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Original article

A new deep eutectic solvent-based green gel for the removal of polymeric coating from mural painting

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ABSTRACT

It is challenging to extend the species of deep eutectic solvent (DES) based gels, particularly in forming non-toxic polymer gels with good mechanical properties. In this study, we propose an eutectogel system for cleaning purposes in the field of culture heritage conservation. Green gels containing ChCl-EG-GVL-PVA and ChCl-EG-PVA are produced by combining choline chloride (ChCl), ethylene glycol (EG) and polyvinyl alcohol (PVA) with or without γ-valerolactone (GVL). The crosslinking of the gels is primarily formed by ChCl-EG and PVA through hydrogen bonding. The additional green solvent GVL is compatible with the gel composition and plays an important role in cleaning. The developed gels exhibit good mechanical properties and fine microstructures, making them easy to handle and suitable for cleaning cultural relics. Therefore, the gels have been tested on a mockup coated with Paraloid B72® to examine their cleaning efficiency. Furthermore, the selected gel has been validated on a Yuan dynasty mural painting for the removal of aged acrylic coating. The results from both the mockup and the real case study demonstrate the effective cleaning efficiency of the ChCl-EG-GVL$_2$-PVA$_2$ gel and highlight its potential usefulness in the field of cultural heritage conservation.

1. Introduction

Natural and synthetic resins are frequently utilized in works of art to serve as a protective layer and enhance their aesthetic appeal [1]. As the outermost layer, the coating is the most susceptible part of the cultural artifact, becoming brittle, yellowed, and losing its transparency after a few decades [2]. Therefore, careful removal of degraded coatings from the surface of cultural relics has become a primary objective in the field of heritage conservation [3].

The most common cleaning method involves applying solvents using cotton swabs. The mechanical action on the surface can often be extremely detrimental to the work of art, and the limited control over solvent application may lead to leaching and swelling of the underlying layers.

Over the last decade, various methods including gels [4–8], nanostructured fluids [9,10], plasma jets [11] and lasers [12,13] have been investigated for the removal of varnishes from different objects. Among these, gels offer several advantages in terms of cleaning performance and ease of application. Gels are capable of retaining the solvent and exhibiting a controlled superficial release. They can be classified as chemical gels or physical gels based on their structure [14].

In particular, chemical gels feature covalent crosslinking, while physical gels are characterized by intermolecular interactions. As a result, chemical gels exhibit greater stability compared to physical gels due to their thermally irreversible nature driven by permanent covalent crosslinking. In contrast, physical gels are less stable and typically exhibit thermal reversibility, as their physical interactions are dynamic and influenced by temperature.

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The consistency of the gel depends on the crosslinking density and the amount of solvent; thus, both physical and chemical gels may be soft, weak, and brittle [15]. The consistency of the gel is particularly critical; indeed, soft gels (such as those based on cellulose and polyacrylic acid) are difficult to remove from artworks, even with rinsing solvents and mechanical action [16]. In contrast, rigid networks make the gels less prone to sticking to surfaces, thereby reducing the presence of residues after cleaning. Rheological properties can determine the strength of chemical and physical gels. For rigid gels, the dynamic modulus is frequency-independent and the storage modulus (G') is usually one magnitude higher than the loss modulus (G'') [17].

Since the preparation of chemical gels for cleaning usually involves more complex procedures for both synthesis and loading compared to physical gels, this research focuses on the development of a green nonaqueous rigid physical gel. In recent years, particular attention has been devoted to developing restoration materials that are safe not only for cultural artifacts but also for the operator's health and the environment [18].

DESs are a new generation of economic and environmentally friendly green solvents that have similar properties to ionic liquids [19]. The biodegradability of DESs depends on the properties of their individual components, and ChCl-based DESs have a promising green profile [20]. Owing to their low vapor pressure, good conductivity, nonflammability, and cost-effectiveness, DESs have been widely applied in various fields, such as catalysis, electrochemistry, nanotechnology, electrolytes, and biomass pretreatment. In recent years, DESs have been employed for the removal of unwanted coatings on various objects in the cultural heritage conservation field [21–24]. However, despite their diverse physicochemical properties and wide applications, the ability of DESs to form gels has not been fully studied [19].

Polyvinyl alcohol (PVA) is a water-soluble semicrystalline synthetic polymer produced by the hydrolysis of poly (vinyl acetate) (PVAc), which involves replacing acetate groups with hydroxyl groups. The degree of hydrolysis has significant effects on chemical properties [25]. PVA has attracted considerable interest due to its biocompatibility, degradability, and favorable physicochemical properties [26]. Recently, green gels based on various types of DESs and PVA or its composites have been reported for their excellent frost resistance, conductivity, adhesive and recoverable performance, demonstrating potential applications in the sensor field [27–30]. The poor solubility of PVA in DES can induce the folding and crystallization of PVA chains, leading to the formation of microcrystalline domains that provide remarkable mechanical properties to the eutectogel gel [29].

Compared with PVA chemical gels, PVA physical gels exhibit very low toxicity due to the absence of residual crosslinkers, which is why they have garnered more attention in the biomedical and biomaterials research fields [31]. In the cultural heritage conservation field, the gel-forming capability of PVA has been used for cleaning since the 2000s. PVA-based hydrogels have shown promising results when loaded with versatile cleaning agents [32]. However, hydrogels must be used carefully in the restoration of water-sensitive surfaces. In particular, it is known that natural polysaccharide-based hydrogels display lower efficacy in water retention and may cause alterations to the original materials [33,34].

GVL is a colorless low-viscosity liquid that can be readily obtained from cellulose-based biomass [35]. It has been widely used as a replacement for toxic, nonrenewable solvents due to its stability, biodegradability, and recyclability. Previous studies have explored GVL and poly-3-hydroxybutyrate (PHB) organogels for the removal of terpenic and acrylic varnishes from paintings [5,36]. However, GVL based PHB gels are not flexible enough to bend freely. Subsequently, a combined material consisting of PHB-GVL gel and PVA electrospun mat was produced to improve ease of use and reduce superficial solvent release [37].

2. Research aim

The present study aims to create a green rigid nonaqueous gel system that may provide a controlled release of GVL to remove polymeric coatings. To this end, we developed an eutectogel using GVL in combination with DES choline chloride-ethylene glycol and polyvinyl alcohol (ChCl-EG-GVL$_2$-PVA$_2$). We compared this gel with one obtained without the addition of GVL (ChCl-EG-PVA$_2$), as well as with formulations that varied the content of GVL and PVA. The physical and chemical properties of the developed gels were investigated using rheological measurement (RM), total attenuated reflectance FTIR analysis (ATR-FTIR), scanning electron microscope (SEM) and thermogravimetric analysis (TGA). The performance of both gels was tested to remove Paraloid B72® coatings applied to a standard sample. Subsequently, the ChCl-EG-GVL$_2$-PVA$_2$ gel was also tested on a real case: a Yuan dynasty mural painting that had been covered with Paraloid B72® during a previous detachment and transfer process [38].

3. Materials and methods

3.1. Materials

Choline chloride (ChCl, 98 %), ethylene glycol (EG, 99 %), γ-valerolactone (GVL, 98 %) and gelatin (Gel strength 100 g Bloom) were purchased from Aladdin. Polyvinyl alcohol (PVA, 1788, with a polymerization degree of 1700 and hydroxyl contents of 88 %) was purchased from Kelong Chemical Company. Red ocher was purchased from Nantian Coating Company. Paraloid B72® was purchased from Rohm & Haas Company.

3.2. Preparation of the gels

ChCl-EG was produced by mixing ChCl (2.0 g) and EG (1.78 g) at the mole ratio of 1:2 in a Petri dish. The mixture was stirred at 100 °C for 5 min until a homogeneous colorless liquid was obtained. The gels were defined as ChCl-EG-GVL$_x$-PVA$_y$, where x represents volume of GVL and y represents the quality of PVA in the gel formulation. ChCl-EG-PVA$_2$ gel was prepared by adding PVA (2.0 g) to the obtained ChCl-EG, then hand stirring at 100 °C until it gets thickened, the gel was formed after cooling to room temperature. ChCl-EG-GVL$_2$-PVA$_2$ gel was prepared by mixing PVA (2.0 g) in a mixture of ChCl-EG (3.78 g) and GVL (2.0 mL). The mixture was stirred at 100 °C until getting thickened, the gel was obtained after cooling to room temperature. All gel formulations by varying of GVL and PVA contents were prepared with the same method and shown in Table S1.

3.3. Characterization of the gels

The morphology of both gels was using a scanning electron microscope (SEM, Thermo Fisher Axia ChemiSEM) at an accelerating voltage of 15 kV. During the preparation of SEM samples, the gel needs to undergo solvent replacement and supercritical drying processes. The choice of solvent is crucial as using an improper solvent can alter the gel's structure. We employ a concentration gradient of ethanol/ethylene glycol (EG) at 40 %, 70 %, and 100 % to remove original liquids from the gels. Supercritical drying (Quorum Technologies K850) was applied to dry the samples. Afterwards, the dried gel samples were sputtered with gold to 3 nm thicknesses using sputter coater (Leica EM ACE 200).

Rheology measurements were carried out on a Netzsch Kinexus Pro + Rheometer using a 25 mm diameter sensor plate with a gap of 1 mm, the oscillatory amplitude sweep experiments (γ: 0.01–100 %) were carried out to determine the linear viscoelastic (LVE) range at a constant frequency of 1 Hz. The obtained storage module G' (Pa), loss module G" (Pa) and complex module(η^*) reflect elastic character, viscos character and stiffness of the gel, respectively. Rheological measurements were performed on a set of 3 replicates for both gels and the trend showed no significant differences.

^{1}H NMR analysis was using a spectrometer (Bruker, 400 MHz), by transferring the ChCl, EG, ChCl-EG, GVL and ChCl-EG-GVL$_{0.1-3}$ mixtures into NMR tubes using dimethyl sulfoxide-d$_6$ (DMSO–d$_6$) as a reference solvent.

Thermogravimetric analyses (TGA) were carried out using a Mettler Toledo TGA/DSC1 instrument. The thermograms were recorded from room temperature to 700 °C at a heating rate of 10 °C/min under the N$_2$ atmosphere.

3.4. Sample preparation

ChCl-EG-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_2$ gels were tested on a mockup consisting of a thin layer of Paraloid B72® coating applied to a hydrophilic tempera surface, with egg as the binder for the pigment layer. The painting mockup was prepared following traditional painting techniques, with both the preparatory and painting layers applied using brushes. The preparation layer was created by dissolving 1.0 g of gelatin in 5.0 mL of hot distilled water at 60 °C, followed by the addition of 6.0 g of finely ground calcium carbonate. A gelatin sealing layer was then applied over the preparation layer by dissolving gelatin in distilled water at a 1:2 mass ratio. The pigment layer was prepared by mixing 1.0 g of red ochre with 1.0 mL of an egg binder mixture, composed of egg white, yolk, and distilled water in a 1:1:1 vol ratio. As a natural mineral pigment, red ochre may contain silicate impurities. The coating was prepared by dissolving 1.5 g of Paraloid B72® in 10 mL of acetone, creating a 15:100 (m/v) solution. This coating was applied with a single brush and allowed to dry at room temperature for over one month before conducting the cleaning tests.

3.5. Cleaning procedure

To evaluate cleaning efficiency, ChCl-EG-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_2$ gels were initially tested on the mockup. Following these tests, the ChCl-EG-GVL$_2$-PVA$_2$ gel was selected for application in the real case study. This study focused on a valuable tomb mural painting from the Yuan Dynasty (A.D. 1271–1368). The presence of Paraloid B72® coating on the mural was identified via micro-FTIR analysis and confirmed by reviewing archaeological excavation records. The coating was sprayed as part of a preliminary consolidation campaign during the mural's detachment and transfer in 2005. For the cleaning procedure, the gel was applied directly onto the surface of the mockup or mural painting for 5 min. Afterward, the gel was removed using tweezers, and the surface was further cleaned with two dry cotton swabs to eliminate any coating residues and excess liquid.

3.6. Evaluation of the cleaning performances

Attenuated total reflectance (ATR) analyses were performed with a Thermo Nicolet (Thermo Fisher Scientific, Waltham, MA, USA), iN10MX imaging microscope, fitted with a mercury-cadmium-telluride detector cooled by liquid nitrogen. Measurements were performed using a slide-on ATR objective, equipped with a conical germanium crystal, in the range 4000–675 cm^{-1}, at a spectral resolution of 4 cm^{-1} with 64 scans and an optical aperture of 150 × 150 μm. Portable FTIR spectrometer (Bruker Alpha II) with reflectance mode was applied to determine the cleaning performance for the real case study, the spectra were collected with 4 cm^{-1} spectral resolution and 32 scans in the range 4000–600 cm^{-1} and a measuring spot of 6 mm in diameter. Spectroscopic analysis has been performed on 3 different cleaning areas and in each area 4 spectra have been collected.

4. Results and discussion

4.1. Gel characterization

ChCl-EG-PVA$_2$ gel and ChCl-EG-GVL$_2$-PVA$_2$ gel were prepared using a simple heating and cooling procedure. As shown in Fig. 1, the ChCl-EG-PVA$_2$ gel has a higher degree of transparency and adhesive than the ChCl-EG-GVL$_2$-PVA$_2$ gel. Both gels exhibit good mechanical properties, as they can be bent without breaking the structure. Owing to their high flexibility and bendability, they are suitable for cleaning purposes, as they allow for easy peeling off from treated surfaces and avoid the presence of polymer residues like soft gels.

Rheological measurements were employed to investigate the mechanical properties of the two gels. The elastic and viscous characteristics of the samples are represented by the storage and loss moduli, respectively. As shown in Fig. 2a, the storage modulus (G') of both gels is approximately an order of magnitude higher than their loss modulus (G'') in the linear viscoelastic region (LVE) of 1 %. This corresponds with the gel property and demonstrates the gel-like structure of the two samples. Furthermore, the G' and G'' values of both gels are significantly higher than those previously reported for a ChCl-urea agar gel formulation [21]. This suggests that the network structures of the current gels are stronger. Fig. 2b shows that the complex viscosity of ChCl-EG-GVL$_2$-PVA$_2$ gel is greater than the ChCl-EG-PVA$_2$ gel, indicating a more rigid formulation in the gel which contains GVL.

^{1}H NMR spectra were used to investigate the interactions within the ChCl-EG-GVL liquid system. The formulations are shown in Table S2 and the relevant spectra are displayed in Fig. 3. Upon mixing ChCl with EG, the chemical shift of the -OH in ChCl shifted upfield from 5.63 ppm to 5.50 ppm, while the -OH in EG shifted downfield from 4.43 ppm to 4.49 ppm. These shifts indicate the formation of a DES through hydrogen bond interactions between ChCl and EG [39]. Upon the addition of GVL to ChCl-EG, no significant chemical shift of GVL was observed. The slight upfield shift of the -OH in the ChCl-EG DES is attributed to the presence of water [40]. This result demonstrates that the additional GVL does not impact the interactions within the ChCl-EG DES.

ATR-FTIR analyses were conducted to further investigate the formation mode of ChCl-EG-GVL-PVA gels. The spectra of PVA powder, ChCl, EG, ChCl-EG, and GVL are presented in Fig. S1. Table S3 lists the major vibrations attributed to PVA and ChCl-EG. The vibration observed at 3274 cm^{-1} in PVA powder corresponds to its O–H stretching, primarily due to PVA's hydrogen bonds [41]. As shown in Fig. 4a, the spectra of ChCl-EG-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_2$ gels display the O–H band at higher wavenumbers compared to pristine PVA powder, specifically at 3300 cm^{-1} and 3317 cm^{-1}, respectively. This indicates a partial disruption of the hydrogen bond networks initially formed in PVA, while hydrogen bond networks between PVA and ChCl-EG facilitates the formation of the gels' crosslinked structure.

Additionally, the influence of GVL and PVA on the ChCl-EG-PVA gel was examined by varying the GVL and PVA content. The spectra of the five fresh gels (Table S1) presented in Fig. 4, indicate that upon the addition of 1 mL of GVL, the O–H stretching shifts to a higher wavenumber, suggesting that the additional GVL partially disrupts the hydrogen bond networks formed by ChCl-EG and PVA. However, increasing the GVL content to 2 mL does not result in

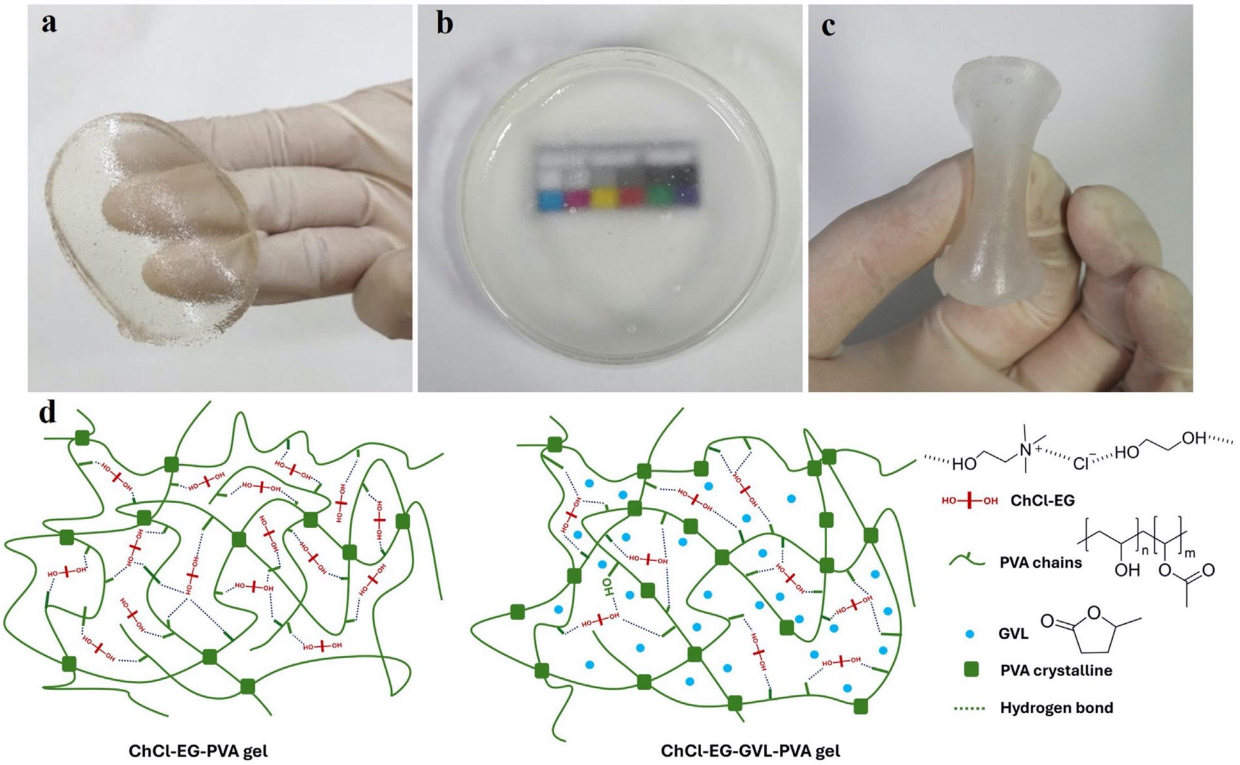

Fig. 1. Images of (a) ChCl-EG-PVA$_2$ and (b, c) ChCl-EG-GVL$_2$-PVA$_2$ gel, (d) schematic illustration of ChCl-EG-PVA and ChCl-EG-GVL-PVA gel structure.

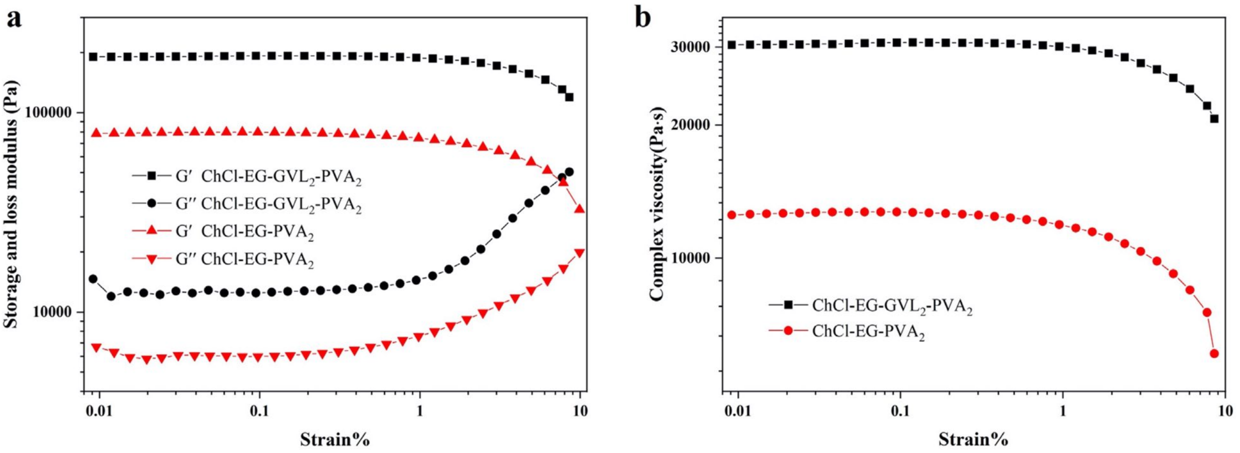

Fig. 2. Strain dependence of (a) storage and loss modulus (G' and G"), and (b) complex viscosity of ChCl-EG-GVL$_2$-PVA$_2$ gel (black) and ChCl-EG-PVA$_2$ gel (red).

a significant shift compared to 1 mL of GVL, while the intensity of the O–H stretching decreases with the increasing GVL content. This finding suggests that the hydrogen bonding interaction mode remains unchanged in the ChCl-EG-GVL-PVA system, but the addition of GVL dilutes the ChCl-EG DES, thereby reducing the extent of hydrogen bonding between the ChCl-EG and PVA. Similar results are observed in Fig. 4b, in the presence of 2 mL of GVL, altering the PVA content from 1 to 3 g does not induce a shift in the O–H stretching, while the intensity of the O–H stretching increases with increasing PVA content. This indicates that the hydrogen bonding can be strengthened by increasing the PVA content. The results from ^{1}H NMR and ATR-FTIR analyses demonstrate that GVL primarily acts as a diluent, influencing the degree of hydrogen bond crosslinking in the gels. Conversely, the main function of GVL in the gels is as a detergent for cleaning, while the ChCl-EG is responsible for the physical crosslinking with PVA through hydrogen bonding.

SEM micrographs of ChCl-EG-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_2$ gels are presented in Fig. 5. Microparticles are evident in both gels, which can be attributed to the crystallization of PVA due to its poor solubility in ChCl-EG and ChCl-EG-GVL. The bundles of fibers associated with these microparticles form a promising three-dimensional network that enhances the mechanical properties of the gels. The surface morphology analysis also indicates that the ChCl-EG-PVA$_2$ gel exhibits a higher prevalence of fibrous structures compared to the ChCl-EG-GVL$_2$-PVA$_2$ gel. These fibers create strong

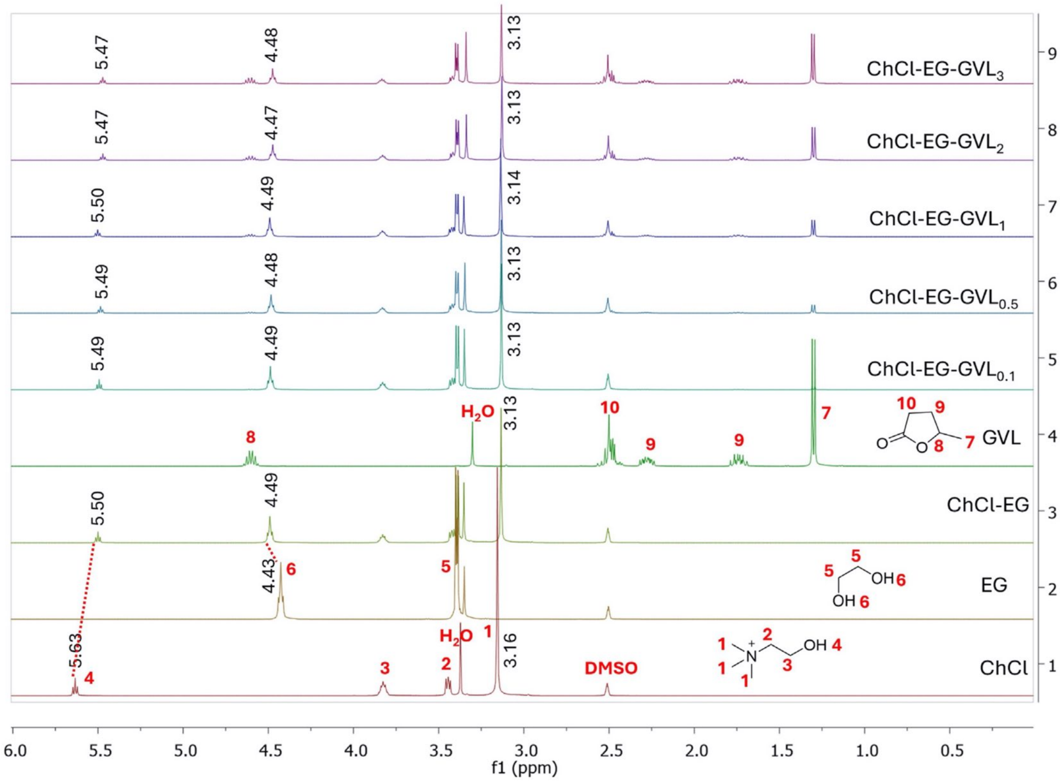

Fig. 3. ^{1}H NMR of ChCl, EG, ChCl-EG, GVL and ChCl-EG-GVL$_{0.1-3}$ mixtures.

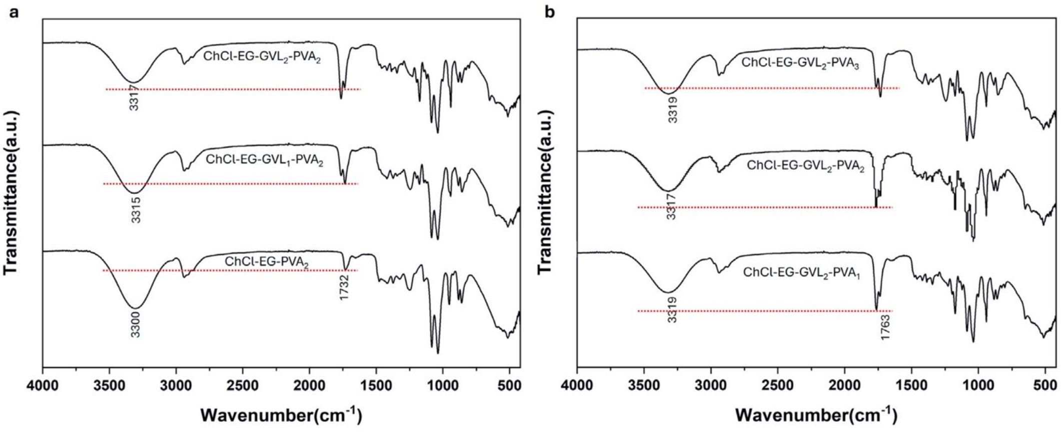

Fig. 4. ATR-FTIR spectra of (a) ChCl-EG-PVA$_2$, ChCl-EG-GVL$_1$-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_2$ gel, (b) ChCl-EG-GVL$_2$-PVA$_1$, ChCl-EG-GVL$_2$-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_3$ gel.

entanglements with PVA crystals, resulting in a rougher surface for the ChCl-EG-PVA$_2$ gel, which suggests a more stable network structure. In contrast, the addition of GVL partially disrupts and dilutes the degree of hydrogen bonding, leading to a reduction in fibrous structures and a more compact surface, thereby increasing the rigidity of the gel. In light of these conclusions, a schematic illustration of the structures of ChCl-EG-PVA and ChCl-EG-GVL-PVA gels is presented in Fig. 1d.

TGA-DSC measurements were used to examine the thermal degradation behavior of the ChCl-EG-PVA$_2$ gel and the ChCl-EG-GVL$_2$-PVA$_2$ gel. Fig. 6 and Table S4 report their weight losses corresponding to various temperature ranges. ChCl-EG, ChCl-EG-GVL and their compositions were also examined for comparison (Fig. S2). Three steps of weight loss were identified for the pristine PVA powder. The high hygroscopicity of PVA results in a slight weight loss observed at low temperatures, which can be attributed to the evaporation of moisture. The second stage occurs between 250 °C and 410 °C, related to the polymer's thermal degradation, accounting for 72.67 % of the total weight loss. In this stage, two maximum decomposition temperatures of 319 °C and 358 °C were observed [42]. The final decomposition of the remaining organic compounds results in a weight loss of 16.68 % over 410 °C [43].

For the ChCl-EG DES, decomposition occurs at around 320 °C. The weight loss of 41.49 % is attributed to the evaporation of EG

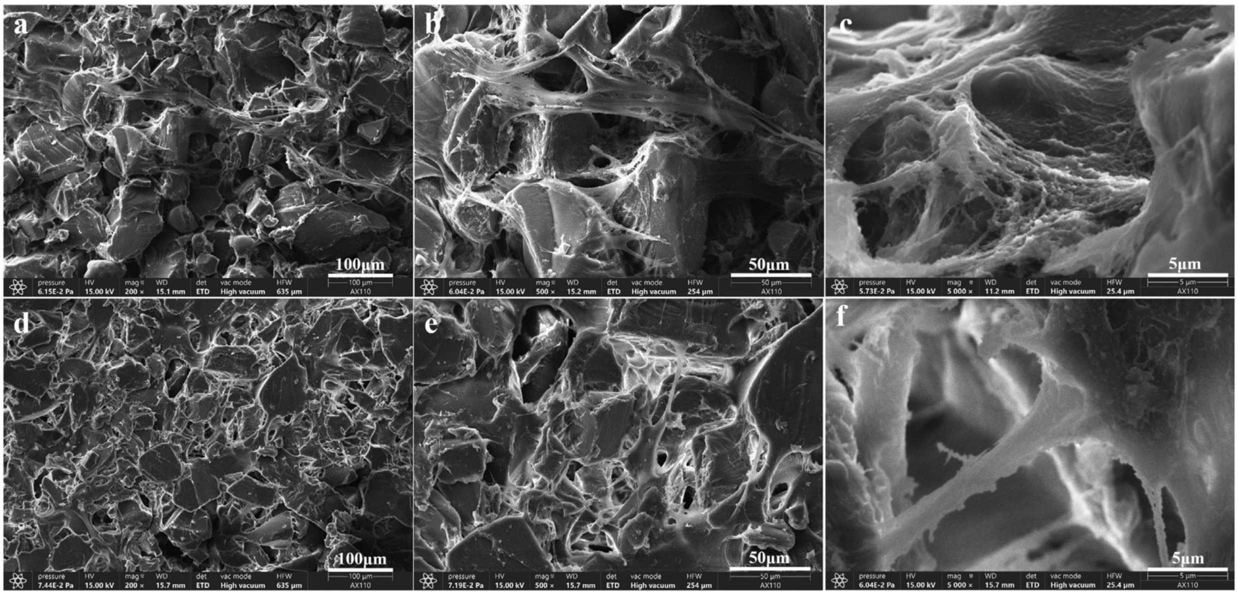

Fig. 5. SEM micrographs of ChCl-EG-PVA$_2$ gel (a, b, c) and ChCl-EG-GVL$_2$-PVA$_2$ gel (d, e, f) at different magnifications.

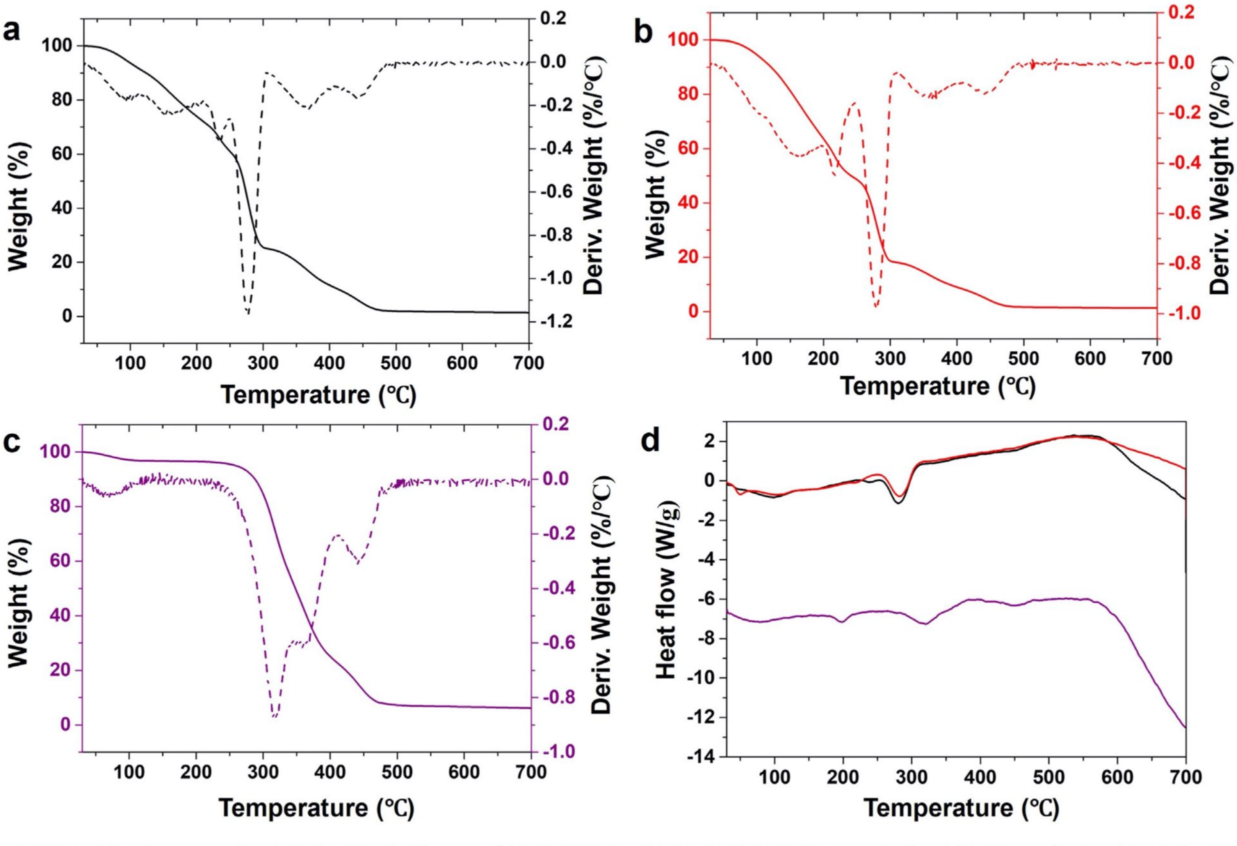

Fig. 6. TGA (solid) and corresponding derivative TGA (dash) curves of (a) ChCl-EG-PVA$_2$ (black), (b) ChCl-EG-GVL$_2$-PVA$_2$ (red) and (c) PVA powder (purple); (d) the DSC of ChCl-EG-PVA$_2$ (black) and ChCl-EG-GVL$_2$-PVA$_2$ (red) and (c) PVA powder (purple).

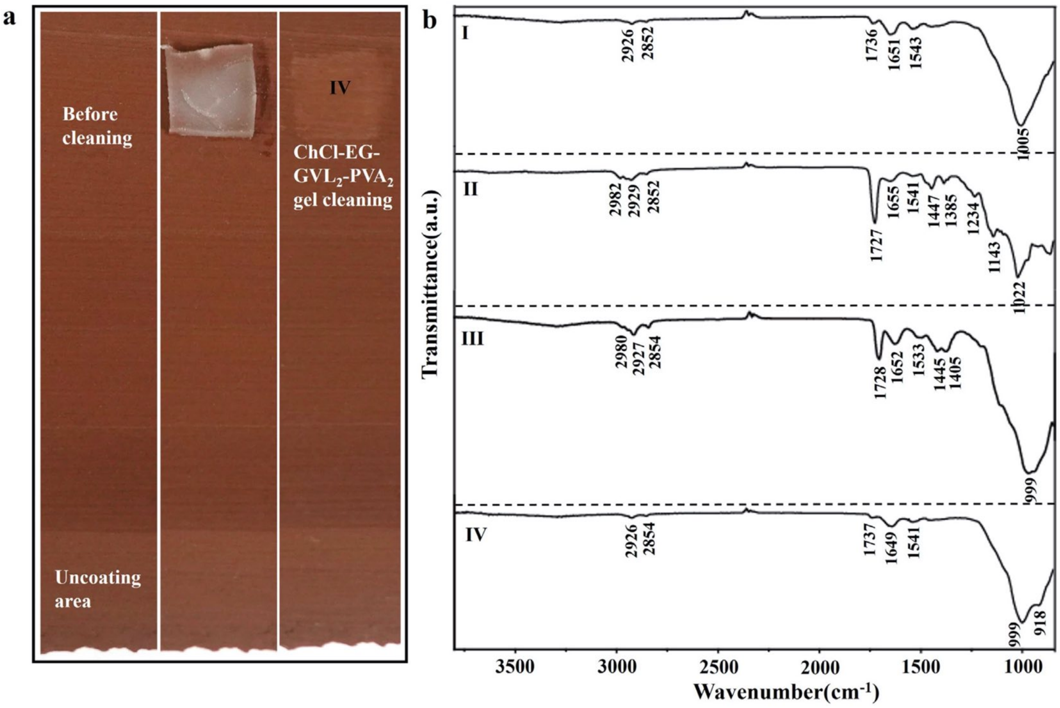

Fig. 7. The aspect of the mock-up (a) at the cleaning procedure; Micro-FTIR (b) acquired on (I) an uncoating area, (II) Paraloid B72® coating area, (III) after ChCl-EG-PVA$_2$ gel cleaning, (IV) after ChCl-EG-GVL$_2$-PVA$_2$ gel cleaning.

below its boiling point. From 236 °C to 276 °C, the temperature reaches and exceeds the boiling point of EG, resulting in its complete vaporization and a weight loss of 16.28 %. This vaporization temperature is higher than that of pure EG, which is 180 °C, indicating that the DES is more stable after its formation [44]. The weight loss of 42.23 % between 276 °C and 320 °C is associated with the decomposition of choline chloride [44]. The addition of GVL to the ChCl-EG DES increases the weight loss to 54.81 % in the temperature range of 30 °C to 210 °C, however, it does not affect the complete decomposition attributed to ChCl.

The ChCl-EG-PVA$_2$ gel exhibits an 8.69 % weight loss between 30 °C and 115 °C, which is associated with a broad endothermic peak in the DSC curve, attributed to the evaporation of water and EG. Between 115 °C and 210 °C, a weight loss of 19.28 % occurs due to the evaporation of EG below its boiling point. From 210 to 250 °C, the temperature reaches and exceeds the boiling point of EG, resulting in its complete vaporization and a weight loss of 11.04 %. The weight loss of 36.11 % observed between 250 °C and 310 °C is primarily linked to the decomposition of choline chloride and partial thermal degradation of PVA, accompanied by a strong endothermic peak in the DSC curve. At this stage, the decomposition of the DES in the ChCl-EG-PVA$_2$ gel is complete. The weight loss observed afterward is related to the decomposition of the remaining PVA.

The ChCl-EG-GVL$_2$-PVA$_2$ gel exhibits two weak endothermic peaks in the DSC curve, along with an initial weight loss of 8.54 % at lower temperatures, ranging from 30 °C to 115 °C. This weight loss is attributed to the evaporation of water and the partial evaporation of GVL and EG. A notable 31.41% weight loss occurs as the temperature increases to the boiling points of EG and GVL. Both GVL and EG completely vaporize between 210°°C and 250 °C, resulting in an additional 11.48 % weight loss. The main cause of the 30.48 % weight loss observed between 250 °C and 310 °C is the decomposition of choline chloride and the partial thermal degradation of PVA, accompanied by a strong endothermic peak. The subsequent weight loss is associated with the decomposition of the remaining PVA.

TGA results show that only a small amount of water and liquids evaporate from the ChCl-EG-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_2$ gels below 100 °C, indicating that the gels have good thermal stability in the environment. The stability of the gels, along with the high boiling points of EG and GVL, ensures that the liquid components are effectively retained within the gel matrix, increasing the durability of the gels in cleaning applications. Additionally, ChCl-EG contains abundant hydroxyl groups that interact with hydroxyl groups at PVA chains through hydrogen bonding, thereby strengthening the gel network and improving its mechanical properties. In this case, the coating layer can gradually swell and dissolve with the controlled release of the cleaning agent, which can ultimately be removed by peeling off the gel after treatment.

4.2. Evaluation of the cleaning performances

To assess the potential usefulness of DES-based gels in the field of culture heritage conservation, ChCl-EG-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_2$ gels were tested for their ability to remove Paraloid B72® from a mockup prepared as described in the sample preparation section. The cleaning efficiency of the gels was investigated using micro-FTIR, which was performed on the mockup surface before and after cleaning (Fig. 7a). In the uncoated area signals related to egg binder and red ocher can be observed (Fig. 7bI). As shown in Fig. 7bII, the characteristic bands of Paraloid B72® are identified by the presence of vibrations at 1727 cm^{-1} (C=O stretching), 1447 and 1385 cm^{-1} (C–H bending), and 1234 cm^{-1} and 1143 cm^{-1} (C–O-C stretching) [45]. Fig. 7bIII indicates that treatment with the ChCl-EG-PVA$_2$ gel was ineffective as the characteristic bands of Paraloid B72® remained evident. Conversely, after cleaning with the ChCl-EG-GVL$_2$-PVA$_2$ gel, the characteristic bands of Paraloid B72® disappeared completely. Additionally, vibrations at 999 and 918 cm^{-1}, attributed to the silicate components in the painting layer, can

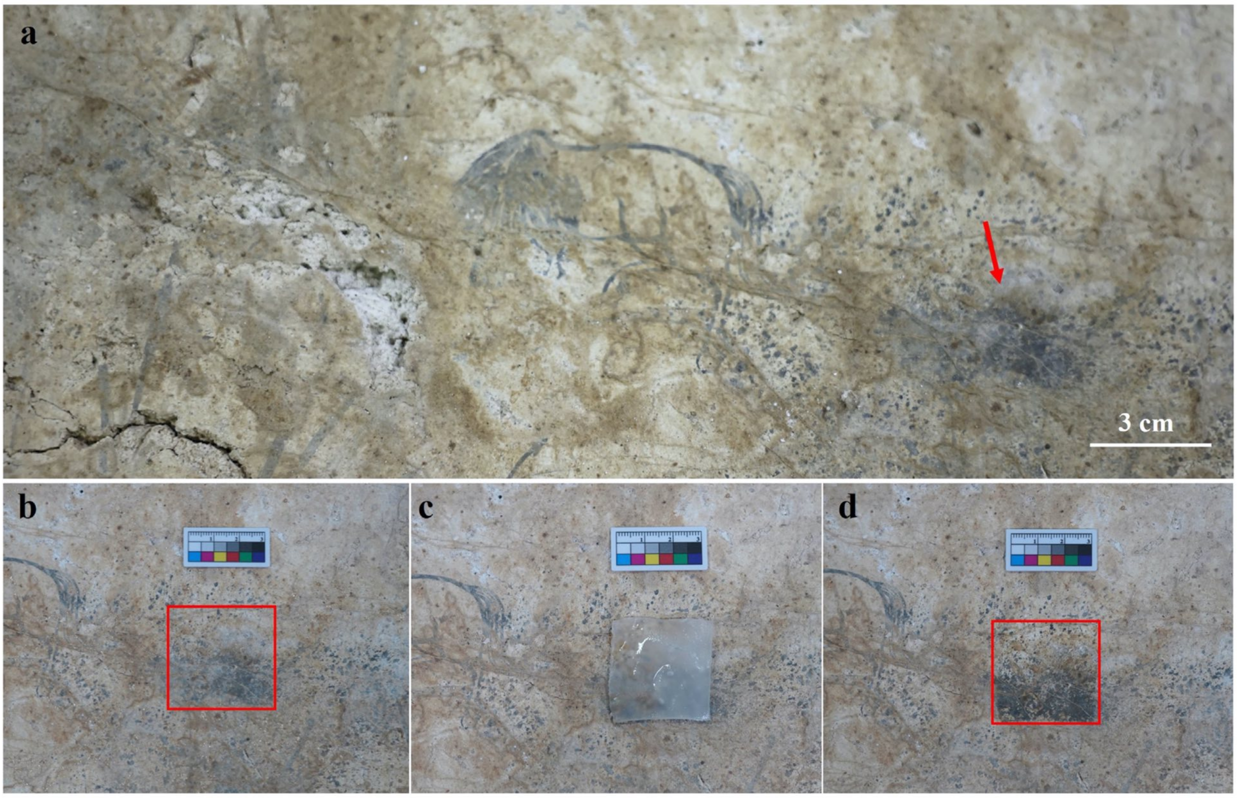

Fig. 8. Images of mural painting (a) cleaning test area and the cleaning procedure of (b) before cleaning, (c) ChCl-EG-GVL$_2$-PVA$_2$ gel application and (d) after cleaning.

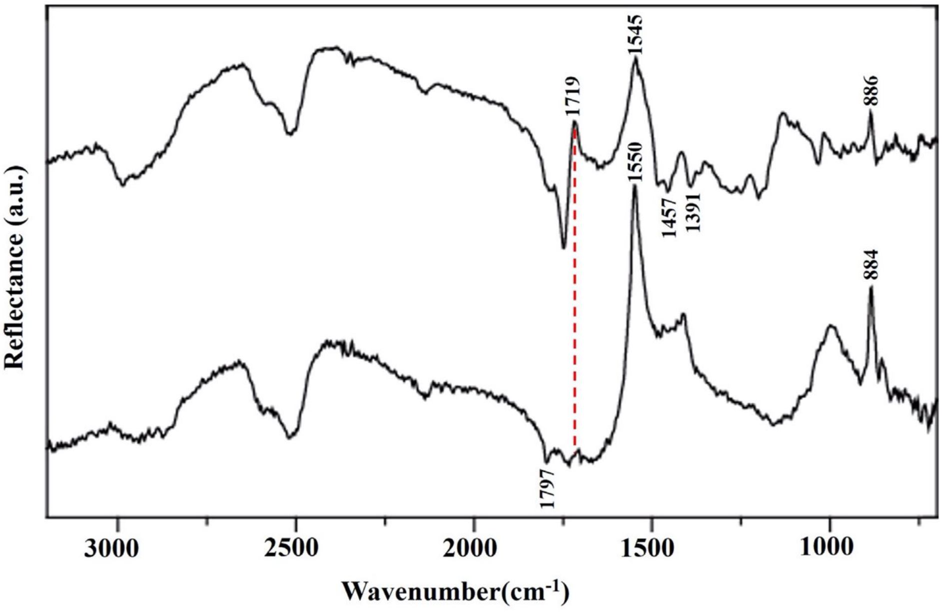

Fig. 9. Reflectance FTIR spectra of the area in the mural painting before cleaning (up), after ChCl-EG-GVL$_2$-PVA$_2$ gel cleaning (down).

be clearly identified after cleaning. Fig. S3 presents graphs of the cleaning areas treated with both gels, where dry cotton swabs were used to remove the swollen coating and gel residues. No residues from the gel or coating were detected in the cleaned area treated with the ChCl-EG-GVL$_2$-PVA$_2$ gel. However, the coating was not significantly reduced after cleaning with ChCl-EG-PVA$_2$ gel and dry cotton swabs. The results indicate that the ChCl-EG-GVL$_2$-PVA$_2$ gel, using GVL as a cleaning agent, can effectively remove the Paraloid B72® coating without leaving any residues.

After evaluating the cleaning efficiency on the mockup, the ChCl-EG-GVL$_2$-PVA$_2$ gel was tested on a mural painting from the Yuan Dynasty. The surface of the mural exhibited a Paraloid B72® coating that was applied during a previous consolidation campaign. The apparent yellowing and darkening of the coating may indicate degradation over time. For the cleaning process (Fig. 8 and Fig. S4), the ChCl-EG-GVL$_2$-PVA$_2$ gel was applied directly for 5 min, and two dry cotton swabs were used to remove the swelling residues. Subsequently, in situ and noninvasive analysis using FTIR in reflectance mode was performed to evaluate the gel's cleaning performance. As shown in Fig. 9, before cleaning, the characteristic vibrational bands of Paraloid B72®, including C=O stretching at 1719 cm^{-1} (inverted), and C–H bending at 1484 cm^{-1}, 1457 cm^{-1} and 1391 cm^{-1}, were identifiable [46]. Following treatment, not only did the signal for Paraloid B72® disappear, but there was also a significant increase in the intensity of inverted bands at 1550 cm^{-1}(CO_3^{2-} antisymmetric stretching) and 884 cm^{-1}(CO_3^{2-} out-of-plane bending), which can be attributed to calcium carbonate [47]. Comparable results were observed in a different testing area (Fig. S5). The findings from this case study indicate that the ChCl-EG-GVL$_2$-PVA$_2$ gel demonstrates effective cleaning efficiency for removing the Paraloid B72® coating from the mural.

5. Conclusion

Green gels prepared using DES and PVA are proposed in this study. Their physical interactions through hydrogen bonds were explored via ^{1}H NMR and ATR-FTIR. In this arrangement, PVA acted as the gelator to form a fibrous structure and interact with ChCl-EG, while GVL was added as the cleaning agent. The selected ChCl-EG-PVA$_2$ and ChCl-EG-GVL$_2$-PVA$_2$ gels exhibit commendable mechanical properties, allowing for ease of handling and peeling. Their mechanical and thermal characteristics were assessed through rheological measurements and thermogravimetric analyses. The cleaning efficiency of both gels was tested on a mockup and evaluated using micro-FTIR. The ChCl-EG-GVL$_2$-PVA$_2$ gel demonstrated exceptional effectiveness in removing the Paraloid B72® coating, leaving no residues in the treated area. Consequently, this gel was selected for further evaluation of its capacity to remove aged acrylic coating from a mural painting. The cleaning performance was assessed in situ using FTIR in reflectance mode, confirming the efficacy of this formulation for the removal of acrylic coating.

In conclusion, the proposed eutectogels demonstrate promising mechanical properties, the ability to retain solvents without leaving residues after treatment, and the potential to avoid water, making them suitable for treating even water-sensitive surfaces. The use of DES in the preparation of the gels will enable future applications to tailor their wetting ability by adjusting the amounts of DES and GVL according to the polarity of the coatings to be removed.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at

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