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Silver nanoparticles-based hydrogels synthetized by ionizing radiation for cleaning of tangible cultural heritage surfaces

Maria José Alves Oliveira [a,*], Larissa Otubo [a], Adriana Pires [b], Rodrigo Fernando Brambilla [a], Ana Cristina Carvalho [b], Paulo S. Santos [a], Almir Oliveira Neto [a], Pablo Vasquez [a]

[a] Nuclear and Energy Research Institute-IPEN-CNEN/SP, Av. Professor Lineu Prestes, 2242, Cidade Universitária, CEP 05508-000, São Paulo, SP, Brazil
[b] Laboratório de Restauração do Palácio dos Bandeirantes endereço, Avenida Morumbi, 4500, São Paulo, SP, Brazil

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ABSTRACT

The surfaces of the works of art are one of their most important parts since they interact directly with the observer's perception. On the other hand, they are also in direct contact with physical, chemical and biological agents that can induce degradation and signs of aging. Dust deposits, stains and aged layers of protection can degrade, causing irreversible damage to works of art. In this way, the removal of undesirable materials from artistic surfaces is essential to preserve cultural heritage articles. The aim of this work was to develop silver nanoparticles-based hydrogels and to study the behavior regarding solvent concentration, stability and ability to clean dirt samples based on paper and canvas. The hydrogels were synthesized (reticulated) by gamma rays having the simultaneous formation of silver nanoparticles (AgNP) in the same process. The samples were characterized by swelling tests, attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR), Raman spectroscopy, differential scanning calorimetry (DSC), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and optical microscopy (OM). The results showed the removal of dirt from the paper samples, as well as the softening of the dirt from the canvas, without leaving residues and without affecting the integrity of the art works submitted to treatment.

1. Introduction

The need for innovative techniques to facilitate the process of surface cleaning is particularly increasing when considering the field of restoration of modern and contemporary art (Montis et al., 2019). In fact, the physical-chemical properties of many of the new materials employed by modern and contemporary artists challenge in some cases, even the use of methodologies consolidated among conservatives (Bonelli et al., 2018; Baij et al., 2020; Baij et al., 2019).

The works of arts, including canvases and delicate papers, are objects that suffer deterioration caused by several factors, among them, the atmospheric action, that, because its composition of solid particles, liquids and gases, is capable of compromising the integrity of the collections over time (Foster et al., 2003). Among the most aggressive pollutants to the works, dust and acid gases due to the burning of fuels are highlighted. The continuous deposition of dust on the artifacts impairs the aesthetics of the parts, favors the development of microorganisms and can accelerate the deterioration of the documentary material due to the contained acids (Baglioni et al., 2021a). Furthermore, acid gases quickly damage the chemical structure of the materials constituting the parts of the collection (Monico et al., 2011). The speed of degradation is caused by atmospheric pollutants and also by the relative humidity present in the collection (Baij et al., 2020). In conservation, cleaning is considered one of the most challenging tasks during the process of restoration of an artistic surface, due to the variety of materials of the artifacts, the environmental conditions (Pensabene Buemi et al., 2020), oxidation and undesirable dirt that must be removed (Baij et al., 2019).

The literature presents techniques for cleaning works of arts using polymeric hydrogels synthesized by chemical and physical processes (Baglioni et al., 2012; Mastrangelo et al., 2020; (Bonelli et al., 2019; Mazzuca et al., 2017). Although this material presents good results, it has weaknesses in covering the range of specificities of the materials to be treated by the restorers (Baglioni et al., 2021b). Given the complexity and varieties of the compositions of works of art, there is a need for further studies to improve these hydrogels, aiming to increase cleaning

* Corresponding author.
E-mail address: mariajhho@gmail.com (M. José Alves Oliveira).

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efficiency without damaging the integrity of the works.

The use of synthetic and modified natural polymers has stimulated the application of nanotechnology in polymeric systems formed by new structures (Peppas et al., 2006; Franco and De Marco, 2020). There are several techniques for the modification of polymers, including the physical process by freezing and thawing cycles (Bacelar et al., 2016), the chemical crosslinking (esterification) (Akhtar et al., 2016; Parhi, 2017; Timaeva et al., 2020) and ionizing radiation of cobalt-60 source, which has shown great efficiency in these modifications over the years, addicionally promoting simultaneous sterilization (Jagur-Grodzinski, 2010). Among the development of polymeric nanotechnology, hydrogels are known as actuators in the drug delivery (Henke et al., 2005; Nurkeeva et al., 2004; Khutoryanskiy, 2007), plays the function of maintaining soil moisture in agriculture (Lopes Monteiro Neto et al., 2017), and are tool of controlled release of cleaning agent in the treatment of delicate surfaces in restoration of works of arts (Carretti et al., 2003; Calzolari et al., 2017).

Ionizing irradiation is a technology that ensures the modification (cure) of the polymer, that, in a single process promotes crosslinking, sterilization and, in the case of using silver ions, occurs the *in situ* formation of AgNP, without using any reticulating additive nor reducers, allowing long time of stockage without losing its validity characteristics (Alc â ntara et al., 2020; Jeong et al., 2020; Ikada et al., 1977).

The exposure of Ag^{+} ions to gamma radiation in an aqueous medium leads to the formation of $Ag^{\mathbf{0}}$ in a redox reaction induced by the products of H_2O radiolysis, including hydrogen atom (H) and hydrated electron (e^-_{aq}) (Chen et al., 2007), as indicated in the following reactions.

$$H_2O \rightarrow e^-_{aq}, OH, H, H_3O^+, H_2, H_2O_2 \quad (1)$$

$$Ag^+ + e^-_{aq} \rightarrow Ag^{\mathbf{0}} \quad (2)$$

$$Ag^+ + H^{\bullet} \rightarrow Ag^{\mathbf{0}} + H^+ \quad (3)$$

In a medium containing a stabilizing agent or in a polymer matrix, the formation of AgNPs occurs (Sedlacek et al., 2017).

2. Materials and methods

2.1. Materials

Gellan gum (GG) (type Kelcogel®CG-LA) were kindly provided by CP Kelco (Limeira, SP, Brazil), Poly (N-2-vinylpyrrolidone)(PVP) K90, Mw = 360,000, (Exôdo); 44 ppm silver ions supplied by ADP Soluções.

Practical tests were performed in an artwork of the author Augustus, entitled "*Portrait of Pedro de Magalhaes Padilha*" (1972), oil technique which presented fungi, dirt and oxidation, canvas provided by the laboratory "*Restauração do Palácio dos Bandeirantes*' and in the sheets (paper) of a book from the collection "*Biografia de Patronos Brasileiros*', private collection.

2.2. Synthesis of hydrogels using ionizing radiation

The polymers were separately solubilized: 2 wt% PVP and 2 wt% gellan gum (GG) in a 44 ppm silver ion solution, at approximately 25 °C for 24 h. Post solubilization, they were mixed in an autoclave and heated at 100 °C in a water bath for 6 min. The bain-marie favors a homogeneous distribution of temperature around the autoclave containing the formulation. In this step, the homogenization of the polymer occurs and the integrity of gellan gum (which is a natural polymer) is maintained, without thermal degradation. Formulation samples were placed in molds, sealed and subjected to ionizing irradiation with absorbed doses of 5, 10, 15 and 25 kGy at a dose rate of 5 kGy/h to induce the polymer crosslinking and formation of AgNP, simultaneously. Samples were irradiated at the Multipurpose Gamma Irradiation Facility of the Radiation Technology Center/CETER/IPEN, São Paulo-SP, Brazil.

The Ag nanoparticles were synthesized in the absence of any alcohol. Namely, in the presence of 2-propanol, the OH* and H* radicals, created by water radiolysis, abstract hydrogen from the alcohol to produce alcohol radical. These radicals effectively reduce Ag ions to metal in an aqueous medium. On the other hand, it is well known that the radiation crosslinking of polymer molecules is mainly induced by OH* radicals in an aqueous medium (with the G value of irradiation-induced intermolecular crosslinking 0.48) (Demeter et al., 2022). In the case of simultaneous crosslinking of polymers, and the reduction of Ag ions, the presence of alcohol in the reaction mixture would limit crosslinking in a certain amount.

3. Characterizations

3.1. Swelling tests

The synthesized hydrogels samples were dried in an oven at 60 °C, until reach a constant weight. The dried hydrogels samples were immersed in several different solvents: Milli-Q water with pH = 7, aqueous solution with pH = 4, methanol, ethanol, ethyl acetate and acetone. Samples were weighted at intervals of time during a total period of 48h for the determination of the degree of swelling. The results were obtained using equation (A), according to ASTM D 570 standard test method (ASTM D 570, 2018; Ma et al., 2016).

$$Increase\ in\ weight\ (\%) = \frac{wet\ weight - conditioned\ weight}{conditioned\ weight} \times 100 \quad (A)$$

whose unit is (%) and in which wet weight is the mass of the swelled polymer and *conditioned weight* is the mass of the dried polymer.

3.2. Attenuated total reflection in Fourier transformation of infrared spectroscopy

The ATR-FTIR analysis was performed on an ATR accessory (MIRacle with a ZnSe Crystal Plate Pike®) installed on a Nicolet® 6700 FT-IR spectrometer equipped with a cooled MCT detector with N_2 liquid.

3.3. Raman spectroscopy

Raman analysis was used to analyze whether changes occurred in the silver spectrum with the hydrogel after cleaning the surface of the analyzed substrate. Raman analysis was performed on a Macroram Horiba, Laser 785 nm.

3.4. Differential exploratory calorimetry (DSC)

The DSC analyses of the freeze-dried hydrogels were performed using about 5–6 mg of the sample, which was heated in aluminum crucibles from 30 °C to 300 °C temperature range, at a heating rate of 10 °C. min^{-1}, under N_2 atmosphere. The equipment used was a PerkinElmer DSC 6000, Differential Scanning Calorimeter.

3.5. Scanning electron microscopy (SEM)

The formation of pores and cracks of the surface hydrogels were analyzed by SEM. The freeze-dried samples were fractured and fixed with a double-sided conducting carbon. The analyses were carried out in a field-emission scanning electron microscope (model JSM-6701F, Jeol), operating at 3 kV.

3.6. Transmission electron microscopy (TEM)

Transmission electron microscopy was used to verify the silver nanoparticles distribution in the hydrogel. A very thin layer of the hydrogel was directly deposited on a 400 mesh copper grid, let to dry and then covered by carbon evaporation. The dried samples were

Fig. 1. AgNP hydrogel irradiated with a 10 kGy dose.

analyzed in a JEM-2100, Jeol transmission electron microscope, operating at 200 kV.

3.7. Practical tests on paper

AgNP hydrogel samples synthetized at 10 kGy were used to perform the practical tests. Synthetized hydrogel were applied on the paper surface and analyzed for a period of 15 h. Pages 16 and 17 of the book “Biografia de Patronos Brasileiros” were selected and treated with the hydrogel since presented stains and dirt.

Photographic records were taken before and after placing the hydrogel on the stain of the paper. A paper sheet was used to avoid the contact between the treated page and the previous ones, preventing humidity transfer from the hydrogel.

3.8. Optical microscopy (OM)

Optical microscopy was used to verify modifications in the paper fibers and the ink present in the writing. Analyzes were performed in the sample before and after the hydrogel treatment.

3.9. Practical test on canvas

A hydrogel with AgNP 44 ppm, synthetize at 10 kGy was placed on the canvas surface for 20 min. The process results were photographically registered.

4. Results

4.1. Hydrogels

The AgNP hydrogels were synthesized by ionizing radiation with absorbed doses of 6, 10, 15, 20 and 25 kGy, then analyzed to verify their integrity, malleability and resistance of being removed from packing and handling. The hydrogel sample synthesized at 6 kGy showed less resistance to being unpacked and greater amount of moisture compared to the others. The hydrogel sample obtained at 10 kGy dose, shown in Fig. 1, presented the best malleability as well as handling and resistance of being unpacked, among the samples produced. For this reason, the hydrogel synthesized at 10 kGy was chosen to perform the practical analyses on paper and canvas. Higher radiation doses used (15, 20, and 25 kGy) lead to a brittle and rigid hydrogel, due to degradation of the gellan gum polymer (natural polymer).

PVP was chosen because it is an amphoteric polymer and shows good crosslinking with other polymers in hydrogel synthesis. It is also a good AgNP stabilizer. Gellan gum was chosen because it is a natural and hygroscopic polymer. Literature presents studies of doped hydrogels used for paper cleaning (De Filpo et al., 2016). In addition, it provides consistency to the formulation prior to the gamma irradiation process. One of the main goals was to use the minimum percentage between the two polymers. The first selection criteria for composition were to verify: malleability, tackiness, and moisture of the hydrogel. Analyzing these

Table 1
Hydrogel swelling tests results with AgNP at 10 kGy using several solvents.

Solvents	Hydrogel mass (%)					Water recovery t = 2h
	t = 0h	t = 1h	t = 3h	t = 5h	t = 7h	No
H_2O pH 7	1.3	74.6	154.6	209.3	225.3	No
H_2O pH 4	1.3	66.9	153.8	210	226.9	No
Methanol	1.3	1.19	1.16	1.15	1.14	Yes
Ethanol	1.3	0.90	0.82	0.82	0.85	Yes
Ethyl acetate	1.3	0.188	0.18	0.16	0.17	Yes
Acetone	1.3	0.321	0.296	0.283	1.393	Yes

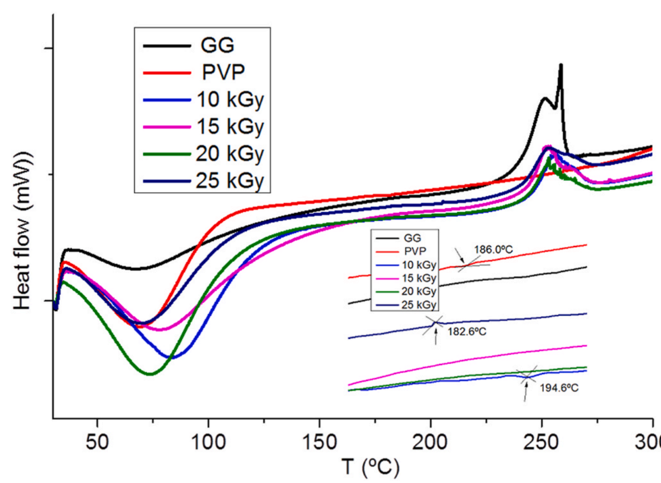

Fig. 2. DSC curves of gellan gum (GG), PVP and hydrogels with AgNP irradiated at 10, 15, 20 kGy and 25 kGy doses.

parameters, another composition of PVP/gellan gum for cleaning paper and canvases would not be feasible. Percentages below showed stickiness and left residues while percentage above lost the malleability and moisture of the hydrogel.

4.2. Swelling tests

Hydrogel synthesized samples at 10 kGy were subjected to swelling tests using several solvents for a specified time. Table 1, shows that the organic solvents used did not induce sample swelling, actually had the opposite effect and dehydrated the samples. This dehydration process proved to be reversible and these samples were recovered after being soaked in water for 2 h, without losing their initial characteristics. Hydrogel samples tested with pH7 and pH4 aqueous solutions

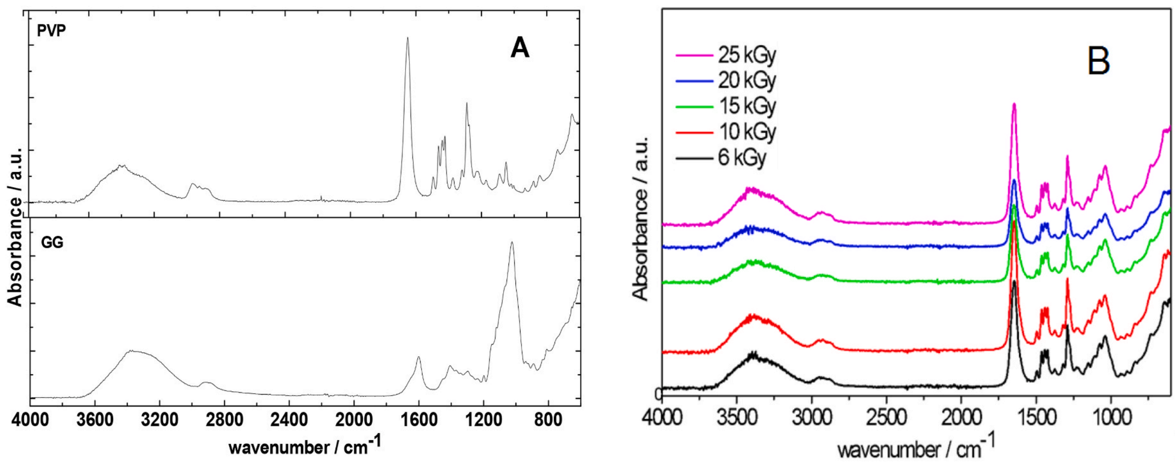

Fig. 3. ATR-FTIR spectra of (A) PVP pure and gellan gum pure (B) spectra of AgNP in dried irradiated hydrogel.

maintained physical integrity of their handling characteristics and flexibility until t = 7h, with approximately 225% of swelling. After 7h of swelling test, residues of the samples were released into the solutions, losing their physical integrity.

4.3. DSC

Fig. 2 shows the DSC analysis of the pure non-irradiated PVP, gellan gum (GG) and the containing AgNP hydrogels irradiated at different doses. The pure non-irradiated PVP presented an endothermic peak at 75 °C due to adsorption water evaporation and the glass transition at 175 °C. Depending on its molecular weight and moisture content, the glass transition temperature (Tg) can vary and the presence of water can manifest itself as a broad endotherm during scanning (Filho, 2021). For the pure GG, the Tg is expected to occur at −25 °C (Prezotti et al., 2014; de Souza et al., 2021), not covered in the measured range. An endothermic peak was observed at 99 °C due to water evaporation and the exothermic peak of the GG decomposition was observed at 250 °C.

After synthesis and irradiation of the hydrogels, the Tg became difficult to observe due to restriction of main chain movement by crosslinkings (Th ü rmer et al., 2014). The 10 kGy sample was the only sample that showed a glass transition at 194.6 °C. This Tg shift to a higher temperature is expected after the reticulation by the irradiation process. For the 25 kGy sample, small exothermic peak can be observed at 182.6 °C, probably due to the increase in the radiation dose applied, that will be explored in future studies. The exothermic peaks between 251 a 258 °C were associated with GG decomposition (de Souza et al., 2021). These results show the miscibility among the PVP/GG polymers, also confirmed by ATR-FTIR in Fig. 3.

4.4. ATR-FTIR

Fig. 3 depicts the IR spectra of pure PVP, GG and the irradiated hydrogels containing AgNP. It shows the vibrations of C=O (1643 cm^{-1}), N–OH complex (1288 cm^{-1}), C–N (1076 and 1039 cm^{-1}) of PVP (Wang et al., 2005). In addition, for GG it is observed the bands of aromatic C–C stretching (1424 cm^{-1}) as reported by Ismail et al. (Razali et al., 2020). The characteristic bands of PVP and GG in all samples are present with equal definition, indicating that crosslinking occurred between PVP and gellan gum during gamma irradiation. The C–O band of GG, centered at 1026 cm^{-1} was shifted to 1036 cm^{-1} in hydrogel, overlapping with the C–N bond stretching of the PVP. Additionally, in the hydrogel spectra, it is possible to see a shoulder at 1600 cm^{-1} corresponding to the characteristic absorption band of carboxyl in GG (Xu et al., 2007), on the band corresponding to C=O of PVP, indicating the reticulation of hydrogel.

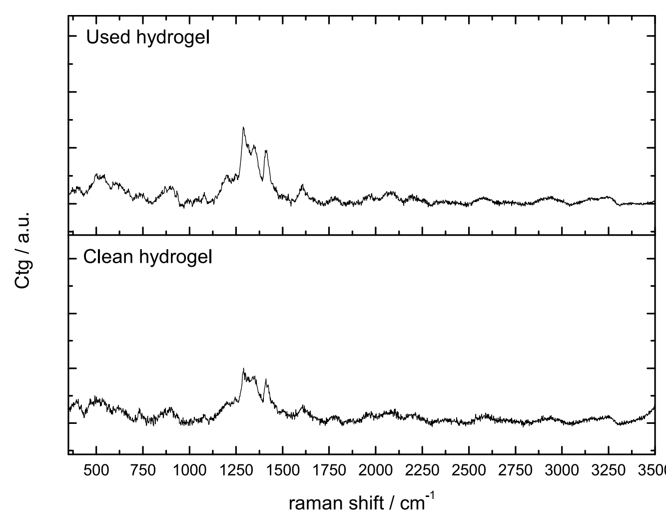

Fig. 4. Raman spectra of the hydrogels before and after cleaning the substrate surface.

4.5. Raman

The reason for using Ag nanoparticles and their role in cleaning surfaces was particular to the bactericidal and fungicidal action of AgNPs (Alc â ntara et al., 2020). These pathological agents are found in most cultural artifacts, arising from long storage periods without restoration of these objects. AgNPs nanoparticles do not absorb dirt but have an antibacterial and fungicidal role on the surface of the materials. This is observed by the Raman spectra of clean hydrogel and used hydrogel, Fig. 4.

4.6. SEM

As can be observed in the scanning electron micrographs of the 10 and 25 kGy dose-irradiated hydrogels in Fig. 5, the morphology of the sample is determined according to the hydrogel crosslinking: the higher the irradiation dose, the greater the interlacing of the polymer network. This determines the space between the chains, controlling the swelling of the polymer, the release of active ingredients or solvents and also where dirt adsorption occurs.

4.7. TEM

A drop of the formulation was placed on the sample grid for TEM and

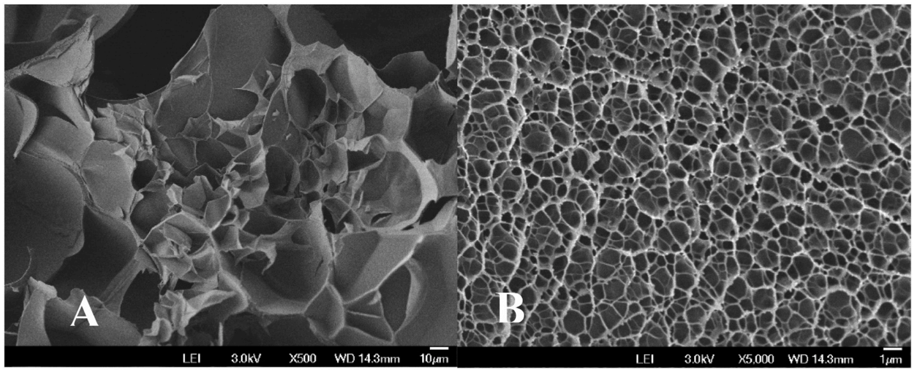

Fig. 5. SEM of the reticulated hydrogel with (A) 10 kGy and (B) 25 kGy doses.

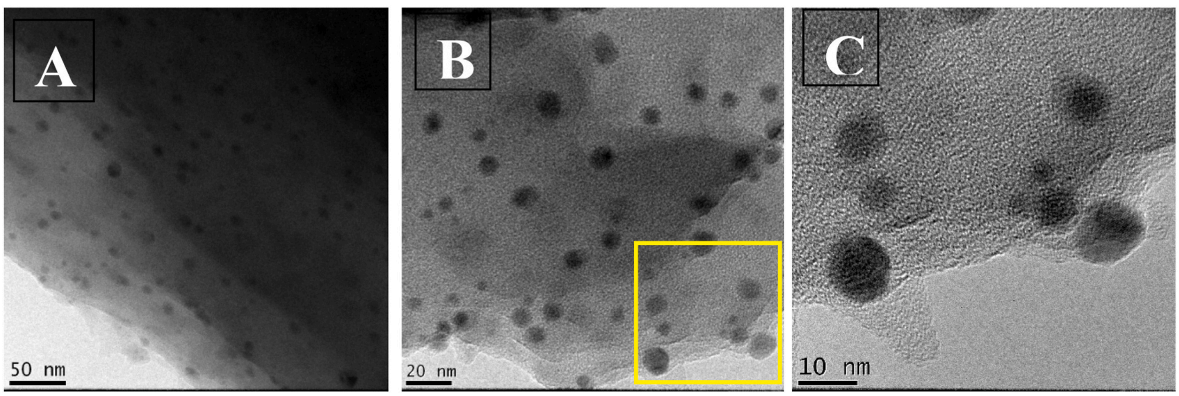

Fig. 6. (A) and (B) TEM images of hydrogel with AgNP irradiated at 25 kGy showing the distribution of the NP embedded in the hydrogel matrix; (c) is the inset highlighted in (b) showing some more detailed AgNP.

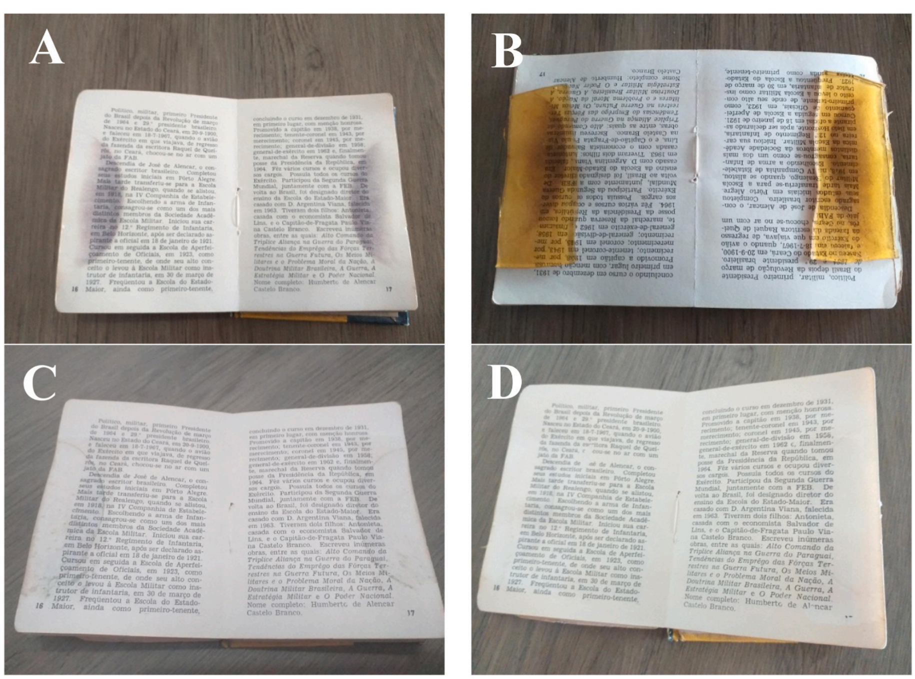

Fig. 7. (A) Paper with unknown dirt on the edges, (B) Paper with hydrogel applied on the surface with dirt during the cleaning period, (C) Paper with removal of dirt after 3h of contact with the hydrogel on the surface, (D) removal of dirt after 15 h.

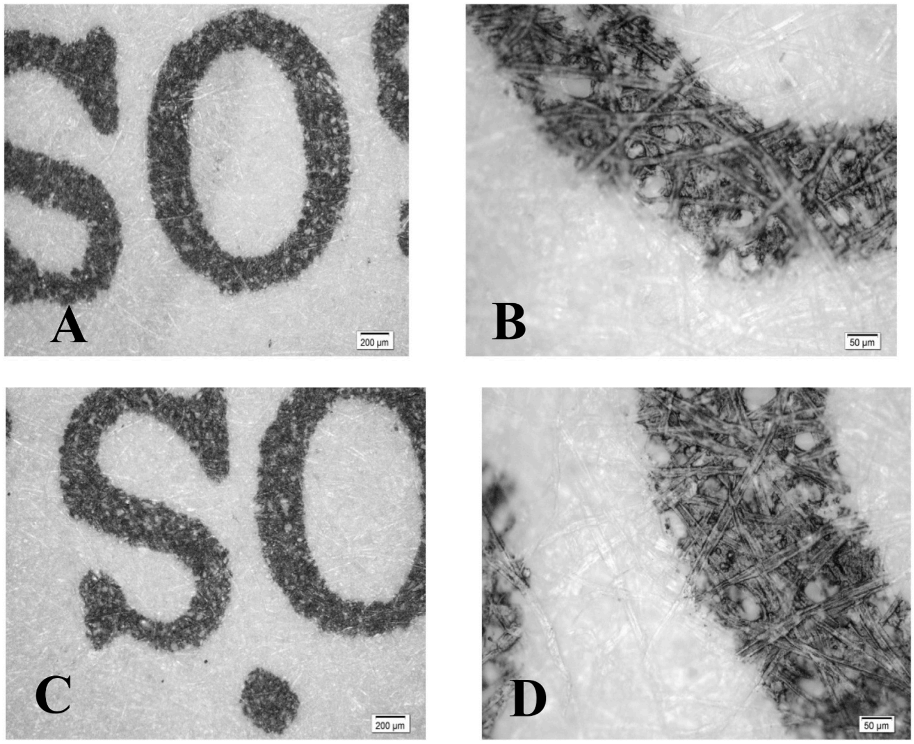

Fig. 8. Optical microscopy images of (A–B) a stain region before cleaning and (C–D) region after the cleaning process.

irradiated for crosslinking (curing) of the hydrogel and concomitant formation of the AgNP. Fig. 6, depicts the film of the 25 kGy dose-hydrogel, with AgNP distributed in the hydrogel. The mean diameter of the AgNP observed was 7.2 nm ± 1.8 nm (with a D_{90} = 9.5 nm).

It's important to know that the antibacterial properties of the hydrogel nanocomposites do not originate from the released nano-particles. They're trapped in a polymer matrix. The antibacterial properties of Ag hydrogel nanocomposite are predominantly from Ag ions released into the fluid from the surface of nanoparticles due to oxidation. That's why the surface of the nanoparticles and their size, as well as oxidation potential, are important. The shape of particles could affect a specific surface of particles, i.e. the surface available for oxidation and thus affect antibacterial efficacy. In addition, it is well known from the literature that Cu nanoparticles have antibacterial properties (Grass et al., 2011) and could therefore be a potential replacement for Ag nanoparticles hydrogel filler for cleaning of tangible cultural heritage surfaces.

4.8. Practical testing on paper

A book from the collection "Biografia de Patronos Brasileiros", kept stored inappropriately, was submitted to dirt cleaning tests. Besides the darkening of the aged paper, it presented dark stains with bluish characteristic, caused by solvent or unidentified paints, as can be seen in Fig. 7A. A hydrogel sample was placed covering the whole stain on paper (Fig. 7B) and the effect on the surface of the paper was analyzed for a 15h treatment (Fig. 7C and D).

Fig. 7C shows the stain after 3h. Although the stain ton was diminished, it was still visible. The hydrogel was replaced on the same initial position for another 12 h, thus totaling 15 h of treatment. After 15 h, the picture in Fig. 7D shows that very good result in the removal of the stain and dirt from the treated paper.

The hydrogel is composed of 20% of polymeric material, the rest being water. When this material is reticulated (cured) by ionizing radiation, three-dimensional networks form. The containing water is trapped inside this net in solid form. The SEM images in Fig. 3 show pores and gaps in the hydrogel microstructure after the water was removed by freeze-drying process. The retained water in the hydrogel is what gives flexibility, softness and moisture to the hydrogel. Additionally, this spaces between the chain provides a controlled release of the solvent, facilitating the absorption of dirt.

In this process, it is assumed that the moisture was transfer from the hydrogel to the paper, softening the dirt. As soon as the hydrogel was dehydrated by losing water to the paper and to the environment simultaneously, the reverse process occurred and it reabsorbed the moisture from the paper, capturing together the dirt on the surface of the paper. It is noticed that after 3 h, the result is satisfactory and after 15h, it presents almost total absence of dirt, without damaging or leaving residues on the paper.

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4.9. Optical microscopy

Analyzing the paper through the optical microscope is a direct experiment, for being a nondestructive technique. Essentially, the paper is a web of vegetal fibers that were put together to form flat sheets. The composition of fibers may vary according to the type of vegetal used at the manufacture of the paper. Therefore, the use of optical microscopy allows to identify and expose physical evidences in documents, that otherwise, would be invisible to the naked eyes (Diaspro and Usai, 2006; Connell, 2002). It is possible to see by optical microscopy images in

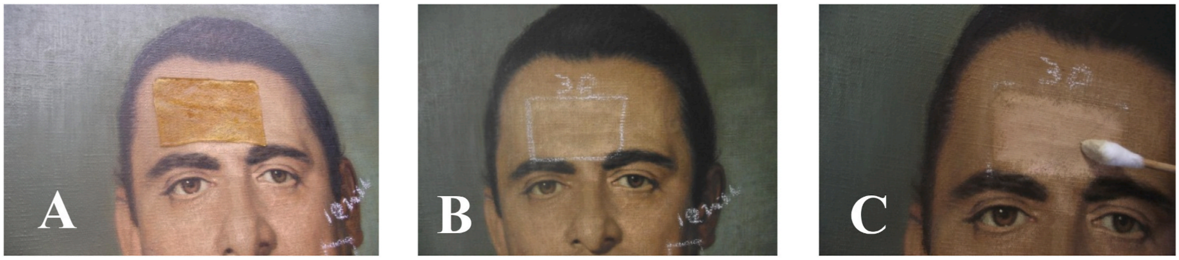

Fig. 9. (A) Hydrogel applied on the surface of the artwork; (B) hydrogel removed from the surface after 30 min (C) Final result of the cleaning region of the artwork.

Fig. 8, that the region subjected to the dirt-cleaning process using AgNP hydrogel, cleaned the exposed stain at the written area (Fig. 8 A and B) but did not compromised the fibers structure or the written itself (Fig. 8 C and D), if compared to a sample that wasn't exposed to the cleaning treatment.

4.10. Practical testing on canvas

The painting from the author Augustus, entitled Portrait of Pedro de Magalhães Padilha, from 1972, oil on canvas technique was submitted to the cleaning test, using hydrogel with silver nanoparticles, Fig. 9. The hydrogel stayed in direct contact with the canvas for 30 min, at a region that presented dirt, mold, fungus and oxidation varnish. The hydrogel withdrew the dirt, the oxidation varnish, and the rest was cleaned with a solution of turpentine and ethyl alcohol. It stands out that the solvents mix described does not show the same cleaning effect in this kind of dirt without the previous action of the hydrogel. The hydrogel cleaned and softened the rest, making the final cleaning easier.

The results shown in this paper indicate that the surface properties influence the cleaning efficiency. Each surface has a unique structure in terms of surface roughness, porosity, and surface energy. At the point of contact of hydrogel with the surface, the surface dynamic process of liquid absorption occurs, involving phenomena such as wetting, penetration, diffusion, and swelling. In general, surface energy of the substrate is a good measure of its wettability and consequently the possibility of clearing with hydrogels. For water to effectively wet out a surface, its surface energy must be as low or lower than the surface energy of the substrate. The surface energy of water is 72.8 mJ m^{-2}. From this follows that the surface energy value for works of art based on paper is greater, while for the canvas it is lower. Therefore, the value of the surface energy can predict the possibility of removal of undesirable materials from artistic surfaces using hydrogel nanocomposites.

5. Conclusion

The experiments showed that AgNP hydrogels based on gellan gum-PVP were successfully synthesized using ionizing radiation, which was responsible for the polymer reticulation and the *in situ* formation of AgNP, with a mean diameter of 7.2 nm ± 1.8 nm, embedded in the polymer matrix, but also influences on the mechanical properties as increasing the dose to higher than 15 kGy could initiate the polymer degradation. It was observed that the crosslinking of hydrogels is a determining factor for the porosity of the polymer matrix, that controls the amount of moisture, flexibility and malleability of the hydrogel. The tested AgNP hydrogel showed excellent results cleaning book paper stain and the dirt of the canvas painting. Therefore, this study demonstrated that it is possible to prepare hydrogels by radiation process, according to the proposal of usage, such as cleaning dirt from complex material such paper or canvas, corroborating with valuable information for the development of new materials, which can support the cleaning of cultural artifacts.

Author statement

Maria José Alves Oliveira: Conceptualization; Investigation, Methodology, Project administration, Supervision, Writing - original draft, Writing - review & editing. Larissa Otubo: Investigation, Writing - review & editing. Adriana Pires: Investigation, Writing - review & editing. Rodrigo Fernando Brambilla: Investigation, Writing - review & editing. Ana Cristina Carvalho: Resources. Paulo S. Santos: Resources. Almir Oliveira Neto: Resources. Pablo Vasquez Conceptualization, Methodology, Supervision, Writing - review & editing.

Declaration of competing interest

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

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