

INNOVATIVE METHOD FOR THE CLEANING OF WATER-SENSITIVE ARTIFACTS: SYNTHESIS AND APPLICATION OF HIGHLY RETENTIVE CHEMICAL HYDROGELS

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Abstract

Cleaning is one of the most important processes for the conservation of cultural heritage artifacts, but also one of the most delicate and potentially damaging to the original materials. Nowadays, aqueous cleaning is usually preferred to cleaning with organic solvents, because it is environmental friendly and less aggressive to artifact's materials. However, in some circumstances, such as cleaning paper documents, easel paintings and textiles, water-based systems can be invasive. The interaction of water with the hydrophilic support favors mechanical stresses between substrate and paint layers, which can eventually lead to paint detachment or paint leaching. Water-based detergent systems (such as micellar solutions and oil-in-water microemulsions) offer several advantages in terms of selectivity and gentle removal of hydrosoluble (e.g. grime) and hydrophobic (e.g. aged adhesive) materials. The confinement and controlled release of these water-based systems is achieved through the synthesis and application of chemical hydrogels specifically designed for cleaning water-sensitive cultural heritage artifacts. These gels are based on semi-interpenetrating p(HEMA)/PVP networks. Semi-IPN hydrogels are prepared by embedding linear polyvinylpyrrolidone physically into a network of poly(2-hydroxyethyl methacrylate). Water retention and release properties were investigated. The micro-porosity was studied by Scanning Electron Microscopy. To demonstrate both efficiency and versatility of the selected hydrogels in confining the most appropriate water-based cleaning system a representative case study is presented.

Keywords: *Semi-IPN hydrogels; Cleaning; Nanocontainers; Gel structure.*

Introduction

In general, most of the materials and methods used for conservation treatments are initially designed for application in other fields and then adapted by restorers for their specific purposes. This implies that the common procedure may not have the most suitable features demanded by each particular case study. In the last decades our research group is being concerned in providing

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conservators new tools based on nanotechnology that are specifically designed to answer different issues in conservation of cultural heritage [1-3].

Usually, a cleaning process is carried out to remove superficial layers that may induce further degradation to the artifact. These layers can be hydrophilic (e.g. superficial grime) or hydrophobic (e.g. aged varnishes and adhesives). While the removal of hydrophilic layers is easily performed with aqueous methods, the removal of hydrophobic layers is commonly carried out through the use of pure organic solvents. Most organic solvents are toxic and do not allow a controlled cleaning since they can quickly diffuse into inner layers [4, 5].

Dissolving hydrophobic materials, such as polymers, through non-confined pure solvents can cause their penetration within artifacts' porous matrix. After solvent evaporation polymer residues may remain within the substrate porosity.

Nanostructured fluids (e.g. oil-in-water microemulsions, micellar solutions) have been developed by the CSGI (Center for Colloid and Surface Science) to address this problem [6-8]. A microemulsion is a high-performing cleaning tool since it can remove hydrophobic layers using a small amount of organic solvents. The microemulsion droplets contain the appropriate solvent able to swell or solubilize the polymeric layers, while the water in the dispersing phase can penetrate within the porous substrate of the artifact, avoiding the risk of redeposition of the dissolved polymers, because of its affinity with the hydrophilic pores of the surface.

The use of confining tools that are able to retain capillary penetration of water-based systems is particularly important in the specific case of water-sensitive substrates (e.g. paper manuscripts, canvas paintings).

Nowadays the most used confining methods in conventional conservation practice include the use of cellulose pulp poultices and some physical gels [9, 10] (cellulose derivatives, polyacrylic acids, polysaccharide-based gels, and others), which do not have the suitable retentive features for the cleaning of water-sensitive artifacts. For this reason, highly retentive chemical "sponges" that allow a controlled release of the cleaning system, limiting its action only to the first few layers of the painted surface, were developed. For this, efforts were focused on the polymer gel technology.

Gels can be divided into two major categories, depending on the nature of their bonds: physical and chemical gels. Physical gels are formed by electrostatic interactions between polymeric chains, so they are usually viscous systems that can respond to heat or be disrupted by mechanical forces. Polysaccharide based gels (e.g. agar-agar or gellan gum) are an example of physical gels and are, at present, one of the most promising tools used by conservators with the intent of retaining the cleaning agent [11]. These gels, however, are fragile and do not have the suitable retention features.

Chemical gels are, on the other hand, characterized by the presence of covalent bonds. They have a specific shape given during synthesis and have strong gel cohesion, so no gel residues are expected after treatment using chemical gels. Chemical gels are more versatile because depending on the components (monomer, cross-linker, liquid medium, etc.) and the quantitative proportions it is possible to obtain gels with different chemical-mechanical properties [12-14]. In the specific case of cleaning water-sensitive artifacts, the ideal container would be a highly retentive soft hydrogel. In this paper we present the potential application of highly retentive hydrogels based on semi-interpenetrating polymer networks (semi-IPN) composed by a cross-linked polymer network of polyhydroxyethylmethacrylate (p(HEMA)) and an interpenetrating linear polymer of polyvinylpyrrolidone (PVP) that does not form covalent bonds with HEMA. These two polymers are biocompatible materials, largely used in the biomedical and pharmaceutical areas. The amount of PVP modulates the hydrophilicity and softness of the final product, while p(HEMA), constituting the

three-dimensional network, largely determines the mechanical properties. A high equilibrium water content (EWC) of hydrogels, which is correlated to pore dimensions, and hydrophilicity of the polymer network, is consistent with high hydrogel softness. Moreover, polymer network hydrophilicity is related to hydrogels' retention capacity, because the interaction forces of aqueous system/polymer network may prevail over the ones of aqueous system/artifacts surface.

Materials and Methods

Synthesis of p(HEMA)/PVP hydrogels

HEMA monomer and the cross-linker N,N'-methylenebisacrylamide (MBA) were mixed together in a water solution with linear PVP (average Mw~1300 kDa). The reaction mixture was bubbled with nitrogen for 5 minutes to remove oxygen and then radical initiator 2,2'-Azobis(2-methylpropionitrile) was added in a 1:0.01 monomer/initiator molar ratio. The reaction mixture was gently sonicated for 30 minutes in pulsed mode to eliminate possible gas bubbles. The polymerization reaction, started by thermal homolysis of the initiator, was performed for 4h at 60°C. After polymerization, hydrogels were placed in containers with distilled water.

Table 1. Composition (w/w) of three representative semi-IPN p(HEMA)/PVP hydrogels already applied for cleaning of cultural heritage artifacts.

Hydrogel	HEMA	PVP	MBA	H ₂ O	Monomer/cross-linker ratio	HEMA/PVP ratio
H50	25.0%	24.9%	0.2%	49.9%	1:1 x 10 ⁻²	1:1
H58	16.8%	25.1%	0.2%	57.9%	1:1.5 x 10 ⁻²	1:1.5
H65	10.5%	24.5%	0.2%	64.9%	1:2 x 10 ⁻²	1:2.3

Hydration cycle

To investigate how much water a semi-IPN hydrogel can load after synthesis until equilibrium is reached, hydrogel weight was registered at different times, as follows:

$$\text{Water uptake (\%)} = \frac{W_i - W_{0^*}}{W_{0^*}} \times 100 \quad (1)$$

where W_i is the hydrogel weight obtained at time i , W_{0^*} is the hydrogel weight immediately after synthesis.

Fourier Transform Infrared Spectroscopy (FTIR)

A FTIR spectrometer (Thermo Nicolet Nexus 870) in attenuated total reflectance mode (ATR-FTIR), equipped with a Golden Gate diamond cell was used to verify the absence of gel residues after direct contact with canvas. Data were collected with a MCT detector with a sampling area of 150 μm^2 . The spectra were obtained from 128 scans with 4 cm^{-1} of optical resolution.

Scanning Electron Microscopy (SEM)

A FEG-SEM ΣIGMA (Carl Zeiss, Germany) was used to acquire images from xerogels (freeze-dried hydrogels) using an acceleration potential of 1 kV and a working distance of 1.9 mm.

Results and Discussion

The investigated semi-IPN hydrogels were designed to address the problem of cleaning water-sensitive surfaces. Accordingly, the most important gel features are transparency, softness, high-retention and gel cohesion to avoid any gel residues on the surface after cleaning treatment. Each of these hydrogels' features is discussed in more detail further in this work.

Hydrogels' transparency and softness

Semi-IPN p(HEMA)/PVP hydrogels are transparent and soft, as highlighted in figure 1. The material's transparency is very important in restoration treatments because it allows the restorer a visual control of the cleaning process. These hydrogels can load as well other aqueous systems and pure solvents without losing their transparency. Their softness permits an acceptable adhesion to most surfaces, as illustrated in figure 1 (left). Furthermore, these hydrogels can remain attached to surfaces both in vertical position and upside down, allowing treatments on wall paintings or painted ceilings.

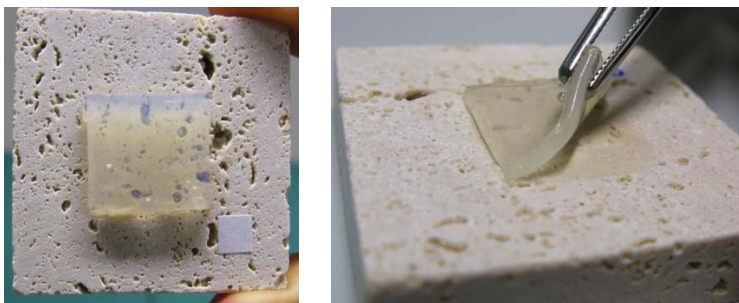


Fig. 1. Semi-IPN hydrogel (H65) on a travertine stone. On the left, the hydrogel applied in vertical position; on the right, the hydrogel removal is shown. It is worth noting that the stone surface is wet only in correspondence with the contact area.

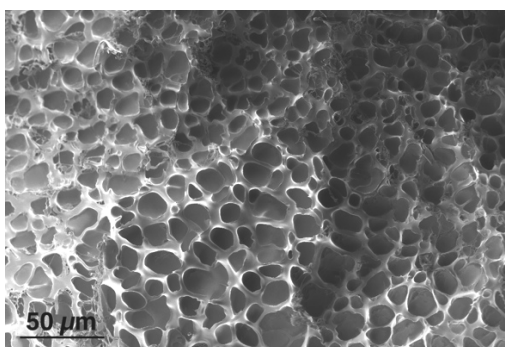


Fig. 2. SEM image of semi-IPN H65 hydrogel in xerogel form (lyophilized hydrogel).

Semi-IPN hydrogels present a mesoporosity that was investigated using a Scanning Electron Microscope (SEM). The SEM image of H65 xerogel's porosity is presented in figure 2. A sponge-like structure is noted, with pore dimensions varying from 5 to 40 μm . Hydrogels' porosity is mainly given by the presence of water during synthesis. Formulations with higher initial water amount in the reaction mixture show higher porosity.

Hydrogels' hydrophilicity and retention capacity

Three formulations were devised for addressing the specific demands of different case studies (see table 1). The main differences between gel formulations are the softness and retention capacity. The softer hydrogels are also the most hydrophilic. Hydrophilicity is correlated with the water content inside hydrogels, so less hydrophilic hydrogels have less water content. The water amount in the reaction mixture is 50% (w/w) in H50 and 65% (w/w) in H65. After the synthesis, the newly formed semi-IPN sponge can still load a high quantity of water until equilibrium water content (EWC) is reached. Curves in figure 3 show the difference in water loading capacity (i.e. hydrophilicity) of two hydrogel formulations (H50 and H65). H65 hydrogel, the most hydrophilic one, displays a water uptake of $\sim 134\%$, while H50 have a water uptake of $\sim 64\%$.

The hydration cycle permits to investigate the time required to reach the EWC after synthesis; all the investigated gel formulations need about 6 days. Only when the EWC is reached, can the hydrogels be used for cleaning procedures. Furthermore, if needed, it is possible to exchange the already water-loaded hydrogels with another water-based system, such as oil-in-water microemulsions, or pure organic solvents, by putting them in a filled container with the liquid to be loaded inside hydrogels. This exchange takes approximately 12h.

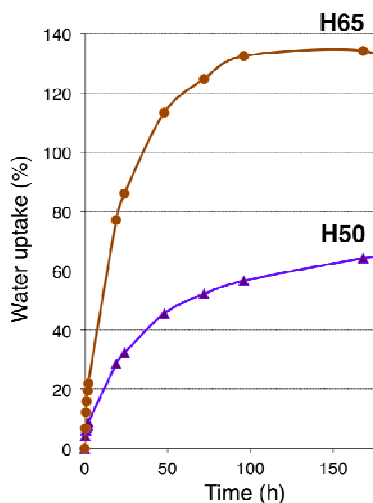


Fig. 3. Hydration cycle for two semi-IPN hydrogel formulations.

After 4h exposure to the air in a controlled environment (55% relative humidity and 20°C), water-loaded hydrogels (shaped as a 1 cm square, with 2 mm thickness) still maintain a water content of around 90% with respect to EWC. This means that these hydrogels limit the

liquid evaporation rate and, thus, allow a longer contact between cleaning system and artifact's surface.

Hydrogels' cohesion

The cross-linked polymer network of semi-IPN hydrogels implies very high gel cohesion, which prevents gel residues on the surface after cleaning treatments.

To confirm this statement, ATR-FTIR spectra, shown in figure 4, were collected from a cotton canvas, which is a very hydrophilic surface, after direct contact with semi-IPN hydrogels. For instance, the characteristic intense bands assigned to the carbonyl stretching vibration of both HEMA and PVP (respectively 1724 and 1654 cm^{-1}) are not visible in the spectra of cleaned canvas; this confirmed that no detectable gel residues are left on canvas due to gel contact.

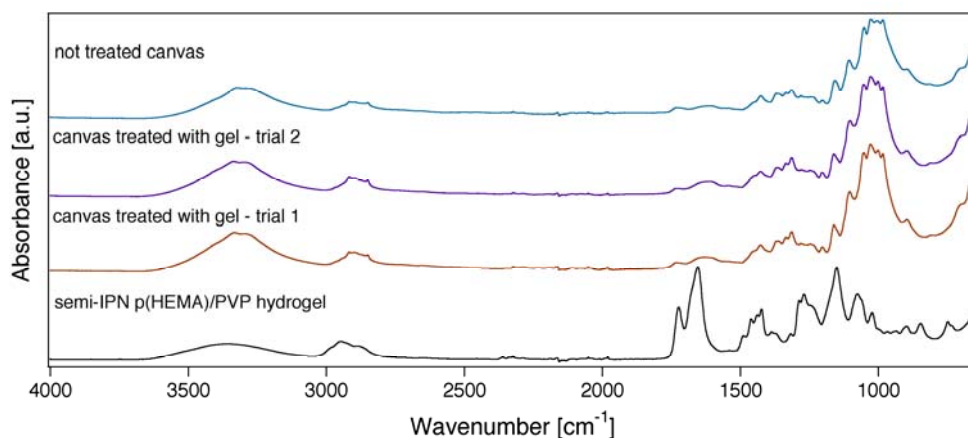


Fig. 4. ATR-FTIR spectra to verify the absence of gel residues on canvas after direct contact with semi-IPN hydrogels.

Cleaning tests

These semi-IPN hydrogels permit a highly controlled cleaning and could replace the common methods used in conservation, such as the use of a wetted cotton-swab (largely used for the application of water or other solvents directly over the painted surface). In order to make a comparison between these two techniques a mock-up sample of a water-sensitive material (canvas) was prepared. Acrylic and vinyl tempera were used to paint the canvas. On the top of the paint layer, a thin deposit of the hydrophilic artificial grime mixture developed by Wolbers [15] was applied. It is well known that acrylic and vinyl color applied on canvas tend to lose adhesion with the support when in contact with water. For that reason, this mock-up sample was a good reference material to check the efficiency of this new gel-based technique. Cleaning tests were carried out using different hydrogel formulations, and compared with a classic wetted cotton-swab cleaning. Results are summarized in figure 5. None of the hydrogel formulation led to color removal. The best cleaning result was achieved with formulation H65. On the other hand, evident color traces were noted on cotton-swab after its use (Fig. 5 right), due to the swelling and loss of adhesion of the paint layer favored by water.

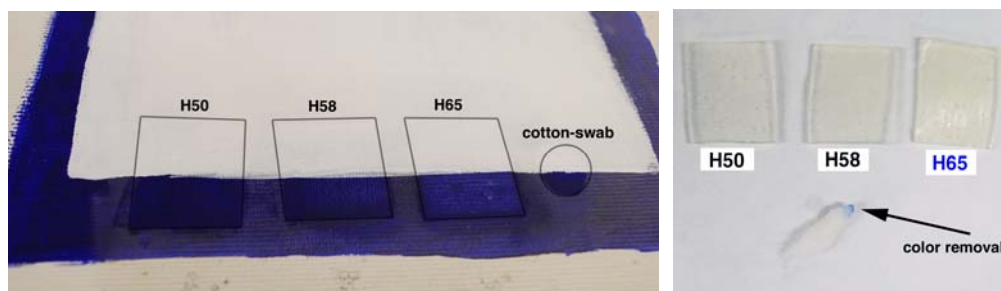


Fig. 5. Cleaning tests on a canvas painted with modern tempera (acrylic/vinyl resins) and coated with artificial grime. Cleaning was performed with water-loaded semi-IPN hydrogels applied for 5 minutes. Cotton-swab wetted with water was used for comparison purpose.

Conclusions

Chemical semi IPN hydrogels are a suitable tool to achieve a controlled cleaning action on water-sensitive cultural heritage artifacts. They are transparent and easy to manipulate, can load high quantities of water-based cleaning systems and keep them in contact with surfaces for the time required for the cleaning. Several advantages in respect to traditional cleaning methods (physical gels and cotton swab) were observed: due to the strong gel cohesion no residues are left on the surface after cleaning and no pigments removal was observed after contact with water-sensitive paint layers.

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