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Polymeric membranes grafted by ionizing radiation for uranium adsorption

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Abstract: Fuel elements production by IPEN-CNEN has a perspective to be increased to attend Brazilian Multipurpose Reactor, under construction. This production generates liquid waste that requires proper treatment to minimize environmental impacts, promoting more sustainable practices. Considering the rise on nuclear power energy generation, and that there is global lack of terrestrial uranium sources, the increasing demand for this element has been leading to uranium exploit alternatives. So, several researches are available on uranium adsorption from sea water. Adsorption is one of process for removing metals from wastewater, due to its high selectivity and low environmental impact. Taking into account this scenary, in this study, Winged Polypropylene (WPP) fabric was grafted via ionizing radiation (RIG) with the monomer Bis[2-(methacryloyloxy) ethyl] phosphate (B2MP). RIG promotes functionalization of WPP with phosphate groups that are prone to capture U from solution. Synthesized WPP-*g*-polyB2MP membranes were characterized by Scanning electron microscopy (SEM), Raman spectroscopy, thermogravimetry and, uranium adsorption capacity by ICP-OES and gamma spectrometry. WPP-*g*-polyB2MP membranes were successfully synthesized by ionizing radiation grafting direct method. Reaction parameters, like reactants concentration, radiation absorbed dose, affected the degree of grafting (DoG). By physico-chemical characterization results it was possible to observe DoG differences with parameters variation. Optimization of these parameters was sought in order to achieve uranium adsorption, and to increase the adsorption capacity of the membrane.

Keywords: Uranium adsorption, ionizing radiation grafting, fuel element production.

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Membranas poliméricas enxertadas por radiação ionizante para adsorção de urânio

Resumo: A produção de elementos combustíveis pelo IPEN-CNEN tem perspectiva de aumento para atender ao Reator Multipropósito Brasileiro, em construção. Essa produção gera resíduos líquidos que requerem tratamento adequado para minimizar os impactos ambientais, promovendo práticas mais sustentáveis. Considerando o aumento da geração de energia nuclear e a escassez de fontes terrestres de urânio no mundo, a crescente demanda por esse elemento tem incentivado a busca por alternativas de exploração de urânio. Assim, várias pesquisas estão disponíveis sobre a adsorção de urânio da água do mar. A adsorção é um dos processos para remoção de metais de águas residuais, devido à sua alta seletividade e baixo impacto ambiental. Levando em consideração esse cenário, neste estudo, o tecido de Winged polipropileno (WPP) foi enxertado via radiação ionizante (RIG) com o monômero Bis[2-(metacriloiloxi) etil] fosfato (B2MP). A RIG promove a funcionalização do WPP com grupos fosfato que são propensos a capturar urânio da solução. As membranas WPP-g-polyB2MP sintetizadas foram caracterizadas por microscopia eletrônica de varredura (MEV), espectroscopia Raman, termogravimetria e a capacidade de adsorção de urânio foi determinada por ICP-OES e espectrometria gama. As membranas WPP-g-polyB2MP foram sintetizadas com sucesso pelo método direto de enxertia via radiação ionizante. Por meio dos resultados de caracterização físico-química, foi possível observar que as variações dos parâmetros de reação, como a concentração de reagentes e a dose de radiação absorvida, afetaram o grau de enxertia (DoG). A otimização desses parâmetros foi buscada para atingir a adsorção de urânio e aumentar a capacidade de adsorção das membranas.

Palavras-chave: Adsorção de urânio, enxertia por radiação ionizante, produção de elemento combustivel.

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1. INTRODUCTION

The Brazilian Multipurpose Reactor (RMB) is under construction to meet the growing demand for radiopharmaceuticals production. With greater power and operational capacity than IPEN's IEA-R1 Research Reactor, the RMB aims to enable national production of the Mo-99 radioisotope, reducing dependence on imported radionuclides for Tc-99m generating kits and seek for Brazil's autonomy [1]. Nuclear fuel for materials testing research reactor (MTR) has been produced by Nuclear Fuel Center (CECON) of IPEN. During fuel element production, solid and liquid waste is generated that requires treatment before disposal to meet permissible levels for conventional disposal [2]. Radioactive waste management in Brazil is overseen by the National Commission for Nuclear Energy (CNEN) through five stages: waste classification and characterization, temporary storage, treatment to reduce volume, concentration, or toxicity, and final disposal in protected repositories. Legislation outlines guidelines for site selection, construction, licensing, operation, inspection, custody, civil liability, and guarantees [3]–[5]. Effluent treatment can be performed by different methods, such as precipitation, ion exchange, biosorption and adsorption by polymeric membranes [6].

In recent years, land-based uranium mining has faced political, logistical, and environmental challenges globally. A 45% increase in nuclear power generation is projected within 15 years, potentially consuming up to 20% of terrestrial uranium reserves by 2035 [7]. So, several countries have been exploited uranium removal from sea water, it is still a critical challenge, and conventional methods such as ion exchange, membranes, solvent extraction, electrochemical processes, adsorption, chemical precipitation, flotation, and coagulation offer various advantages and limitations. Ion exchange is effective but presents high costs

and operational challenges. Chemical precipitation is simple and inexpensive but generates a lot of sludge and is ineffective at low concentrations. Adsorption stands out for its high removal efficiency (99%), even though being an effective process for removing metals from wastewater, it is costly and difficult to reproduce [8].

Among the methods to enhance adsorption, Radiation Induced Grafting (RIG) is notable for incorporating functional monomers into base polymers using high-energy radiation, such as gamma rays from Cobalt-60 or electron beams as chemical reaction initiators. Studies have shown promising results in removing uranium and vanadium from seawater with polymeric membranes synthesized via RIG [9], [10]. By using the same grafting parameters and adsorption applied to membranes synthesis for U adsorption from seawater; in this study it was adapted for uranium adsorption from liquid effluents of nuclear fuel production process at IPEN.

RIG can be performed using indirect or direct methods. In the indirect approach, the base polymer film is first irradiated without monomer or solvents, and the free radicals generated react afterwards by heating in contact with non-irradiated monomer chains, resulting in copolymerization. The direct method involves simultaneous irradiation of the monomer, base polymer, and solvent. In this study, Winged polypropylene fabric (WPP) and the monomer Bis[2-(methacryloyloxy)ethyl] phosphate (B2MP) were grafted using the direct method by electron beam irradiation at IPEN to create membranes for uranium adsorption from liquid effluents from the nuclear fuel production process at IPEN [11]. WPP fabric from Allasso Industries was chosen due to its high specific surface area of about 140,000 cm^2/g, enhancing grafting efficiency and increasing uranium extraction capacity [12]. The B2MP monomer, a hydrophilic compound with a bifunctional structure comprising two methacrylate groups and one phosphate group, improves the polymer's properties and broadens its applications [13], [14]. The synthesized WPP-*g*-polyB2MP membranes were characterized using Raman spectroscopy, scanning electron microscopy

(SEM), and thermogravimetry. Adsorption capacity was assessed using gamma ray spectrometry with a high-purity germanium detector (HPGe) and inductively coupled plasma optical emission spectrometry (ICP-OES).

2. MATERIALS AND METHODS

2.1. Materials and equipment

The materials used included winged polypropylene (WPP) fabric, manufactured by Alasso Industries and kindly provided by the University of Maryland; Bis[2-(methacryloyloxy) ethyl] phosphate and polyoxyethylene sorbitan monolaurate (Tween 20) from Sigma-Aldrich; ammonium and iron (II) sulfate (Mohr's salt) from Carlo Erba. Ultrapure water from Ultra Water Purifier from Gehaka, ethanol P.A., Sciavicco and, acetone P.A from Alphatec. Drying was performed in a Marconi MA 030/12 vacuum oven. Ohaus Pioneer balance, with a range of 0.001 g to 220 g, and a Shimadzu 224 model, with a range of 10 mg to 220 g. Ultrasonic cleaning was performed using an Elmasonic, 60H model device.

2.2. Sample preparation and grafting

WPP sample was cut with a surgical scalpel, weighed on an analytical balance, then the films placed in ziplock bags, identified with WPP, date and radiation absorbed dose (kGy). The grafting solution was prepared with B2MP, Tween 20 (2%), water, ethanol and Mohr's salt. The Mohr's salt was weighed on an analytical balance and dissolved in water before adding the B2MP. The B2MP monomer is dissolved in ethanol and added to the previous solution. The concentrations of each substance were adjusted to reduce gel formation in the membrane. Purging is performed with argon or nitrogen for about 20 minutes. The samples were irradiated with an electron beam using the Dynamitron Electron Accelerator (IPEN-CNEN) with an energy of 0.809 MeV and a beam current of 0.7 mA, with a dose rate of 4.02 kGy/s. The absorbed radiation doses were 50, 70, and 100 kGy. The samples were cleaned

with ultrapure water and ethanol, using ultrasound for thorough cleaning. Drying was done in an oven at 50°C for at least 2 hours to ensure the membranes are dry enough for weighing stabilization for the real degree of grafting (DoG) measurement. DoG is a quantitative weight measure of the proportion of grafted groups relative to the base polymer (Equation 1). Determining the degree of grafting is essential to verify if the grafting occurred satisfactorily.

$$DoG\ (\%) = \frac{M_F - M_I}{M_I} \times 100 \quad (1)$$

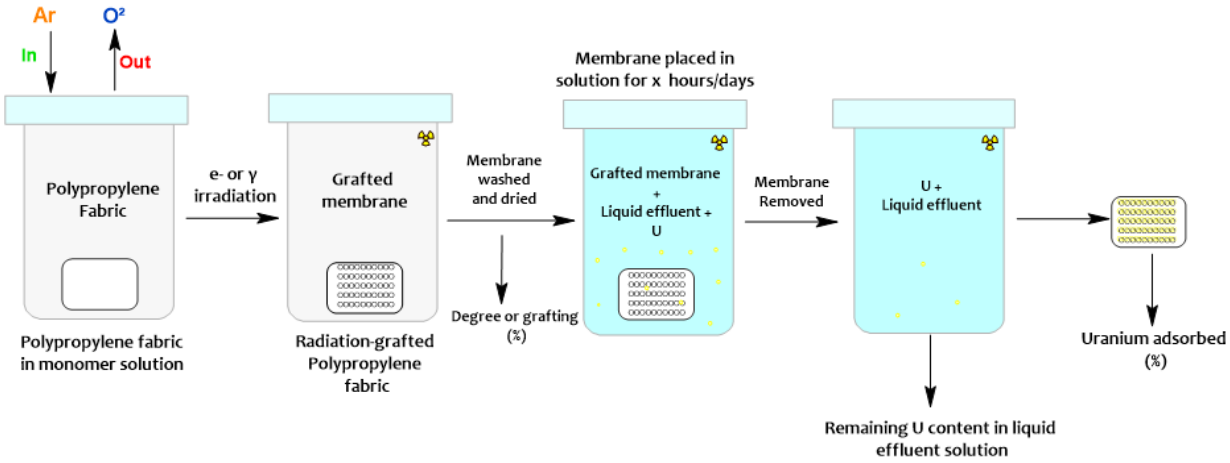
Where: M_F:Final mass M_I:Initial mass

2.3. Uranium adsorption

The liquid effluent from nuclear fuel production containing uranium tetrafluoride was provided by CECON. The initial pH of the sample, determined using pH strips in the range of 0 to 14 (Merck), was extremely acidic (0), resulting in the disintegration of the synthesized membranes in contact with the effluent. So, in order to adjust the pH, 1mol/L KOH was used, with a purity of 85%, raising the pH of the sample to 6.0.

Synthesized membranes were prepared for adsorption tests by placing each membrane in labeled vials. Each membrane was immersed in 20 mL of pH corrected liquid effluent for 7 days. After immersion, membranes were removed, washed with acetone and dried in an oven. The remained solution after membrane removal and dried membranes were analyzed using a germanium detector, while the solution was subjected to analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). Figure 1 illustrates the entire process, from preparation through uranium adsorption and its subsequent determination.

Figure 1: Membrane preparation scheme and adsorption process



Source: Author, 2024.

2.4. Characterization of grafted membranes

Scanning Electron Microscopy (SEM): Provides high-resolution analysis, essential for examining structures such as polymeric membranes and revealing details like the growth of grafted monomer chains on fibers [15]. The samples were coated and images of the non-grafted and grafted membranes were obtained using a Thermo Scientific Prisma E.

Raman spectroscopy: Raman spectroscopy identifies chemical compounds and their structures by analyzing the inelastic scattering of light in a sample. The energy shift in the reflected light provides information about chemical bonds and molecular structure [16]. It was used to observe the Raman bands of pristine fabric and to analyze changes in the Winged Polypropylene fibers after grafting with B2MP. Raman spectra were obtained using a Horiba JobinYvon spectrometer, model SyncerityTM CCD Detector with a resolution of 4 cm^{-1}, and LabSpec6 software from IPEN.

Thermogravimetric Analysis (TGA): Monitors the mass variation of a sample as a function of temperature or time in a controlled environment, using a thermobalance that continuously weighs the sample during heating. The experiments produce curves that provide information on thermal stability and decomposition behavior, evaluating weight

changes (m) as a function (f) of temperature (T) and/or time (t)[17]. For the analysis, it was cut 1 cm^2 of each sample (grafted and without grafting).

2.5. Determination of uranium adsorption capacity

Analytical technique for radionuclide determination by gamma spectrometry: Performed using HPGe (high-purity germanium) detectors that employs highly purified germanium crystals to detect ionizing radiation with high efficiency. The HPGe operates based on the germanium's ability to generate electron-hole pairs when struck by radiation, which produces an electrical signal proportional to the energy of the incoming radiation. This signal is then amplified and analyzed to determine the energy and intensity of the incident radiation. Due to its high sensitivity and energy resolution, HPGe is widely used in gamma spectrometry for both quantitative and qualitative analyses of radioactive samples [18].

The WPP-*g*-polyB2MP membranes prepared in this study were placed in quartz vials containing 20 mL of aqueous effluent solution (pH adjusted to 6) and were kept for 7 days. The uranium adsorption by the membrane was determined by analyzing the resulting solution (after removing the membrane) using a high-purity germanium detector, Ortec brand, model DSEPEC, with Maestro software. the chosen measurement (counting) time was 1200s and the energy of the U-235 photopeak considered was 185 keV.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES): Is an analytical technique used to identify and quantify chemical elements in various samples. It uses argon plasma to excite atoms, allowing for the measurement of the radiation emitted as these atoms return to their ground state. ICP-OES is widely applied in the analysis of metals, metalloids, rare earth elements, and environmental samples to detect metals. For the ICP-OES analysis in this study, the liquid effluent was examined after the removal of the adsorption membranes synthesized in this work.

3. RESULTS AND DISCUSSIONS

3.1. Degree of grating (DoG)

Preliminar RIG tests were conducted with a solution containing 632 mg of ammonium iron (II) sulfate (Mohr's salt), 7.5 mL of B2MP, 2 mL of Tween 20, and 92.5 mL of H_2O, making up a total of 100 mL of solution. However, the grafting degree results were unsatisfactory (DoG < 5%). Previous study in the literature [19] has shown that B2MP has low solubility in water, and Tween 20 was used to increase its solubility. Nonetheless, using only water as a solvent result in an excess of homopolymers after RIG, while ethanol reduces the grafting degree [19]. Mohr's salt stabilizes free radicals during irradiation [20]. In this work, new tests were conducted by varying the concentration of the reagents in the solution to reduce the content of homopolymers during the grafting reaction. The main results are presented in Table 1 below:

Table 1: Variation of parameters for the RIG aiming to reduce the amount of homopolymers

Solution	Dose (kGy)	Mohr's Salt (mg)	B2MP (mL)	Tween 20 (mL)	EtOH (mL)	H_2O (mL)	DoG (%)	Observation
1	50	63.2	2.2	0.45	8.6	8.6	70	Reduced in homopolymers
2	70	126.4	3.0	0.40	8.3	8.3	263	High in homopolymers
3	100	63.2	3.0	0.40	8.3	8.3	97	Low in homopolymers

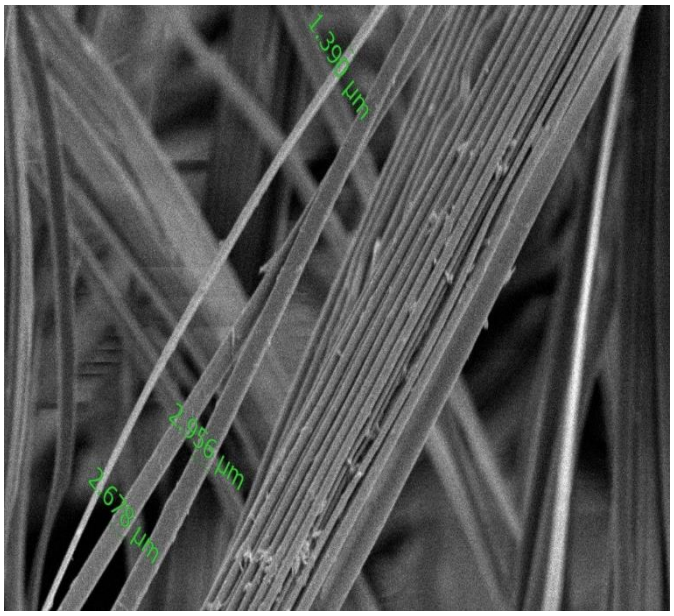
The first solution was irradiated at 50 kGy and resulted in a DoG 70% without significant homopolymer formation. However, WPP irradiated at 70 kGy resulted in a DoG of 263%, but with excessive homopolymer formation, leading to a rigid membrane. Irradiation of WPP at 100 kGy achieved a DoG of 97%, but showed significant gel formation on the membrane surface. Previous studies investigating uranium adsorption from seawater indicate that DoG above 100% ensure higher uranium extraction, with an ideal DoG of 120% [21].

Higher radiation doses lead to excessive homopolymer formation on the membrane surface, creating a gel layer that hinders adsorption by reducing membrane porosity [22].

3.2. Scanning electron microscopy (SEM)

The pristine WPP fabric had fine, loose fibers (1.390 μm to 2.956 μm in diameter) with a smooth surface and some lint, indicating uniformity (Figure 2).

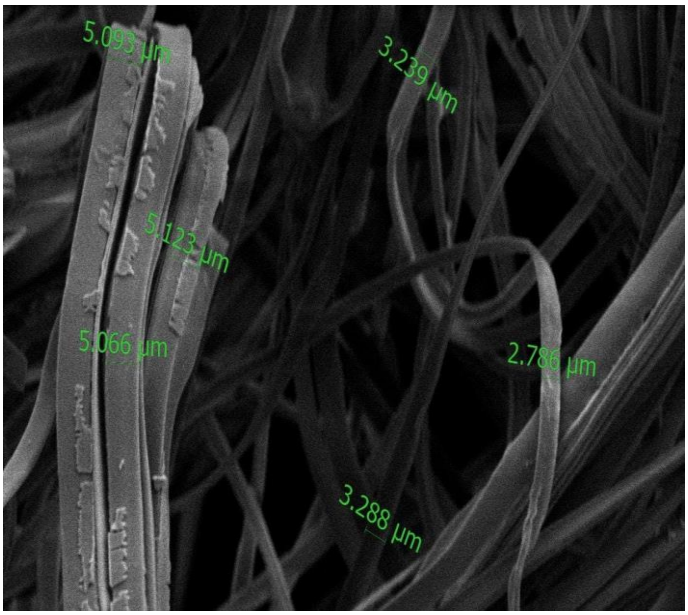
Figure 2: SEM Image of pristine WPP fabric fibers



Source: Authors, 2022

The **WPP-g-polyB2MP** with DoG of 97% presented partially loose fibers, with accumulation of homopolymer on the surface and thickness ranging from 2.786 μm to 5.123 μm, indicating changes in the polymer matrix (Figure 3).

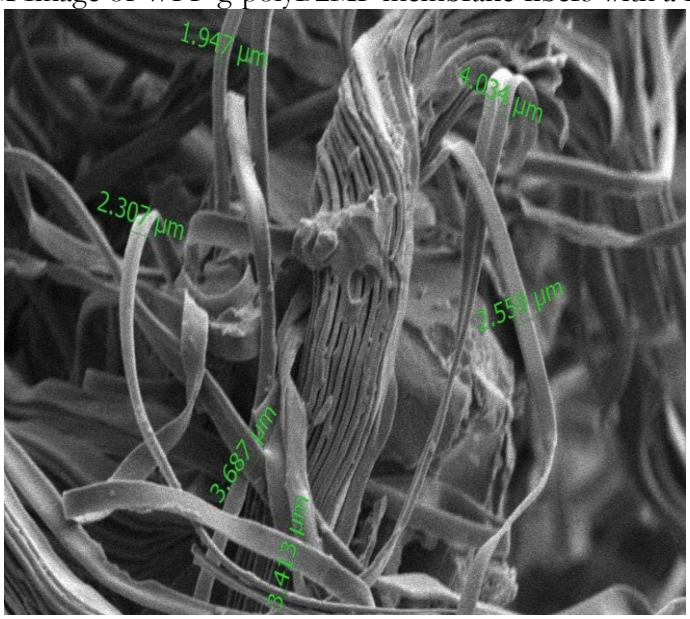
Figure 3: SEM Image of WPP-g-polyB2MP membrane fibers with a DoG of 97%



Source: Authors, 2022

Figure 4 shows a membrane with a DoG of 263% with fibers from 1.947 µm to 4.034 µm in diameter, highly fused and with extensive accumulation of homopolymer on the surface, highlighting significant structural changes in the polymer matrix.

Figure 1: SEM Image of WPP-g-polyB2MP membrane fibers with a DoG of 263%

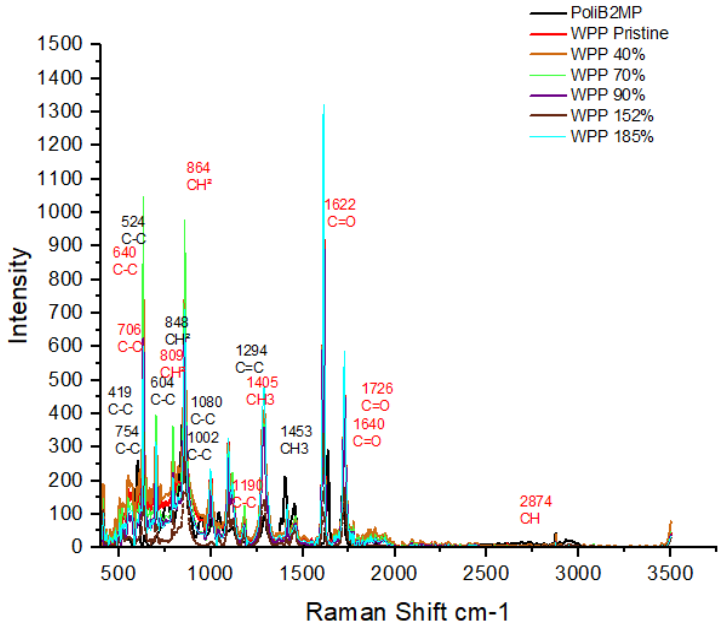


Source: Authors, 2022

3.3. Raman Spectroscopy

In Figure 5 it is possible to observe Raman spectra of pristine and grafted membranes with varying degrees of grafting. The attribution of the functional groups were obtained and compared with literature.

Figure 5: Raman spectrum PolyB2MP, Pristine WPP and WPP-*g*-polyB2MP.



Source: Author, 2024.

Gopanna *et al.*[23] and Furukawa *et al.*[24] identified vibrations between 810 and 842 cm^{-1} in the Raman spectrum of Polypropylene (PP), corresponding to molecules in the crystalline phase and helical molecules in the amorphous regions. In the spectrum of Winged Polypropylene (WPP), these vibration frequencies were observed at 848 cm^{-1} for stretching of C-C bonds, 998 cm^{-1} for rocking of CH_3 groups, and 1460 cm^{-1} for asymmetric deformation of CH_3 groups. Furthermore, vibration frequencies at 809 cm^{-1} (CH_2 swing), 864 cm^{-1} (C-C stretch) and 1190 cm^{-1} (C-C stretch) in the spectrum also support these structural features.

In the literature, Tissot *et al.*[22] established the following vibration frequencies in the Raman spectrum of the B2MP monomer: C=O stretching at 1724 cm^{-1}, ethylene

unsaturation at 1635 cm^{-1}, C=C stretching at 1294 cm^{-1}, C-C stretching at 1294 cm^{-1}, C-C stretch at 1002 cm^{-1} and 1080 cm^{-1}. In our data, we find these same vibration frequencies at 1002 cm^{-1} and 1080 cm^{-1} for C-C stretching, 1294 cm^{-1} for C=C stretching, 1640 cm^{-1} and 1726 cm^{-1} for C=O stretching in the B2MP spectrum. The B2MP grafting process introduces new functional groups into the WPP, resulting in additional peaks and changes in the intensities of existing peaks, such as the peaks at 1726 cm^{-1} and 1640 cm^{-1}, attributed to the C=O stretching of the ester. Furthermore, grafting changes the structure and composition of WPP, causing new peaks, such as 419 cm^{-1}, 524 cm^{-1}, and 604 cm^{-1}, to appear and change in intensity, indicating the presence of new C-C complex bonds. The intensity of the peaks can also be influenced by the relative concentration of the functional groups, with certain peaks increasing or decreasing as the percentage of grafting varies, such as the peaks at 864 cm^{-1} and 998 cm^{-1}, which increase in intensity at WPP 40% and 70 % due to the increase in C-C and CH_3 groups in relation to pristine WPP.

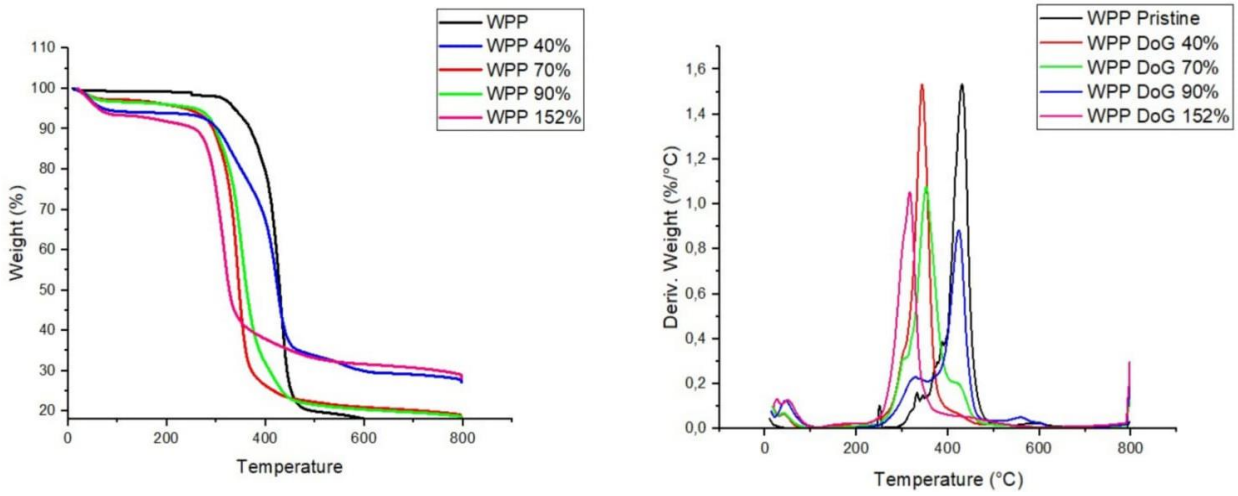
3.4. Thermogravimetry (TGA)

TGA was performed on WPP (pristine) and four samples with varying degrees of grafting, so that we could evaluate the changes in the thermal properties of the samples. In Figure 6 it is possible to observe the weight loss curves and the derivative of the weight loss of pristine WPP and WPP-*g*-polyB2MP with different DoG.

For a better understanding of the data, information on temperature, mass loss, residues and initial mass were added in Table 2:

The membranes grafted with B2MP began to degrade at lower temperatures than pristine WPP, indicating lower thermal stability. The WPP grafted at 152 %, in particular, exhibits a lower weight loss temperature (318.6 °C) and a lower initial degradation temperature (127.0 °C), likely due to the excess of polyB2MP, which may have introduced many functional groups and resulted in a less stable polymer structure.

Figure 6: TG/DTG curves of pristine WPP and WPP-*g*-polyB2MP (DoG 40, 70, 90 and 152 %)



Source: Author, 2024

Table 2: Temperatures of main events and weight loss of WPP without grafting and grafted with different DoG by TG/DTG

Sample	DoG (%)	Weight (mg)	Events	Temperature (°C)	Weight Loss (mg)	Weight Loss (%)
WPP-Pristine	0		Initial temp	220.3	-	
		11.74	1st peak	433.4	7.31	79.4
			Residue			20.6
WPP-g-polyB2MP	40		Initial temp	134. 2		
		11.95	1st peak	344.4	8.80	73.9
			Residue			26.1
WPP-g-polyB2MP	70		Initial temp	138.2		
		11.90	1st peak	352.3	8.70	73.1
			Residue			26.8
WPP-g-polyB2MP	90		Initial temp	142.3	-	-
		11.57	1st peak	422.6	7.46	64.4
			Residue			35.6
WPP-g-polyB2MP	152		Initial temp	127.0		
		13.58	1st peak	318.6	7.31	61.4
			Residue			38.6

This suggests that high concentrations of B2MP may compromise the material's thermal stability. In contrast, some grafted membranes, such as WPP-*g*-polyB2MP with DoG 90 %, have a higher weight loss temperature, reflecting in improved thermal resistance.

3.5. Uranium Adsorption

Analysis of uranium using ICP-OES

The analysis of uranium in aqueous solutions exposed to WPP-g-polyB2MP membranes was performed using ICP-OES, complemented by measurements with a high-purity germanium detector for comparison of the results. Initially, the stock solution of UF4 with pH correction was analyzed and showed a uranium concentration of 0.15 ± 0.02 mg/L. This value was used as a reference for comparing the adsorption efficiency of the WPP-g-polyB2MP membranes. The results are presented in Table 3.

Table 3: Uranium Concentration in Aqueous UF_4 Solution in Analysis Performed by ICP-OES

SAMPLE	DoG (%)	U CONCENTRATION (mg/L)
Stock Solution	-	0.15 ± 0.02
YK-1	254	<0.1
YK-2	263	<0.1
YK-3	74	<0.1
YK-4	97	<0.1

After adsorption by the membranes and their removal from the solution, the remaining solutions, identified as YK-1, YK-2, YK-3, and YK-4, showed uranium concentrations below 0.1 mg/L. These results indicated that the membranes synthesized in this work adsorbed uranium from the solution. Although the reduction in uranium concentration is indicative that the membranes promoted the reduction of uranium from the solutions, it is worth noting that the initial uranium concentration in the solution was already close to the detection limit of the technique.

Gamma emission peak analysis of uranium using the Gamma Spectrometry - HPGe detector:

The effectiveness of uranium adsorption by the membranes was evaluated by measuring the amount of uranium in the solution (20 mL) before and after contact with the membranes. The difference was used to estimate the percentage of uranium adsorbed and the amount of uranium adsorbed per weight of the membrane. These values were then compared by adsorption performance of the membranes, as shown in the Table 4:

Table 4: Uranium adsorption by different membranes, membrane weight and adsorption efficiency.

SAMPLE	Membrane weight (mg)	Volume (mL)	U (mg)	U adsorption (%)	U (µg of U/g de membrane)
Stock Solution	-	20	0.003	100	-
WPP DoG: 42%	175.8	-	-	61	10.40
WPP DoG: 70%	483.4	-	-	54	4.311
WPP DoG 90%	322.2	-	-	89	8.28
WPP DoG 124%	375.8	-	-	60	3.72

The efficiency of uranium adsorption on polypropylene membranes (WPP) increases with the degree of grafting up to a certain point. However, when the grafting degree is too high, the amount of uranium adsorbed per gram of membrane tends to decrease. The membrane with a 90% grafting degree showed the highest adsorption (89 %) but the lowest amount of uranium adsorbed per gram (8.285 µg /g). This pattern suggests that excessively high grafting levels may not proportionally improve adsorption capacity and may even reduce the total amount of uranium adsorbed. Therefore, finding a balance in the grafting degree is crucial to maximize adsorption effectiveness.

4. CONCLUSION

At this stage of study, we obtained polypropylene (WPP) membranes grafted with the monomer B2MP using ionizing radiation (RIG), demonstrating it is a viable alternative for uranium adsorption from aqueous effluents. The variation in the degree of grafting (DoG) affects the physical, chemical, and thermal properties of the membranes, influencing their uranium adsorption capacity.

Characterization by SEM and Raman spectroscopy revealed structural and chemical changes due to grafting, indicating successful integration of B2MP functional groups into polypropylene. TGA showed that DoG impacts the thermal stability and resistance of the membranes, reflecting the structural complexity of samples with higher DoG.

Adsorption tests using ICP-OES and HPGe confirmed the membranes' effectiveness in removing uranium, with the best performance observed in samples with around 90% DoG. Future research will focus on optimizing grafting conditions and evaluating the durability of the membranes under real-world conditions.

Results indicated that the uranium adsorption efficiency of B2MP-grafted WPP membranes (WPP-g-polyB2MP) was influenced by the grafting degree. Variations in grafting degree directly affected adsorption capacity, with a tendency for the amount of uranium adsorbed per gram of membrane to decrease at excessively high grafting degrees. Therefore, optimizing the grafting degree was crucial to achieve ideal uranium adsorption efficiency.

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CONFLICT OF INTEREST

All authors declare that they have no conflicts of interest to disclose.

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