

PERFLUORINATED POLYMER GRAFTING: INFLUENCE OF PRE-IRRADIATION CONDITIONS

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ABSTRACT

The technological interest of perfluorinated polymers is related to its specific properties like low chemical reactivity and high mechanical and temperature resistance. The development of polymeric membranes for PEM fuel cell dispositives requires beyond these characteristics, a long-life time performance and low cost compared to Nafion membranes. By these material have high crystallinity, the radiation grafting indeed occurs but this process generate a low mechanical resistance aggregate. In this way, it is necessary to render the polymer with a low crystallinity or even amorphous. Generally, irradiation under polymer melt temperatures makes the crystallinity breaking and polymer crosslinking. The main objective of this work was promoting the crosslinking process into perfluorinated polymers by pre-irradiation method and to precede styrene grafting by electron beam irradiation in a second step. The experimental methodology consists in pre-irradiate perfluorinated polymers films like PTFE and PFA under high temperature (> 300 °C) and vacuum conditions by electron beam irradiation at 5 kGy to 30 kGy doses and 2,85 kGy/s to 22,4 kGy/s dose rates. To obtain temperatures above 300 °C, it was necessary construct a vacuum chamber with a heating system where temperature process could be follow up in real time. Some molecular alterations in polymeric matrix were analyzed by Mid-ATR-FTIR spectroscopy; macroscopic changes are verified by gravimetry. The styrene grafting onto these samples is realized by electron beam irradiation at doses between 30 and 100 kGy. These results are discussed.

1. INTRODUCTION

Radiation induced grafting of styrene into fluoropolymer films and subsequent sulfonation offers an attractive way to prepare proton exchange membranes for use in fuel cells. This process is an advantageous means of modifying base polymers because grafting frequently results in the superimposition of properties related to the backbone and the grafted chains.

Fluoropolymers have an excellent chemical and thermal stability beyond to present sensibility to ionizing radiation. If the irradiation is performed at room temperature, most of the fluoropolymers undergo predominantly chain scission and it is decrease the mechanical resistance.

The PTFE can be crosslinked by irradiation in its molten state in an oxygen-free atmosphere [1,2]. Evidence of crosslinking in PTFE was derived directly from structural information using ^{19}F solid-state NMR [3]. Radiation-induced grafting of styrene in crosslinked PTFE was reported for the first time [4-6].

In this study, the perfluorinated films PTFE (polytetrafluoroethylene) and PFA (polytetrafluoroethylene-co-perfluoropropylvinylether) were submitted to electron beam irradiation under vacuum and high temperatures to precede the crosslinking process. In the literature, the requirement for it is irradiation in vacuum at temperatures above the glass transition temperature; also, PFA can be branched and crosslinked by irradiation under special conditions [7,8].

After crosslinking step, these films have been irradiated to perform the subsequent grafting of styrene.

2. EXPERIMENTAL

The fluoropolymer films (100 μm thickness) were purchased by Goodfellow and styrene monomer was commercial grade purified by molecular sieves contact. Electron beam irradiation was supplied by an Electron Beam Accelerator JOB 188 (Dynamitron®) energy 1.5 MeV (Figure 2), beam current 25 mA, scan 60 to 120cm, beam power 37.5 kW. The fluoropolymer samples were irradiated at temperatures from 290 $^{\circ}\text{C}$ to 350 $^{\circ}\text{C}$ close to polymer melting points (PTFE: m.p. = 327 $^{\circ}\text{C}$ and PFA: m.p. = 305 $^{\circ}\text{C}$) and at irradiation doses from 1.25 kGy to 70 kGy (dose rates of 2.83 kGy/s used on PTFE samples and 22.4 kGy/s used on PFA samples).

The percent of mass variation was determined by gravimetry and the values were the average of triplicate measures. After irradiation, the films were removed of vacuum chamber and immersed in grafting solution (styrene:butanol-1 at 1:1 proportion) and irradiated at 100 kGy. The grafted films were washed in toluene and soaked in ethanol to precipitate the homopolymer PS. The ATR-Mid-FTIR spectra were evaluated by a spectrophotometer Bomem MB100.

3. RESULTS AND DISCUSSION

The percent mass of fluoropolymers pre-irradiated under high temperature is presented in figure 1. We can observe PFA has higher loss mass than PTFE. It happens because PFA is submitted to high doses without lose its mechanical resistance; PTFE do not support doses above 10 kGy because its C-C bonds are radiation sensitive; low mechanical resistance is the macroscopic effect observed in this case.

All samples lose weight and the average mass changes. Temperature and irradiation dose are important parameters that play role in weight loss values on analysed polymers: PTFE lose mass below 0.2 % (maximum loss weight at 340 $^{\circ}\text{C}$, 5 kGy and 2.83 kGy/s) but at 320 $^{\circ}\text{C}$ the weight loss decrease to 0.1 % at 10 kGy and the same dose rate; PFA lose more than 2 % of mass at 290 $^{\circ}\text{C}$ and at 70 kGy, but 0.3 % weight loss is observed at 50 kGy and at the same temperature.

The figure 2 shows the degree of grafting of these samples. For PFA samples pre-irradiated at 290 °C and at 50-70 kGy (22.4 kGy/s), was achieved an average value of 1.4 % degree of grafting, that is a greater value if compared to grafted PFA original sample (0.65 %). An average of 4.88 % was the degree of grafting achieved in PTFE sample pre-irradiated at 320 °C and at 10 kGy irradiation dose (dose rate 2.83 kGy/s); this value is greater than degrees of grafting for another pre-irradiated films.

Pre-irradiation under high temperature allows polymer crosslinking and its microscopic effect is the crystallinity breakage; an increase in mechanical resistance of polymer films is observed as a macroscopical effect. The high degree of grafting achieved in perfluorinated polymer samples pre-irradiated at temperatures around 300 °C compared to original films can be an indicative of polymer crosslinking; in this case, reactivity increases in a less organized material.

The Mid-ATR-FTIR spectroscopy was performed to these perfluorinated films. In figure 3, non-grafted PTFE pre-irradiated films show 1200 cm^{-1} and 1140 cm^{-1} absorption bands, related to $-\text{CF}_2-$ deformation, less intense than those in original film; this behavior can be attributed to degradation caused by high temperature/irradiation dose effects. The 320 °C pre-irradiated film shows these absorption bands more intense than 340 °C and 350 °C pre-irradiated films; it suggests that temperatures above 320 °C can contribute to degradation material effect. Otherwise, 340 °C and 350 °C pre-irradiated films have the same intensities in these mentioned absorption bands, despite lower weight loss (-0.08 %) at 350 °C pre-irradiated film, that absorbed the smaller irradiation dose (1.25 kGy) compared to 340 °C pre-irradiated film (5 kGy) in the same dose rate, where a great material degradation should be present; this behavior can be related to crystallinity breakage in function of temperature/dose irradiation parameters and this physical change must be investigated more extensively. The PTFE high temperature pre-irradiated films were styrene grafted (styrene:butanol-1 1:1 mixture) under atmosphere air/room conditions and irradiation dose of 100 kGy; the grafting on these films is confirmed by 1055 cm^{-1} and 690 cm^{-1} absorption bands in these spectra, that referred to vibrations in plane of aromatic C-H and out of plane aromatic ring bend respectively.

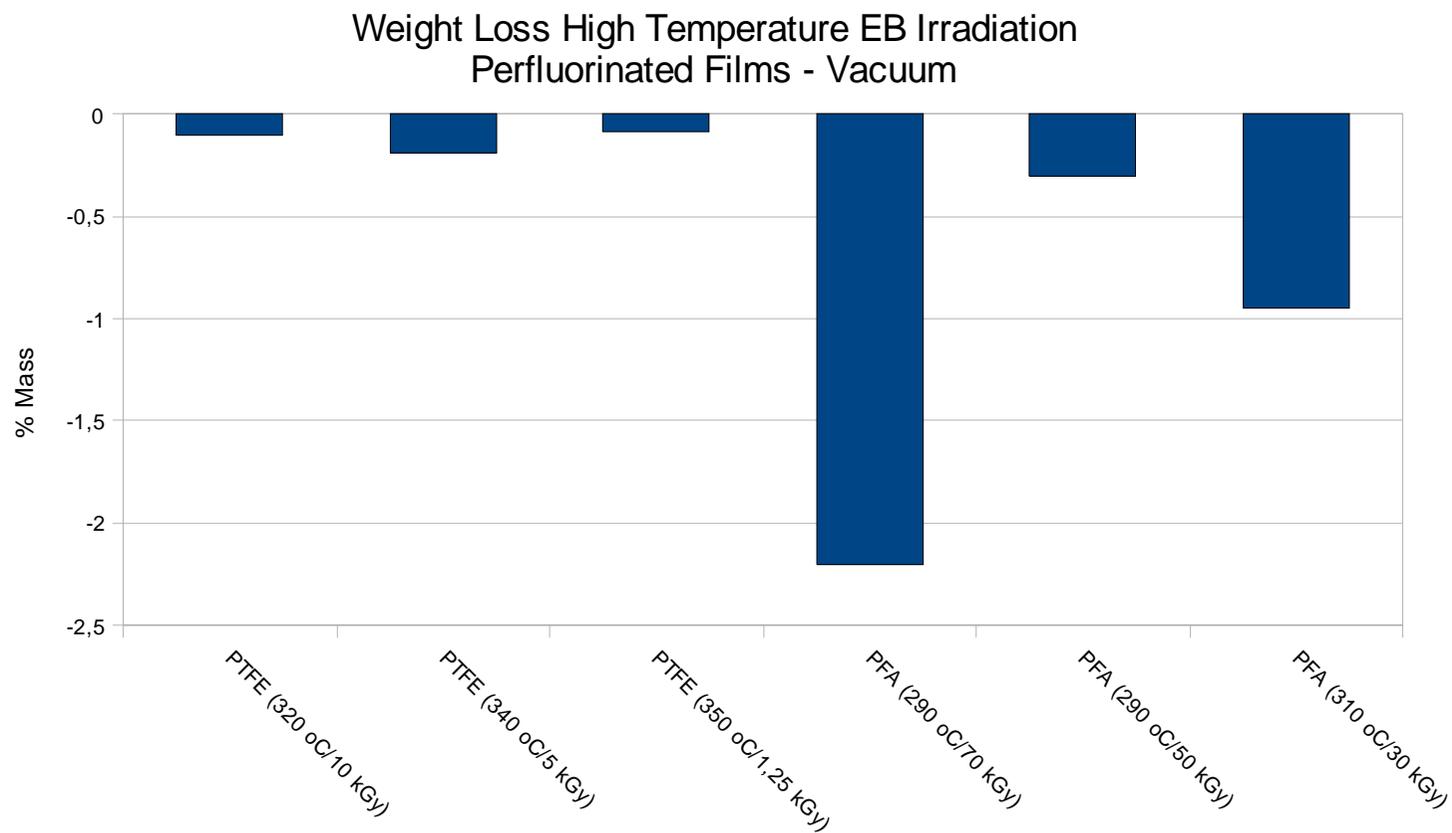


Figure 1 – Percent of weight loss in perfluorinated pre-irradiated films.

High Temperature Pre-irradiation
Grafting under atmosphere air - Styrene:Butanol-1 1:1

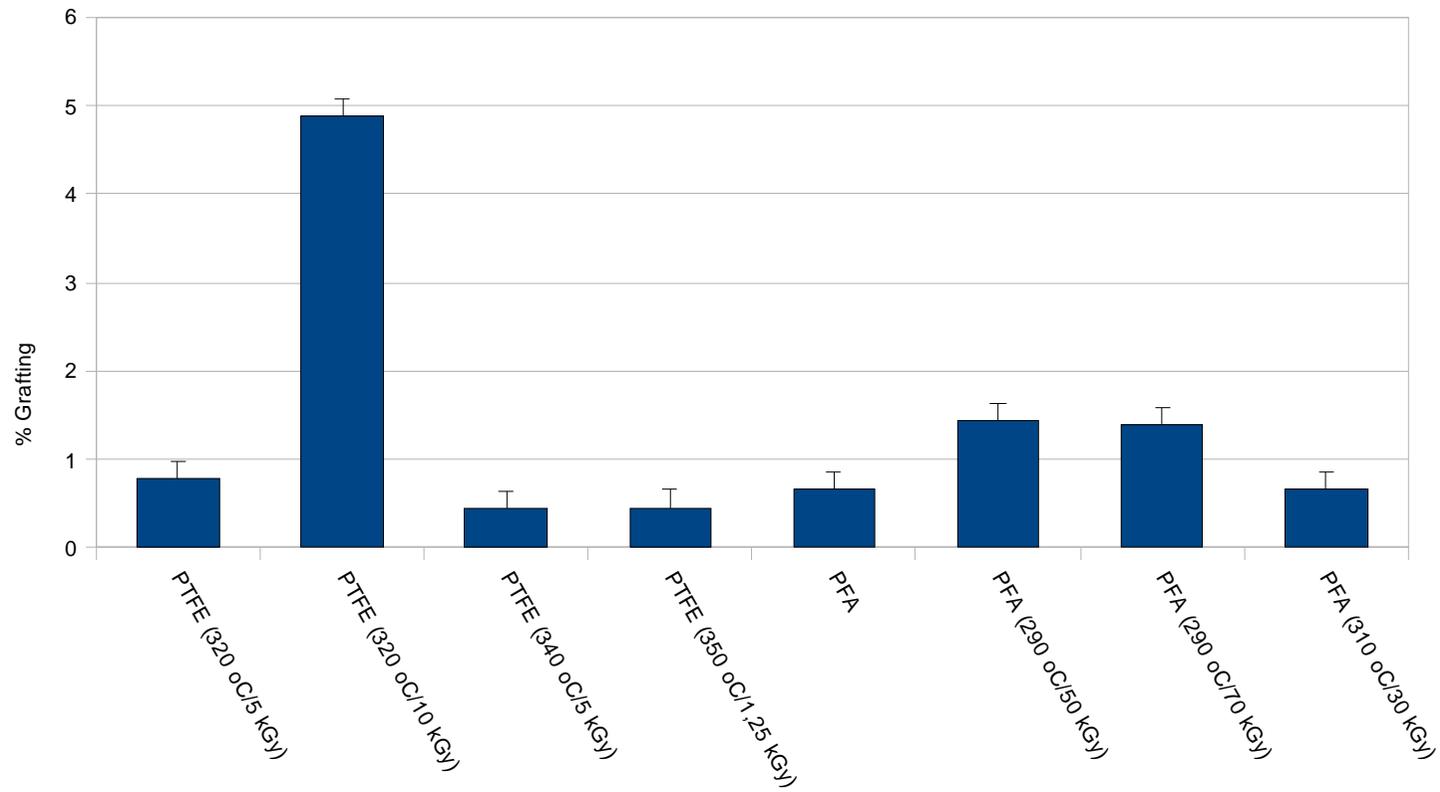


Figure 2- Degree of grafting of pre-irradiated samples.

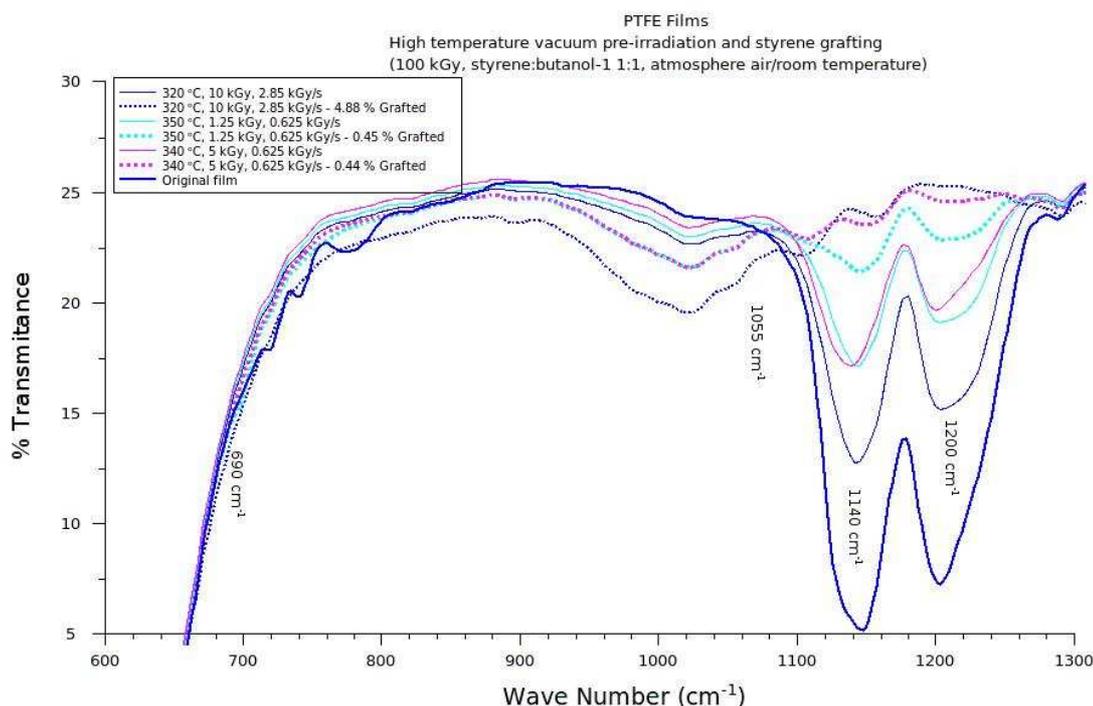


Figure 3 - High temperature vacuum pre-irradiated PTFE films Mid-ATR-FTIR spectra compared to PTFE original film. The grafting at high temperature pre-irradiated films was performed in atmosphere air/room conditions, irradiation dose of 100 kGy and styrene:butanol-1 1:1 mixture.

The figure 4 show Mid-ATR-FTIR spectra for grafted and non-grafted PFA films at high temperature pre-irradiation. In 1200 cm^{-1} and 1140 cm^{-1} absorption bands non-grafted films present similar behavior than those presented in figure 3; the intensities of these bands in original film and in PFA film pre-irradiated under $290 \text{ }^\circ\text{C}$ and 50 kGy irradiation dose are almost the same and it suggests no degradation or a little degradation occurring at these conditions, but the low intensities for these absorption bands in PFA film pre-irradiated under $290 \text{ }^\circ\text{C}$ and 70 kGy irradiation compared to original film indicate material degradation when it is exposed under these conditions. Grafted PFA pre-irradiated films show absorption bands in 1055 cm^{-1} and 690 cm^{-1} , that confirms the styrene presence in these samples.

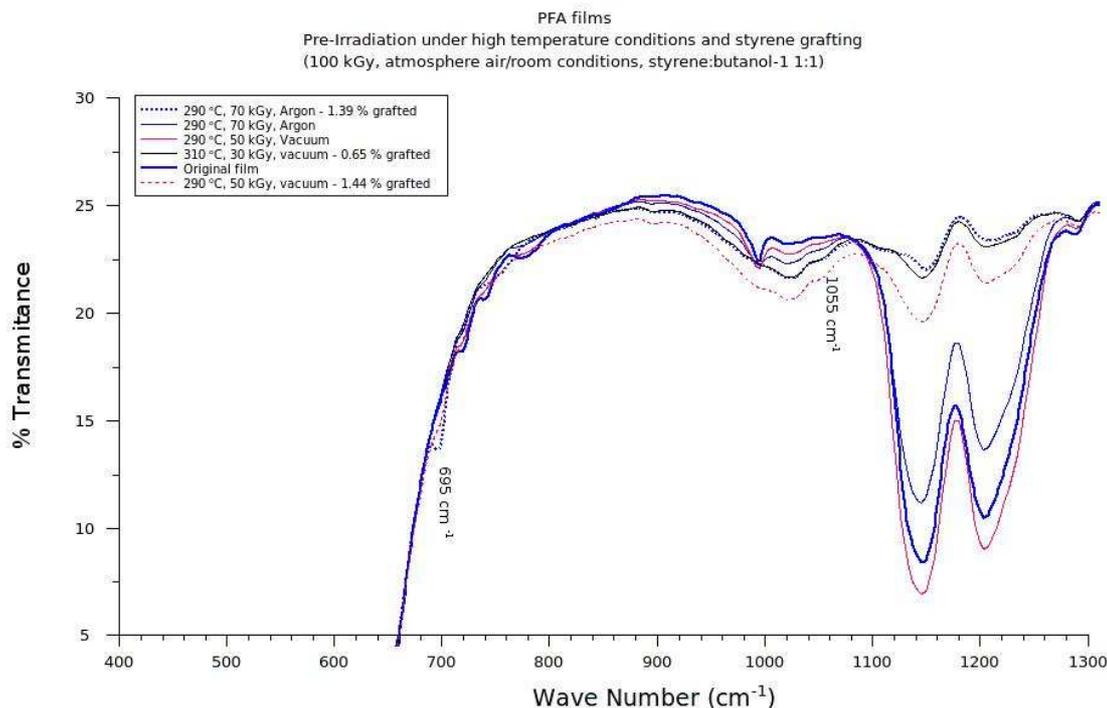


Figure 4 - High temperature vacuum pre-irradiated PFA films Mid-ATR-FTIR spectra compared to PFA original film. The grafting at high temperature pre-irradiated films was performed in atmosphere air/room conditions, irradiation dose of 100 kGy, dose rate of 22.4 kGy/s and styrene:butanol-1 1:1 mixture.

3. CONCLUSIONS

The PFA samples pre-irradiated under high temperature resist more at high doses and at high dose rates than PTFE samples and it is related to the distinct backbone molecular structure at both perfluorinated polymers. All polymers present weight loss when distinct irradiation dose and temperature are setted; it is not verified weight loss proportionality when the polymer samples are irradiated at different doses, but at the same temperature. Perfluorinated polymers present less degradation when pre-irradiation process occur at temperatures below its melting points. We observed styrene grafting is better achieved in perfluorinated samples pre-irradiated at temperatures below its melting points.

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