

New membranes obtained by grafted irradiated PVDF foils

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ABSTRACT

The present work describes a new method to produce membranes of poly(Acrylic-acid-Xmonomer) using the grafting procedure. PVDF foils irradiated with Ar⁺ beam with energies between 30 and 150 keV were employed as substratum. Different combinations of monomers in water solutions were used: acrylic acid (AAc); acrylic acid-glycidyl methacrylate (AAc-GMA); acrylic acid-styrene (AAc-S), acrylic acid-N-isopropyl acrylamide (AAc-NIPAAm) and acrylic acid-N-isopropyl acrylamide-glycidyl methacrylate (AAc-NIPAAm-GMA). A large percentage of grafting results for specific values of: ion fluence and energy, AAc and sulfuric acid concentration, and different substrata PVDF polymorphous (alpha or beta). At a particular time of the grafting process, the poly(AAc-Xmonomer) membranes detach from the substratum and continue their grafting in the solution. This method is useful to produce increased replicated membranes of the irradiated original surface.

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1. Introduction

Irradiation of polymers with gamma, X photons or electrons has been used extensively to obtain homogeneous graft copolymers [1–3]. The random distribution of deposited energies produces a homogeneous grafted zone in the bulk, which modified the substrate [4].

Different polymer substrates grafted with several monomers are suitable for a great number of applications, such as: (a) membranes obtained by grafting of AAc were found to be promising for dialysis, (b) radiation grafted carboxylic acid membranes such as poly(AAc) were tested for the production of NaOH by electrolysis of NaCl, (c) membranes prepared by grafting of monomers such as AAc were tested for water desalination, (d) radiation grafted membranes prepared by grafting of AAc onto polymers showed superior pervaporation properties, (e) AAc grafted membranes also showed superior permeability towards methanol compared to methacrylic acid equivalent [5].

Our group has performed several studies analyzing the grafting characteristic of irradiated polymers with different ions at high energy [6–12]. The present work continues with this research program using low energy ion beams. These ions have ranges of a few hundred of nanometers, inducing changes near the material surface. Therefore, the grafting process modifies the physical and chemical material properties, without modifying the bulk properties [13,14]. This characteristic opens the possibility of merging the physical and chemical properties of the substrate with the characteristics of the monomers for the production of new advanced materials. According to Chapiro [1]: “The grafting operation can also be purposely limited to the surface of a polymer for the production of interesting medical devices”.

Several works were published studying the irradiated grafting process [13–16]. In particular, a systematic study using low energy ions takes heed of different methods, monomers and polymers to measure the grafting yield as a function of different parameters, such as: fluence, grafting time, monomer concentration, etc. [13].

Our study describes a new method to produce a thin layer of AAc growing on the PVDF surface irradiated with an Ar⁺ beam with different energies. A new effect is reported: the grafting process begins on the irradiated surface, the membrane detaches from it, and continues growing in the grafting solution, disassociated from the substratum.

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2. Materials and methods

Argon ion beams between 30 and 125 keV were used, provided by the 200 keV ion implanter (Instituto de Física, Porto Alegre, Brazil) to irradiate the polymer films with fluences ranging from 1.10^{12} to 50.10^{13} cm^{-2} .

The targets were films of α and β -PVDF from Solvay (Belgium) with different thicknesses. Synthesis quality S, GMA and NIPAAm monomers (from Aldrich Chemical Company Inc.), and AAC monomer (from Merck Ltd.) were used "as received". All irradiated foils were stored at -20 °C temperature in air until the grafting experiments were performed.

The grafting yield Y was calculated by $Y(\%) = (m_f - m_i)/m_i$, where m_i and m_f represent the sample weight before and after grafting, respectively.

The aqueous solutions used for the grafting process in addition to different monomers and sulfuric acid, have 0.1% Mohr salt concentration.

3. Results and discussion

3.1. Acrylic acid grafting solution

Fig. 1 shows the results of the grafting yields using 25 m -PVDF films. Fig. 1(a) shows the grafting yield as a function of the AAC concentration for 0.2 M sulfuric acid in aqueous solution for 2 h. of grafting time. The ion energy and fluence were 100 keV and 10^{13} cm^{-2} , respectively.

The grafting yield increases steadily up to 50 vol.% of AA due to an increase of the polymerization rate. Then a rapid rise up to more than 120% at 79 vol.% of AA where the grafting yield is at a peak is observed. For higher AA concentrations, a sharp decrease of the grafting yield occurs.

We think that the $\text{CH}_2=\text{CH}-\text{COOH}\cdot\text{H}_2\text{O}$ species are the optimal ones to the grafting copolymerization to proceed, so 0.5 M fraction

of water is the maximum concentration (100%) in the grafting solution. This explains why the maximum grafting yields appears at 79% v/v, where an exact equimolarity exists between AA and water molecules. At lower AA concentrations, there is a small amount of activated species, because of a dilution effect in water. On the opposite case, at greater AA concentrations, there is less activated species, in consequence of a dilution effect in AA.

Fig. 1(b) shows the grafting yield as a function of sulfuric acid concentration, for 79% AAC in aqueous solution and for 9 h of grafting time. The ion energy and fluence were 100 keV and 10^{13} cm^{-2} , respectively. The maximum grafting yield was obtained for 0.2 M of sulfuric acid.

Fig. 1(c) shows the grafting yield as a function of the ion fluence for 100 keV energy and for: 79% AAC, 0.2 M sulfuric acid in aqueous solution and 22 h grafting time. The maximum grafting yield is observed at 10^{13} cm^{-2} ion fluence. For these previous conditions and during the grafting process, the grafted poly acrylic acid membrane detached itself from the original substratum. It continued the grafting reaction in the aqueous solution. In order to analyze the ion fluence values where this effect occurred, later experiments were performed and they determined that this effect appears at 5.10^{12} cm^{-2} , then increases at 10^{13} cm^{-2} and is not observed at 5.10^{13} cm^{-2} ion fluence.

The appearance of these maximum suggests that some kind of interference effect exists between the latent tracks. A possible mechanism to explain this interference effect was proposed before [10,17]. They suggested the existence of a deactivated zone around the ion incidence axis. Inside this zone the irradiation dose is so high that no active site remains for the grafting process. Then the latent track consists in a relative small region deactivated around the incident axis surrounded by a large region in which there are active sites for grafting. When two latent tracks intersect each other the deactivated zone of one latent track can eliminate a zone, previously available for grafting, on the other one. Then, this suggested mechanism can induce a reduction of the total grafting at certain values of the fluence [6].

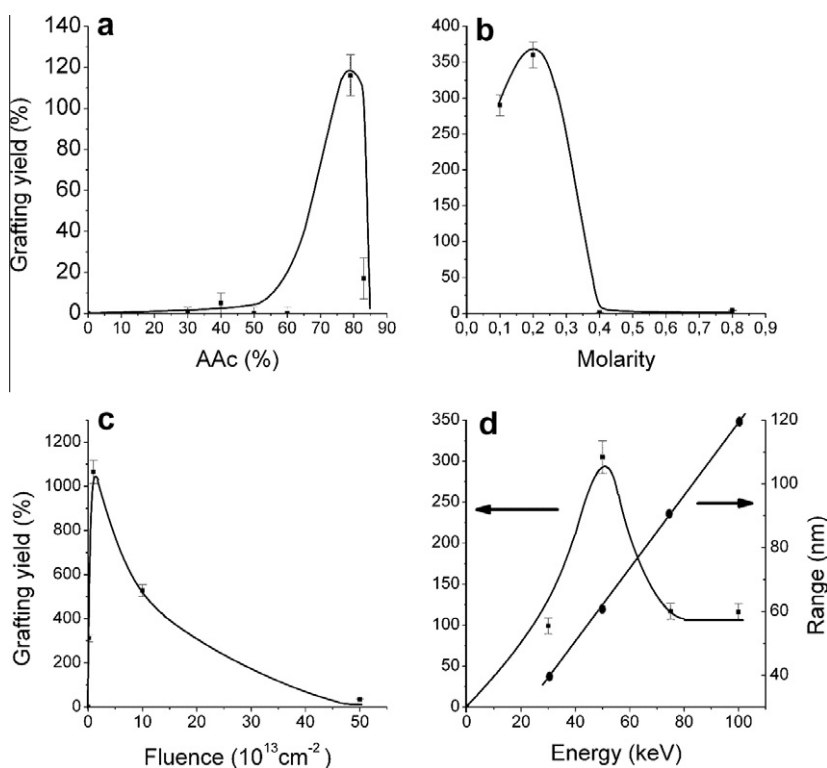


Fig. 1. Grafting yield as a function of: (a) acrylic acid percentage, (b) H_2SO_4 molarity, (c) ion fluence and (d) ion energy (left scale) and ion range (right scale).

Fig. 1(d) shows the grafting yield as a function of the ion energy for 79% AAC, 0.2 M sulfuric acid in aqueous solution and 5 h of grafting time. A maximum is observed for 50 keV. The detachment effects were observed for 50 and 100 keV but not for higher energies such as 125 and 150 keV. The ion range as a function of energy is also shown. As can be seen, the grafting yield increases up to the maximum at 50 keV which corresponds to 60 nm ion range. For greater energies the grafting yield decreases, probably due to the difficulty of the monomer solution to diffuse across the grafted region.

For the range of energies studied, nuclear stopping power (NSP) is predominant over electronic stopping power (ESP). When energy increases, at the same fluence, the amount of active sites also increases, so the grafting yield is greater. On the other hand, the maximum nuclear stopping power is obtained for energies lower than 50 keV, and that is why, taking into account that NSP is the most important one that creates active sites, as long as we increase the energies ($E < 50$ keV), these sites are more likely to be at the inner part of the substratum. The inner the active sites are, most difficult is to AA monomers to reach them because of hindered diffusion, so the remaining active sites decay before the grafting solution can reach them. This explanation is also consistent with the previous report of García Bermúdez et al. [18].

Fig. 2 shows a picture of two pairs of samples, where the smaller ones (gray color) are the original substrata and the larger ones correspond to the grafting replica. As can be seen in Fig. 2, the area increases, between the original substrata and the grafting replica. This increment was about three times the area of the substratum. The experimental parameters are 79% AAC, 0.2 M sulfuric acid in aqueous solution, 22 h grafting time, 10^{13} cm⁻² ion fluence and 100 keV ion energy. The maximum grafting at 50 keV, showed in Fig. 1(d), can explain the increase observed in the area.

Using the obtained set of parameters that optimizes the grafting yield, we observed the detachment effect for β -PVDF (4.5, 9 and 25 μ m thickness) substratum but not for the polymorphous α -PVDF (14 and 25 μ m thickness) one. This could be explained by the grafting proceeding in volume more easily in the case of the amorphous β -PVDF than for the crystalline α -PVDF. This effect could increase the probability to find particular regions or spots that hold the grafted films to the substratum and prevent it from detaching. On the other hand, as the crystalline region is more dif-



Fig. 2. Shows a picture of two pairs of samples in which the smaller ones are the original substrata and the larger ones the grafted replicas. The experimental parameters were 79% AAC, 0.2 M sulfuric acid in aqueous solution, 22 h grafting time, 10^{13} cm⁻² ion fluence and 100 keV ion energy.

icult to be grafted, then the number of anchor spots is reduced promoting the chance of detachment to happen.

In order to make clear the detachment effect, we performed the FTIR spectra analysis shown in Fig. 3 for both the PVDF substratum and the grafted replica. Fig. 3(1) shows the asymmetric and symmetric stretching vibrations of the CH₂ group which belongs to PVDF polymer, at 3025 and 2985 cm⁻¹, respectively. Fig. 3(2) shows the C=O vibration of free and hydrogen-bonded acid groups which belong to Poly(AAc) at 1716 cm⁻¹, with a shoulder at 1740 cm⁻¹ [13]. The characteristic PVDF peaks can be observed in Fig. 3(1,3,4) and 4, corresponding to the PVDF films, the remaining substratum after the grafting process and the grafted detached film, respectively. The information obtained could indicate that some fragments of the original PVDF film were also detached, becoming part of the final Poly(AAc) membrane.

In addition, the characteristic Poly(AAc) peaks are present in the Poly(AAc) monomer solution, as shown in Fig. 3(2), as well as in the Poly(AAc) membrane in Fig. 3 and 4, indicating that the monomer was really grafted. The small peak obtained for the remaining substratum, in the same region, indicates that part of the grafted foil remains in the substratum.

A possible explanation for this behavior could be that the grafting proceeds in volume more easily in the case of the amorphous α -PVDF than for the crystalline β -PVDF. This effect could increase the chance of appearance of regions or spots where the grafted films are held to the substratum and prevented it from detaching. On the other hand, as the crystalline region is more difficult to be grafted, and then the number of anchor spots is reduced, promoting the occurrence of detachment.

3.2. Different monomer mixtures

The following section analyses the detachment effect using several monomer mixtures, developing membranes with different mechanical and chemical properties. Grafting yield is determined for 2 h of grafting time, ion energy of 100 keV and fluence of 10^{13} cm⁻².

Fig. 4(a) shows the grafting yield as a function of GMA percentage, for two hours of grafting time. The grafting solution was 78.25% of AAC-GMA and 0.2 M sulfuric acid in aqueous solution. As GMA percentage increases, the grafting yield increases and

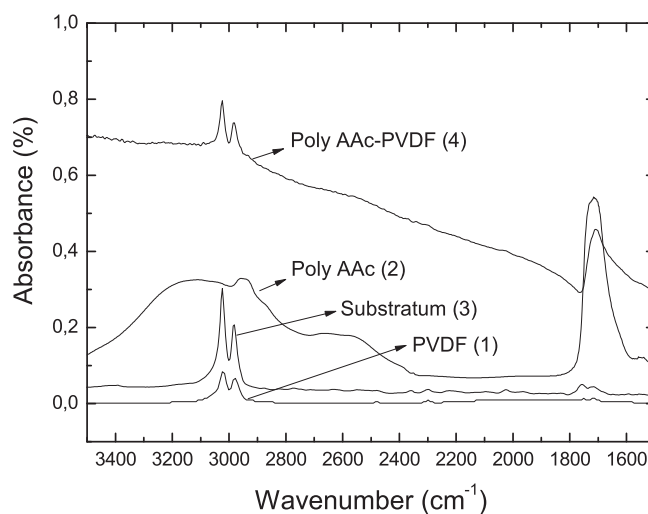


Fig. 3. FTIR spectra for: (1) β -PVDF control film of 25 μ m; (2) control film of poly(acrylic acid); (3) the remaining substratum film after the grafting procedure; (4) the Poly(acrylic acid) membrane obtained after the grafting procedure. The grafting conditions were: 79% AAC, 0.2 M sulfuric acid in aqueous solution, for 9 h of grafting time. The ion energy and fluence were 100 keV and 10^{13} cm⁻², respectively.

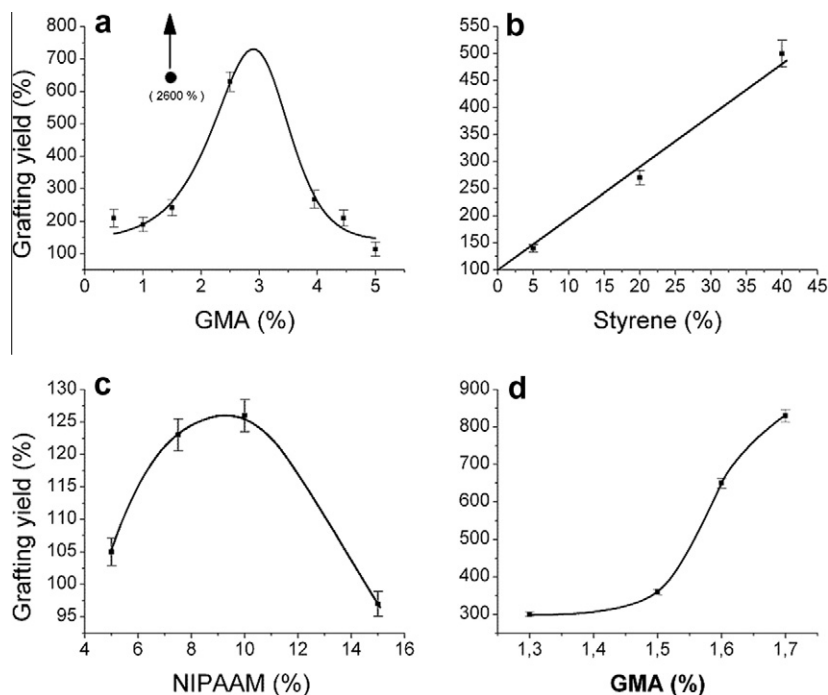


Fig. 4. Grafting yield as a function of GMA, styrene, NIPAAm and GMA percent in: (a) AAC + GMA water solution, (b) AAC + Styrene water solution, (c) AAC + NIPAAm water solution and (d) AAC + GMA + NIPAAm water solution, for 2 h of grafting time. The ion energy and fluence were 100 keV and 10^{13} cm^{-2} , respectively.

the Poly(AAc-co-GMA) film detaches from the substrate up to 2.5% GMA. After that, the grafting yield decreases and the film continues attached to the substratum. The grafting yield of 2600%, shown in Fig. 4(a), corresponds to 3 days of grafting time and 1.5% GMA monomer. In this case, the Poly(AAc-co-GMA) film also detached itself from the substratum.

It has been previously suggested that in acidic conditions, GMA monomer reacts through the epoxide ring-opening mechanism (preferential pathway), which explain that the molecule is attached onto the AAC structure, enabling a crosslinking polymerization reaction [19]. The maximum in the grafting yield (Fig. 4(a)) might be explained assuming this mechanism. Taking into account that the GMA monomer not only takes part on the grafting reaction but also on the crosslinking process, as GMA concentration increases, the crosslink should also increase. This induces a cross-linked structure which hinders or obstructs the diffusion of the grafting solution to reach active sites, resulting in lower grafting yields.

Fig. 4(b) shows the grafting yield as a function of styrene concentration. The grafting solution was 78% of AAC-Styrene, 0.2 M sulfuric in aqueous solution. As styrene percentage increases, the grafting yield also increases and the Poly(AAc-co-styrene) film detaches from the substratum.

Fig. 4(c) shows the grafting yield as a function of NIPAAm percentage. The grafting solution was 80% of AAC-NIPAAm, 0.2 M sulfuric acid in aqueous solution. As NIPAAm percentage increases, the grafting yield increases up to 10% NIPAAm concentration. The Poly(AAc-co-NIPAAm) film detaches from the substratum in all cases.

Fig. 4(d) shows the grafting yield as a function of GMA percentage. The grafting solution was 69% of AAC, 9.8% NIPAAm, X% GMA, 0.2 M sulfuric acid in aqueous solution. As GMA percentage increases, the grafting yield increases and the Poly(AAc-co-NIPAAm-co-GMA) film detaches from the substratum.

FTIR spectra of detached membranes and substratum of Poly(AAc-co-NIPAAm) are shown in Fig. 5. The comparison of both spectra exhibits some differences: an absorbance band which can

be assigned to carboxylates and other to carbonyls from Poly-AAC at 1550 and 1700 cm^{-1} , respectively [12,20]. Furthermore, the characteristic absorption bands of PNIPAAm can be identified from the sample spectra: amide I at 1650 cm^{-1} and amide II at 1548 cm^{-1} [21]. Concluding, the FTIR spectra shows the presence of the Poly AAC and the Poly NIPAAm in the membrane as well as in the remaining substratum.

The addition of these monomers has the advantage of changing the properties of the grafted membranes. For instance, when NIPAAm is added, it allows controlling the hydration rate, obtaining temperature responsive polymers for targeted drug delivery [22]. GMA is used to improve the mechanical properties of the membrane and, at the same time, provides a reactive group for immobilization of compounds [23]. Furthermore, styrene can be

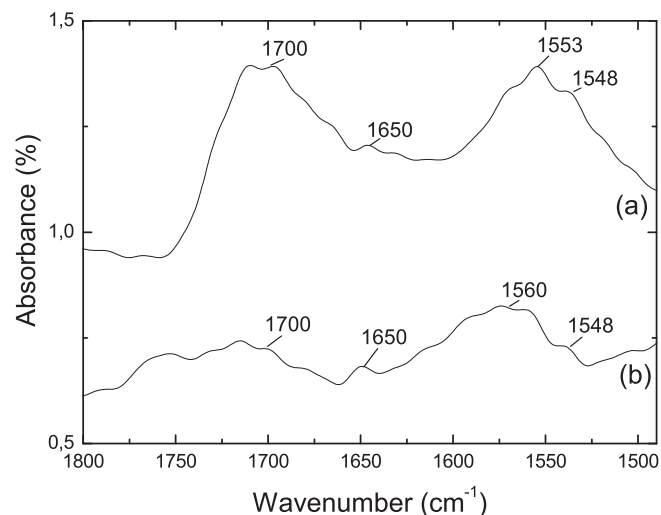


Fig. 5. FTIR spectra obtained for a detached membrane of poly (AAC-NIPAAm) (a) and for the remaining substratum (b).

incorporated for the development of polymers for fuel cell applications.

4. Conclusions

Concluding, we describe a new method to produce membranes from previously irradiated surfaces. This technique allows the production of enlarged replicas of a certain pattern on the surface of a substratum, by irradiating with an ion beam through a mask. In addition, by choosing particular monomer mixtures it might be possible to develop the detached membranes for specific applications. The mechanism underlying this phenomenon is not clear and certainly needs further research.

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