

Chemical semi-IPN hydrogels for the removal of adhesives from canvas paintings

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Received: 9 July 2013 / Accepted: 8 November 2013 / Published online: 29 November 2013
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Abstract Semi-interpenetrating (IPN) poly (2-hydroxyethyl methacrylate)/polyvinylpyrrolidone hydrogels were synthesized and used for the removal of adhesives from the back of canvas paintings. The high water retention capability and the specific mechanical properties of these gels allow the safe cleaning of water-sensitive artifacts using water-based detergent systems. The cleaning action is limited to the contact area and layer-by-layer removal is achieved while avoiding water spreading and absorption within water-sensitive substrates, which could lead, for example, to paint detachment. The use of these chemical gels also avoids leaving residues over the treated surface because the gel network is formed by covalent bonds that provide high mechanical strength. In this contribution, the physicochemical characterization of semi-IPN chemical hydrogels is reported. The successful application of an o/w microemulsion confined in the hydrogel for the removal of adhesives from linen canvas is also illustrated.

1 Introduction

Several conservation issues are continuously demanding innovative materials and techniques capable of providing efficient long-term preservation of cultural heritage artifacts. Cleaning is very challenging because of the difficulty in removing soiling materials with efficiency and with a

high selective and controlled action. Wet cleaning provides several tools for gentle removal of unwanted materials, but the use of neat solvents has limitations due to the porosity of the artifact that favors the capillary absorption of the liquid phase, with the consequent spreading of the solubilized materials within the original artwork's materials [1]. Moreover, in the case of easel paintings, the low control of solvents penetration may cause swelling or leaching of the artifacts' organic materials [2].

Recently, several nanostructured fluids have been formulated with enhanced properties in terms of cleaning capability. Most of them are water-based systems efficient in the swelling, solubilization and removal of hydrophobic coatings, e.g. microemulsions, micellar solutions. Moreover, oil-in-water microemulsions guarantee the confinement of the specific solvent for the material to be removed within oil microemulsion droplets preventing the spreading into the artifact [3, 4]. These systems are very versatile and optimal for several applications, yet, in some cases, limitations could still persist. In fact, in the case of water-sensitive artifacts (e.g. paper manuscripts or canvas paintings), the strong interaction between the aqueous continuous phase of the microemulsion/micellar solution and the hydrophilic substrates can lead to deformations, halos and detachment of material. For this reason, in order to benefit from these nanofluids, it is of paramount importance to use highly retentive containers capable of efficiently confining these detergent systems, with the aim of limiting their cleaning action merely at the interface.

Solvent gels, i.e. solvents in their thickened state, are one of the present methods used by conservators to minimize solvent penetration into the artifact [5]. However, the use of solvent gels entails a considerable risk related to the residues that remain on the surface after cleaning. In fact, after the cleaning procedure it is always necessary to

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perform an appropriate removal of the residues through the use of organic solvent blends. To overcome this limitation, conservators and scientists have recently devised new confining methods, one of which is the use of polysaccharide-based physical gels (e.g. agar-agar, gellan gum) for the cleaning of various types of materials [6]. However, these physical gels do not exhibit the appropriate features for cleaning water-sensitive artifacts, since the weak bond interactions of the gel structure can lead to excessive water release. Chemical hydrogels, on the other hand, have a polymeric network constituted by covalent bonds and, therefore, exhibit improved mechanical features. Moreover, in latter studies chemical gels have shown to have high retention capability and controlled water release without leaving any gel residues on the artifact [7, 8]. Chemical gels can be shaped in the desired form during the synthesis and can load high amounts of liquid phase, without undergoing gel solubilization.

In this paper we report the innovative use of hydrogels based on semi-interpenetrating polymer networks (semi-IPN) loaded with an *o/w* microemulsion for the removal of aged adhesives from a backside of a canvas painting. In relation to previous acrylamide/bisacrylamide hydrogels [7], semi-IPN hydrogels have similar hydrophilic features, but are more resistant, transparent and are highly retentive and, therefore, appropriate for cleaning water-sensitive artifacts. In a previous work (see reference [8]) hydrophilic layers of grime were removed from a Thang-Ka (water-sensitive substrate based on tempera magra technique) using water-loaded semi-IPN hydrogels. In this paper we used p(HEMA)/PVP hydrogels to remove hydrophobic layers, such as aged polymers, using the appropriate detergent system (a microemulsion) confined into the gel network. We showed that these gels are very versatile and can be used to remove different kinds of materials from various types of water-sensitive substrates.

The semi-IPN hydrogels described here are constituted by a network of poly(2-hydroxyethyl methacrylate) [p(HEMA)], which contributes to the hydrogel mechanical strength, and the interpenetrated linear polymer polyvinylpyrrolidone (PVP), that contributes to the hydrogel hydrophilicity. Some of the most important characteristics of these hydrogels are the softness [9] and their capability

to confine the cleaning action exclusively to the contact area, where only the first few layers of the artwork's surface are in contact with the solvent system [8] allowing a controlled layer-by-layer cleaning treatment. The hydrogels' capability to load different cleaning systems (e.g. pure and mixed solvent systems, micellar solutions, microemulsions) is shown here for the first time.

The case study reported is a lining removal. A lining consists of a structural treatment where a new canvas is attached to the backside of the canvas support (see Fig. 1, left). Aging of linings leads to an accelerated degradation of the painting caused by acid formation due to molecular decay of the used adhesives, so lining removal is often necessary. Adhesives removal is very stressful for the painting because, on one hand the use of pure solvents can transport the dissolved polymer into the canvas fibers and, in the worst cases, into the preparation layers (see Fig. 1, right) and, on the other, canvas can easily absorb water-based systems, leading to the swelling of the hydrophilic layers of the painted artifact, which may lead to paint detachment.

2 Experimental

2.1 Synthesis of hydrogels

The semi-IPN hydrogels were prepared by embedding PVP (average $M_w \approx 1,300$ kDa) physically into the forming hydrogel network of HEMA. For this purpose HEMA monomer and the cross-linker *N,N'*-methylenebisacrylamide (MBA) were mixed together in a water solution with linear PVP. The reaction mixture was bubbled with nitrogen for 5 min to remove the oxygen and then the radical initiator α , α' -azoisobutyronitrile was added in a 1:0.01 monomer/initiator molar ratio. The reaction mixture was gently sonicated for 30 min in pulsed mode to eliminate the possible gas bubbles. Different formulations of hydrogels were prepared by varying the proportions of monomer/

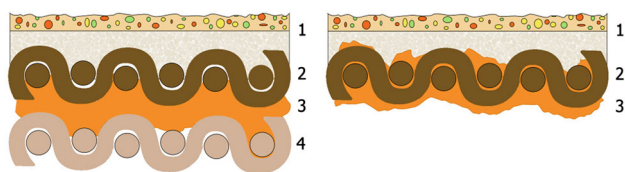


Fig. 1 Schematic cross-section of a painting with a lining (left) and after its removal using solvent technology (right). 1 Preparation and painted layers; 2 original canvas; 3 adhesive; 4 canvas used for lining

Table 1 Compositions (w/w) of the selected semi-IPN hydrogels; HEMA/MBA and HEMA/PVP ratios

	H50	H58	H65
HEMA (%)	25.0	16.8	10.5
MBA (%)	0.2	0.2	0.2
PVP (%)	24.9	25.1	24.4
Water (%)	49.9	57.9	64.9
HEMA/MBA ratio	$1:1 \times 10^{-2}$	$1:1.5 \times 10^{-2}$	$1:2 \times 10^{-2}$
HEMA/PVP ratio	50/50	40/60	30/70

The acronym HXX refers to the XX percentage of water in the reaction mixture

cross-linker ratio with PVP and water percentages. The composition of the three investigated systems is reported in Table 1. The polymerization reaction by thermal homolysis of the initiator was performed for 4 h at 60 °C. After polymerization, the hydrogels were washed and placed in containers with distilled water.

Polysaccharide-based physical gels (agar–agar and gelatin gum) were also prepared by dispersion of dry powders in water with 3 % (w/w). Powders were supplied by C.T.S. Italy (trademarks AgarArt and Kelcogel).

2.2 Physicochemical characterization

The gel content (G) gives the fraction between the mass of the final semi-IPN p(HEMA)/PVP hydrogel and the mass of the two components in the initial mixture, which can be calculated as follows [10]:

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

where W_d is the dry weight of the hydrogel and W_0 is the weight of HEMA and PVP in the initial reaction mixture. The equilibrium water content (EWC) of hydrogels gives information on the polymer network hydrophilicity and can be calculated as follows:

$$\text{EWC} = [(W_w - W_d)/W_w] \times 100 \quad (2)$$

where W_w is the weight of the water swollen hydrogel in equilibrium obtained at least 7 days after polymerization reaction.

Water release feature provides a better understanding of the retention capability of each gel system. The surfaces of fully swollen hydrogels were gently dried and the gel was put on three sheets of Whatman® filter paper inside a plastic Petri dish with lid to avoid water evaporation. The sheets of filter paper were weighed before and after 30 min of gel application.

The loading gel capacity toward different cleaning systems was calculated by immersing the lyophilized H58 hydrogel into the selected solvents. Squared hydrogel films of about 1 cm² and 2 mm of thickness were used. Both hydrogel weights and size were registered before and after immersion in the solvent to estimate the quantity of loaded solvent by each gel. The solvents were chosen from those commonly used by conservators [11].

A FTIR spectrometer (Thermo Nicolet Nexus 870) in attenuated total reflectance FT-infrared mode (ATR-FTIR), equipped with a Golden Gate diamond cell was used to investigate on possible gel residues after a cleaning treatment. Data were collected with an MCT detector with a sampling area of 150 μm². The spectra were obtained from 128 scans with 4 cm⁻¹ of optical resolution.

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 1.4 mm.

2.3 Removal of aged polymer adhesives

To evaluate the effectiveness of the prepared hydrogel systems, cleaning tests on model samples were performed. Linen canvas samples were previously treated with two different polymers widely used in lining procedure, Mowilith® DM5 (vinyl acetate/*n*-butyl acrylate copolymer) and Plextol® B500 (ethyl acrylate/methyl methacrylate copolymer). To simulate the natural aging process samples were submitted to an artificial aging as described in the literature [12].

The hydrogels were loaded with EAPC o/w microemulsion [1] through immersion for at least 12 h before application on canvas. This microemulsion is composed of water (73.3 wt%), sodium dodecyl sulfate (3.7 wt%), 1-pentanol (7.0 wt%), propylene carbonate (8.0 wt%) and ethyl acetate (8.0 wt%). The hydrogel loaded with the microemulsion EAPC was kept in contact with the canvas surface for 4 h. To avoid evaporation of the microemulsion, the hydrogel was covered with a plastic foil. A Whatman® filter paper was placed on the backside of the canvas to verify the absence of dissolved polymer or solvent diffusing through the canvas. After the gel application, the aged polymeric adhesive was swollen and softened and could be easily removed with gentle mechanical action.

3 Results and discussion

The three p(HEMA)/PVP hydrogels formulations here presented were designed to address different needs in conservation concerning cleaning. The gel content (G) in this type of hydrogels is usually low because there are no chemical bonds between polymer network and interpenetrated linear polymer, so any excess of the latter can be washed out. H50 hydrogel presents a G value of 90 % (Table 2), which is comparable with the G of acrylamide

Table 2 Some physicochemical properties of the selected p(HEMA)/PVP, acrylamide [7] and polysaccharide hydrogels

	G (%)	EWC (%)	Water release (mg/cm ²)
H50	90	72	8
H58	78	80	15
H65	74	87	16
Acrylamide “Hard”	95	95	27
Acrylamide “Soft”	88	97	56
AgarArt	-	97	30
Kelcogel	-	97	33

chemical gels. This is a considerable fact since there is a 50/50 p(HEMA)/PVP ratio. This sustains the presence of hydrogen bonds between HEMA and PVP [13]. However, increasing linear PVP amount with respect to HEMA leads to a substantial drop in G at a specific p/(HEMA)/PVP ratio, meaning that the available area of HEMA network is not enough to encompass more PVP.

In general, all the synthesized semi-IPN hydrogels are transparent and soft. The systems differ mainly in hydrophilicity, i.e., water loading and water release features. These properties can be tuned before synthesis by variation of their component ratios (HEMA/PVP, HEMA/cross-linker, water/reaction mixture). In particular, from H50 to H65 the hydrophilicity character increases as demonstrated by the EWC values reported in Table 2. The physical gels

Table 3 Amount of loaded solvents in hydrogel H58 and loading percentage with respect to the water loaded gel

	Solvent/xerogel (w/w)	%
Acetic acid	11.17	270
Benzyl alcohol	10.70	254
2-Methoxyethanol	4.02	33
Ethylene glycol	3.98	32
Ethanolamine	3.81	26
Water	3.02	0
Ethyl alcohol	2.97	-2
Propylene glycol	2.72	-10
Methyl alcohol	2.47	-18
2-Butanol	1.74	-42
Cyclohexane	n.l.	n.l.
Heptane	n.l.	n.l.
<i>p</i> -Xylene	n.l.	n.l.
Triethanolamine	n.l.	n.l.
Toluene	n.l.	n.l.
Acetone	n.l.	n.l.
Butyl acetate	n.l.	n.l.
2-Butoxyethanol	n.l.	n.l.
Methyl ethyl ketone	n.l.	n.l.
Propylene carbonate	n.l.	n.l.

n.l. not loaded

(AgarArt and Kelcogel) have an EWC of 97 %, which correlates with an excessive water release for cleaning water-sensitive substrates, as illustrated in a previous work [8]. In fact, water release test shows that physical gels release water at least twice as much as semi-IPN hydrogels. Acrylamide gels have a high EWC and show an higher water release with respect to semi-IPN hydrogels, which are for that reason more suitable for the cleaning of water-sensitive substrates.

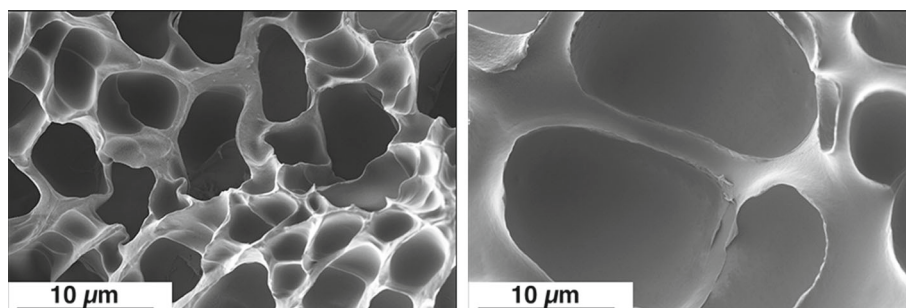
Semi-IPN p(HEMA)/PVP hydrogels are capable to load pure solvents as well. The loading capacity for some pure solvents is presented in Table 3. As expected, only the more polar solvents are loaded in semi-IPN hydrogels.

Mesoporosity was investigated through FEG-SEM images obtained from freeze-dried hydrogels (xerogels). It is known that some structure collapse may occur when ice forms. To verify this, EWC was calculated before and after freeze-drying process. A difference was noticed especially for H65 hydrogel that showed an EWC decrease of ca. 8 % that has to be considered when analyzing FEG-SEM images. FEG-SEM images of H50 and H65 hydrogels (Fig. 2) show the presence of a sponge-like structure. The difference between H50 and H65 hydrogels' porosity is mainly due to the quantity of water in the reaction mixture (50 and 65 % w/w, respectively), but also to PVP loss after polymerization, noted from G value, which contributes to larger pores due to the volume fraction of the macromolecule.

To confirm that these chemical gels do not leave residues on the surface after a cleaning treatment ATR-FTIR spectra were performed on canvas previously in contact with water-loaded semi-IPN gels. ATR-FTIR spectra reported in Fig. 3 show two reference spectra (a cotton canvas and a H50 hydrogel) and spectra from two canvas samples treated with H50 and H65. The characteristic carbonyl stretching vibration bands of HEMA and PVP are not present in the spectra of the treated canvases, proving that no detectable gel residues are left after the cleaning procedure.

The removal of aged adhesives from the back of canvas paintings can be done using oil-in-water microemulsions. However, in order to ensure a controlled cleaning process, the confinement of this cleaning tool inside hydrogels is

Fig. 2 FEG-SEM images of H50 (left) and H65 (right) xerogels



important to minimize fibers swelling due to contact with the water phase. It has been recently shown that an ethyl acetate/propylene carbonate based microemulsion (μ EAPC) can be effectively loaded inside acrylamide

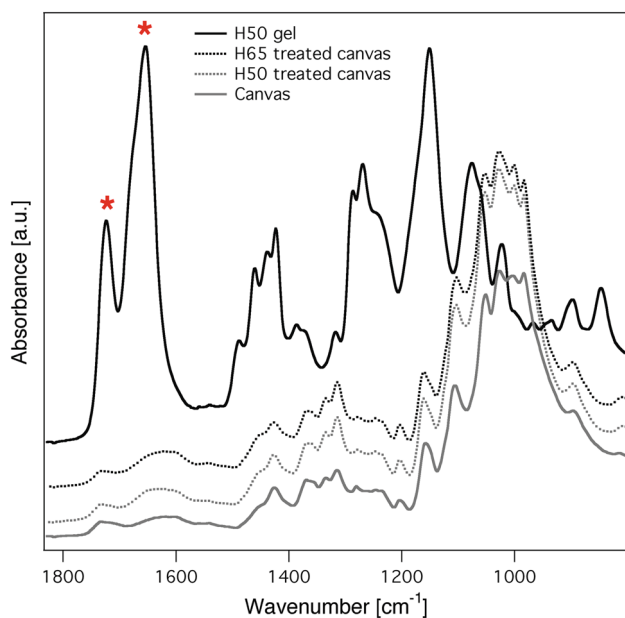


Fig. 3 ATR-FTIR fingerprint region spectra of a canvas, of H50 hydrogel and of canvases previously in contact with p(HEMA)/PVP hydrogels H65 and H50. Marked bands (*asterisk*) correspond to characteristic C=O stretching vibration of HEMA ($1,724\text{ cm}^{-1}$) and PVP ($1,654\text{ cm}^{-1}$)

hydrogels and provide an efficient removing of lining adhesives [7]. The use of p(HEMA)/PVP hydrogels loaded with this microemulsion was considered mainly because of the high water retention capability. The application of μ EAPC loaded hydrogels H50 and H65 for the removal of aged adhesives is illustrated in Fig. 4.

The artificially aged polymer adhesives, swollen after application of p(HEMA)/PVP hydrogels loaded with EAPC, are easily removed by gentle mechanical action. In Fig. 4 (centre and right), the enhanced swelling of these adhesives, after contact with the microemulsion confined inside hydrogels, is clearly detectable. In addition, the Whatman[®] filter paper placed on the backside of the canvas samples did not show traces of polymer transported by the microemulsion on the backside of the canvas. This confirms the hydrogel's effectiveness in confining the cleaning action only at the interface. The H65 hydrogel showed better efficacy in swelling both polymers making it the most appropriate confining tool for this kind of cleaning procedure under these circumstances. The required application time of 4 h allows the swelling and the partial solubilization of the polymer by the microemulsion. We have observed that a shorter application time results in a non complete swelling of the polymer leading to an inhomogeneous removal. The cleaning results are highlighted by optical microscopy images given in Fig. 5. The adhesive removal obtained through the application of H50 shows an incomplete cleaning action (Fig. 5, right) since the amount of microemulsion confined into the gel available for the cleaning is lower than in the H65 hydrogel. As a result, the

Fig. 4 Application of H50 hydrogel on the canvas glued with Plextol[®] adhesive, which, after swelling, could be removed by gentle mechanical action (*left and center*); removal of Mowilith[®] adhesive after application of H65 hydrogel (*right*)



Fig. 5 Optical microscopy images ($\times 100$ magnification) of the canvas with Plextol[®] before (*left*) and after removal of the aged adhesive using EAPC microemulsion confined in H65 (*center*) and H50 (*right*) hydrogels

canvas cleaned with H65 hydrogel presents a better cleaning, without visible damage of canvas fibers (Fig. 5, center).

4 Conclusions

Water-sensitive artifacts, i.e. artifacts that are constituted by hydrophilic materials, are always a concern for conservators that must apply gentle and controlled methods for efficient and safe removal of soiling materials, adhesives or aged varnishes. Chemical hydrogels based on semi-IPNs of p(HEMA)/PVP have demonstrated to be highly retentive and with good cleaning efficiency for the removal of hydrophobic layers, such as aged polymers, through the confinement of high-performing nanostructured fluids. This efficient combination of hydrogels and cleaning systems confined into the chemical gel network is a step forward in the conservation of cultural heritage and could be potentially applicable to different case studies.

Acknowledgements The authors acknowledge Dr. Chelazzi for providing the aged canvas samples. J. D. acknowledges financial support provided by *Fundação para a Ciência e a Tecnologia* (FCT) through a Ph.D. research grant (SFRH/BD/73817/2010). This work was partly supported by the CSGI, the European Union, Project NANOFORART (FP7-ENV-NMP-2011/282816) and the Ministry for Education and Research (MIUR, PRIN-2009-P2WEAT).

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