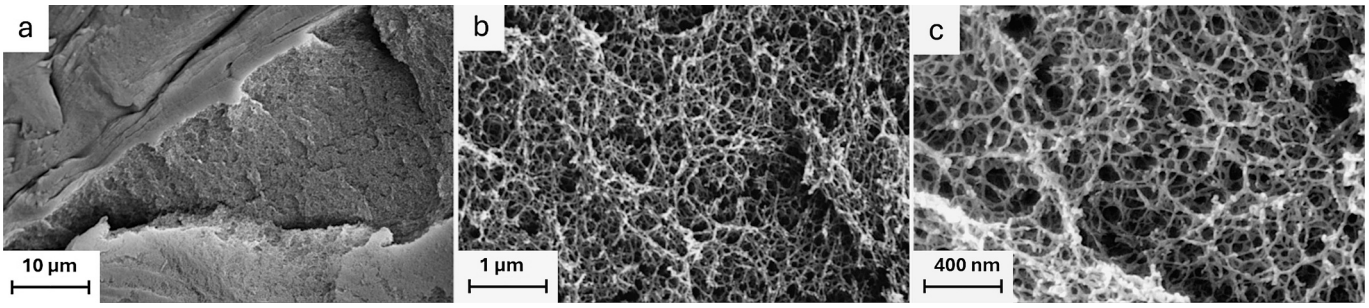

Fig. 5. SEM images of G2 gel. The images were obtained with different magnifications: a) 2 k; b) 20 k; c) 50 k.

Table 4
Percentage absorption (Abs%) values for the gel formulations G1, G2, G3, G4, G5 with different solvents.

Solvent	Abs (%)				
	G1	G2	G3	G4	G5
MEK	95.0 ± 0.6	85.3 ± 1.1	93.7 ± 0.5	91.3 ± 0.8	93.4 ± 0.6
2-propanol	94.2 ± 0.6	90.6 ± 0.7	92.5 ± 0.7	95.6 ± 1.0	91.8 ± 0.9
Water/ethanol 30:70	92.3 ± 0.8	91.1 ± 0.5	91.1 ± 0.8	92.2 ± 0.7	–
Ethanol	95.0 ± 0.7	90.4 ± 0.6	91.2 ± 0.4	91.3 ± 0.7	–
DMC	96.0 ± 0.3	92.9 ± 0.5	93.8 ± 0.7	93.1 ± 0.5	–

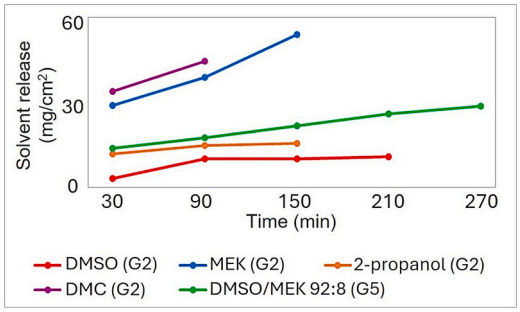

Fig. 6. Release values (mg/cm^2) over time (min) until a constant weight was achieved of G2 gels loaded with DMSO, MEK, 2-propanol and DMC, and G5 gels as such.

resulting from the reaction of water with unconverted isocyanate groups still present in the three-dimensional structure and not detectable in the FT-IR spectra. As a result, the water/ethanol mixture was excluded from further testing. The G2 gel loaded with MEK exhibited slight volumetric shrinkage, which is also observed during the solidification phase of the G5 gel, prepared directly in MEK containing 8 % DMSO, whereas gels loaded with isopropanol, dimethyl carbonate, and ethanol retained their transparency and elasticity, showing no volumetric shrinkage. 2-propanol was chosen for further tests, as it is often used in conservation.

The solvent release was also evaluated, and different gels (G1-G5) show distinct release behaviors (Fig. 6). In particular, comparing G2 synthesized in DMSO and G5 obtained with MEK/DMSO mixture (without solvent exchange), the latter demonstrates a significantly higher release capacity at 30 min, likely due to much lower surface tension of DMSO (0.55 hPa at 20 °C) compared to MEK (105 hPa). However, the limited release observed for DMSO is positive considering its potential hazards to certain materials; this highlights the suitability of PVB-based gels as controlled cleaning systems. Instead, the MEK/DMSO mixture provides steady, gradual release, enhancing control during cleaning as a result of the simultaneous presence of MEK with 8 % DMSO. In contrast, the gel synthesized in DMSO and loaded with MEK (without DMSO residues) exhibits a high initial release rate that decreases over time, reducing its effective duration. The gel loaded with DMC (57 hPa) releases even faster, confirming that the MOW-based matrix retains solvents with higher surface tensions less effectively. Finally, the isopropanol-loaded gel shows a slightly lower 30-min release rate but maintains a consistent release profile over time.

Evaporation tests were also carried out on G2 gel as such (containing DMSO) and G2 loaded with MEK, 2-propanol, or DMC. Additionally, a G5 gel was tested as such (Fig. 7). For G2 as such, the low volatility of DMSO prevents evaporation, while an increase in weight is observed as the loaded gel absorbs moisture from the air. However, comparing the trend with the behavior of the same amount of free DMSO, the results show that the gel effectively slows down the water absorption by DMSO, demonstrating its hydrophobic properties. For the MEK/DMSO gel (G5), solvent content remains above 20 % in both the gel and the free mixture. However, the small DMSO content allows some environmental water absorption, affecting weight measurements. The evaporation curve

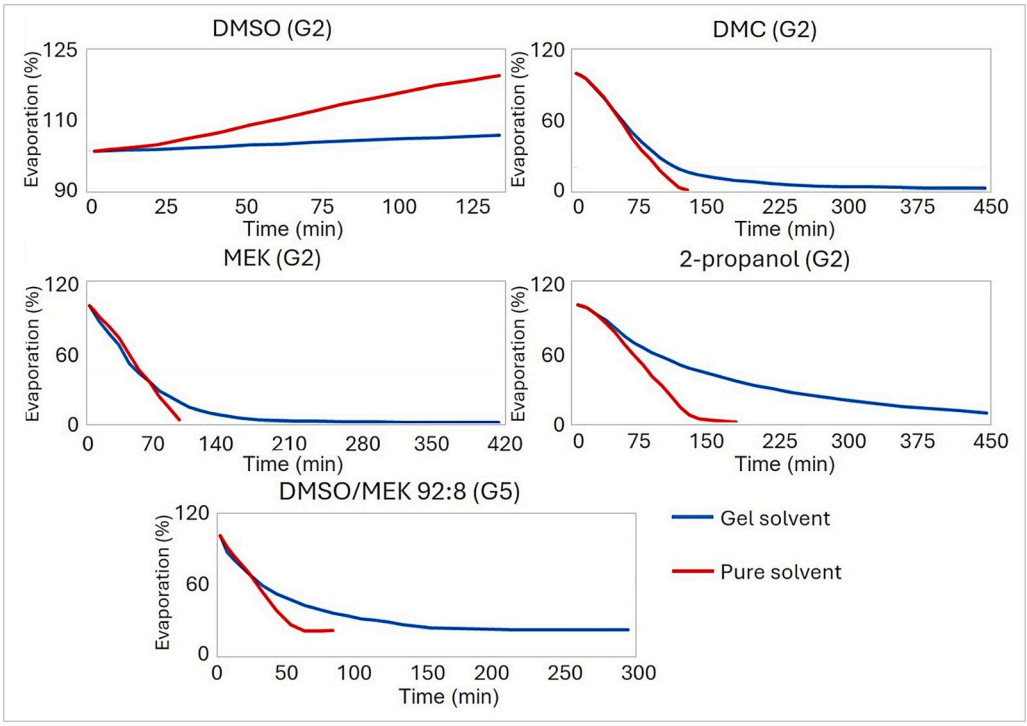

Fig. 7. Comparison between the evaporation curves of G2 gel loaded with organic solvent (DMSO, DMC, MEK and 2-propanol) and G5 gel with MEK/DMSO 92:8 versus the corresponding pure solvent/mixture.

confirms the gel reduces MEK evaporation, consistent with observations on G2 where DMSO was completely replaced by MEK. PVB-based gels show excellent retention of isopropanol and dimethyl carbonate, maintaining solvent presence even after 2 h of ambient exposure. This retention is particularly notable for 2-propanol, whose evaporation rate within the gel differs markedly from that of the pure solvent.

The results concerning the release and evaporation rate of the solvents confirm the importance of the interaction of the solvents with the gel components; these rates are affected not only by the vapor pressure of the solvents but also by the secondary interactions between polymeric components and solvents, and the microporosity of the gel structure.

3.4. Cleaning tests

MOW-based gels were developed to remove traditional varnishes and synthetic coatings with low molecular weight.

Two different cleaning tests were performed to analyze the behavior of the gels on the two different coatings. The first series of tests was carried out on a wooden surface protected with DF6 [43], a reversible fluorinated oligomer, whose dispersion into the environment during cleaning could create critical environmental issues if not confined in the cleaning system. The ability to remove the DF6 coating from beech wood samples was tested using G2 gels loaded with MEK or isopropanol. A quarter of the 5 cm diameter gel was applied to the coated samples, with cleaning efficacy evaluated via Water Contact Angle (WCA) measurements and colorimetric analysis before and after cleaning. The WCA of DF6-coated samples decreased steadily during cleaning, reaching 88° after 4 h, indicating wood hydrophilicity almost completely restored with both solvents (Table 5). This final angle remained slightly higher than the untreated wood (average $\theta = 68°$). The application of DF6 on beech wood induced a color variation of about $\Delta E \approx 4.5$. Although this value slightly exceeds the threshold of human eye perceptibility, it can be considered acceptable for protective treatments in wood conservation, as the resulting tone remains consistent with the natural color spectrum of wood. Upon removal of the coating with the PVB-based gel, the observed color variation ($\Delta E^* > 3$) limited to the gel-contacted areas

Table 5
WCA values of DF6-coated beech wood surfaces at time zero and after 1, 2, 3, and 4 h of contact with G2 gels loaded with MEK or 2-propanol.

Gel	WCA (°)				
	Pre cleaning	After 1 h	After 2 h	After 3 h	After 4 h
(G2) MEK	115 ± 2	110 ± 3	102 ± 2	88 ± 6	88 ± 1
(G2) 2-propanol	120 ± 3	111 ± 1	96 ± 2	94 ± 5	88 ± 2

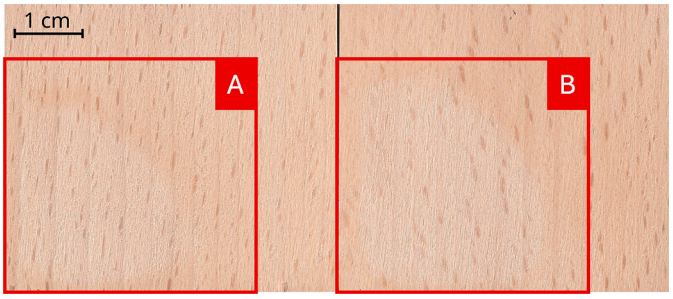

Fig. 8. Macroscopic aspect of DF6-coated beech samples after contact with G2 gels loaded with MEK (A) or 2-propanol (B).

Table 6
Colorimetric measurements on DF6-coated beech wood surfaces after cleaning with G2 gels loaded with MEK or 2-propanol.

Gel	ΔL*	Δa*	Δb*	ΔE*
	Δ = post cleaning – pre cleaning			
(G2) MEK	2.16 ± 0.26	−1.14 ± 0.03	−3.50 ± 0.03	4.27
(G2) 2-propanol	2.04 ± 0.02	−1.32 ± 0.01	−5.32 ± 0.05	5.85
	Δ = post cleaning – original wood color			
(G2) MEK	2.60 ± 0.02	−0.86 ± 0.01	−0.87 ± 0.03	2.88
(G2) 2-propanol	1.48 ± 0.04	−0.72 ± 0.02	−0.77 ± 0.02	1.82

(Fig. 8), though the treated samples showed a* and b* values comparable to the original wood (Table 6). Thus, the PVB-based gel loaded with MEK, or isopropanol effectively restored the characteristics of wood prior to DF6 treatment confining the removed material inside the gel.

The second type of cleaning involved the removal of a varnish. Tests were conducted on canvas mock-ups coated with Dammar resin using a gel loaded with MEK, 2-propanol, DMC, or DMSO. Cleaning efficiency was evaluated under UV and visible light before and after 15 min of gel application. Visible surface changes were confined to the treated area (Fig. 9B), with UV fluorescence confirming the positive effect (Fig. 9A). DMC achieved the most complete varnish removal, followed by MEK and isopropanol, while DMSO was less effective, leaving varnish with bluish reflections. Although DMC dissolved Dammar well, its fast release caused excessive penetration, potentially damaging to the paint layer. Consequently, for controlled cleaning, PVB-based gels with MEK and 2-propanol were most suitable. Post-treatment observations (Fig. S4) showed minimal volume changes in the gels. All gels retained transparency but developed a yellowish tint in visible light due to terpene resin absorption, this is also confirmed by the faint fluorescence that the gels exhibit under UV irradiation after the cleaning trials. The results obtained with MEK and 2-propanol highlight the effectiveness of MOW-based gels for cleaning varnished surfaces.

Within the detection limit of FT-IR, any evidence of residue emerged from the analysis of treated surfaces. However, the absence of residues was expected due to the nature of the gel. Indeed, chemical cross-linking with strong covalent bonds guarantees a highly cohesive material resistant to mechanical stress, as confirmed by rheological tests.

Compared to other innovative systems reported for Dammar removal, such as thiolene photocured organogels [45] and PHB-based composite gels combined with nonwoven fabrics [46], our novel organogel represents a significant advancement. Unlike thiolene photocured systems, PVB-based gels do not require initiators or irradiation. Their lower rigidity and markedly higher solvent uptake capacity (e.g., DMC) further enhance cleaning efficiency. Similarly, while the PHB-based composite gels remove Dammar through swelling and peeling due to adhesion to fabric fibers, they leave residues that must be removed with cotton swabs. In contrast, our system minimizes mechanical stress, avoids strong adhesion to the substrate, and eliminates the need for additional cleaning. Moreover, its high elasticity and cohesion are achieved through structural optimization of the gel itself, without coupling with electrospun fabrics, resulting in a straightforward preparation process and a single-component gel with superior properties.

4. Conclusions

Novel polyvinyl butyral (PVB)-based chemical gels have been designed, produced and characterized to their use as organogels for cleaning works of art. The gels were synthesized starting from commercially available low environmental impact products and obtaining excellent characteristics without the need for additives to improve the properties of the gel. Five formulations were prepared, varying the gelling agent-to-cross-linker ratio, gelling product type, reaction temperature, and solvent. A 1:2 ratio produced cohesive, elastic, transparent gels, with FT-IR confirming complete polyisocyanate reaction and polyurethane formation together with the simultaneous formation of small amounts of polyurea which increase in the presence of contact with air humidity.

All gels presented high Gel Fraction (G%), though lower G% and higher Equilibrium Water Content (EWC) were observed with MOW B 30 T/B 30 HH blends due to lower amount of hydroxyl groups. PVB-based gels, typically synthesized in DMSO and then loaded by washing with other solvents, can also be synthesized in MEK, enabling direct application without additional washing cycles when MEK is a suitable cleaning solvent. This streamlines preparation and minimizes solvent waste, which could still be recovered after washing in a highly sustainable process.

The high volatility of MEK complicates both the synthesis and storage of MEK-based gels. In contrast, DMSO-based formulations offer excellent reproducibility and long-term stability when preserved in their synthesis solvent. Notably, for gels with a MOW/EAS ratio of 1:2, solvent exchange is straightforward and does not compromise transparency, volume, or elasticity. Their high absorption capacity and restricted solvent release made them ideal for controlled cleaning, slowing evaporation, particularly with isopropanol and DMC.

Rheological tests confirmed strong viscoelastic properties, and SEM imaging revealed a porous, interconnected structure. Cleaning tests on wood treated with a fluorinated agent and Dammar-varnished canvas

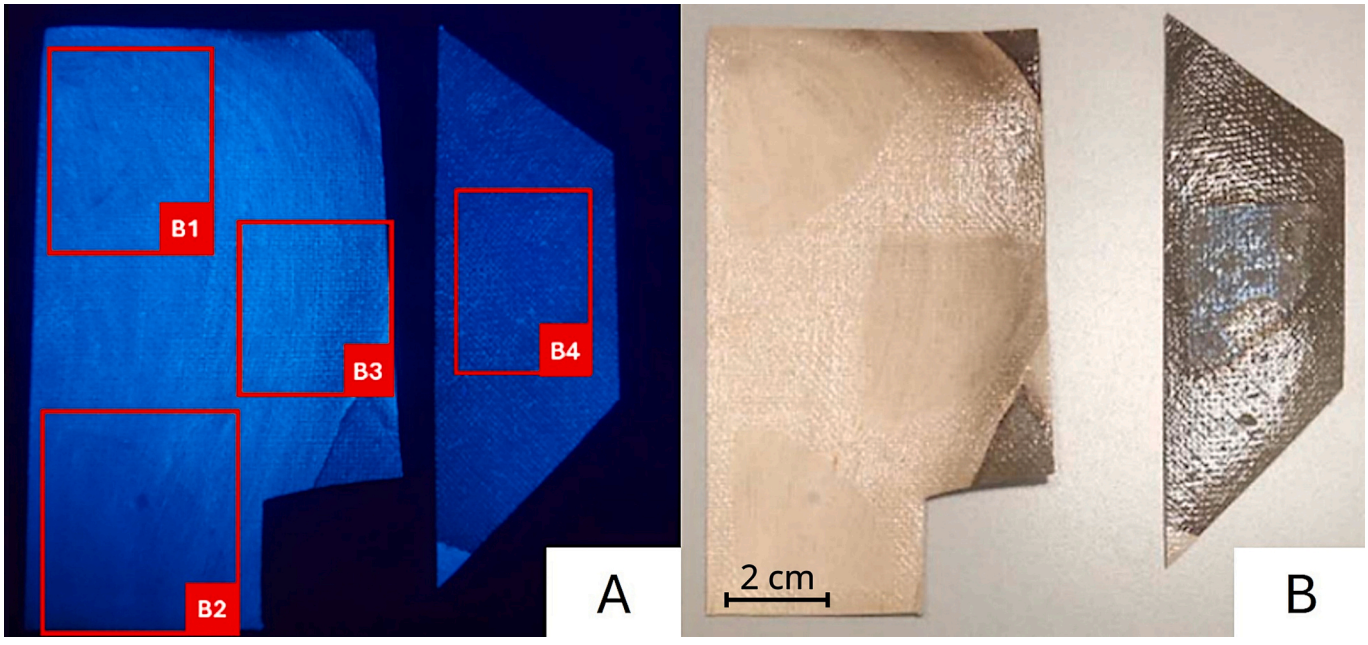

Fig. 9. Results of the cleaning process. A) UV light photo of the selected area after 15 min of G2 gel application, where B1 = gel loaded with 2-propanol, B2 = gel loaded with DMC, B3 = gel loaded with MEK, B4 = gel loaded with DMSO; B) Visible light photo of the selected area after 15 min of G2 gel application.

demonstrated the effectiveness of these gels, highlighting their potential for cleaning delicate surfaces in the conservation of Cultural Heritage.

Specially for G2, the optimized MOW/EAS ratio and closed-system synthesis yield a highly cross-linked, homogeneous network. This dense network underlies the gel mechanical robustness, with a predominantly elastic behavior. The uniform nanoscale porosity enables efficient solvent uptake while maintaining cohesion, explaining the superior performance of G2. Moreover, the systematic preparation of the gels confirmed the reproducibility of these properties.

CRediT authorship contribution statement

Laura Vespignani: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Yuewen Pan:** Visualization, Validation, Investigation, Formal analysis, Data curation. **Rodorico Giorgi:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization. **Antonella Salvini:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Leonardo Bellandi (University of Florence) is kindly acknowledged for assistance with rheology measurements. We thank MIUR-Italy ("Progetto Dipartimenti di Eccellenza 2023−2027" for the funds allocated to the Department of Chemistry "Ugo Schiff"). Laura Vespignani acknowledges NOP Research and Innovation 2014-2020, financed by ESF REACT-EU resources, Action IV.4 "PhD programs and research contracts on innovation topics" and Action IV.5 "PhD programs on green topics", for partly funding this work. Rodorico Giorgi acknowledges PRIN 2022CNNRWZ- REAGENERA, financed by the Next Generation EU- Mission 4, component 1, CUP H53D23003830006, for partly funding this work. Rodorico Giorgi also acknowledges CSGI for supporting this research.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.porgcoat.2025.109730.

Data availability

No data was used for the research described in the article.

References

[1] C. Cucci, J.K. Delaney, M. Picollo, Reflectance hyperspectral imaging for investigation of works of art: old master paintings and illuminated manuscripts, Acc. Chem. Res. 49 (10) (2016) 2070–2079, https://doi.org/10.1021/acs.accounts.6b00048.

[2] Z. Ma, L. Yang, L. Wang, V. Pitthard, T. Bayerova, G. Krist, X. Zhao, The influence of natural aging exerting on the stability of some proteinaceous binding media commonly used in painted artworks, Coatings 12 (10) (2022) 1522, https://doi.org/10.3390/coatings12101522.

[3] M. Martínez-Weinbaum, L. Maestro-Guijarro, P.M. Carmona-Quiroga, S. Siano, D. Ciofini, M. Castillejo, M. Oujja, In-depth structural and compositional assessment of aged Terpenoid varnish layers by nonlinear optical microscopy, J. Cult. Herit. 62 (2023) 170–180, https://doi.org/10.1016/j.culher.2023.05.026.

[4] A.E. Vâlcea, I. Mariș, A.D. Negrea, N. Cimpoeșu, G. Gârbea, D. Grecu, S.G. Moga, B. Istrate, F.N. Finta, A.D. Rizea, D.-C. Anghel, C. Munteanu, M.I. Petrescu, M. Abrudeanu, Interdisciplinary research on medieval fresco subjected to degradation processes in the Corbii de Piatră cave church, Materials 16 (15) (2023) 5257, https://doi.org/10.3390/ma16155257.

[5] S. Sotiropoulou, Z.E. Papliaka, L. Vaccari, Micro FTIR imaging for the investigation of deteriorated organic binders in wall painting Stratigraphies of different techniques and periods, Microchem. J. 124 (2016) 559–567, https://doi.org/10.1016/j.microc.2015.10.002.

[6] R.-M. Ion, L. Iancu, R.M. Grigorescu, S. Slamnoiu-Teodorescu, I.D. Dulama, I. A. Bucurica, Degradation products assessment of the wooden painted surfaces from a XVIIth heritage monastery, Appl. Sci. 13 (4) (2023) 2124, https://doi.org/10.3390/app13042124.

[7] S. Sotiropoulou, G. Sciutto, A.L. Tenorio, J. Mazurek, I. Bonaduce, S. Prati, R. Mazzeo, M. Schilling, M.P. Colombini, Advanced analytical investigation on degradation markers in wall paintings, Microchem. J. 139 (2018) 278–294, https://doi.org/10.1016/j.microc.2018.03.007.

[8] P.N. Maravelaki, Surface cleaning: implications from choices & future perspectives, in: Conserving Stone Heritage. Cultural Heritage Science, Springer, Cham, 2022, pp. 37–74, https://doi.org/10.1007/978-3-030-82942-1_2.

[9] M. Baglioni, T. Guaragnone, R. Mastrangelo, F.H. Sekine, T. Ogura, P. Baglioni, Nonionic surfactants for the cleaning of works of art: insights on acrylic polymer films Dewetting and artificial soil removal, ACS Appl. Mater. Interfaces 12 (23) (2020) 26704–26716, https://doi.org/10.1021/acsami.0c06425.

[10] C. Biribicchi, A. Macchia, G. Favero, R. Strangis, B. Gabriele, R. Mancuso, M.F. La Russa, Sustainable solutions for removing aged wax-based coatings from cultural heritage: exploiting hydrophobic deep eutectic solvents (DESs), New J. Chem. 47 (12) (2023) 5991–6000, https://doi.org/10.1039/d3nj00228d.

[11] B. Ormsby, A. Bartoletti, K.J. van den Berg, C. Stavroudis, Cleaning and conservation: recent successes and challenges, Herit. Sci. 12 (1) (2024) 10, https://doi.org/10.1186/s40494-023-01113-0.

[12] P. Baglioni, D. Berti, M. Bonini, E. Carretti, L. Dei, E. Fratini, R. Giorgi, Micelle, microemulsions, and gels for the conservation of cultural heritage, Adv. Colloid Interf. Sci. (2014) 361–371, https://doi.org/10.1016/j.cis.2013.09.008. Elsevier B. V.

[13] D. Chelazzi, R. Bordes, R. Giorgi, K. Holmberg, P. Baglioni, The use of surfactants in the cleaning of works of art, Curr. Opin. Colloid Interface Sci. 45 (2020) 108–123, https://doi.org/10.1016/j.cocis.2019.12.007.

[14] G. Cavallaro, S. Milioto, L. Nigamatzyanova, F. Akhatova, R. Fakhrullin, G. Lazzara, Pickering emulsion gels based on Halloysite nanotubes and ionic biopolymers: properties and cleaning action on marble surface, ACS Appl. Nano Mater. 2 (5) (2019) 3169–3176, https://doi.org/10.1021/acsanm.9b00487.

[15] P. Pérez Benito, J.L. Regidor Ros, P. Roig Picazo, Emulsion system without surfactant as an alternative to the use of a solvent gel, Conserv. Patrim. 34 (2020) 101–108, https://doi.org/10.14568/cp2018051.

[16] M. Ioan, D.F. Anghel, I.C. Gifu, E. Alexandrescu, C. Petcu, L.M. Diţu, G.A. Sanda, D. Bala, L.O. Cinteza, Novel microemulsions with essential oils for environmentally friendly cleaning of copper cultural heritage artifacts, Nanomaterials 13 (17) (2023) 2430, https://doi.org/10.3390/nano13172430.

[17] N. Khaksar-Baghan, A. Koochakzaei, Y. Hamzavi, An overview of gel-based cleaning approaches for art conservation, Herit. Sci. 12 (1) (2024) 248, https://doi.org/10.1186/s40494-024-01369-0.

[18] A. Sannino, C. Demitri, M. Madaghiele, Biodegradable cellulose-based hydrogels: design and applications, Materials (2009) 353–373, https://doi.org/10.3390/ma2020353.

[19] C. Chang, L. Zhang, Cellulose-based hydrogels: present status and application prospects, Carbohydr. Polym. (February 11, 2011) 40–53, https://doi.org/10.1016/j.carbpol.2010.12.023.

[20] K.J. De France, E. D'Emilio, E.D. Cranston, T. Geiger, G. Nyström, Dual physically and chemically crosslinked regenerated cellulose – gelatin composite hydrogels towards art restoration, Carbohydr. Polym. 234 (2020) 115885, https://doi.org/10.1016/j.carbpol.2020.115885.

[21] E. Carretti, M. Bonini, L. Dei, B.H. Berrie, L.V. Angelova, P. Baglioni, R.G. Weiss, New Frontiers in materials science for art conservation: responsive gels and beyond, Acc. Chem. Res. 43 (6) (2010) 751–760, https://doi.org/10.1021/ar900282h.

[22] C. Stavroudis, Carbopol 934, Ethomeen C25, Ethomeen C12, Armeen CD: now available from conservation materials, Newsletter (Western Association for Art Conservation) *12* (2) (**1990**).

[23] C. Mazzuca, L. Severini, M. Missori, M. Tumiati, F. Domenici, L. Micheli, M. Titubante, M. Bragaglia, F. Nanni, G. Paradossi, A. Palleschi, Evaluating the influence of paper characteristics on the efficacy of new poly(vinyl alcohol) based hydrogels for cleaning modern and ancient paper, Microchem. J. 155 (2020) 104716, https://doi.org/10.1016/j.microc.2020.104716.

[24] N. Bonelli, G. Poggi, D. Chelazzi, R. Giorgi, P. Baglioni, Poly(vinyl alcohol)/poly (vinyl pyrrolidone) hydrogels for the cleaning of art, J. Colloid Interface Sci. 536 (2019) 339–348, https://doi.org/10.1016/j.jcis.2018.10.025.

[25] M. Bonini, S. Lenz, E. Falletta, F. Ridi, E. Carretti, E. Fratini, A. Wiedenmann, P. Baglioni, Acrylamide-based magnetic nanosponges: a new smart nanocomposite material, Langmuir 24 (21) (2008) 12644–12650, https://doi.org/10.1021/la802425k.

[26] G. Pizzorusso, E. Fratini, J. Eiblmeier, R. Giorgi, D. Chelazzi, A. Chevalier, P. Baglioni, Physicochemical characterization of acrylamide/Bisacrylamide hydrogels and their application for the conservation of easel paintings, Langmuir 28 (8) (2012) 3952–3961, https://doi.org/10.1021/la2044619.

[27] D. Gulsen, A. Chauhan, Effect of water content on transparency, swelling, lidocaine diffusion in p-HEMA gels, J. Membr. Sci. 269 (1–2) (2006) 35–48, https://doi.org/10.1016/j.memsci.2005.06.024.

[28] J.A.L. Domingues, N. Bonelli, R. Giorgi, E. Fratini, F. Gorel, P. Baglioni, Innovative hydrogels based on semi-interpenetrating p(HEMA)/PVP networks for the cleaning

of water-sensitive cultural heritage artifacts, Langmuir 29 (8) (2013) 2746–2755, https://doi.org/10.1021/la3048664.
[29] M. Shibayama, X. Li, T. Sakai, Precision polymer network science with tetra-PEG gels—a decade history and future, Colloid Polym. Sci. 297 (1) (2019) 1–12, https://doi.org/10.1007/s00396-018-4423-7.
[30] P. Baglioni, N. Bonelli, D. Chelazzi, A. Chevalier, L. Dei, J. Domingues, E. Fratini, R. Giorgi, M. Martin, Organogel formulations for the cleaning of easel paintings, Appl. Phys. A 121 (3) (2015) 857–868, https://doi.org/10.1007/s00339-015-9364-0.
[31] M.D. Pianorsi, M. Raudino, N. Bonelli, D. Chelazzi, R. Giorgi, E. Fratini, P. Baglioni, Organogels for the cleaning of artifacts, Pure Appl. Chem. 89 (1) (2017) 3–17, https://doi.org/10.1515/pac-2016-0908.
[32] P. Ferrari, D. Chelazzi, N. Bonelli, A. Mirabile, R. Giorgi, P. Baglioni, Alkyl carbonate solvents confined in poly (ethyl methacrylate) organogels for the removal of pressure sensitive Tapes (PSTs) from contemporary drawings, J. Cult. Herit. 34 (2018) 227–236, https://doi.org/10.1016/j.culher.2018.05.009.
[33] A. Zuliani, S. Chen, R. Giorgi, Re-usable cross-linked poly(ethyl methacrylate) gels for cleaning purposes of artworks, Appl. Mater. Today 30 (2023) 101716, https://doi.org/10.1016/j.apmt.2022.101716.
[34] G. Poggi, H.D. Santan, J. Smets, D. Chelazzi, D. Noferini, M.L. Petruzzellis, L. Pensabene Buemi, E. Fratini, P. Baglioni, Nanostructured bio-based castor oil organogels for the cleaning of artworks, J. Colloid Interface Sci. 638 (2023) 363–374, https://doi.org/10.1016/j.jcis.2023.01.119.
[35] D. Bandelli, R. Mastrangelo, G. Poggi, D. Chelazzi, P. Baglioni, Tailoring the properties of Castor oil polyurethanes organogels with green oligoesters, Colloids Surf. A Physicochem. Eng. Asp. 698 (2024) 134528, https://doi.org/10.1016/j.colsurfa.2024.134528.
[36] K. Ellinas, A. Tserepi, E. Gogolides, Durable superhydrophobic and superamphiphobic polymeric surfaces and their applications: a review, Adv. Colloid Interf. Sci. 250 (2017) 132–157, https://doi.org/10.1016/j.cis.2017.09.003.
[37] Y. Zheng, Y. He, Z. Wang, Y. Zhao, L. Sun, Fabrication of a photothermal self-repairable antifouling coating for achieving enhanced superamphiphobic durability, J. Ind. Eng. Chem. 135 (2024) 572–585, https://doi.org/10.1016/j.jiec.2024.01.069.
[38] H. Wang, D. Gao, Y. Meng, H. Wang, E. Wang, Y. Zhu, Corrosion-resistance, robust and wear-durable highly amphiphobic polymer based composite coating via a simple spraying approach, Prog. Org. Coat. 82 (2015) 74–80, https://doi.org/10.1016/j.porgcoat.2015.01.012.
[39] Y. Cao, A. Salvini, M. Camaiti, One-step fabrication of robust and durable superamphiphobic, self-cleaning surface for outdoor and in situ application on building substrates, J. Colloid Interface Sci. 591 (2021) 239–252, https://doi.org/10.1016/j.jcis.2021.02.001.
[40] E.M. Sunderland, X.C. Hu, C. Dassuncao, A.K. Tokranov, C.C. Wagner, J.G. Allen, A review of the pathways of human exposure to poly- and perfluoroalkyl substances (PFASs) and present understanding of health effects, J. Expo. Sci. Environ. Epidemiol. 29 (2) (2019) 131–147, https://doi.org/10.1038/s41370-018-0094-1.
[41] S.L. Nason, J. Koelmel, N. Zuverza-Mena, C. Stanley, C. Tamez, J.A. Bowden, K. J. Godri Pollitt, Software comparison for nontargeted analysis of PFAS in AFFF-contaminated soil, J. Am. Soc. Mass Spectrom. 32 (4) (2021) 840–846, https://doi.org/10.1021/jasms.0c00261.
[42] D. Prat, A. Wells, J. Hayler, H. Sneddon, C.R. McElroy, S. Abou-Shehada, P.J. Dunn, CHEM21 selection guide of classical- and less classical-solvents, Green Chem. 18 (1) (2016) 288–296, https://doi.org/10.1039/C5GC01008J.
[43] Y. Zhang, L. Vespignani, M.G. Balzano, L. Bellandi, M. Camaiti, N. Lubin-Germain, A. Salvini, Low fluorinated oligoamides for use as wood protective coating, Coatings 12 (7) (2022) 927, https://doi.org/10.3390/coatings12070927.
[44] Conservazione Dei Beni Culturali - Metodi Di Prova - Misura Del Colore Delle Superfici, UNI EN 15886:2010. UNI Ente Italiano di Normazione, November 2010.
[45] Y. Çakmak, E. Çakmakçi, N.K. Apohan, R. Karadag, Isosorbide, pyrogallol, and limonene-containing thiol-ene photocured bio-based organogels for the cleaning of artworks, J. Cult. Herit. 55 (2022) 391–398, https://doi.org/10.1016/j.culher.2022.04.013.
[46] Y. Jia, T. Zhang, M. Liu, J. Zhang, Y. Han, Organogel coupled with microstructured electrospun polymeric nonwovens for the effective cleaning of sensitive surfaces, ACS Appl. Mater. Interfaces 12 (2020) 39620–39629, https://doi.org/10.1021/acsami.0c09543.