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Radiation Induced Graft Polymerization (RIG) of B2MP onto Nylon Fabric for Uranium Adsorption

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1. Introduction

Minimization of waste generation and the practice of recycle and reuse can improve process economics and can minimize the potential environmental impact [1,2,3,4] in addition, increasing the public acceptance of nuclear technology. Brazil has a demand to increase the use of radiopharmaceuticals on medical diagnostics and therapies, being Mo 99 the most used radioisotope in nuclear medicine. It is currently acquired from the international market, manufactured at Nuclear and Energy research Institute (IPEN) and distributed in Brazil in ^{99m}Tc generator kits. In order to allow national production, Brazilian Multipurpose Reactor (RMB) under construction will operate at longer shifts and higher power (30MW), compared to the IEA-R1 research reactor of IPEN (currently at 4.5 MW). Nuclear Fuel fabrication by Nuclear Fuel Centre (CECON) at IPEN is scaling up of an order of 6 to assure the fuel supply for the RMB operation, resulting in more than 40 fuel elements per year. In this scenario, currently around 3000 L of liquid radioactive waste are generated annually by the production process of 8 nuclear fuel elements (NFE's). Waste minimization can be accomplished by source reduction, recycling and reuse and waste management optimization [1]. That have been partially attained by the development of new materials for uranium separation from liquid waste. For instance, polymeric membrane for adsorption, in which different means of grafting has been researched, that depends on reactants used for functionalization [5, 6,7,8,9,10,11. One of them is the synthesis of the adsorbent fabrics performed by radiation induced grafting (RIG) method, in which ionizing radiation acts as chemical reaction initiator to attach desirable functional groups onto a durable polymeric substrate. Compared to conventional grafting methods, RIG has the benefit of simple cost-effective, manageable reaction parameters along with tunable composition and distribution of grafted polymeric chains [12,13]. One method to obtain the grafting of the active monomer on the polymer is by indirect grafting, consisting of irradiating the polymer in the absence of oxygen, and then placing it in an oxygen-free B2MP solution. This occurs by addition of the radiolytically produced carbon centered radicals (Nylon●) to the double bonds of the B2MP to initiate the grafting [14]. However, the main disadvantage that the amount of free radicals on the polymer substrate initiates to instantly decay, with subsequent consumption and exclusion of potential grafting positions [15]. The other method is through direct where the polymer (ultra-high surface area Winged™ Nylon 6) is irradiated immersed in aqueous, oxygen-free B2MP solution [12,14] and, it was suggested that the best results have been obtained using direct grafting. In this sense we selected RIG through direct method and presented is this study. Radiation Induced Grafting (RIG) of several systems polymer-monomer and/or type of functionalization of produced grafted films or fibers for the capture of uranium mostly for its recovery from sea water can be found in the literature [14,15]. Considering those findings, best results were obtained using Bis[2-(methacryloyloxy) ethyl] phosphate (B2MP) [14]. Winged fibers provide higher surface areas to RIG monomer and consequently greater superficial area to the uranium extraction to occur, as it was reported in the literature to have an average specific surface area of ~140,000 cm^2/g [14,15]. In this study we synthesized membranes through RIG of B2MP onto winged nylon fabric by direct method. So, for this research, several systems and conditions for RIG polymeric membrane synthesis. Main application is to separate uranium from NFE waste aqueous solutions. Characterization of membranes have been performed through determination of gravimetric degree of grafting (DoG), Raman spectroscopy, thermal properties (DSC, TGA).

2. Methodology

All reactants were analytical grade. Bis[2-(methacryloyloxy) ethyl] phosphate (B2MP) Sigma Aldrich (CAS: 32435-46-4), $Fe(NH_4)_2(SO_4)_2.6H_2O$ (Mohr´s salt) Aldrich, Ethyl Alcohol Exodus and Ultrapure Water (UPW). Nylon 6 (Winged® Nylon was kindly supplied by Prof Mohamad Al-Sheikhly, produced by Allasso Industries). Solutions were prepared adapted according to already published in the literature [12,14]: Mohr´s salt dissolved in water (632 mg 100 mL^{-1}) to suppress possible gel formation [16]. 300 mM B2MP, ethyl alcohol:UPW, 50:50 (v:v), surfactant TWEEN 20 from Sigma-Aldrich. Adapted from the cited concentration, we variated by using 2X B2MP concentration, or 2X tween 20, or just UPW and monomer, either half Mohr´s salt. Fabric was cut into small pieces up to 2 X 3 cm^2 placed inside a vial, 4-20 mL (depending on the size of nylon fabric, being the same within replicates) of prepared solution and sealed. Argon as purge gas by 15 min. Sealed Vials with films and grafting solution were arranged inside sample chamber of a Gammacell 220 Irradiator from Atomic Energy of Canada Limited (AECL). Dose rate 376-351 Gy h^{-1}. Radiation absorbed doses from 15 kGy up to 100 kGy. Also, we performed gamma irradiation at Multipurpose Irradiator (IM, dose rate of 6 kGy h^{-1}) and electron beam irradiation using a Dynamitron Continuous Electron Beam Unit from RDI- Radiation Dynamics Inc. USA, model DC 1500/25/4 - JOB 188 with maximum energy of 1.5 MeV of IPEN/CNEN. The energy used in this study was 0.55 MeV, beam current of 5.74 mA, and dose rate of 39.97 kGy s^{-1}. Low temperature (~ -10 ◦C), was achieved by placing the films with grafting solution inside polyethylene plastic zip bags above a bed of dry ice during irradiation, with 50 and 100 kGy absorbed doses.
Gravimetric degree of grafting was calculated through weight differences considering initial, *Wi* (pristine fabric) and final grafted membrane, *Wg* according to Eq. 1:

$$DoG\ (\%) = \frac{W_g - W_i}{W_i} \times 100 \quad (1)$$

Thermogravimetric analysis (TGA) of samples (~5 mg in alumina pan) was conducted using TGDTA SDT Q 600 model, TA Instruments, with a heating rate of 10 °C min^{-1}, RT to 800 °C, N_2 100 mL min^{-1}. Differential Scanning Calorimetry (DSC) measurements were carried out at DSC 6000 Perkin Elmer, and samples of ~5 mg were put into aluminum pan and sealed. The measurements were performed at heating-cooling-heating of 30 – 300 °C, rate of 10 °C min^{-1} under N_2 flow (50 mL min^{-1}). The DSC data were estimated using first heating scan. Degree of crystallinity was calculated considering WN melting peak enthalpy for pristine and its fraction on grafted samples, compared to 100% crystalline melting enthalpy of nylon [17,18]. Raman spectra were recorded on a Horiba JobinYvon, model XploRA-PLUS spectrometer with a laser wavelength 785 nm, power of 85 mW, objective lens 50 x 0.50 N.A., HORIBA Instruments Incorporated/SyncerityTM CCD Detector and a resolution of 4 cm^{-1}, software LabSpec6.

3. Results and Discussion

The most important factor controlling the capacity of the adsorbent for uranium is the grafting density (DoG) of the monomer onto the polymer [14]. It was possible to observe the influence of absorbed dose of radiation, dose rate, type of radiation, chemical composition of grafting solution on the degree of grafting (DoG). Some difficulties found in this study were concerning cleaning membranes with high homopolymer formation besides grafting. Samples that presented very high DoG in the Fig. 1 (IM irradiated and double monomer concentration) could not be cleaned appropriately even after using various solvents and ultrasound. Similar high DoG were found in the literature [15] and attributed to B2MP be prone to easily suffer crosslinking and so, grafting. It is possible to observe of dose rate and monomer concentration influences on DoG. Even though it had been reported a scission predomination at higher dose rates, damaging the substrate [15], it was not possible to visually observe in this study on membranes irradiated with 10 fold gamma dose rates, neither with EB irradiated samples, in this case irradiated at dry ice temperature. DSC curves display melting peaks of nylon pristine at 220 ºC, WN (2X tween) at 193 ºC and WN (1/2 Mohr) at 212 ºC (Fig. 2). Assessment of polyamide-6 crystallinity by DSC and the melting enthalpy of WN were estimated according to literature [17,18]. Degree of crystallinity reduced slightly with increasing DoG above 50%. In Fig. 3 it possible to observe the presence of grafted B2MP onto WN because of two steps degradation instead of one observed in WN degradation. Presence of B2MP decreases thermal stability of WN by about 100ºC, ascribed to B2MP depolymerization. In Fig. 4 it is possible to observe Raman spectra of pristine WN, WN-*g*-B2MP with DoG of 257% and 48% and polyB2MP, and functional groups peaks attribution, respectively, according to the literature [19,20,21,22,23].

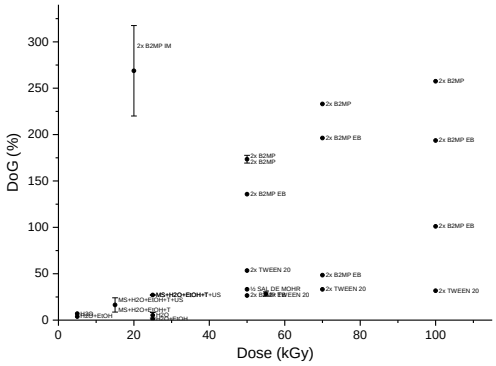

Figure 1: Influence of absorbed dose of radiation, chemical composition of grafting solution on DoG. * IM – Multipurpose Gamma Irradiator; EB -Electron Beam.

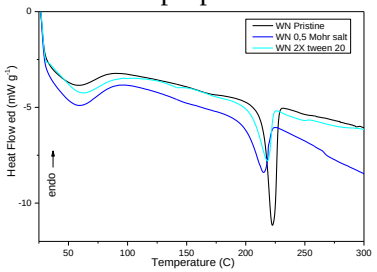

Figure 2: DSC curves of pristine WN (black), WN-*g*-B2MP with DoG of 33% (light green) and 49% (blue).

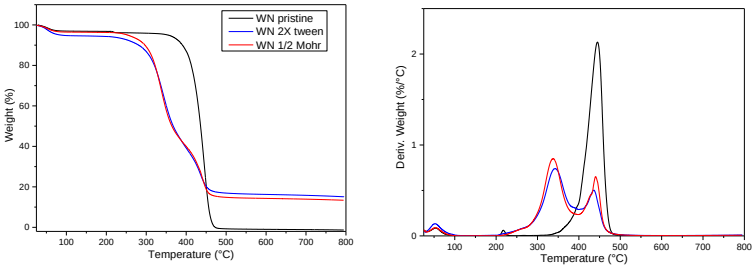

Figure 3: TG curves of pristine WN (black), WN-*g*-B2MP with DoG of 30% (red) and 48% (blue).

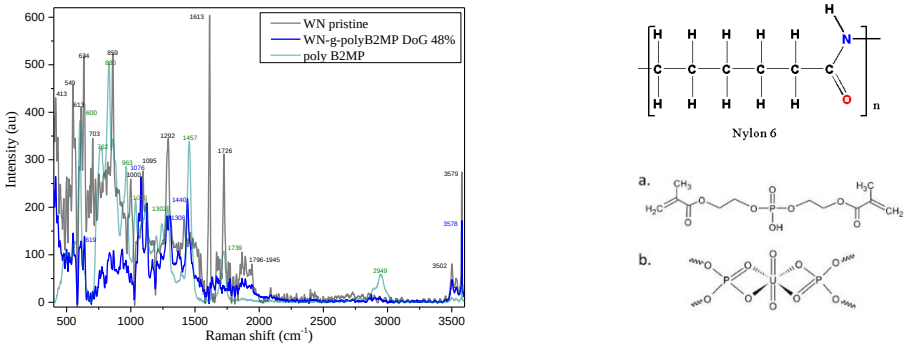

Figure 4: Raman spectra of pristine WN (black); WN-*g*-B2MP with DoG of 257% (blue), DoG of 48% (red); and polyB2MP (gray).

4. Conclusions

For this research, several systems and conditions for RIG polymeric membrane synthesis was tested. Best path for RIG of B2MP onto winged nylon fabric was through direct method. Characterization of membranes have been performed through determination of gravimetric degree of grafting (DoG), Raman spectroscopy, scanning electron microscopy (SEM), thermal properties (DSC, TGA).

Future work: Next steps envisage the estimation of the separation efficiency of uranium from solutions the volume reduction and chemical stability of uranium concentrates from chemical treatment and concentrate uranium forms from solution that are impractical to recover. Efficiency of adsorption will be estimated by uranium concentration measurement by ICP-OES, and HyperpureGe detector. We will test uranium adsorption by prepared membranes in two different pH values.

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