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DEVELOPMENT OF NANOSTRUCTURED POLYMERIC MATERIALS BY E-BEAM TECHNOLOGY FOR CLEANING CULTURAL HERITAGE ARTIFACTS

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Abstract.

The research and development of nanostructured polymeric materials have significantly expanded across several application fields. However, a gap in the literature remains regarding the use of electron beam (E-beam) technology for the synthesis of such materials, as gamma irradiation has been more widely employed. In this study, E-beam crosslinked nanostructured polymeric materials were developed for the controlled release of cleaning agents used in the conservation of cultural heritage objects, particularly aged canvases and paper-based materials. Polymeric hydrogels were prepared using polyvinylpyrrolidone (PVP), Polyvinyl alcohol (PVA), agar, ethylenediaminetetraacetic acid (EDTA), and polyethylene glycol (PEG 300) at different concentrations. The resulting systems were evaluated as potential alternatives for surface cleaning applications in cultural heritage conservation, aiming to replace conventional organic solvent-based methods that pose risks to both conservators and the environment.

Key Words: electron beam (E-beam); hydrogels; crosslinking; nanostructured polymers; cultural heritage conservation.

1. Introduction

The search for more efficient and safer surface-cleaning methods has intensified, particularly in the conservation of modern and contemporary artworks, whose constituent materials often exhibit high sensitivity to conventional treatments. Historically, organic solvents have been extensively employed in cleaning procedures; however, their use presents significant limitations, including incompatibility with certain pigments and paint layers, as well as toxicological risks associated with the exposure of conservation professionals. In response to these challenges, increasing research efforts have focused on the development of alternative materials capable of enabling more selective, safer, and more effective cleaning processes [1],[2]. Among the investigated alternatives, hydrogels have emerged as highly promising materials for applications in the conservation of cultural heritage objects [3],[4],[5],[6].

Hydrogels are three-dimensional polymeric networks capable of retaining large amounts of water while maintaining structural integrity through crosslinking [7]. The properties and performance of these materials are strongly dependent on the crosslinking method employed. Conventional approaches typically involve chemical crosslinking [8], which may generate potentially hazardous residues, or physical crosslinking, which often requires specific processing temperatures, presents storage limitations, and is generally restricted to semi-crystalline polymers. In recent years, radiation-induced crosslinking using cobalt-60 gamma sources has gained considerable attention due to several advantages, including the simultaneous formation of the polymeric network and sterilization of the material, as well as improved storage stability [9],[10]. Despite these

advances, a significant gap remains in the literature regarding the use of electron beam irradiation for the production of hydrogels intended for the cleaning and consolidation of cultural heritage surfaces. From a process-engineering perspective, electron beam technology offers important operational and economic advantages over gamma irradiation. Electron accelerators can be switched off when not in operation, eliminating continuous radiation emission and reducing shielding and safety management demands associated with cobalt-60 sources. Additionally, electron beam processing enables high dose rates, shorter irradiation times, and greater flexibility for industrial scale production.

Therefore, the present study aimed to develop polymeric hydrogels crosslinked by electron beam irradiation and containing EDTA as a complexing agent for application in surface-cleaning processes of cultural heritage objects. The proposed system seeks to combine the selective cleaning capability of EDTA with the controlled solvent delivery and residue minimization provided by hydrogel matrices, while leveraging the operational advantages of electron beam radiation technology.

2. Methodology

2.1 Formulation Preparation

Four polymeric formulations were prepared: (i) PVP/agar/PEG/EDTA containing 85 mL of water; (ii) PVP/PEG/EDTA containing 86 mL of water; (iii) PVA/agar/PEG/EDTA containing 85 mL of water; and (iv) PVA/PEG/EDTA containing 86 mL of water. The formulations containing agar were heated and homogenized until complete dissolution of all components, then cast into suitable moulds and vacuum sealed prior to irradiation (Fig. 1A). The formulations without agar remained in the liquid state after preparation and were poured into moulds, which were subsequently placed in appropriate containers for transport and irradiation processing (Fig. 1B).

2.2 **Electron beam irradiation**

Electron beam irradiation was carried out at the Radiation Technology Center of the Nuclear and Energy Research Insitute (IPEN, São Paulo, Brazil) using a JOB 188 electron accelerator (Radiation Dynamics Inc., USA). The accelerator operates at a maximum energy of 1.5 MeV, with a beam current of up to 25 mA and an effective scanning width of 120 cm. All samples were irradiated using an electron beam accelerator and exposed to absorbed doses of 20 and 25 kGy. The irradiation process was performed under controlled conditions to promote polymer crosslinking and hydrogel formation.



FIG. 1. *Samples (A) and (B) positioned for irradiation*

2.2 Characterization

Fourier Transform Infrared (FTIR) spectra were recorded using an Agilent Cary infrared absorption spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector and an Attenuated Total Reflectance (ATR) accessory with a single-reflection diamond crystal. Measurements were performed at a spectral resolution of 4 cm^{-1}, with 128 accumulated scans per spectrum, in order to identify the characteristic functional groups and absorption bands of the samples. The surface morphology of the hydrogels was investigated by Scanning Electron Microscopy (SEM) using a benchtop field emission gun (FEG) electron microscope (Phenom Pharos G2, Thermo Fisher Scientific), equipped with an energy-dispersive X-ray spectroscopy (EDS) system and a secondary electron detector (SED). The swelling degree was determined to evaluate the solvent uptake capacity of the hydrogels relative to their initial dry mass, without compromising the integrity of their three-dimensional polymeric network. For this purpose, the percentage of solvent absorbed by the samples was calculated until swelling equilibrium was reached. Following material characterization, practical cleaning tests were performed using the developed hydrogels on an artist's canvas. The tests consisted of the removal of surface contaminants from pre-defined and delimited regions of the canvas in order to evaluate the cleaning efficiency of the formulations.

3. Results

4.1 Electron Beam–Crosslinked Hydrogel

Electron beam irradiation offers a significantly shorter processing time compared to cobalt-60 gamma irradiation systems [11],[12]. Under the conditions employed in this study, hydrogel crosslinking was achieved in approximately ten minutes, including equipment setup and operational adjustments. The required absorbed doses were delivered in three irradiation cycles. This stepwise dose application was necessary to prevent thermal degradation of the material, since continuous exposure to the electron beam may lead to localized overheating and consequent structural deterioration of the polymer network.

Immediately after irradiation, the formation of uniformly distributed bubbles throughout the samples was observed, resulting in a foam-like appearance (Fig. 2A). This effect is attributed to ongoing post-irradiation crosslinking reactions and the generation of gaseous species associated with water radiolysis within the hydrogel matrix [13]. After 24 hours, a marked reduction in bubble content was observed, enabling safe removal of the samples from their packaging without compromising structural integrity (Fig. 2B). By the fourth day post-irradiation, the polymeric network exhibited progressive stabilization, allowing the hydrogels to be handled without fragmentation or material loss during application to treated surfaces (Fig. 2C). These results indicate that, although crosslinking is initiated during irradiation, the final stabilization of the three-dimensional hydrogel structure continues in the post-irradiation period, leading to a more mechanically stable material over time.

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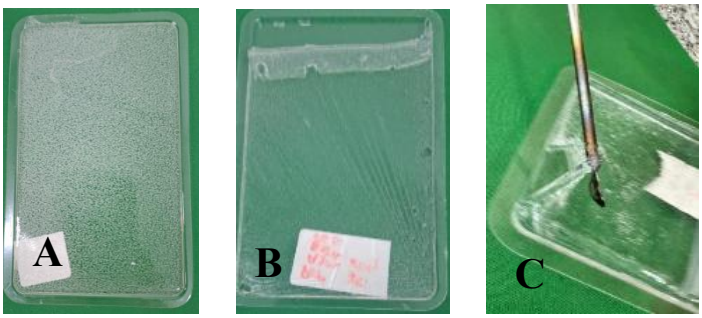

FIG. 2. *(A) immediately after irradiation; (B) 24 h post-irradiation; (C) 4 days post-irradiation, showing network stabilization.*

3.2 FTIR Analysis

The FTIR spectra of the PVP and PVA based hydrogels exhibited characteristic absorption bands associated with the constituent polymers and the additives incorporated into the formulations. In all samples, a broad band in the 3200–3600 cm^{-1} region was observed, attributed to O–H stretching vibrations arising from agar, PEG, EDTA, and adsorbed water within the polymeric matrix. The pronounced broadening of this band suggests the formation of extensive hydrogen-bonding interactions among the hydrogel components.

For the PVP-based hydrogels, a distinct absorption band at approximately 1650 cm^{-1} was observed, corresponding to the C=O stretching vibration of the lactam group in the polymer backbone (Fig. 3A). In addition, bands in the 1280–1320 cm^{-1} region were assigned to C–N stretching vibrations of the pyrrolidone ring, while bands between 1050 and 1150 cm^{-1} were associated with C–O–C stretching of PEG as well as glycosidic linkages in agar.

In the PVA based hydrogels, characteristic bands were observed in the 1080–1140 cm^{-1} region, attributed to C–O stretching vibrations of the polymer backbone (Fig. 3B), as well as bands in the 1410–1450 cm^{-1} region, related to CH_2 bending vibrations. The presence of agar led to subtle changes in the intensity of bands associated with hydroxyl groups, indicating intermolecular interactions between the hydrogel components.

The absence of new significant absorption bands in the FTIR spectra suggests that radiation-induced crosslinking occurred predominantly through intermolecular bonding between polymer chains, without the formation of new functional groups detectable by FTIR. The observed variations in band intensity and broadening further indicate changes in hydrogen-bonding interactions and in the structural organization of the hydrogel three-dimensional network.

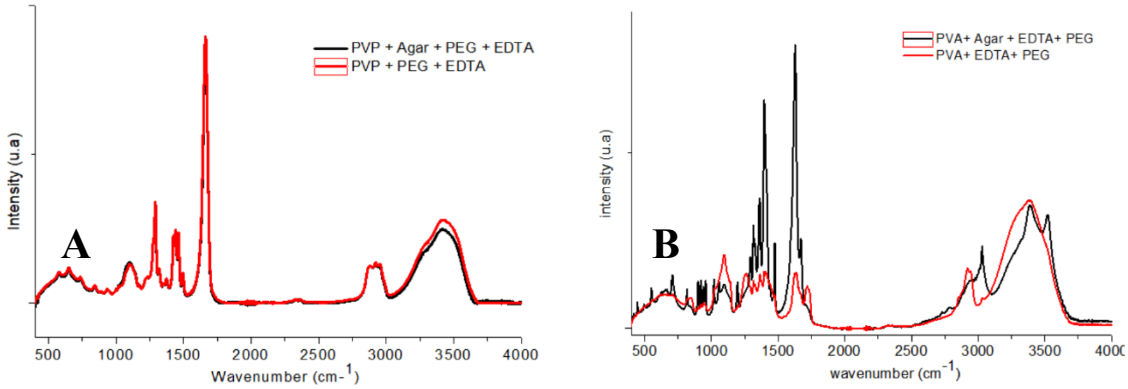

FIG. 3. *FTIR spectra of the hydrogels: (A) PVP based hydrogel and (B) PVA based hydrogel, highlighting characteristic absorption bands.*

4.3 Scanning Electron Microscopy (SEM)

Due to the high water content of the hydrogels (approximately 85%) [14], the samples were dehydrated at room temperature (25 °C) prior to morphological analysis to enable SEM characterization.

Figure 4A shows the PVP based hydrogel containing agar. The highlighted regions reveal a wrinkled surface morphology, attributed to the formation of a three-dimensional polymeric network induced by the crosslinking process. These features become more pronounced after water removal during dehydration.

In contrast, Fig. 4B presents the PVP based hydrogel without agar, which exhibits a surface characterized by irregularly distributed voids interspersed with smoother regions, indicating a less homogeneous network structure.

Figure 5A corresponds to the PVA based hydrogel containing agar, in which dehydrated regions (indicated by circles) display more developed and well defined morphological structures compared to the PVP/agar system. Conversely, the PVA based hydrogel without agar (Fig. 5B) shows a predominantly smooth and homogeneous surface, with morphology resembling a continuous polymeric film.

Overall, these results indicate that the presence of agar significantly influences the organization of polymer chains during the crosslinking process, promoting the formation of more defined three-dimensional structures and markedly affecting the surface morphology of the hydrogels after dehydration.

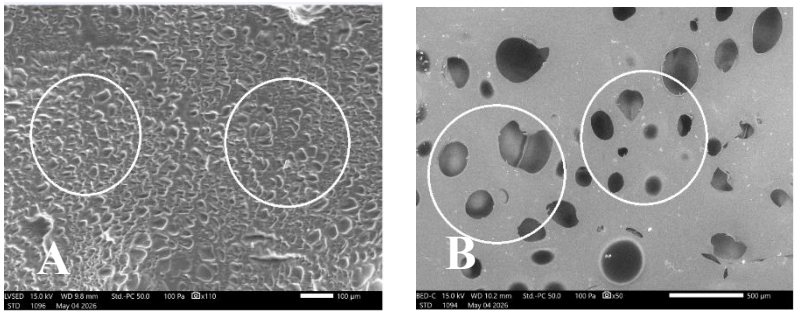

FIG. 4. *SEM micrographs of dehydrated PVP based hydrogels (25 °C): (A) with agar; (B) without agar.*

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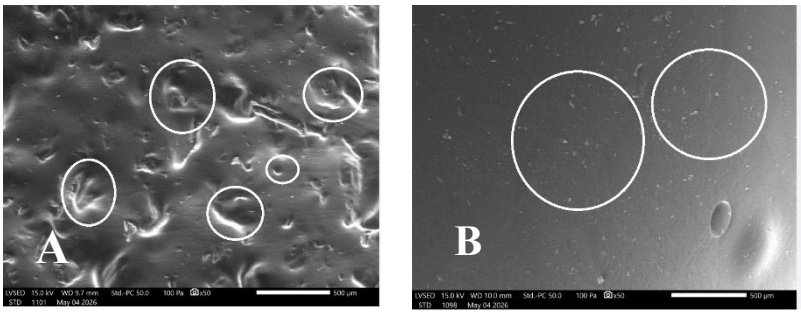

FIG. 5. *SEM images of dehydrated PVA hydrogels at 25 °C showing the influence of agar addition: (A) PVA/agar; (B) PVA without agar.*

3.4 Sweling Behavior

The PVP and PVA based hydrogels containing agar (Fig. 6A and Fig. 7B, respectively) exhibited similar swelling behavior, reaching approximately 250% water uptake without loss of structural integrity. In contrast, the PVP based hydrogel without agar did not exhibit sufficient mechanical stability during the test, fragmenting in the solution after approximately 30 minutes of immersion, which prevented accurate determination of the swollen mass.

The PVA based hydrogel without agar showed significant swelling capacity; however, the extent of swelling was lower than that observed for the agar containing formulations. This behavior may be attributed to the presence of hydrophilic functional groups in the agar structure, which enhance interactions with water molecules and increase the overall absorption capacity of the hydrogel. In addition, agar incorporation likely contributed to the formation of a more stable and interconnected polymeric network, capable of maintaining structural integrity during the swelling process.

These results are consistent with the SEM observations (Figs. 4 and 5), where agar-containing formulations exhibited more organized and porous morphologies, which facilitate water diffusion and retention within the polymeric matrix.

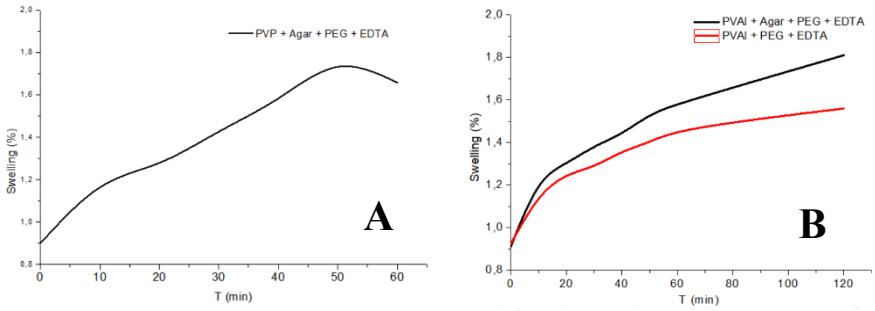

FIG. 6. *Swelling profiles of PVP and PVA based hydrogels showing water uptake as a function of time: (A) PVP; (B) PVAI.*

4.5 Practical Cleaning tests

Following physicochemical and morphological characterization, the hydrogels exhibiting the most favorable structural properties were selected for practical cleaning evaluations. For this purpose, an acrylic-painted canvas exhibiting a high level of surface soiling was

used as the test substrate. The hydrogel samples were applied directly to selected areas of the artwork and maintained in contact for 30 minutes.

The results demonstrated that both the PVP-based hydrogel containing agar (Fig. 7A) and the PVA-based hydrogel containing agar (Fig. 7B) were effective in removing surface contaminants from the canvas. After removal of the hydrogels, efficient cleaning was observed without the need for additional mechanical action using swabs, indicating a strong capability of these formulations to adsorb and remove surface soiling.

In contrast, the PVA based hydrogel without agar (Fig. 7C) exhibited lower structural stability during application. After removal, residual hydrogel fragments were observed adhering to the canvas surface, requiring swab-assisted cleaning to ensure complete removal of the material. The PVP based hydrogel without agar was not suitable for practical application due to insufficient mechanical integrity, which compromised handling and prevented reliable removal after the contact period.

Overall, agar containing formulations demonstrated superior performance in terms of handling, structural stability, and clean removal, leaving no detectable residues on the treated surface. These results highlight the potential of the developed hydrogels for applications in the conservation and restoration of cultural heritage materials, combining effective soil removal with improved operational safety and environmental sustainability [15].

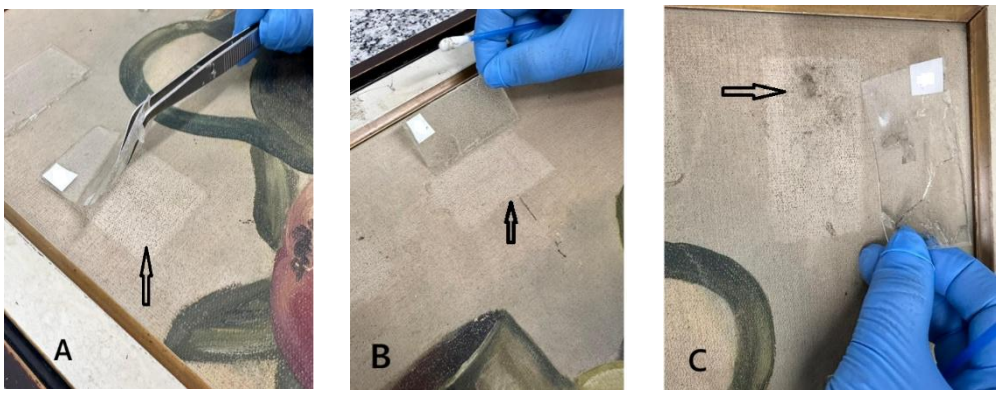

FIG. 7. *C Practical cleaning tests on an acrylic painted canvas using hydrogels: (A) PVP/agar; (B) PVA/agar; (C) PVA without agar.*

5. Conclusion

The results obtained demonstrate that the incorporation of agar plays a key role in enhancing the structural integrity and handling resistance of the hydrogels, which are essential properties for their application in the cleaning of artistic surfaces. In addition, owing to their predominantly aqueous composition and the use of EDTA as a complexing agent for soil removal, the developed hydrogels present a promising and more sustainable alternative to conventional cleaning systems based on organic solvents. Therefore, their application may contribute to reducing occupational exposure of conservators to potentially toxic substances, while also minimizing the environmental impact associated with the use and disposal of traditional chemical solvents.

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Conflicts of interest

The authors declare that they have no conflicts of interest

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