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Poly(vinyl alcohol)/poly(vinyl pyrrolidone)

Hydrogels for the Cleaning of Art

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KEYWORDS

Hydrogels, cleaning, contemporary art, poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), conservation, gellan gum

ABSTRACT

The cleaning of modern and contemporary paintings is a delicate and challenging operation. Many contemporary paintings exhibit rough, clotted and pitted surfaces, where the removal of soil is difficult. Gels are among the most efficient tools to achieve controlled and efficient cleaning of works of art. However, most gels used in the conservation practice are too rigid to adapt rough surfaces, or too mechanically weak to be removed without leaving polymer residues. Several formulations of physically cross-linked poly(vinyl alcohol) (PVA)-based hydrogels, obtained by cast-drying or freeze-thawing of aqueous polymeric solutions, were formulated and characterized.

The viscoelastic properties, porosity, and crystallinity of the gels were studied, along with the behavior of water inside the polymeric network. It was shown that the properties of the gels were improved through blending with poly(vinyl pyrrolidone) (PVP). The most promising gel formulation, in terms of mechanical properties and water retentiveness, was assessed for the removal of soil from an alkyd painting mock-up. A traditional gel, gellan gum, was also tested as a reference system. The effectiveness of soil removal was investigated by 2D Fourier transform infrared (FTIR) microscopy, using a Focal Plane Array (FPA) detector. In conclusion, it was shown that the newly developed formulation grants the residue-free removal of soil from rough and irregular artistic surfaces, overcoming the limits of traditional cleaning methods.

INTRODUCTION

The removal of unwanted materials from works of art is a common yet challenging operation. Research in conservation science is constantly addressing the development of innovative, highly technological materials, tailored to specific conservation challenges.

Ideal cleaning systems must allow high control and selectivity of the cleaning action. The use of gelled systems, which has been recently introduced in the conservation practice, is one of the most successful strategies to achieve highly effective and non-invasive cleaning.¹⁻⁵ Most gels used in the conservation practice are physical gels;⁶⁻⁹ more recently, chemical gel formulations have been introduced.¹⁰⁻¹⁵ Conservators usually label gels based on their macroscopic mechanical behavior. Accordingly, two different classes are identified: *rigid gels* and *soft gels*. Rigid gels have fixed shape, and they usually grant controlled release of cleaning fluids. The strong cohesion forces of these networks result in their feasible removal from treated surfaces, leaving no polymer residues.

However, rigid gels do not adhere homogenously on rough surfaces, as shown in Figure 1-A. This hinders homogenous cleaning of artistic surfaces. Rigid gels include physical polysaccharide-based hydrogels, such as Agar Agar and gellan gum, and chemical semi-interpenetrated (semi-IPN) poly(2-hydroxyethyl methacrylate)/poly(vinyl pyrrolidone) (p(HEMA)/PVP) hydrogels and organo-gels.^{10,11}

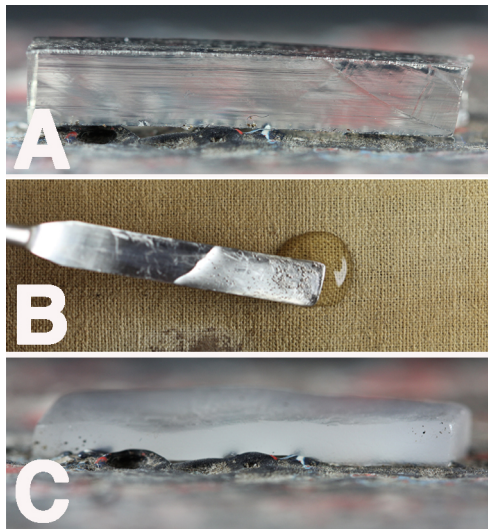


Figure 1. Gels used in conservation: (A) a *rigid gel* – gellan gum 3%; (B) a *soft gel* - Klucel™ 4%; (C) a poly(vinyl alcohol)/poly(vinyl pyrrolidone) (PVA/PVP) hydrogel. The rigid gellan gum does not adhere as homogenously as a PVA/PVP hydrogel to a rough painted layer that mimics a modern/contemporary painting.

The soft gels class includes materials that display a *jam-like* texture, as hydroxypropylcellulose (e.g. Klucel™) (see Figure 1-B) and polyacrylic acid (PAA). The main advantage of soft gels is their adhesion to rough surfaces. However, it has been shown that the complete removal of

cellulose- and PAA-based gels after cleaning is not achieved even using rinsing solvents and mechanical action.¹⁶⁻¹⁸

Poly(vinyl alcohol) (PVA)-based hydrogels are commonly used in human tissue engineering or membranes formation, thanks to specific properties such as high water content, viscoelasticity, biocompatibility and non-toxicity.¹⁹⁻²² Freeze-thawing (FT) and cast-drying (CD) are two common procedures for preparing these gels.^{19,23,24} Gel formation is induced by phase separation of the polymer solution in freeze-thawing, or by solvent evaporation in cast-drying, leading to the formation of small crystalline nuclei. The growth of the nuclei induces the formation of crystallites, which act as tie points within the polymeric network. The resulting gels have optimal mechanical strength and, at the same time, display good adhesion to rough surfaces, as shown in Figure 1-C. These were deemed as optimal characteristics for the cleaning of pitted and clotted painted surfaces, which are frequently met in modern/contemporary art.

Here, PVA-based hydrogels were prepared from aqueous polymer solutions, using both cast-drying and freeze-thawing. The viscoelastic properties, porosity, and crystallinity of the gels were investigated, as well as the behavior of water inside the polymeric network. The properties of these gels can be tuned by blending PVA with poly(vinyl pyrrolidone), PVP, a highly hydrophilic polymer recently proposed in semi-interpenetrated (semi-IPN) hydrogels for the cleaning of cultural heritage artifacts.^{11,25} The influence of PVP on specific properties (e.g. hydrophilicity, porosity, and rheological behavior) was investigated.

A PVA/PVP formulation with ideal mechanical properties and retentiveness was characterized and assessed for the removal of artificial soil from a painting mock-up sample with a rough surface, which mimics the artworks of Action Painters (e.g. Jackson Pollock and Willem de Kooning). Micro-reflectance Fourier transform infrared (FTIR) 2D imaging was carried out on painting

mock-ups using a Focal Plane Array (FPA) detector with the largest array currently available (128x128 pixels), in order to evaluate both the cleaning efficacy and the presence of gel residues through molecular mapping with high spatial resolution (down to few microns). Gellan gum was also tested as a reference.

EXPERIMENTAL SECTION

MATERIALS

PVA (av. M_w 146000-186000 g/mol, assay 98-99%) and PVP (av. M_w 1300000 g/mol, assay 95%) were purchased from Sigma-Aldrich (Germany). KELCOGEL® Gellan Gum (technical grade) was purchased from CTS (Italy). Klucel™ (technical grade) was purchased from Phase Restauro (Italy). Chemicals were used as received. Water used for the preparation of polymer solutions was purified by a Millipore system (resistivity >18 MΩ cm).

PREPARATION OF GELLAN GUM AND KLUCEL™

Gellan gum (3%) was prepared according to a procedure reported elsewhere.²⁶ A solution of Klucel™ (4% w/w) was obtained by adding powdery hydroxypropyl cellulose to water. The mixture was stirred overnight until a clear viscous polymer dispersion was obtained.

PVA/PVP HYDROGEL PREPARATION

Aqueous polymer solutions were obtained by dissolving PVA powder into purified water at 95°C in a double neck flask equipped with a condenser, to avoid water evaporation during heating. After complete dissolution of PVA, PVP is added, and the solution is stirred at 80°C for 4 hours

to achieve complete homogenization. To obtain a transparent solution, gas bubbles due to stirring are removed through 15 minutes sonication in pulsed mode in an ultrasonic bath. Polymer solutions (7.5 g each) were then poured in glass Petri dishes (diameter = 50 mm) and subjected to cast-drying or freeze-thawing processes.

CAST-DRYING METHOD

To obtain hydrogels through cast-drying method, Petri dishes containing the polymer solution were stored in an oven for 12 hours at 50°C under nitrogen flow, to attain complete evaporation of the liquid fraction. The obtained xerogels, which are transparent and glassy, are rehydrated with purified water to yield elastic hydrogel films (ca. 1 mm thick). After washing in purified water, films are stored in water-filled falcons.

FREEZE-THAWING METHOD

To prepare cryogels through freeze-thawing method, Petri dishes containing the aqueous PVA or PVA/PVP solutions were subjected to repeated freezing (8 hours at -23°C) and thawing cycles (16 hours at room temperature). Petri dishes were covered with a lid, and sealed to prevent evaporation during the thawing cycles. After gelation, hydrogels were washed to extract ungelled components, and stored into containers filled with purified water.

PHYSICOCHEMICAL CHARACTERIZATION OF GELS

Gel fraction

The gel fraction is determined gravimetrically through the formula²⁷

$$G(\%) = (W_d/W_0) * 100 \quad (1)$$

where W_0 is the dry weight of the sample with residual soluble components (not extracted), while W_d is the dry weight after extraction of soluble components. Dry weights are determined after drying in oven at 120°C until constant weight is reached. G% data are reported in Table 1. The measurements were repeated at least five times.

Water content and free water index

The equilibrium water content (EWC) provides information on the hydrophilicity of the gel network. EWC is calculated according to the formula²⁸

$$EWC (\%) = ((W_w - W_d)/W_d) * 100 \quad (2)$$

where W_w is the weight of the swollen hydrogel measured 7 days after preparation, and W_d is the dry weight of the hydrogel, determined by differential thermogravimetry (DTG). The measurements were repeated at least three times.

Free water index (FWI) gives the fraction of water, within hydrogels' structure, which acts as bulk water, i.e. available for the exchange processes involved in the cleaning process. The FWI was calculated as follows²⁹

$$FWI = \Delta H_{exp}/(WC * \Delta H_{theo}) \quad (3)$$

where ΔH_{exp} (J/g) is the experimentally measured melting enthalpy of water for the given sample (at least three measurements), calculated by integration of the differential scanning calorimetry (DSC) peak around 0°C, ΔH_{theo} is the theoretical value for the melting enthalpy of bulk water (333.61 J/g),³⁰ while WC is the water content, which corresponds to EWC for fully swollen hydrogels.

Gel samples (5-10 mg for cast-drying method, and 18-22 mg for freeze-thawing method) were analyzed in a Tzero™ aluminum hermetic pans using a DSC Q1000 (TA Instruments) apparatus. Temperature scan was from -60 °C to 25 °C, with a 0.5 °C/min heating rate. After DSC measurements, hermetic pans were drilled, and the water content was determined using a SDT Q600 (TA Instruments) apparatus. The temperature scan was from 20 °C to 450 °C with a heating rate of 10 °C/min.

Water release

The amount of water released on a porous hydrophilic substrate provides information about the retention capability of gels. After gently drying with blotting paper, a fully swollen hydrogel was placed in a Petri dish over filter paper, and covered with a lid to avoid water evaporation. After 30 minutes, water release was determined gravimetrically by weighting the Petri dish and the filter paper. The measurements were repeated at least three times.

Porosity

In order to investigate the meso- and macroporosity, hydrogels were freeze-dried, obtaining xerogels whose porous structure is as close as possible to that of swollen hydrogels. Images were

acquired with a FEG-SEM SIGMA (Carl Zeiss, Germany) using an acceleration potential of 1 kV and a working distance of 1.4 mm. For the analyses, gold-metallization of xerogels was performed with an Agar Scientific Auto Sputter Coater.

Rheology

Oscillatory rheology measurements were performed using a Discovery HR-3 rheometer from TA Instruments, equipped with a parallel plate geometry (40 mm diameter) and a Peltier temperature control system. The storage modulus, G' , and the loss modulus, G'' , were recorded. The linear viscoelastic region was previously determined through amplitude sweep runs (strain 0.01-40%; 1Hz). Presented data are average of at least two measurements.

Crystallinity of hydrogels

The degree of crystallinity, defined as the fractional amount of crystallinity in semi-crystalline polymer samples,³¹ can be determined by measuring the specific melting enthalpy of PVA in the samples. The degree of crystallinity is calculated as follows

$$X_c = (\Delta H_{\text{exp}}/\Delta H_{100}) * 100 \quad (4)$$

where ΔH_{exp} is the measured specific melting enthalpy of PVA in the samples, and ΔH_{100} the specific melting enthalpy of a completely crystalline PVA over the same temperature range. Measurements were carried out using a SDT Q600 (TA Instruments) apparatus that provides the weight corrected heat flow (J/g); samples were analyzed between 20 °C and 450 °C, with a heating rate of 10°C/min. The measurements were repeated at least three times. Crystallinity of hydrogels

was determined by integration of the melting peak between 200-250°C, as reported in the literature,^{21,32,33} and then calculated according to (4) using the specific melting enthalpy of completely crystalline PVA (161 J/g).³⁴

APPLICATION TESTS

To perform the cleaning tests, a mock-up sample was prepared using industrial alkyd paints diluted in turpentine, which were extensively used by prominent artists such as J.Pollock or P.Picasso.³⁵⁻³⁷ Alkyd colors (*Vermillion GR. 1*, *Prussian blue GR. 1*, *Ivory black GR. 1* and *Titanium white GR. 1*) were purchased from Winsor & Newton (product line *Giffin*). Colors were applied on canvas simulating the *dripping* technique, so as to obtain a highly irregular painted layer. Prior to the cleaning tests, the mock-up was covered with an artificial soil mixture that simulates atmospheric particulate.³⁸

The PVA/PVP hydrogel formulation with optimal mechanical behavior and water retentiveness was tested for the removal of artificial soil from the mock-up sample. Gellan gum was used as a reference, as it is traditionally employed for the cleaning of paintings.

The 2D imaging-FTIR analysis of the mock-up was carried out using a Cary 620-670 FTIR microscope, equipped with an FPA 128x128 detector (Agilent Technologies). This set up allows the highest spatial resolution currently available to FTIR microscopes. The spectra were recorded directly on the surface of the samples (or of the Au background) in reflectance mode, with open aperture and a spectral resolution of 4 cm⁻¹, acquiring 128 scans for each spectrum. A “single-tile” analysis results in a map of 700 x 700 μm² (128 x 128 pixels), and the spatial resolution of each imaging map is 5.5 μm (i.e. each pixel has dimensions of 5.5 x 5.5 μm²). Five different tiles were

acquired both before and after treatment of the mock up with the gels. In order to improve the readability of the spectra, the background noise was reduced using the “smooth” tool (set at 11) of the Igor Pro software (Wavemetrics), taking care not to alter any diagnostic information deemed useful to this investigation. In each 2D map, the intensity of characteristic bands of the alkyd paint layer, of the artificial soil, or of the gel, was imaged. The chromatic scale of the maps shows increasing absorbance of the bands as follows: blue < green < yellow < red. Subtraction between spectra, where needed, was carried out using the “Autosubtract” tool of the ResPro software, which automatically calculates an optimized subtraction factor, multiplies the reference spectrum by such factor, and subtracts it from the active spectrum. The subtraction factor is calculated to minimize the sum of the mean-square differences between the mean-centered sample spectrum and the mean-centered reference spectrum in the selected region(s).

RESULTS AND DISCUSSION

The aim of this work is the formulation of gel systems that can be safely used for the cleaning of rough, clotted and pitted surfaces, typically found in the paintings of several Action Painters. In this regard, gels should be sufficiently viscous to adapt to the surface they are put in contact with. At the same time, gels should display strong cohesion forces to allow their complete removal after cleaning. Moreover, gels should contain high amounts of cleaning fluid, i.e. water, but they should also be retentive so as to avoid excessive and uncontrolled wetting of the surface.

Several hydrogel formulations were prepared using both cast-drying (CD) and freeze-thawing (FT) methods, at different PVA concentrations. It was found that a minimum PVA concentration

(> 3% w/v) is needed to obtain hydrogel films using the cast-drying method. However, films with good applicative features, i.e., elasticity and mechanical strength, are obtained for PVA concentrations between 6-12% w/v. Thus a 9% w/v PVA (named PVA_CD), and two formulations with increasing PVP content (named PVA/PVP(3:1)_CD and PVA/PVP(1:1)_CD) were selected for characterization. In Table 1, the names and compositions of the cast-drying films are indicated.

Figure 2 shows the phase diagram of several formulations of PVA-based cryogels (FT), including formulations that contain variable amounts of PVP. A minimum number of freezing cycles, n , is needed to obtain a gel for each of the investigated compositions. In Figure 2, the capital letter A indicates the area where gelation of systems does not take place (*sols*). On the other hand, gel formulations in area B are too fragile, and thus difficult or impossible to manipulate. Finally, formulations in area C are the most interesting systems from the applicative point of view. In particular, formulations prepared with 9% w/v PVA, yield gels with the most appealing macroscopic characteristics, i.e., elasticity and mechanical strength. Therefore, three different formulations with 9% w/v PVA and increasing PVP content were selected for characterization. Formulations having the same composition were prepared by increasing the number of freezing cycles (namely $n=3$ and $n=7$), in order to study the influence of freeze-thawing cycles on the gels' characteristics. In Table 1, the names and compositions of freeze-thawing films are indicated.

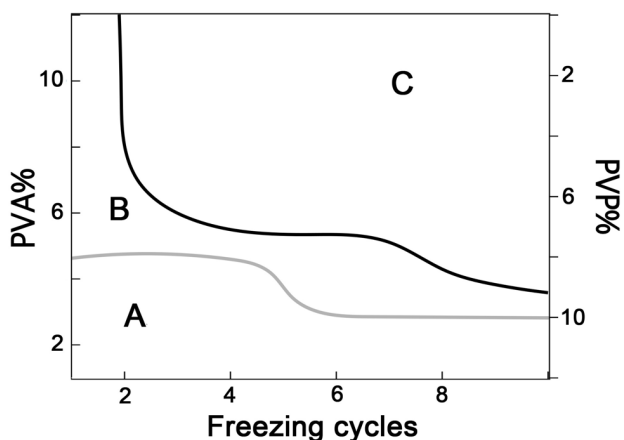


Figure 2. Phase diagram for a PVA/PVP/water system as a function of the number of freezing cycles n , and of polymer concentrations. Formulations in area A are *sols*; formulations in areas B and C are *gels*. Formulations in C exhibit the most interesting characteristics (elasticity, mechanical strength) from an applicative point of view.

Table 1: Composition and gel fraction (G%) of the selected hydrogel formulations.

Name	Method	PVA (w/v %)	PVP (w/v %)	nr. of cycles (n)	G (%)
PVA_CD	Cast-Drying	9	0	-	88.0±2.3
PVA/PVP(3:1)_CD		9	3	-	73.8±3.1
PVA/PVP(1:1)_CD		9	9	-	46.9±2.5
PVA_FT3	Freeze-Thawing	9	0	3	77.7±0.5
PVA_FT7				7	87.3±1.5
PVA/PVP(3:1)_FT3		9	3	3	68.3±1.0
PVA/PVP(3:1)_FT7				7	82.5±0.2
PVA/PVP(1:1)_FT3		9	9	3	32.4±0.5
PVA/PVP(1:1)_FT7				7	34.5±0.1

The equilibrium water content (EWC), free water index (FWI), and release properties of the selected hydrogel formulations were studied. The states of water in swollen hydrogels are three: free water, freezable bound water, and unfreezable bound water. Free water has the same

thermodynamic properties of bulk water; freezable bound water displays a freezing point lower than 0°C due to its weak interactions with polymer chains; unfreezable water, strongly hydrogen bonded, does not show a phase transition over the range of temperatures normally associated to the freezing of bound and bulk water. DSC and DTG were used to characterize water behavior inside the prepared PVA-based hydrogels, following established procedures.³⁹⁻⁴¹

Table 2. Equilibrium water content (EWC) and free water index (FWI) of the investigated hydrogel formulations, and water release on filter paper. For comparative purposes, water release data for hydrogels commonly used in conservation are also reported.

Cast-drying	EWC (%)		FWI		Water release (mg/cm ²)	
	n=3	n=7	n=3	n=7	n=3	n=7
PVA_CD	72.7 ± 1.9		0.05 ± 0.01		3.3 ± 0.4	
PVA/PVP(3:1)_CD	76.2 ± 3.2		0.79 ± 0.02		4.1 ± 0.7	
PVA/PVP(1:1)_CD	92.8 ± 4.9		0.94 ± 0.01		13 ± 1	
Freeze-thawing	n=3	n=7	n=3	n=7	n=3	n=7
PVA_FT	92.6 ± 0.6	86.8 ± 1.5	0.94 ± 0.01	0.88 ± 0.01	22 ± 2	14 ± 3
PVA/PVP(3:1)_FT	94.2 ± 1.4	90.5 ± 0.2	0.96 ± 0.01	0.91 ± 0.01	20 ± 1	19 ± 4
PVA/PVP(1:1)_FT	95.3 ± 1.5	86.9 ± 0.3	0.96 ± 0.01	0.88 ± 0.03	<90	<90
Traditional gels						
Klucel™ 4%					36±1	
Gellan Gum 3%	n.a.				33 ^a	
Agar Agar 3%					30 ^a	

^aData extracted from ²⁵

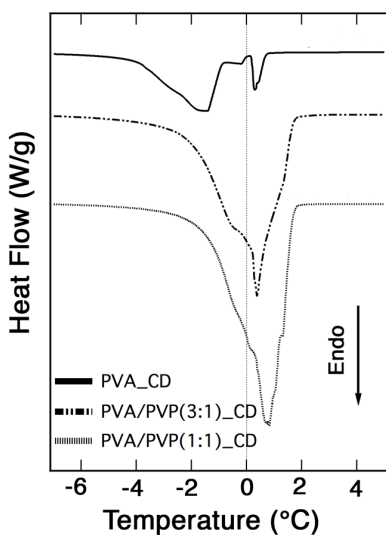


Figure 3. DSC thermograms of pure PVA and blended PVA/PVP hydrogels obtained by cast-drying. Endothermic peaks are related to the melting of water. The vertical line highlights the phase transition temperature of bulk water.

Figure 3 shows DSC thermograms of three hydrogel formulations prepared by cast-drying. The observed thermal transition is related to the melting of water contained within the hydrogels. PVA hydrogel sample (solid line) shows a multi-peak profile with a narrow peak at a temperature slightly higher than 0° , which is related to the melting of free water, and a broader melting peak below 0° , due to freezable bound water. The thermograms related to PVA/PVP formulations (samples PVA/PVP(3:1)_CD and PVA/PVP(1:1)_CD) show a single peak, with a shift toward higher temperatures for increasing PVP content, indicating that most of the water behaves as free water. Therefore, the presence of PVP induces a change in the state of water within PVA hydrogels obtained by cast-drying. This evidence is confirmed by the values of EWC and FWI, reported in Table 2, showing a significant increase with respect to the PVA formulation (PVA_CD). SEM pictures, reported in Figure 4, provide further insight: the PVA formulation (PVA_CD) (Figure 4-

A) exhibits a smooth, homogeneous and quite compact surface where porosity at the micron-scale is not observed. Water is probably entrapped in the so-called molecular porosity, and swelling of the gel is due to an increase of the space between polymer chains.⁴² Thermal analysis indicated that water in the network behaves like bound water (see Table 2), confirming its strong interaction with polymer chains. On the other hand, the PVA/PVP blended formulation (PVA/PVP(3:1)_CD) displays a highly interconnected net-like porous structure (Figure 4-B). In this formulation, pores size ranges from hundreds of nanometers to several microns: water contained in these pores behaves as bulk water, as indicated by the higher FWI (see Table 2). PVP acts as a porogen during gel formation upon solvent evaporation, keeping PVA chains distant, and allowing the formation of pores. The higher the amount of PVP in the initial polymer solution, the higher the amount of free water.

Cast-drying and freeze-thawing of polymer solutions with the same starting concentration lead to the formation of markedly different hydrogels, as shown in the SEM pictures reported in Figure 4-A and 4-C. In fact, sample PVA_FT3 displays a homogenous distribution of macropores, with a diameter of several hundreds of nanometers, while, as discussed above, PVA_CD does not show porosity on the same scale. In gels obtained by freeze-thawing, the main mechanism responsible for pores formation is water crystallization, which occurs during a solid-liquid phase separation process (nucleation of the ice crystals) within the polymer poor-phase (i.e., water). This process creates regions with increasing PVA concentrations and bigger ice crystals, which, once melted, leave empty pores. In the cast-drying method, on the other hand, the main mechanism of gel formation is the evaporation of the solvent in a polymer solution, which cannot lead to the formation of big pores in the absence of a porogen, i.e., PVP.

Figure 4 shows that in cryogels, the increase of freeze-thawing cycles leads to the formation of larger pores and thicker pore walls, as also reported in the literature.⁴³ Water freezes and expands with each cycle, pushing the PVA chains into close contact with each other, and increasing the difference between the polymer-rich zones, which become denser, and the polymer-poor zones, where water crystallize in bigger crystals. However, a significant decrease in EWC and FWI with the number of freezing cycles is observed. This behavior is probably related to the lower swelling of the denser polymer zones, where water is strongly hydrogen bonded, and behaves as bound water.

The addition of about 25% of PVP to the initial PVA solution (PVA/PVP(3:1)_FT) leads to the formation of bigger pores, without significant variations in EWC and FWI, after 3 and 7 freeze-thawing cycles. In general, SEM pictures of cryogels show that smaller pores can be found in the PVA formulation (mean pore size $<1\mu\text{m}$) with respect to PVA/PVP blended system (mean pore size $>1\mu\text{m}$). The role of PVP in pores formation during freeze-thawing cycles is mainly due to its hydrophilicity: in the blended systems, the crystallization of water occurs at lower temperature with respect to pure PVA formulations, resulting in the formation of less nuclei; this may lead to bigger ice crystals and, thus, bigger pores. Moreover, because PVP does not participate in the crystallization process, it may act as a porogen since it is partly washed out during storage in water, as confirmed by G% values in Table 1.

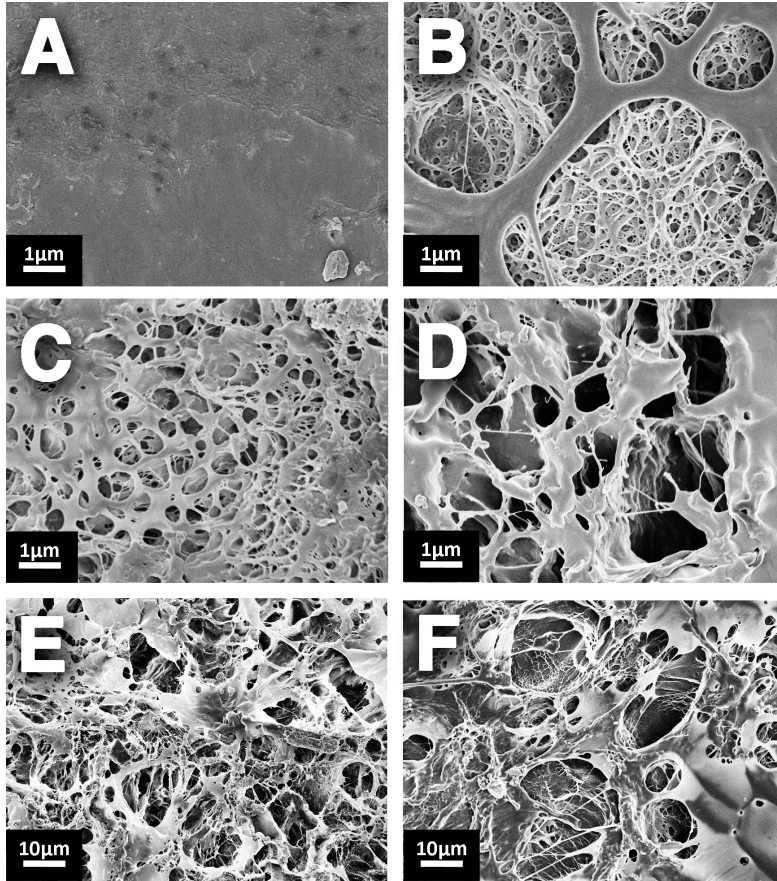


Figure 4. FEG-SEM images for different hydrogel formulations obtained through cast-drying (CD) or freeze-thawing (FT): (A) PVA_CD; (B) PVA/PVP(3:1)_CD; (C) PVA_FT3; (D) PVA/PVP(3:1)_FT3; (E) PVA_FT7; (F) PVA/PVP(3:1)_FT7.

Changes in the viscoelastic behavior as a function of the systems' composition, preparation method (FT or CD), and number of freezing cycles (for cryogels), were studied through rheological measurements.

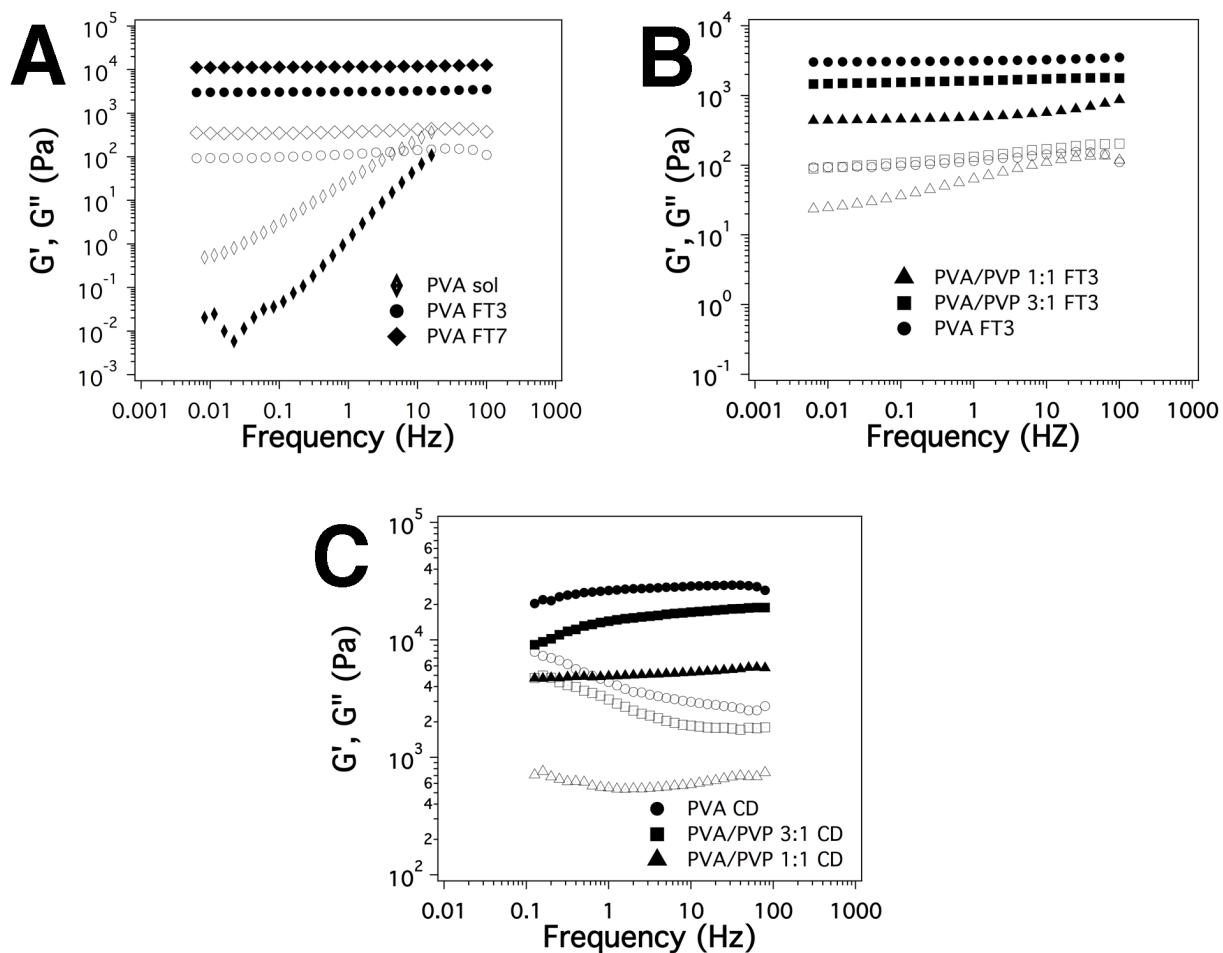


Figure 5. Log-log plots of the storage modulus G' (filled marks) and loss modulus G'' (empty marks) for different hydrogel formulations. (A) Frequency sweep of a PVA solution (0 freezing cycles, rhombus) subjected to 3 (circles) and 7 (diamond) freezing cycles. (B) Frequency sweep of PVA cryogels (3 cycles) with increasing PVP content. (C) Frequency sweep of cast-drying PVA-hydrogels with increasing PVP content. Error bars are included in the dimensions of the markers.

Figure 5-A shows the changes in a pure PVA system due to freeze-thawing cycles, from the typical behavior of a concentrated polymeric solution (PVA sol, 0 freezing cycles), displaying a

loss modulus higher than the storage modulus, to the typical behavior of chemical gels, with frequency independent moduli and $G' \gg G''$. This means that, after gelation, deformations in the linear viscoelastic range are essentially elastic or recoverable. An increase in both moduli is observed as a function of the increasing number of freezing cycles, as a result of the formation of stronger networks. Although these hydrogels are flexible, systems with an excessively high elastic modulus are too rigid to adapt macroscopic surface irregularities in the typical range encountered in cultural heritage artifacts (i.e. $\geq 1\text{mm}$). As shown in Figure 5-B, the addition of PVP to hydrogel formulations significantly lowers the elastic modulus. Overall, the PVA_FT3 formulation is too rigid for cleaning purposes, while PVA/PVP(1:1)_FT3, which is the formulation with the highest PVP content, has poor mechanical properties. The best adaptability to surfaces and ease of handling are granted by the formulation with 25% PVP (PVA/PVP(3:1)_FT3), which displays intermediate values of the storage modulus. Figure 5-C shows the viscoelastic behavior of PVA hydrogels obtained through cast-drying method. These systems display an elastic modulus that is one order of magnitude higher than the same formulations obtained through 3 freezing cycles, due to their denser networks and lower water content. The addition of PVP allows a significant lowering of the elastic modulus, as shown by the PVA/PVP(1:1)_CD formulation, which is the most flexible among the cast-dried systems. Nevertheless, this formulation was considered too rigid to be used for the cleaning of rough artistic surfaces.

The degree of crystallinity, X_c , obtained with thermal analyses, is reported in Table 3. Pure PVA formulations show higher X_c than blended PVA/PVP hydrogels (CD or FT). Moreover, a significant decrease in the onset temperature of polymer melting is observed for PVA/PVP hydrogels. This can be explained considering that PVP affects the PVA crystallization process: PVP hydrophilic groups interact with the PVA chains, acting as diluents and reducing the

dimensions of the crystalline regions. Similar effects have been observed when plasticizers, such as glycerin, are added to PVA-based hydrogel systems.⁴⁴ Because crystalline regions confer mechanical strength to the polymeric network, while amorphous regions confer flexibility,⁴⁵ the addition of PVP produces softer hydrogel systems. These results are in accordance with the rheological measurements shown above.

Table 3. Onset and maximum melting temperature (error ± 1 °C), melting enthalpy, and crystallinity degree of PVA, for hydrogels of pure PVA and blended PVA/PVP (3:1) formulations obtained by cast-drying or freeze thawing ($n=3$).

	Onset (°C)	Temp. Peak (°C)	Temp. Enthalpy (J/g)	X _c (%)
Cast-drying				
PVA_CD	210	222	63 \pm 1	39 \pm 2
PVA/PVP(3:1)_CD	207	221	43 \pm 1	27 \pm 1
Freeze-thawing				
PVA_FT3	204	222	56 \pm 1	35 \pm 1
PVA/PVP(3:1)_FT3	199	222	47 \pm 1	29 \pm 1

Finally, the water release of the gel formulations must be taken into account. Gels commonly used in restoration, as Agar-Agar, gellan gum and Klucel™, have a water release of about 30-40 mg/cm². These values are deemed too high to achieve controlled cleaning action on highly water sensitive surfaces⁴⁶. As shown in Table 2, no significant differences in water release are observed passing from pure PVA formulations to hydrogels containing 25% of PVP, both CD and FT. On

the other hand, when PVP content is 50%, water release increases of about 4 times, i.e. ca. 13 mg/cm² for CD, and ca. 90 mg/cm² for FT. Formulations with water release between 12-24 mg/cm² were considered optimal for applicative purposes.

Overall, considering all the investigated parameters, the PVA/PVP(3:1)_FT3 formulation was selected for the removal of artificial soil from a rough artistic surface. Figure 6 shows the cryogel formulation used for the cleaning test: the gel is elastic, semi-transparent and easy to manipulate.

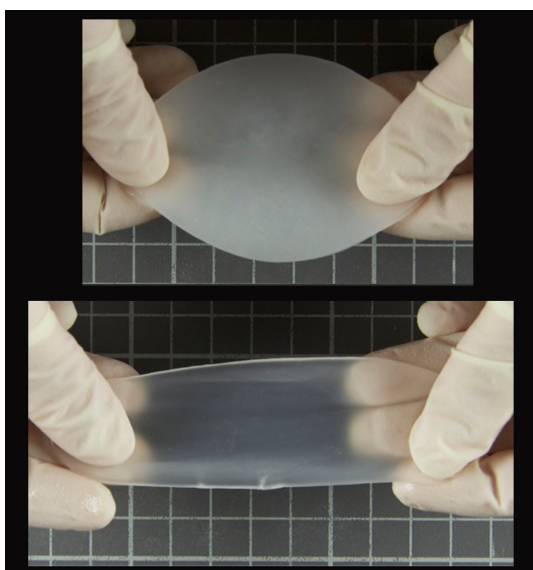


Figure 6. The cryogel formulation used for the cleaning tests, PVA/PVP(3:1)_FT3. The gel is elastic, semi-transparent, and allows an easy manipulation. The squares on the background are 1 cm².

APPLICATION OF HYDROGEL FOR THE REMOVAL OF ARTIFICIAL SOIL

The removal of artificial soil from the painting mock-up was carried out using the PVA/PVP(3:1)_FT3 formulation loaded with water. For comparison, gellan gum was applied

following the same procedure, i.e. three applications of 5 minutes (total contact time = 15 minutes). Due to its rigidity, the gellan gum did not perfectly adhere to the surface; therefore, as shown in Figure 7, only scarce soil removal could be achieved. In this case, the complete removal of soil would require additional mechanical action (e.g. using cotton swabs); however, it has been shown that the repeated use of swabs on painted surfaces may induce unwanted effects such as the removal of water-soluble additives^{47,48} or mechanical stress. On the other hand, the application of the PVA/PVP(3:1)_FT3 formulation led to satisfactory removal of soil with no additional mechanical action needed.

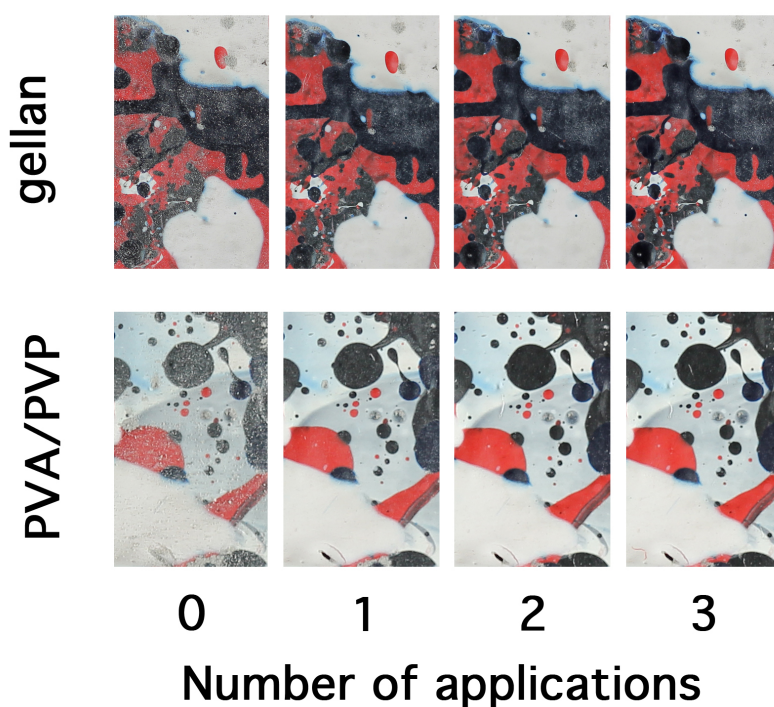


Figure 7. Cleaning tests on a soiled alkyd painting mock-up. The top row shows the partial removal of soil following three gellan gum applications (5 minutes each). Soil residues are clearly observable even after the third application. The bottom row shows the complete removal of soil

after the application of the PVA/PVP(3:1)_FT3 hydrogel. No soil residues are observable already after two applications. Each tile is 5 x 8 mm².

To evaluate the effectiveness of soil removal down to the micron scale, microFTIR 2D imaging was carried out on the mock-up sample, before and after the application of the gels. For comparison, reference spectra were recorded also in areas not covered with artificial soil. In Figure 8, the intensity of the peak at 1517 cm⁻¹ (i.e. the positive part of the derivative band centered at 1475 cm⁻¹, assigned to the CH₂ bending of the alkyd resin³⁶) was imaged between 1560 and 1475 cm⁻¹. The intensity of the band strongly decreases on areas covered with artificial soil, as shown by the presence of prevalently green and yellow pixels (no or low intensity) in the corresponding FTIR 2D maps, with only scarce presence of red pixels (high intensity). Upon cleaning with the PVA/PVP(3:1)_FT3 gel, the map shows prevalently red areas, and the related spectra clearly show the alkyd band. Upon cleaning with a gellan gum, the alkyd band is less intense on areas where the artificial soil was not effectively removed. These results were confirmed by imaging the OH stretching band, between 3730 and 3585 cm⁻¹, of kaolin (present in the artificial soil mixture), which is clearly observable in the spectra of the soiled sample, and no longer observable after cleaning with the PVA/PVP gel. The kaolin bands are still observable on areas where the gellan gel was used. These data confirmed that the artificial soil was efficiently and homogeneously removed using the PVA/PVP gel.

Then, to check the possible presence of PVA/PVP gel residues after cleaning, the spectral region between 1705 and 1641 cm⁻¹ was imaged (see Figure 9), where a band at 1664 (C=O stretching) would suggest the presence of PVP residues⁴⁹. As a reference, we first imaged areas where the gel was purposely left on the surface: the C=O stretching band is clearly observable and imaged as

expected. However, after simply removing the gel (with no further mechanical action), the peak can no longer be observed, as for pristine paint areas where the gel was not applied. Moreover, the spectra obtained by subtracting the absorptions of the cleaned paint layer from those of the pristine paint (“pristine paint – cleaned”) do not show peaks neither at 1664 cm^{-1} , nor at 1094 cm^{-1} (C-O stretching of PVA⁵⁰), suggesting that no gel residue was left after the treatment, down to the sensitiveness of the instrument. To this regard, it must be noticed that the detection limit of an FPA detector has been found to be significantly lower than that of a conventional mercury cadmium telluride (MCT) detector for the FTIR detection of trace amounts of materials. In fact, the heterogeneous distribution of the analyte can result in small areas of localized high concentration, which can be detected thanks to the high spatial resolution of the FTIR FPA imaging approach.⁵¹

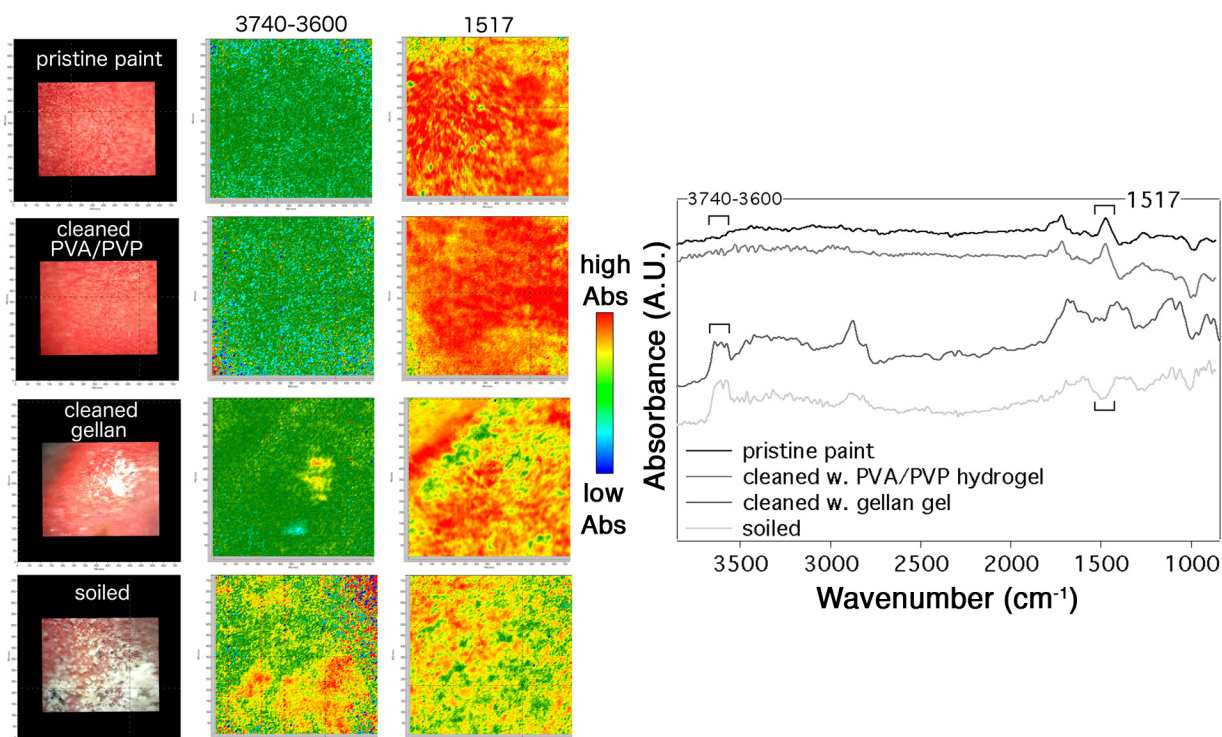


Figure 8. FTIR 2D imaging of a painting mock-up sample. Top row: pristine painted area that was not artificially soiled; Top-center row: area artificially soiled, and then cleaned 15 minutes with PVA/PVP(3:1)_FT3, with no additional mechanical cleaning (“cleaned PVA/PVP”); Center-

bottom row: area artificially soiled, and then cleaned 15 minutes with a gellan gel with no additional mechanical cleaning (“cleaned gellan”). Bottom row: area artificially soiled (“soiled”). For each area, the images beside the visible map show the corresponding 2D FTIR maps, where the intensities of the peaks at 1517 cm^{-1} (CH_2 bending of the alkyd resin) and 3670 cm^{-1} (OH stretching of kaolin in the soiling mixture) were imaged. All maps have dimensions of $700 \times 700\ \mu\text{m}^2$, each axis tick being $50\ \mu\text{m}$. The FTIR Reflectance spectra are shown on the right panel, each spectrum relating to a single pixel ($5.5 \times 5.5\ \mu\text{m}^2$) of the corresponding 2D Imaging map.

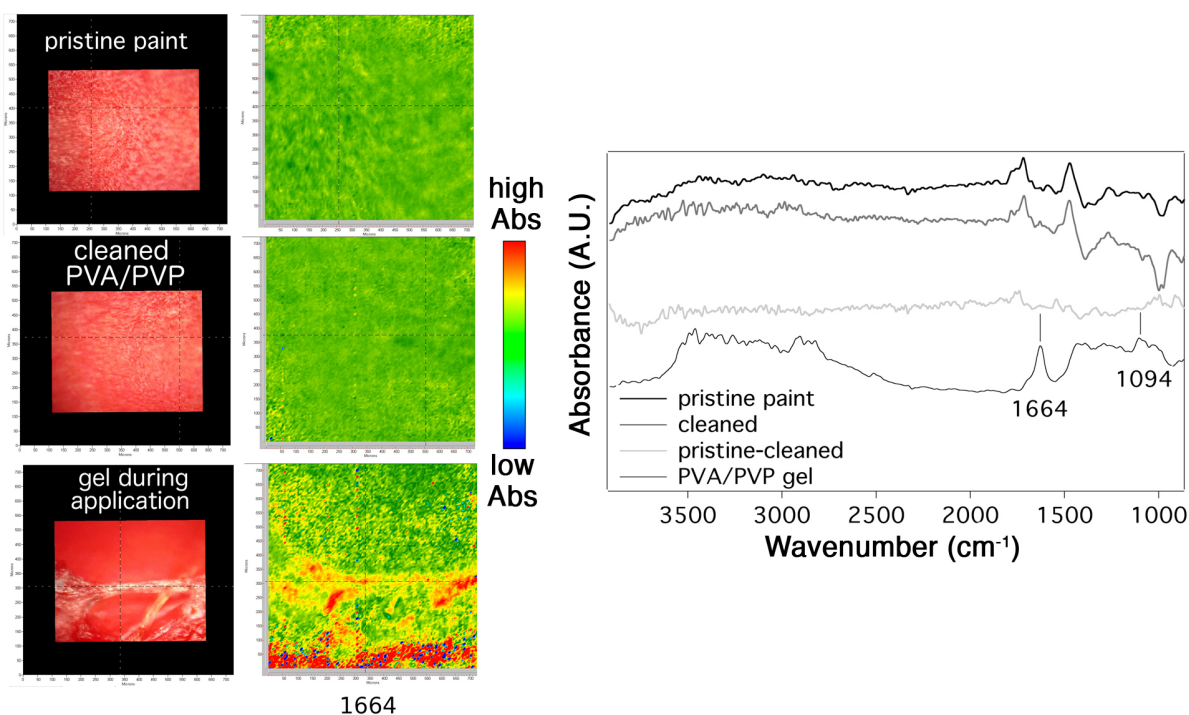


Figure 9. FTIR 2D imaging of a painting mock-up sample. Top row: pristine painted area that was not artificially soiled; Center row: area artificially soiled, and then cleaned 15 minutes with PVA/PVP(3:1)_FT3, with no additional mechanical cleaning (“cleaned PVA/PVP”); Bottom row: paint area during the application of a PVA/PVP(3:1)_FT3 gel (“gel during application”); the gel was purposely kept on the surface to obtain a reference map of possible gel residues, which indeed were not observed after the removal of the gel (no additional mechanical cleaning needed). For

each area, the image beside the visible map shows the corresponding 2D FTIR Imaging map, where the intensity of the band at 1664 cm^{-1} (C=O stretching of PVP) was imaged. All maps have dimensions of $700 \times 700\ \mu\text{m}^2$, each axis tick being $50\ \mu\text{m}$. The spectra of pristine paint, paint treated with PVA/PVP(3:1)_FT3, and the subtraction between these two spectra (“pristine-cleaned”), are shown along with the spectrum of a PVA/PVP gel. Each spectrum relates to a single pixel ($5.5 \times 5.5\ \mu\text{m}^2$) of the corresponding 2D Imaging map.

CONCLUSIONS

Gels commonly used in the conservation practice are inadequate to remove soil from rough surfaces, being too rigid to adapt irregular surfaces or too mechanically weak to be removed without leaving residues.¹⁶⁻¹⁸ Several formulations of physically cross-linked poly(vinyl alcohol) (PVA)-based hydrogels, obtained by cast-drying or freeze-thawing of aqueous polymeric solutions, were prepared and studied. The properties of the PVA hydrogels were improved through blending with poly(vinyl pyrrolidone) (PVP). The addition of PVP significantly changes the porosity of the gels, increasing the amount of free water in the polymeric network. Moreover, PVP hinders the crystallization of PVA during gel formation, producing more elastic gels, which can be used on rough and irregular surfaces. Regarding cryogels, a PVA/PVP ratio of 3:1 gave optimal viscoelastic properties for applicative purposes, while a 1:1 ratio produced brittle hydrogels that are difficult to manipulate. The increase of freeze-thawing cycles leads to more rigid and retentive gels, mainly due to the fact that, with each freezing cycle, the polymer-rich zones, resulting from phase separation, become progressively denser. Cast-dried gels were deemed too rigid (even after blending with PVP) to adapt rough painted surfaces.

The PVA/PVP(3:1)_FT3 formulation was selected for practical tests, based on the results of physico-chemical characterization. The removal of artificial soil from a painting mock-up sample with rough and pitted surface was carried out using the PVA/PVP gel, whose performance was compared with that of gellan gum, a commercial gel widely used in conservation. The PVA/PVP gel allowed the complete removal of soil as demonstrated by FTIR 2D Imaging, while only partial removal was achieved using gellan gum. No measureable PVP and PVA residues were detected by Fourier transform infrared (FTIR) 2D Imaging on the treated surface, following the removal of the gel. In conclusion, it was shown that the newly developed formulation grants the residue-free removal of soil from rough and irregular artistic surfaces, overcoming the limits of traditional cleaning methods.

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