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BRAZILIAN JOURNAL OF RADIATION SCIENCES

doi.org/10.15392/2319-0612.2024.2644
2024, 12(4A) | 01-11 | e2644
Submitted: 2024-08-27
Accepted: 2024-11-25

Paraloid Resins with Polymeric Monomers Cured by Gamma Radiation for Consolidation of Porous Wood

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Abstract: Preservation consists of an action that aims to guarantee the integrity and perpetuity of something, such as a cultural asset. One of the preservation instruments is restoration, an intervention that aims to definitively secure a product of human activity. Cultural heritage presents an extensive diversity of wooden objects, which can be affected by insect attacks, causing severe damage to their structures. To recover this damage, compatible materials are needed to maintain their integrity. Therefore, we propose to study the obtaining of polymeric resins cured by gamma radiation without the use of catalysts for consolidation or restoration of wooden objects. A series of formulations were developed with polymeric resins based on paraloid B72 and polymeric monomers cured by gamma radiation from a cobalt-60 source. These resins were characterized by physicochemical analyses, and the results presented were surprising in terms of reversibility. Gamma radiation replaced the catalyst, curing the resin 100%, indicating new resin options for restoration and/or consolidation in porous wood.

Keywords: resins, paraloid B72, gamma radiation, cultural heritage

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Resinas Paraloides com Monômeros Poliméricos Curadas por Radiação Gama para Consolidação de Madeira Porosa

Resumo: A preservação consiste em uma ação que visa garantir a integridade e a perpetuidade de algo, como um bem cultural. Um dos instrumentos de preservação é o restauro, intervenção que visa assegurar definitivamente um produto da atividade humana. O patrimônio cultural apresenta uma extensa diversidade de objetos de madeira, que podem ser afetados por ataques de insetos, causando graves danos às suas estruturas. Para recuperar esses danos, são necessários materiais compatíveis para manter sua integridade. Portanto, propomos estudar a obtenção de resinas poliméricas curadas por radiação gama, sem uso de catalisador para consolidação/restauro de objetos de madeira. Uma série de formulações foram desenvolvidas com resinas poliméricas à base de paraloide B72 e monômeros poliméricos curados por radiação gama de fonte de cobalto-60. Estas resinas foram caracterizadas por análises físico-químicas e os resultados apresentados foram surpreendentes em termos de reversibilidade. A radiação gama substituiu o catalisador, curando 100% a resina indicando novas opções de resina para restauração e/ou consolidação em madeira porosa.

Palavras-chave: resina, paraloid B72, radiação gama, patrimônio cultural

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1. INTRODUCTION

Wooden artifacts, such as sculptures and ethnographic items, often suffer damage from borers, termites, and fungi that attack wood. They are treated with a wide range of materials [1-2]. These materials can be classified into several categories, including natural polymers and water-soluble glues, acrylic resins dissolved in different organic solvents, waxes, oils, and chemically cured synthetic resins. However, most of these materials have several disadvantages that must be considered in their application. When employing polymer solutions, whether synthetic or natural, a significant amount of solvent is added to reduce viscosity. This implies that only 10 to 20% of the liquid used in impregnation actually contributes to the consolidation of the wood since the solvent evaporates quickly. As a result, the process must be repeated several times to ensure an adequate amount of resin is introduced. Furthermore, this technique not only presents risks of fire and environmental contamination but also poses dangers to the health of the restorer [3-4-5]. A consolidation the thermosetting resins using ionizing radiation without using a catalyst can be a viable alternative for recovering works of art that are compromised by their structure weakened by insect attacks [6-9]. Gamma irradiation processing has been used for several decades as a biocidal effect in the disinfection of cultural heritage artifacts and in the consolidation process, being advantageous in both cases [1-10-11-12]. On the other hand, acrylic resins have stood out as one of the preferred materials in conservation and restoration, being widely adopted by restorers. These resins, known as paraloid, are used for coating and consolidation due to their stability, transparency, mechanical resistance and reversibility [13[. They are suitable for a wide range of materials, including metals, stone, wood, glass and ceramics. However, research indicates that paraloid may have low temperature resistance in some applications. The most common paraloid resin is B72, whose formulation varies according to the desired purpose, be it protection, consolidation or adhesion. For its preparation,

solvents such as acetone, ethanol, toluene, xylene or ethyl acetate can be used, in addition to allowing optimization with polymeric monomers, such as ethyl methacrylate (EMA) and methyl acrylate (MA), among others [14[. To reduce the volume of solvents and improve the thermal stability performance of Paraloid B72 resin, used to consolidate wood affected by insects or deteriorated by aging [6-15-16-17]. This project proposes curing paraloid resin with polymeric monomers via ionizing radiation. These resins are reversible, offering a viable alternative for internal or external impregnation on wooden artifacts [18-19].

2. MATERIALS AND METHODS

The reagents used in the formulations of this search were: paraloid B 72 resin, monomers: methyl methacrylate (MMA) and butyl methacrylate (MaBu), acetone, polyethylene glycol 6000 (PEG 6000), polyester, styrene. Several formulations were prepared with the commercial B72 paraloid resin with adding monomers, (MaBu), (MMA). The concentration was varied between the resin and monomers, or acetone resin or (PEG 6000), and polyethylene glycol 2000 (PEG 2000).

The formulations prepared were, PEG 6000 + water, PEG 6000 + PEG 2000, paraloid B72 + acetone + PEG 2000, paraloid B72 + acetone, paraloid + styrene, paraloid B72 + MMA + polyester, paraloid B72 + MaBu + MMA, paraloid B72 + MaBu, MMA + MaBu, MaBu. The formulations with paraloid were placed in containers, homogenized and left to rest for 72 hours to complete solubilization. After this period, they were homogenized again to eliminate bubbles and then the packaging was sealed. After this procedure, they were placed in the Cobalt-60 Multipurpose Irradiator of the Institute for Energy and Nuclear Research (IPEN) and exposed to gamma radiation, with a dose of 50 kGy and a dose rate of 1 kGy/h. After curing, physical chemical characterizations were carried out, including Gel Fraction and Thermogravimetry (TGA), Spectroscopy (FTIR), Raman Spectroscopy.

3. RESULTS AND DISCUSSIONS

The purpose of this research was to use industrial polymers, resins and polymer monomers to obtain new formulations of crosslinked resins (cured) by ionizing radiation without the use of a catalyst. The proposed formulations with PEG 6000, PEG 2000, no crosslinking occurred and the paraloid formulations with acetone only formed a viscous gel. However, paraloid with polyester and paraloid with styrene crosslinked to form two phases, with different colors in the same sample.

Formulations containing paraloid with MaBu, paraloid with MaBu and MMA, MaBu with MMA, and MaBu alone demonstrated 100% crosslinking after being irradiated with gamma rays, without the need for a catalyst. Detailed descriptions of these formulations are presented in table 1.

Table 1: Presents the results of the study realize out with the formulations proposed in this research for reversible resins.

Formulation	Negative result	Positive result
PEG 6000 + Aqueous solution	X	
PEG 6000 + PEG 2000	X	
Paraloid B72 + acetone + PEG 2000	X	
Paraloid B72 + acetone	X	
Paraloid B72 + acetone	X	
Paraloid + styrene	X	
Paraloid B72 + MMA + polyester	X	
Paraloid B72 + MaBu + MMA		X
Paraloid B72 + MaBu		X
MMA + MaBu		X
MaBu		X

After irradiation at a dose of 50 kGy, the crosslinked samples were subjected to a Soxhlet extractor using xylene as solvent, to obtain the insoluble gel fraction. As seen in table 2, after 12 hours of extraction, the paraloid resin with MaBu was completely reversible. Thus,

while radiation promoted the crosslinking (curing) of these resins, we found that this process is reversible, which is extremely relevant for applications in consolidation and restoration.

Table 2: Gel fraction in percentage of resins after irradiation at a dose of 50 kGy and extraction carried out with xylene for 12h.

Samples	Gel fraction %
MaBu + paraloid	0.5
MaBu + paraloid + MMA	10.3
MMA + MaBu	7.2
MaBu	1.2

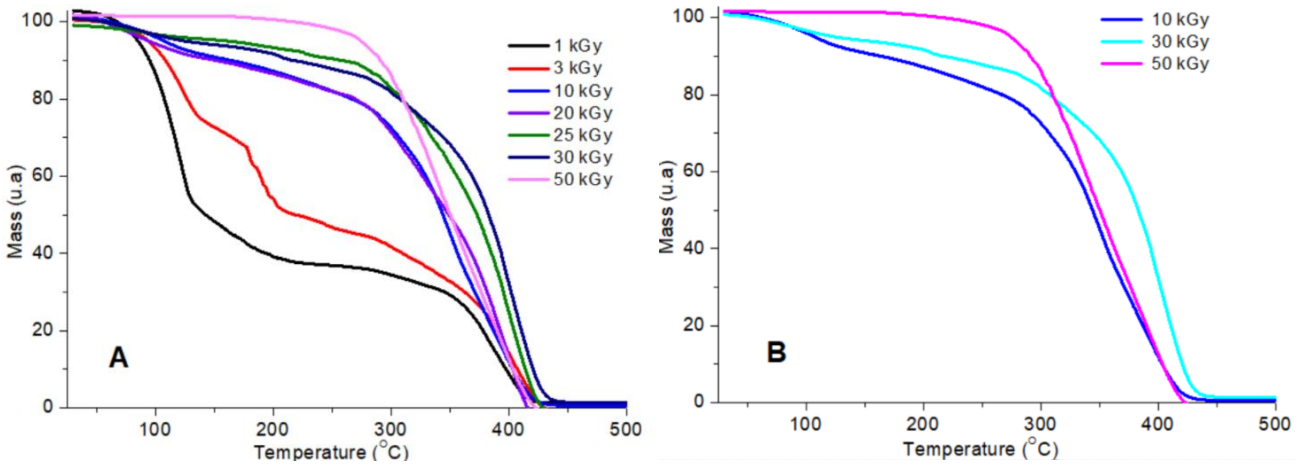
Thermogravimetric analysis (TGA) was used to monitor the mass variation of the cured resin as a function of the dose of ionizing irradiation, expressed in kGy, and temperature, in a controlled environment with a nitrogen atmosphere. Heating occurred at a rate of 10 ºC per minute, until an equilibrium temperature of 20 ºC was reached, with a nitrogen flow of 100 mL per minute. The maximum temperature reached during the analysis was 500 ºC. Samples subjected to irradiation doses of 1, 3, 10, 20, 25, 30 and 50 kGy were evaluated, with the aim of determining thermal stability depending on the ionizing radiation.

In figure 1A, it is observed that the samples subjected to doses of 1 kGy and 3 kGy present variations in mass loss between temperatures of 110 to 380 ºC. These events are associated with the volatilization of solvents and the possible degradation of small molecules.

Radiation doses of 10 kGy and 20 kGy show a similar mass loss, with initial disintegration occurring around 110 ºC and continuing gradually up to 280 ºC. On the other hand, doses of 25 kGy and 30 kGy also show similar behavior, with initial mass loss at 110 ºC, followed by additional disintegrations at approximately 220 ºC, 300 ºC and 380 ºC, respectively. As shown in Figure 1B, the sample irradiated at 50 kGy presents a single mass loss at 300 ºC, demonstrating significant thermal stability compared to the other doses. This indicates that despite being a reversible curing resin (as shown in table 2), it exhibits relevant thermal stability. However, studies carried out by Vinçotte et al 2019 show that films

obtained with paraloid using traditional methods with catalyst or chemical methods degrade at a temperature of 200 ºC [14]. This characteristic makes it a viable alternative to solve problems associated with paraloid B72 resins cured by chemical processes, which tend to soften in environments with temperatures above 32ºC [20].

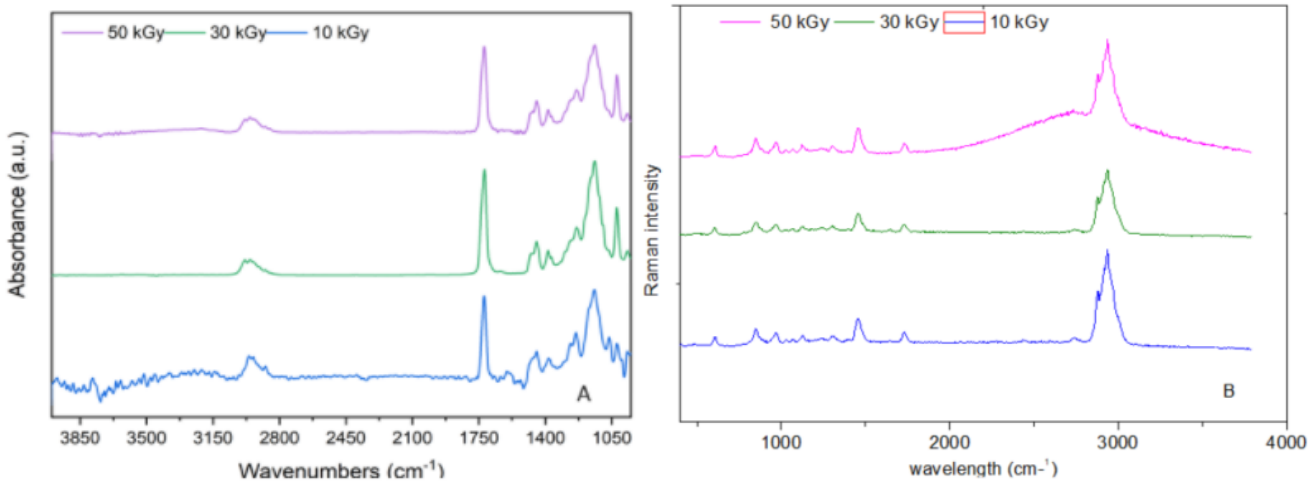
Figure 1 - Thermogravimetry (TGA) curves (A and B) of paraloid+MaBu resin samples cured by ionizing radiation



Thus, it is expected that the study and knowledge of the spectral properties of mixtures containing paraloid such as MaBu forming a resin cured by ionizing radiation will provide useful and vital process parameters maintaining scientific and industrial interest including consolidation of wooden objects. In figure 2A, the infrared spectra of paraloid B72 with the MaBu monomer, present the characteristic bands in the regions of 2900 cm^{-1} C-H stretching, 1750 cm^{-1} carbonyl C=O stretching, 1300 cm^{-1} to 1450 cm^{-1} is associated with C-H, 1200 cm^{-1} C-O and 1149 cm^{-1} C=C-O. These bands are characteristic of paraloid B72[13]. The carbonyl of MaBu is located in the region of 1740-1700 cm^{-1}, it is noted that there was a slight shift in this band, overlapping with the paraloid carbonyl [21-22]. Therefore, similar behavior is observed for the three FTIR spectra, and that the doses of gamma radiation submitted at 10, 30 and 50 kGy, in addition to promoting the curing of the new resin without catalyst, did not cause significant changes in the molecular behavior of the paraloid. Figure 2B shows the

Raman spectra, using WITEC, confocal raman microscope Alpha300 R, green laser, 532 nm; maximum power 45 mW, objective: 50x/0.7. In order to compare with the FTIR result, however, it is noted that there were no changes, the bands present the same behavior for the three irradiation doses submitted.

Figure 2 – FTIR spectrum (A) and raman spectrum (B) of paraloid resin with MaBu cured by ionizing radiation



4. CONCLUSIONS

Through gel fraction analysis, it was concluded that the formulations paraloid with MaBu, paraloid with MaBu and MMA, MaBu with MMA and MaBu cured by ionizing radiation presented 100% crosslinking, without the need for catalyst. In contrast, the paraloid resin with MaBu was characterized by TGA analysis, showing thermal stability from the dose of 10 kGy. The characterization by FTIR and raman indicate that the values of the doses of 10, 30 and 50 kGy maintain the same molecular structure of the resin obtained. The results presented confirm the curing of the formulations forming new resins and the reversibility, indicating new resin options for restoration and/or consolidation in porous wood. both cases.

ACKNOWLEDGMENT

The project: 2020.06. IPEN.02 and International Atomic Energy Agency (IAEA).

FUNDING

Postdoctoral scholarship Intercenter project 2020.06.IPEN.02.PD

CONFLICT OF 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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