



Reversible polymeric resin cured by ionizing radiation for consolidation of wooden artifacts of cultural heritage

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ABSTRACT

This study investigated the application of Paraloid B72 resin, modified with methyl methacrylate (MMA) and butyl methacrylate (MaBu) monomers, to develop new materials for the consolidation and restoration of wooden objects. The curing process was conducted using ionizing radiation from a gamma source (cobalt-60), eliminating the need for organic solvents. After characterization by gel fraction analysis, the Paraloid 30 % formulation with MMA 40 % and MaBu 30 % was selected for further characterizations, including Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), Fourier Transform Infrared Spectroscopy (FTIR), and impregnation tests. The formulation was impregnated into wooden artifacts, cured using ionizing radiation, and subsequently characterized by FTIR, Scanning Electron Microscopy (SEM), and Computed Tomography (CT). The results showed that ionizing radiation replaces the need for catalysts, increasing the thermal stability of the resin and allowing cure control through dose (in kGy) and dose rate (kGy/h). This enabled the resin impregnation without compromising the integrity or the information contained in the consolidated artifact. The development of the methodology and resin formulation presented scientific challenges, particularly in ensuring that the desirable characteristics and reversibility were maintained.

1. Introduction

The use of resins is a well-established practice for the conservation and consolidation of wooden artifacts, as it allows for modeling and filling gaps and pores caused by insects or the natural degradation of wood over time (Access, 2020; Crisci et al., 2010; Carretti and Dei, 2004; Barclay and Mathias, 1989). However, the traditional method of resin curing using catalysts (organic solvents) has limitations, especially regarding temperature variations, which can alter the resin's structure and consequently change the characteristics of the consolidated artifact. The literature presents cultural heritage objects restored with polyester resins cured by gamma radiation, among these objects are wooden artifacts (Vieira et al., 2024; Vujcic et al., 2020; Moise et al., 2019) The gamma radiation-controlled paraloid resin curing procedure is an innovative one, which was developed in this research. After obtaining the resin curing conditions, it was impregnated in wooden artifacts and subjected to gamma radiation for curing.

Acrylic resins have been widely used in the conservation of artifacts since the end of the last century (Koob, 1986). These resins,

commercially known as Paraloid, are employed by conservators as coatings, consolidants, or adhesives due to their relative reversibility, transparency, mechanical strength, and stability (Zhao et al., 2024; Koob, 2021; Mansour and Salem, 2015; Sun et al., 2015). The market offers various types of Paraloid suitable for different materials and easy to handle. However, Paraloid B72 is widely used as a reference for testing and studying new materials (Podany et al., 2001).

These acrylic resins exhibit good compatibility with various solvents such as acetone, ethanol, toluene, xylene, and ethyl acetate, allowing a solvent-resin ratio of up to 70/30 depending on the specific consolidation needs (Chapman and Mason, 2003). For example, Paraloid B72 is a copolymer of ethyl methacrylate (EMA) and methyl acrylate (MA) in a 70/30 ratio. Other widely used acrylic resins in conservation, also commercially available, are copolymers with specific compositions, although their exact proportions are not always disclosed (Magd, 2018; Vaz et al., 2008; Chapman and Mason, 2003). According to the literature, the choice of resin by conservators is guided by the specific application needs and the characteristics of the object to be consolidated. The type of solvent and resin concentration can directly influence

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the outcome of the consolidation process (Vinçotte et al., 2019). However, it is crucial to consider environmental conditions, especially the temperature of the location where the consolidated object will be exposed. Studies conducted by Alexiou et al. evaluated the mechanical properties of chemically cured Paraloid B72 at 0 °C, 30 °C, and 50 °C, showing that this method yields unsatisfactory performance at higher temperatures (Alexiou et al., 2013).

Based on these findings, we proposed developing new resin formulations using Paraloid B72 with the addition of polymeric monomers, cured by gamma ionizing radiation, eliminating the need for solvents. This method offers several advantages. It reduces the environmental impact by avoiding solvent accumulation. It also addresses common challenges faced by conservators, such as unfilled gaps due to low resin concentration or hindered penetration due to high concentration. Moreover, curing with ionizing radiation, in addition to eliminating solvents, allows precise control of crosslinking through dose (in kGy) and dose rate (in kGy/h). The process is performed at room temperature and produces resins with appropriate glass transition temperature (T_g) values for application in various environments, as demonstrated by the results presented in this research. Ionizing radiation has become a valuable tool in preserving cultural heritage objects, being used both for disinfection and for obtaining materials for consolidation/conservation (D'Orsi et al., 2024; Oliveira et al., 2022; Nagai et al., 2021; Bonelli et al., 2019; Moise et al., 2019; Vasquez, 2017; Baglioni et al., 2014).

The innovation of this research is the use of ionizing radiation from a gamma source, this technique brings significant benefits for obtaining new materials for the consolidation and restoration of wooden objects. The main innovative aspects of this work include: (i) Control of resin curing through gamma radiation without the need for catalysts, simplifying the process and reducing environmental impact; (ii) Excellent thermal stability of Paraloid B72 resin after monomer addition and curing through gamma radiation, an essential feature for determining the suitability of Cultural Heritage objects for various exposure conditions. (iii) Reversibility of the resin, a crucial property for consolidation and restoration processes, allowing future interventions without damaging the original object; (iv) Direct impregnation of the resin into the wooden structure, ensuring the effectiveness of the treatment without causing harm to the object's structures.

2. - Materials and methods

2.1. Materials

Paraloid B72 resin, polymeric monomer methyl methacrylate (MMA) and butyl methacrylate (MaBu), the materials were used as received from suppliers, a cylindrical steel reactor with a 7.50 L capacity for resin impregnation into samples, nitrogen (N_2), a vacuum pump, natural wood samples of marupá caxeta (*Simarouba amara*) and rose cedar (*Cedrela fissilis*), a wooden sculpture in the shape of a mask, and a cobalt-60 source located in a multipurpose irradiator.

2.2. Methodology

First Stage: Formulations of Paraloid B72 resin with MaBu at different concentrations, Paraloid B72 with MaBu and MMA at varied concentrations, a mixture of MaBu with MMA in a 1:1 ratio, and a formulation containing only MaBu were prepared. The mixtures were placed in covered beakers for 48 h to ensure complete solubilization of Paraloid. Subsequently, the formulations were homogenized, transferred to 40 mL flasks, and subjected to ionizing irradiation using a gamma source at a dose of 50 kGy and a rate of 1 kGy/h for the curing of the new resins. Following this step, the formulation of Paraloid B72 with MaBu and MMA was selected and subjected to doses of 1, 3, 5, 8, 10, 15, 20, 25, 30, and 50 kGy, at a rate of 1 kGy/h, to study curing behavior as a function of the dose.

Second Stage: In a 10-liter container, a solution was prepared with

30 % Paraloid B72 resin and 40 % MMA, well mixed using a wooden spatula. This was followed by the addition of 30 % MaBu, which was mixed again and left to rest for 48 h to fully solubilize the Paraloid. The resulting solution was transferred to a cylindrical reactor with a 7.5 L capacity, positively pressurized. Inside this reactor, wooden pieces, including caxeta, rose cedar, and a wooden artifact in the shape of a mask, were placed and subjected to N_2 and maintained under vacuum for 24 h. After transferring the resin to the reactor, the mixture was kept under pressure for 72 h to allow resin impregnation into the wooden pieces. After 72 h, the reactor's valve was opened to drain the excess resin. The samples were removed and wrapped in cotton fabric to absorb the excess resin on the surface. Subsequently, the samples were placed in the irradiator chamber and subjected to ionizing radiation using a cobalt-60 source. The fabric with the excess resin was removed from the surface of the samples at a dose of 8 kGy.

2.3. Characterizations

The gel fraction corresponds to the insoluble part of the samples, attributed to the crosslinked (cured) polymeric fraction, obtained from the irradiated samples. For this, 500-mesh stainless steel mesh filter bags, shaped as envelopes, were used to package the crosslinked resin samples. The bags were labeled, weighed individually, and then weighed with the samples. The analysis was performed in triplicate and calculated using the following equation, adapted from ASTM D2765-16 (ASTM D2765-16, 2024).

$$\text{Gel fraction (\%)} = (m_f/m_i) \times 100$$

Where: m_f represents the dry mass of the resin after extraction and drying, and m_i represents the initial mass of the resin before extraction.

Thermogravimetric Analysis (TGA) was employed to monitor the crosslinking (curing) of the samples through the analysis of mass degradation as a function of the gamma radiation dose. The experiments were conducted using alumina crucibles, at a heating rate of 10 °C per minute, in a nitrogen (N_2) atmosphere, with a flow rate of 100 mL per minute and a maximum temperature of 600 °C, using a TA Instruments SDT Q6000 model. Differential Scanning Calorimetry (DSC), was used to determine the polymer transition temperatures, such as melting (endothermic, heat absorption), crystallization (exothermic, heat release), and glass transition, enabling the evaluation of energetic, physical, and/or chemical phenomena occurring during sample heating (Bonfim et al., 2014; Andrade et al., 2008). These analyses were conducted simultaneously with the TGA, under the same conditions, and using the TA Instruments SDT Q6000 model, with the first derivative being analyzed. Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed using a Thermo Nicolet Nexus 670 spectrometer equipped with an Attenuated Total Reflectance (ATR) accessory and a Mercury Cadmium Telluride (MCT) detector. FTIR spectra were acquired in the mid-infrared region (4000-400 cm^{-1}) with a resolution of 4 cm^{-1} , and multiple scans were averaged to improve the signal-to-noise ratio. A background spectrum was collected before each measurement to account for atmospheric contributions. Scanning Electron Microscopy (SEM), was employed to observe the morphological structures of the wood samples before and after resin impregnation and curing through gamma radiation. The analyses were conducted using the SEM-FEG JSM-6701F bench-top microscope by Jeol. Computed Tomography (CT) enabled a detailed exploration of the samples through high-resolution images, offering a non-invasive examination that provided additional information about the artifact, distinguishing density variations (Juanes and Ferrazza, 2012). CT is based on the same principle as radiography, where materials with different compositions exhibit distinct radiation absorption capacities. Denser materials, for instance, absorb a greater amount of X-rays compared to less dense materials, such as a hollow wood structure containing air. The wood samples were subjected to tomographic analyses before and after

Table 1

Gel fraction in percentage of resins after irradiation at a dose of 50 kGy and extraction carried out with xylene for 12h and 24h

Samples	Gel fraction % 12h	Gel fraction % 24h
Paraloid + MaBu	0.5	0.0
Paraloid + MaBu + MAM	10.3	0.0
MAM + MaBu	7.2	0.0
MaBu	1.2	0.0

irradiation using the Ingenuity Elite CT Scanner by Philips, located at the University of São Paulo Hospital. The objective was to identify the presence of pores and cavities in the samples and evaluate whether these areas were filled by the impregnated resin.

3. Results and discussion

The resins formulated with Paraloid and MaBu, Paraloid with MaBu and MAM, MaBu with MAM, and MaBu alone were crosslinked through ionizing radiation from a gamma source, using a dose of 50 kGy and a rate of 1 kGy/h, without the use of catalysts. After irradiation, the samples were subjected to extraction in a Soxhlet extractor, using xylene as the solvent, to obtain the insoluble gel fraction following a procedure adapted of the norm ASTM D2765-16 (ASTM D2765-16, 2024). As presented in Table 1, residues were still present after 12 h of extraction. However, complete solubilization (reversion) of all samples occurred

after 24 h. This indicates that the radiation induced crosslinking (curing) of the resins without a catalyst. Importantly, the process is reversible a characteristic of significant importance for applications in the consolidation and restoration of materials.

3.1. Thermogravimetric Analysis (TGA)

Following the preliminary results of the gel fraction indicating reversibility in the four types of resins, the Paraloid + MaBu + MAM formulation was selected for further characterizations. This formulation was then subjected to ionizing irradiation at doses of 1, 3, 5, 8, 10, 15, 20, 30, and 50 kGy, at a rate of 1 kGy/h, to identify the most effective doses for determining the gel point (crosslinking kinetics). The TGA analyses were divided into two figures for better visualization of the curves.

Fig. 1A shows the behavior of the samples irradiated at doses of 1, 3, and 5 kGy, where the resin and polymeric monomers are still in the viscous phase, and the thermogravimetric curves display three events with similar mass loss among them. In the samples irradiated at 8 and 10 kGy, the onset of crosslinking is observed as the resin transitions to a gel phase. Furthermore, samples irradiated at 15 and 20 kGy exhibit stiffness and stickiness, likely due to increased crosslinking, as noted during sample preparation for analysis. These samples also show greater thermal stability and less defined curves compared to the previous doses.

In the viscous phase, the polymer chains show high mobility. As the

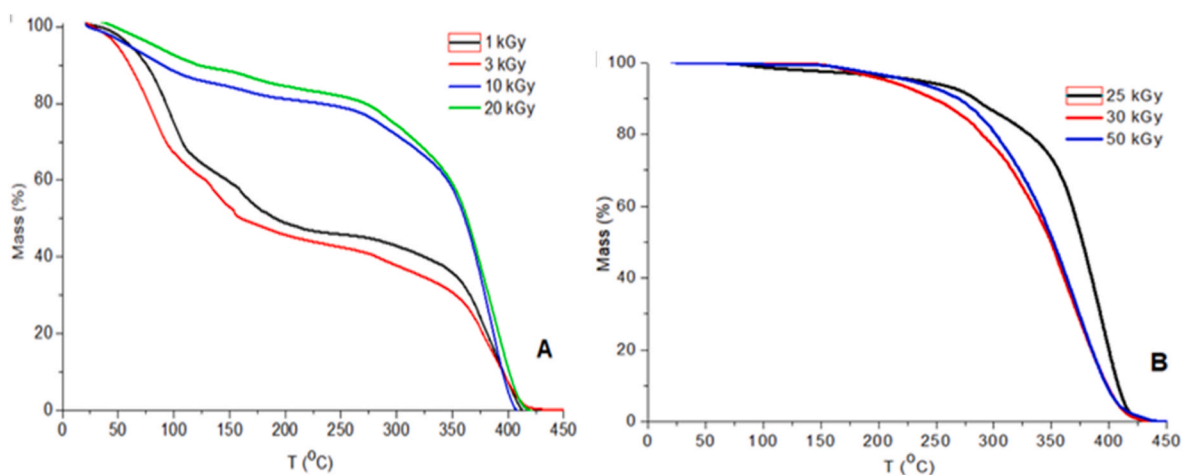


Fig. 1. – A) degradation curves of the paraloid + MaBu + MAM samples irradiated at doses of 1, 3, 5, 8 and 10 kGy and B) degradation curves of the paraloid + MaBu + MAM samples irradiated at doses of 15, 20, 25, 30 and 50 kGy.

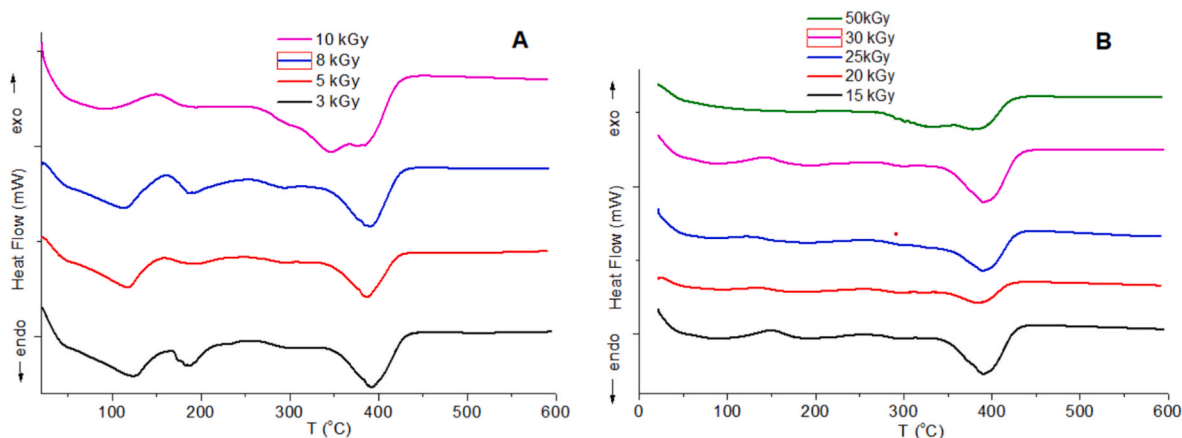


Fig. 2. DSC curves of resin samples cured by ionizing radiation.

Table 2

– The values of the T_g, exothermic, fusion and ΔH_f peaks according to the dose in kGy to which the samples were subjected.

Dose (kGy)	1° peak solvent (°C)	2° peak T _g (°C)	3° peak T _m (°C)	1° peak T _c (°C)	2° peak T _c (°C)	3° peak T _c (°C)	ΔH _f (J/g)
1	105	180	382	–	–	–	140
3	88	97	385	261	–	–	133
5	115	193	390	156	261	–	173
8	98	184	296	143	278	–	136
10	105	200	389	134	257	–	205
15	116	209	394	157	215	–	191
20	101	193	392	137	252	–	295
25	91	300	398	118	262	315	286
30	50–100	270	386	213	308	–	74
50	50	178	383	281	–	–	28

dose increases, mobility decreases, and gel formation occurs, marking the onset of crosslinking. From 25 kGy onward, the polymer chains become rigid, a phenomenon known as curing, which increases thermal stability and makes the polymer more resistant, as shown in Fig. 1B.

For samples irradiated at 25 kGy, three events are observed: T_{onset} at 100 °C, associated with the loss of residual water; at 285 °C, associated

with the degradation of methyl groups and volatile molecules; and at 360 °C, corresponding to the degradation of the main chain. In addition, the sample irradiated at 30 kGy exhibits a T_{onset} event at 180 °C, related to the mass loss of the main chain. Meanwhile, the sample irradiated at 50 kGy shows two events: T_{onset} at 180 °C, associated with the breaking of smaller molecules, and at 250 °C, indicating the degradation of the main molecular chain.

These results indicate that maximum crosslinking, with the highest thermal stability, was achieved for the sample irradiated at 25 kGy, followed by doses of 50 kGy and 30 kGy. It is hypothesized that the 30 kGy dose caused molecular disarrangement, possibly due to chain scission, reducing thermal stability. However, the 50 kGy dose, despite the disarrangement observed at 30 kGy, appears to reestablish molecular

Table 3

– Wood samples' mass in grams (g) before (without resin) and after resin impregnation.

Wood sample	Initial mass (g)	Final mass (g)	Gain mass (g)
Mask	234.00	324.00	100
Natural caxeta	12.38	19.47	7.09
Rose cedar	0.92	1.19	0.27

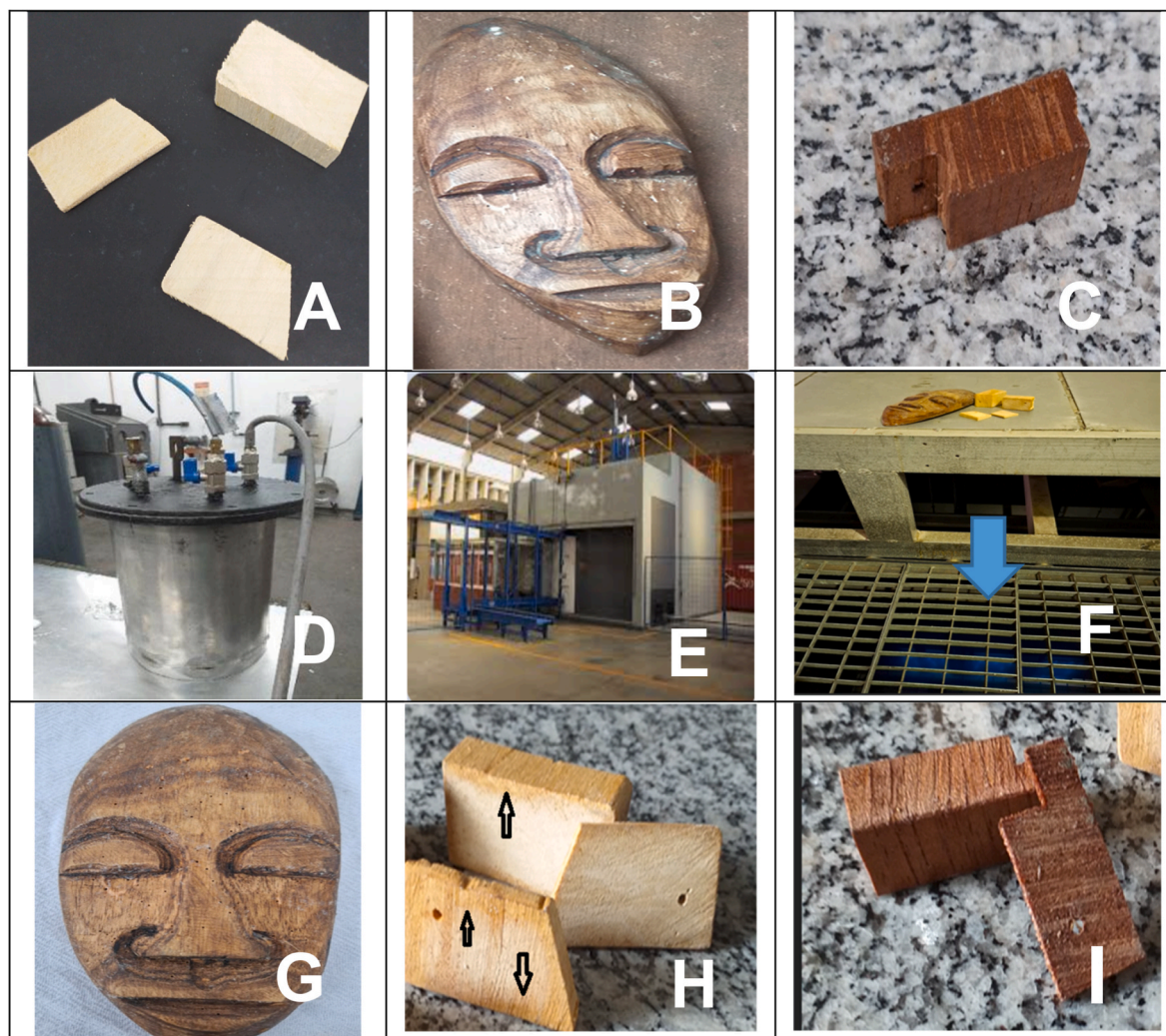


Fig. 3. Samples before and after impregnation and irradiation with Paraloid + MaBu + MAM resin. (3A) natural caxeta, (3B) wooden mask, and (3C) rose cedar (3D) Reactor with the samples and resin under pressure, (3E) External view of the Multipurpose Irradiator, and (3F) Internal view of the irradiator with the samples and cobalt-60 radioactive sources indicated by the arrow, (3G) Impregnated and irradiated mask, (3H) Impregnated and irradiated caxeta, and (3I), impregnated and irradiated rose cedar.

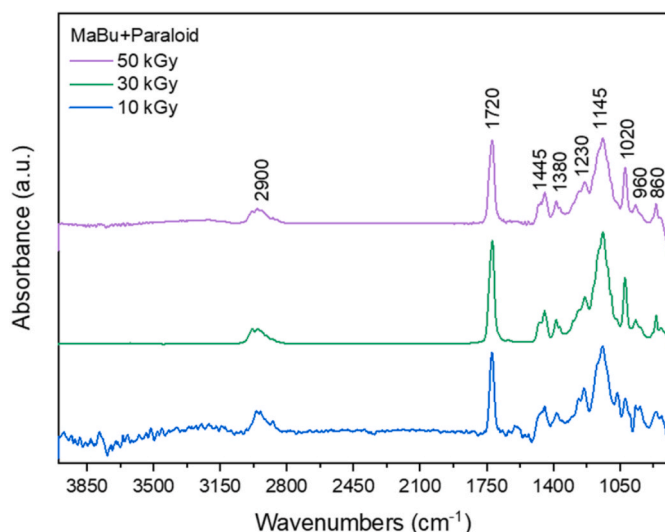


Fig. 4. FTIR spectra of resin after irradiation at a dose of 10, 30 and 50 kGy.

rearrangement, restoring thermal stability and maintaining only two events.

3.2. Differential Scanning Calorimetry analysis (DSC)

In the DSC curves shown in Fig. 2A and B, variations in the intensity and position of peaks occurring before the exothermic peaks are observed. These peaks were associated with excess residual solvent. The second event. These peaks were associated with the glass transition (T_g) regions during the crosslinking process of the samples. The T_g of thermosetting polymers is a property that depends on the degree of crosslinking (Thiessen and Abetz, 2021). The increase in crosslinks reduces the mobility of chain segments and, consequently, increases the glass transition temperature, decreasing the intensity of the signal observed in Fig. 2B. The phenomenon that occurs according to the radiation dose subjected, Vincotte and collaborators reported T_g values for chemically cured Paraloid B72-based adhesives above 40 °C, depending on the addition of solvents (Vinçotte et al., 2019) Table 2 presents the values of the T_g , exothermic, fusion and ΔH_f peaks according to the dose in kGy to which the samples were subjected. It is noted that samples irradiated at doses ranging from 5 kGy to 30 kGy exhibit two exothermic temperature values, indicating the onset of polymer crosslinking in the resin. The resin crosslinked at 25 kGy displayed a high melting point (398 °C). It also showed three endothermic peaks, and the highest enthalpy of fusion

value at 398 (ΔH_f , J/g) compared to the other doses. In contrast, the sample irradiated at 50 kGy showed only one exothermic temperature value and a reduced ΔH_f (J/g). This suggests that crosslinking stability has plateaued due to restricted polymer chain mobility. The DSC results demonstrate that curing of the resin via ionizing radiation is feasible for impregnating wooden artifacts at doses between 20 kGy and 50 kGy. Studies by Andrade et al. (2008) and Schawe (1995), conducted using DSC, show similar results for the chemical curing process of epoxy and polyester resins, where control is achieved through temperature and catalysts (Andrade et al., 2008; Moise et al., 2019; Schawe, 1995).

3.3. Resin impregnated in wood samples and their characterizations

Fig. 3 presents images of the wood samples before and after impregnation and irradiation with Paraloid + MaBu + MAM resin. Fig. 3A, B, and 3C show the natural caxeta wood sample, the cultural artifact mask, and the natural rose cedar wood sample, respectively. Fig. 3D displays the reactor containing the wood samples and the resin formulation for impregnation under pressure. Fig. 3E and F illustrate the external and internal views of the Multipurpose Irradiator, where the impregnated wood samples are placed alongside the cobalt-60 radioactive sources for resin crosslinking via gamma radiation. After irradiation, the mask (Fig. 3G) shows a darker, more uniform coloration. Fig. 3H displays the caxeta sample, with an arrow indicating the darker region where resin penetration occurred. The rose cedar sample (Fig. 3I) exhibits no change in coloration. Similar to our study, Cortela et al. successfully consolidated a wooden boat structure using a polyester resin cured via ionizing radiation. They used a dose of 50 kGy, which is within the range of doses used in our study (Cortella et al., 2020; Moise et al., 2019).

In addition to visual observation, resin impregnation can also be observed through the amount of resin absorbed by the wood, which results in an increase in the sample's mass depending on the quantity and size of natural pores (holes) or those caused by insect attacks. Table 3, presents the mass values of the samples before (without resin) and after resin impregnation and irradiation.

3.4. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) analysis provides detailed information about the chemical composition and molecular structure of materials. By measuring the absorption of infrared radiation by the sample, FTIR spectroscopy can identify specific functional groups and types of chemical bonds present. This technique is particularly valuable in the conservation of cultural heritage objects, as it allows for the non-destructive analysis of a wide range of materials, including

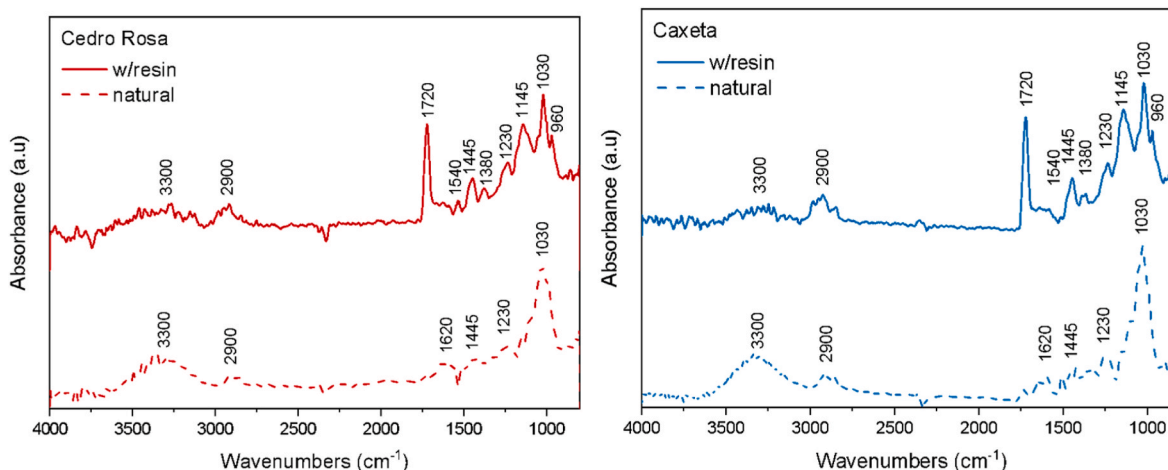


Fig. 5. FTIR spectra of rose cedar (a) and caxeta (b) natural and after impregnated with the resin and cured with gamma radiation.

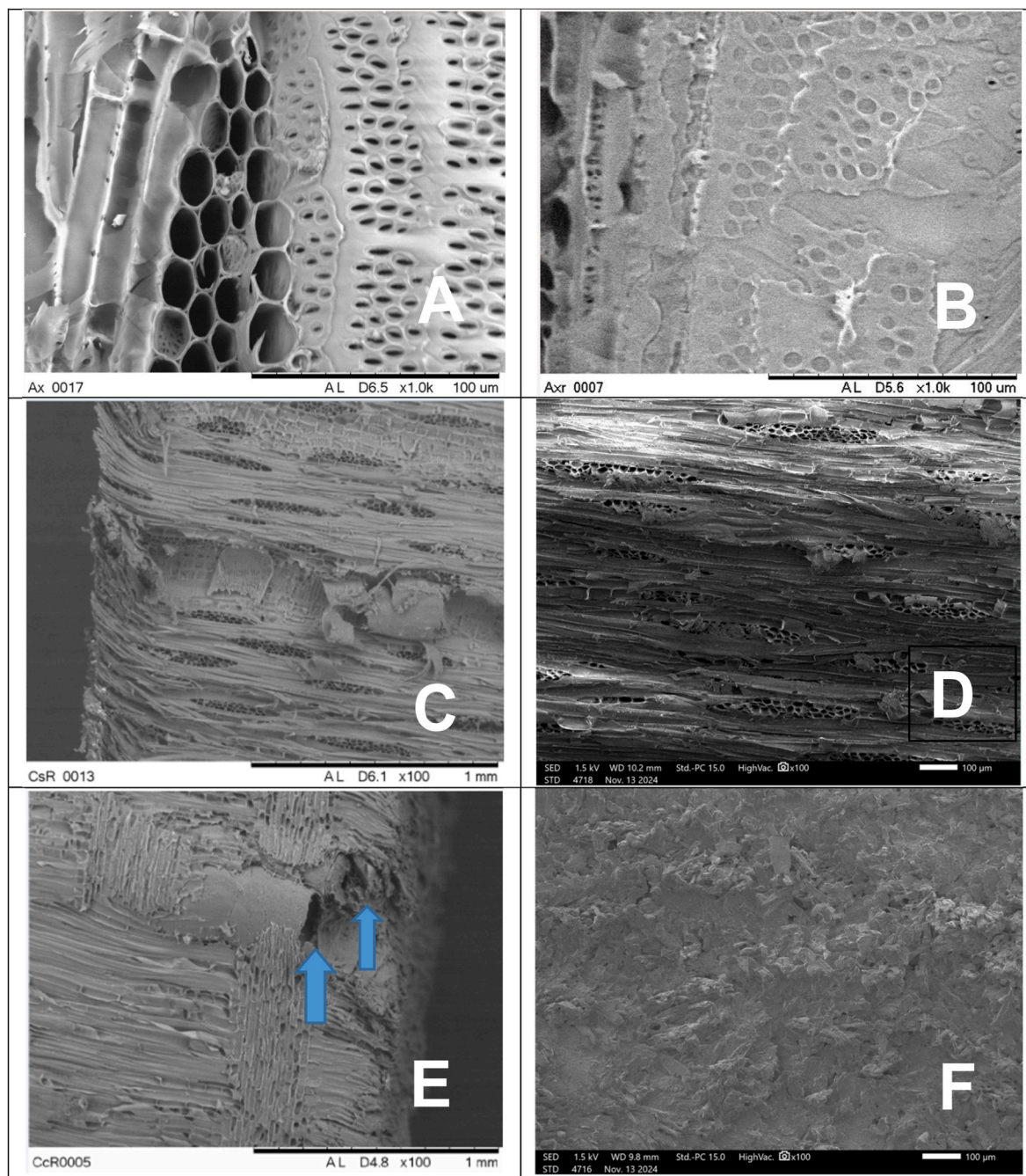


Fig. 6. SEM of wood samples, caxeta without resin (A), caxeta with resin cured by ionizing radiation (B), rose cedar without resin (C and E), rose cedar with resin cured by ionizing radiation (E and F).

coatings, adhesives, and the constituent materials of the objects themselves. In this study, FTIR was employed to investigate the chemical changes in the resin before and after irradiation and wood samples, providing insights into the effects of the treatment on their molecular structures.

The FTIR spectra of the resin in Fig. 4, show characteristic peaks for an acrylic polymer. These include strong absorptions around 1728 cm^{-1} (C=O stretch of the ester group), $1145\text{--}1245\text{ cm}^{-1}$ (C–O stretch), and $2950\text{--}2850\text{ cm}^{-1}$ (C–H stretches). Upon exposure to increasing doses of gamma radiation (10, 30, and 50 kGy), subtle changes were observed. These changes included a slight decrease in the intensity of the C–O stretching peaks ($1145\text{--}1245\text{ cm}^{-1}$) and a broadening of the C=O stretching peak (1728 cm^{-1}), which could indicate some degree of chain scission and a less uniform chemical environment around the ester

groups, respectively. However, there were no significant new peaks or shifts in peak positions, suggesting that the chemical changes induced by gamma radiation in this dose range were relatively minor (Baufleur et al., 2023; Traoré et al., 2016).

Fig. 5 illustrates the FTIR spectra of rose cedar (a) and caxeta (b) in their natural state and after impregnation with the resin and curing with gamma radiation. In their natural state, the FTIR spectra of cedro rosa and caxeta wood displayed characteristic peaks of lignocellulosic materials, including broad O–H stretching ($3300\text{--}3500\text{ cm}^{-1}$), C–H stretching ($2800\text{--}3000\text{ cm}^{-1}$), and various peaks related to cellulose, hemicellulose, and lignin (1735 cm^{-1} , $1500\text{--}1600\text{ cm}^{-1}$, $1000\text{--}1200\text{ cm}^{-1}$).

The impregnation with the resin led to the appearance of the resin's characteristic peaks in the spectra of both wood species, along with some

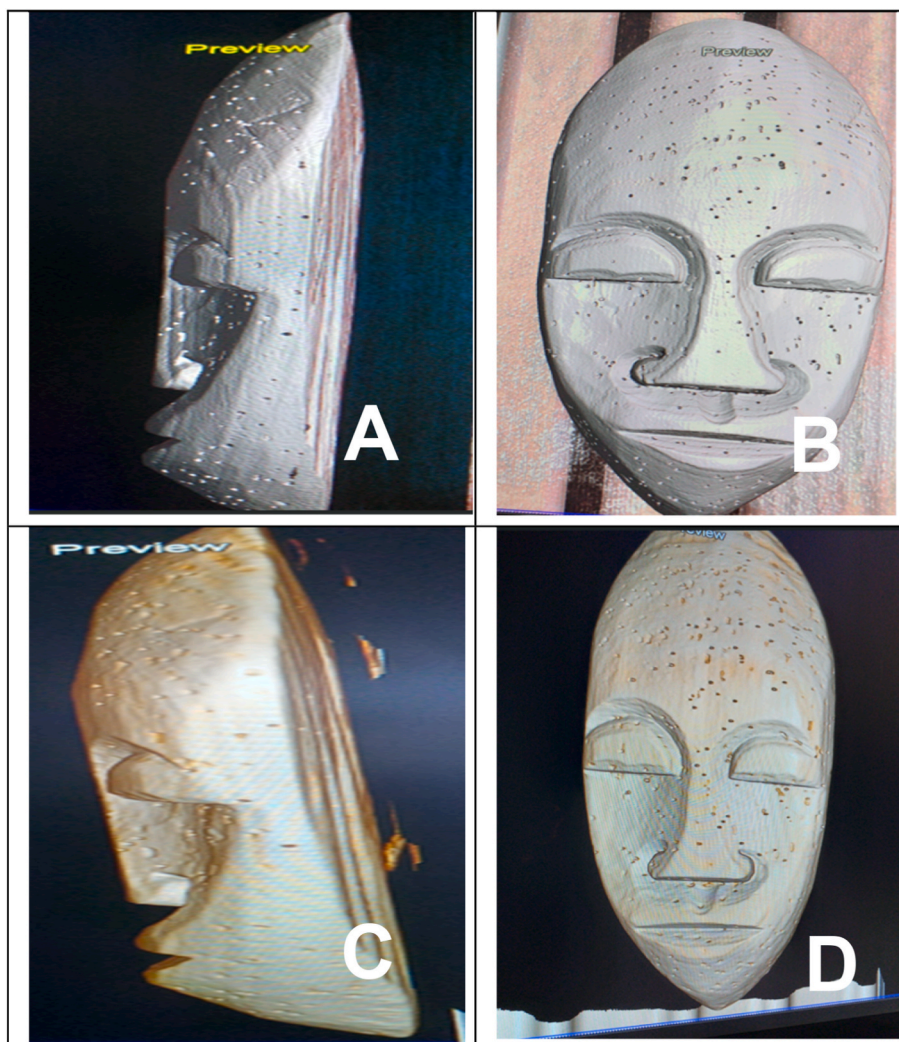


Fig. 7. Computed tomography images (A and B) mask without resin and (C and D) mask with impregnated and irradiated resin.

notable changes in the wood-related peaks. The broad O–H stretching band ($3300\text{--}3500\text{ cm}^{-1}$) decreased in intensity, suggesting a reduction in the number of free hydroxyl groups in the wood, possibly due to interactions with the resin. Additionally, the peaks in the $1000\text{--}1200\text{ cm}^{-1}$ region, associated with C–O stretching and C–O–C vibrations in cellulose and hemicellulose, showed some changes in intensity and shape, indicating potential modifications in the wood structure upon resin impregnation. The characteristic peaks of the resin appeared in the spectra of the impregnated wood without significant shifts in their positions, suggesting that the resin's chemical environment was not drastically altered within the wood matrix. Overall, the changes in the spectra were generally subtle, especially after irradiation, suggesting that the wood species were relatively resistant to gamma radiation in the studied dose range (Baufleur et al., 2023; Brandt et al., 2023; Lazzari and Chiantore, 2000).

3.5. Scanning electron microscopy (SEM)

Since the invention of the compound microscope in the late 17th century by Leeuwenhoek, microscopy in its various forms has revolutionized our understanding of material structures. It has played a key role in understanding the processes of wood cell formation, its hierarchical structure, and the ultrastructure of cell walls (Daniel, 2016). The degradation of wood, whether due to time or attacks by insects, fungi, and bacteria, is one of the main focuses of this type of study. Strictly

speaking, microscopy allows the observation of objects invisible to the naked eye (Balzano et al., 2022; Turkulin et al., 2005).

The wood samples were prepared by removing small splinters, inducing fractures in these splinters, and, without coating, obtaining high-resolution images at a voltage of 5 kV in low vacuum. It was possible to observe small structures, such as pits (pores) and other details of the natural caxeta wood sample, as illustrated in Fig. 6A, while 6B shows the impregnation of crosslinked resin sealing the pores and the structural details of the wood. The rose cedar sample exhibits a morphology with condensed wood grain, where few pores (holes) are observed, spaced apart (Fig. 6C and D). In Fig. 6E, regions can be seen where the resin did not sufficiently penetrate to fill the gaps due to the intercalated fiber arrangement, as indicated by the arrow. In Fig. 6F, it is evident that the resin covers the entire surface of the sample and fills the pores facilitated by the wood's weave.

3.6. Computed tomography (TC)

Like scanning electron microscopy, computed tomography indicates the occurrence of resin impregnation in the samples. This technique, being non-destructive, allows for the visualization of samples without needing to damage them by removing parts for analysis. Fig. 7A and B shows images of the artifact without resin, where pores (holes) caused by termites are observed, scattered across the entire surface of the sample. Termites are insects that attack wood, leaving it riddled with

holes, and if the wood is not sterilized beforehand to eliminate these insects, they can completely destroy its structure. The medical tomography used in this study has a resolution particularly effective for porous and low-density materials, such as bones (Wei et al., 2011). However, in the case of the mask, which is a dense wood sample, it was not possible to observe the depth of the pores; only the superficial pores were visible in the image.

The combination of Paraloid B72 with MaBu and MAM, cured by ionizing radiation, proved to be effective in the consolidation and preservation of wooden artifacts. The process eliminates the need for chemical solutions, reducing environmental impact and potential harm to artisans. In addition, it confirms the successful impregnation and curing of the resin within the wood matrix, increasing its thermal stability and structural integrity without compromising its reversibility for future conservation interventions.

4. Conclusion

The resins formulated with Paraloid B72 and polymeric monomers, irradiated at doses of 20, 25, 30, and 50 kGy, demonstrated suitable characteristics for the impregnation of wooden artifacts, standing out for their high thermal stability—an essential factor for materials exposed to temperature variations. Analyses using FTIR, SEM and computed tomography confirmed the impregnation and curing of the resin in the wooden artifacts used in this research. This suggests that ionizing radiation can be a viable alternative to traditional catalysts in resin curing, offering an environmentally friendly option. Furthermore, the resins maintain their molecular integrity after exposure to different radiation doses and exhibit reversibility, making them potentially useful for wood conservation. This research contributes to the growing body of knowledge on the use of ionizing radiation for the preservation of cultural heritage objects, offering a promising approach for the consolidation and restoration of wooden artifacts.

CRedit authorship contribution statement

Maria José Alves de Oliveira: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization, Maria José Alves Oliveira, Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Mariana Araujo:** Writing – review & editing, Writing – original draft, Validation, Methodology, Formal analysis, Conceptualization. **Larissa Otubo:** Writing – review & editing, Formal analysis. **Sonia Mello-Castanho:** Writing – review & editing, Formal analysis. **Pablo Vasquez:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

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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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Data availability

No data was used for the research described in the article.

References

- Access, S.O., 2020. Wood modification with resin impregnation technology for value-added services. *SVOA Mater. Sci. Technol.*
- Alexiou, K., Müller, N.S., Karatasios, I., Kilikoglou, V., 2013. The performance of different adhesives for archaeological ceramics under mechanical stress. *Appl. Clay Sci., Ancient Ceramics - Analysis and Components* 82, 10–15. <https://doi.org/10.1016/j.clay.2013.05.017>.
- Andrade, H.P.C., Diniz, M.F., Azevedo, M.F.P., Cassu, S.N., Lourenço, V.L., Dutra, R.C.L., 2008. Cure behavior of epoxy adhesive containing mercaptan group evaluated by infrared spectroscopy (MIR/NIR) and differential scanning calorimetry (DSC). *Polímeros* 18, 359–365. <https://doi.org/10.1590/S0104-14282008000400017>.
- Baglioni, M., Raudino, M., Berti, D., Keiderling, U., Bordes, R., Holmberg, K., Baglioni, P., 2014. Nanostructured fluids from degradable nonionic surfactants for the cleaning of works of art from polymer contaminants. *Soft Matter* 10, 6798–6809. <https://doi.org/10.1039/C4SM01084A>.
- Balzano, A., Merela, M., Čufar, K., 2022. Scanning electron microscopy protocol for studying anatomy of highly degraded waterlogged archaeological wood. *Forests* 13, 161. <https://doi.org/10.3390/f13020161>.
- Barclay, R., Mathias, C., 1989. AN epoxy/microballoon mixture for gap filling in wooden objects [WWW Document]. URL. <https://cool.culturalheritage.org/jaic/articles/jaic28-01-003.html>.
- Baufleur, A.M.Y., Stangerlin, D.M., Vasconcelos, L.G. de, Pariz, E., Junior, F.R., Paula, E. A. de O., Melo, R.R. de, 2023. Effect of acetylation on Technological characteristics of Jacaranda copaia wood: part 2 – chemical and colorimetric changes. *Nativa* 10, 283–289. <https://doi.org/10.31413/nativa.v10i2.13666>.
- Bonelli, N., Poggi, G., Chelazzi, D., Giorgi, R., Baglioni, P., 2019. Poly(vinyl alcohol)/poly(vinyl pyrrolidone) hydrogels for the cleaning of art. *J. Colloid Interface Sci.* 536, 339–348. <https://doi.org/10.1016/j.jcis.2018.10.025>.
- Bonfim, F. de S.B.C., Grangeiro Júnior, S., Oliveira, M.A.C. de, Lemos, R.D. de A., 2014. Comparative Study of DSC-Based Protocols for API-Polymer Solubility Determination.
- Brandt, J., Kanaki, E., Fischer, D., Herm, C., 2023. Evaluation of the composition, thermal and mechanical behavior, and color changes of artificially and naturally aged polymers for the conservation of stained glass windows. *Polymers* 15, 2595. <https://doi.org/10.3390/polym15122595>.
- Carretti, E., Dei, L., 2004. Physicochemical characterization of acrylic polymeric resins coating porous materials of artistic interest. *Prog. Org. Coating* 49, 282–289. <https://doi.org/10.1016/j.porgcoat.2003.10.011>.
- Chapman, S., Mason, D., 2003. Literature review: the use of paraloid B-72 as a surface consolidant for stained glass. *J. Am. Inst. Conserv.* 42, 381–392. <https://doi.org/10.2307/3180077>.
- Cortella, L., Albino, C., Tran, Q.-K., Froment, K., 2020. 50 years of French experience in using gamma rays as a tool for cultural heritage remedial conservation. *Radiat. Phys. Chem.* 171, 108726. <https://doi.org/10.1016/j.radphyschem.2020.108726>.
- Crisci, G.M., La Russa, M.F., Malagodi, M., Ruffolo, S.A., 2010. Consolidating properties of Regalrez 1126 and Paraloid B72 applied to wood. *J. Cult. Herit.* 11, 304–308. <https://doi.org/10.1016/j.culher.2009.12.001>.
- Daniel, G., 2016. Chapter 15 - microscope techniques for understanding wood cell structure and biodegradation. In: Kim, Y.S., Funada, R., Singh, A.P. (Eds.), *Secondary Xylem Biology*. Academic Press, Boston, pp. 309–343. <https://doi.org/10.1016/B978-0-12-802185-9.00015-2>.
- D'Orsi, B., Carcione, R., Di Sarcina, I., Ferrara, G., Oliviero, M., Rinaldi, T., Scifo, J., Verna, A., Cemmi, A., 2024. Gamma irradiation for Cultural Heritage conservation: comparison of the side effects on new and old paper. *J. Cult. Herit.* 70, 335–344. <https://doi.org/10.1016/j.culher.2024.10.009>.
- Juanes, D., Ferrazza, L., 2012. Computed tomography studies applied to polychromed sculpture: the making process in three different times. In: Ioannides, M., Fritsch, D., Leissner, J., Davies, R., Remondino, F., Caffo, R. (Eds.), *Progress in Cultural Heritage Preservation*. Springer, Berlin, Heidelberg, pp. 884–893. https://doi.org/10.1007/978-3-642-34234-9_95.
- Koob, S., 1986. The use of paraloid B-72 as an adhesive: its application for archaeological ceramics and other materials. *Stud. Conserv.* 31, 7–14. <https://doi.org/10.1179/sic.1986.31.1.7>.
- Koob, S.P., 2021. The conservation of glass. In: Kanungo, A.K., Dussubieux, L. (Eds.), *Ancient Glass of South Asia: Archaeology, Ethnography and Global Connections*. Springer, Singapore, pp. 203–209. https://doi.org/10.1007/978-981-16-3656-1_7.
- Lazzari, M., Chiantore, O., 2000. Thermal ageing of paraloid acrylic protective polymers. *Polymer* 41, 6447–6455. [https://doi.org/10.1016/S0032-3861\(99\)00877-0](https://doi.org/10.1016/S0032-3861(99)00877-0).
- Magd, M.A.E., 2018. Influence of acrylic coatings and nanomaterials on the interfacial, physical, and mechanical properties of limestone-based monuments. Case Study of “Amenemhat II Temple.”

- Mansour, M.M.A., Salem, M.Z.M., 2015. Evaluation of wood treated with some natural extracts and Paraloid B-72 against the fungus *Trichoderma harzianum*: wood elemental composition, *in-vitro* and application evidence. *Int. Biodeterior. Biodegrad.* 100, 62–69. <https://doi.org/10.1016/j.ibiod.2015.02.009>.
- Moise, V., Stanculescu, I., Vasilca, S., Cutrubinis, M., Pincu, E., Oancea, P., Raducan, A., Meltzer, V., 2019. Consolidation of very degraded cultural heritage wood artefacts using radiation curing of polyester resins. *Radiat. Phys. Chem.* 156, 314–319. <https://doi.org/10.1016/j.radphyschem.2018.11.028>.
- Nagai, M.L.E., de Souza Santos, P., Otubo, L., Oliveira, M.J.A., Vasquez, P.A.S., 2021. Gamma and electron beam irradiation effects for conservation treatment of cellulose triacetate photographic and cinematographic films. *Radiat. Phys. Chem.* 182, 109395. <https://doi.org/10.1016/j.radphyschem.2021.109395>.
- Oliveira, M.J.A., Otubo, L., Pires, A., Fernando Brambilla, R., Cristina Carvalho, A., Santos, P.S., Oliveira Neto, A., Vasquez, P., 2022. Silver nanoparticles-based hydrogels synthesized by ionizing radiation for cleaning of tangible cultural heritage surfaces. *Radiat. Phys. Chem.* 199, 110345. <https://doi.org/10.1016/j.radphyschem.2022.110345>.
- Podany, J., Garland, K.M., Freeman, W.R., Rogers, J., 2001. Paraloid B-72 as a structural adhesive and as a barrier within structural adhesive bonds: evaluations of strength and reversibility. *J. Am. Inst. Conserv.* 40, 15–33. <https://doi.org/10.1179/019713601806113120>.
- Schawe, J.E.K., 1995. Principles for the interpretation of modulated temperature DSC measurements. Part 1. Glass transition. *Thermochim. Acta* 261, 183–194. [https://doi.org/10.1016/0040-6031\(95\)02315-S](https://doi.org/10.1016/0040-6031(95)02315-S).
- Sun, M., Wang, J., Zhang, H., Zhang, B., Fan, Z., Su, B., 2015. Measurement of the reversible rate of conservation materials for ancient murals. *J. Cult. Herit.* 16, 49–56. <https://doi.org/10.1016/j.culher.2014.01.010>.
- Thiessen, M., Abetz, V., 2021. Influence of the glass transition temperature and the density of crosslinking groups on the reversibility of diels-alder polymer networks. *Polymers* 13. <https://doi.org/10.3390/polym13081189>.
- Traoré, M., Kaal, J., Martínez Cortizas, A., 2016. Application of FTIR spectroscopy to the characterization of archeological wood. *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* 153, 63–70. <https://doi.org/10.1016/j.saa.2015.07.108>.
- Turkulin, H., Holzer, L., Richter, K., Sell, J., 2005. Application of the ESEM technique in wood research: Part I. Optimization of imaging parameters and working conditions. *Wood Fiber Sci.* 37, 552–564.
- Vasquez, P.A.S., 2017. The state of the art in radiation processing for cultural heritage in Brazil. Chapter 23. *Uses ioniz. Radiat. Tangible Cult. Herit. Conserv., IAEA Radiation Technology Series* 197–201.
- Vaz, M.F., Pires, J., Carvalho, A.P., 2008. Effect of the impregnation treatment with Paraloid B-72 on the properties of old Portuguese ceramic tiles. *J. Cult. Herit.* 9, 269–276. <https://doi.org/10.1016/j.culher.2008.01.003>.
- Vieira, A.C.D., Salvador, P.A.V., Oliveira, M.J.A. de, Silva, F.A. da, 2024. Preserving cultural heritage through radiation-curing resin consolidation: a case study of an indigenous ceramic vessel. *Braz. J. Radiat. Sci.* 12, e2560–e2561. <https://doi.org/10.15392/2319-0612.2024.2560>.
- Vinçotte, A., Beauvoit, E., Boyard, N., Guilminot, E., 2019. Effect of solvent on PARALOID® B72 and B44 acrylic resins used as adhesives in conservation. *Herit. Sci.* 7, 1–9. <https://doi.org/10.1186/s40494-019-0283-9>.
- Vujčić, I., Masić, S., Obradović, N., Dramićanin, M.D., 2020. Preparation of beechwood/polymer composites using the method of lyophilization and gamma irradiation. *Radiat. Phys. Chem.* 166, 108505. <https://doi.org/10.1016/j.radphyschem.2019.108505>.
- Wei, Q., Leblon, B., La Rocque, A., 2011. On the use of X-ray computed tomography for determining wood properties: a review. This article is a contribution to the series the Role of Sensors in the New Forest Products Industry and Bioeconomy. *Can. J. For. Res.* 41, 2120–2140. <https://doi.org/10.1139/x11-111>.
- Zhao, X., Li, X., Zhang, S., Niu, Q., Li, Z., Xue, C., 2024. Investigation of whitening mechanism on cultural relic surfaces treated with paraloid B72. *Coatings* 14, 1240. <https://doi.org/10.3390/coatings14101240>.