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POST IRRADIATION EFFECTS ON THE GRAFT OF POLY(TETRAFLUOROETHYLENE-CO-PERFLUOROPROPYL VINYL ETHER) (PFA) FILMS

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ABSTRACT

Radiation induced grafting of monomers into fluorinated polymers was designed as an alternative route to polymer modification. In this work, grafting of styrene onto poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) was studied. Radiation-induced grafting of styrene onto PFA films was investigated after simultaneous irradiation (in post-irradiation condition) using a ^{60}Co source. The films of PFA were irradiated at 20, 40, 80 and 100 kGy doses at room temperature and chemical changes were monitored after contact with styrene for grafting. The post-irradiation time was established between 7 and 28 days when films of PFA were maintained in styrene/toluene 1:1 v/v solution at room temperature. After these periods the grafting degrees were evaluated in the samples. The highest degree of grafting was achieved after 14 days. Chemical modifications were evaluated by infrared spectroscopic analysis (FTIR), thermogravimetry (TG), differential scanning calorimetry (DSC) and also by scanning electron microscopy (SEM). The degree of grafting (DOG) was determined gravimetrically. The results showed that irradiated PFA films at 100 kGy exhibited higher grafting degree. Surface analysis by SEM technique of irradiated, grafted and original films have presented an homogeneous surface.

1. INTRODUCTION

Much effort has been devoted to develop cation exchange membranes by radiation induced graft copolymerization techniques [1,2].

Radiation induced grafting of monomers into fluorinated membranes was designed as an alternative route to obtain the proton conduction membranes. Generally, there are two methods for radiation induced grafting:

i) Preirradiation: the base polymer films are irradiated and in the sequence monomer is added and grafted [3];
ii) Simultaneous irradiation: the base polymer films are soaked with monomer solution and then irradiated [4].

The attractiveness of these techniques arises from the ability to introduce desirable properties to a preexisting polymer without altering its properties.

Fluoropolymers are a class of polymers with excellent chemical and thermal stability, low dielectric constants, and low surface energy. Partially fluorinated polymer membranes have also been actively investigated. Nasef et al has reviewed the preparation of various types of ion exchange membranes by radiation induced grafting copolymerization [1, 2, 4-7].

In our laboratory we have studied the radiation-induced graft of styrene onto fluoropolymers [8] and polyolefins**.**

The process of styrene grafting on fluoropolymer is usually conducted at temperatures higher than 50 ºC for high grafting yield [3, 9]. Nevertheless, Walsby et al presented a work on styrene grafting induced by simultaneous irradiation at room temperature, which showed that no polymerization at all takes place. They also reported that the grafts obtained at high temperature were distributed in an uneven way at the surface [1].

In this work, grafting of styrene onto poly(tetrafluoroethylene-co-perfluoropropyl vinyl ether) (PFA) was studied. The innovation of the present work was the study of grafting reaction after simultaneous irradiation, both at room temperature. Radiation-induced grafting of styrene onto PFA films was investigated after simultaneous irradiation (in post-irradiation condition) using a ^{60}Co source. Chemical changes were evaluated by infrared spectroscopic analysis (FTIR), thermogravimetry (TG), differential scanning calorimetry (DSC) and also by scanning electron microscopy (SEM). The degree of grafting (DOG) was determined gravimetrically.

2. EXPERIMENTAL

2.1 Membrane preparation

PFA films with 100 µm thickness purchased from Goodfellow Ltda were used in this study. The graft solution used was styrene monomer mixed with toluene in a proportion of 1:1 (v/v), without purification. Samples with 18 cm^2 in triplicate were used to prepare material for chemical characterization.

The films and graft solution were put into a glass tube and nitrogen was bubbled to guarantee inert atmosphere. The tube was sealed and submitted to gamma radiation at 20, 40, 80 and 100 kGy doses at 5 kGy h^{-1}. After simultaneous irradiation process the samples were kept in the tube at room temperature for periods of 7, 14, 21 and 28 days in order to evaluate the grafting behaviour. The tubes were kept in inert atmosphere during those periods of time to avoiding reactions of free radicals with oxygen. In the sequence, at the end of each period, thermal treatment of the irradiated samples were made in vacuum oven for 4h at 70 °C.

Extraction procedure of the samples was carried out after the thermal treatment in Sohxlet system by using hot toluene as solvent. The extraction to remove the remaining homopolymer was effective in 8 h. The films were dried in vacuum oven to eliminate residual solvents and impurities until constant mass, at the temperature of 70 °C.

2.2. Characterization

Weights increasing of the samples were measured to determine the degree of grafting (DOG) according to the equation (1);

$$DOG\ (\%) = [(w_g - w_o)/w_o)]x100 \qquad (1)$$

where w_g and w_o are the weight of the samples after and before grafting, respectively. All the degree of grafting (%) values at different experimental conditions corresponds to the average value given by three samples for each case.

Infrared spectroscopy was performed at Nexus 670 FTIR of Thermo Nicolet S.A. with samples of the films analyzed by the directly method. The spectra were recorded in samples of the films ungrafted and grafted.

Thermogravimetry (TG) was recorded with a Mettler-Toledo TG / SDTA 851 thermobalance in nitrogen atmosphere, from 25 up to 700 °C at a heating rate of 10 °C min^{-1}.

Differential scanning calorimeter (DSC) was carried out in a 822 Mettler-Toledo under nitrogen atmosphere at a heating rate of 10 °C min^{-1}, in the temperature range of 30 to 350 °C.

The SEM images were obtained in a Phillips XL 30 Microscope and were amplified to 10,000 X. The samples were covered with gold in a Sputter Coater BAL-TEC SCD 050.

3. RESULTS AND DISCUSSION

The overall graft copolymerization process [10] involves three kinetic steps, which may be represented as follows:

$$P \xrightarrow{\gamma\text{-irradiation}} P^{\bullet}\ \text{(substrate radicals)} \qquad (2)$$

$$\text{initiation:}\quad P^{\bullet} + M \rightarrow PM^{\bullet} \qquad (3)$$

$$\text{propagation:}\quad PM^{\bullet} + M \rightarrow PM^{\bullet}_{n+1} \qquad (4)$$

$$\text{termination:}\quad PM^{\bullet}_{n} + PM^{\bullet}_{m} \rightarrow PM_{n+m}\ \text{(grafted polymer)} \qquad (5)$$

where P is the polymer substrate, $P^{\bullet}$ is the primary radical site formed on the substrate, $PM^{\bullet}$ is the initiated graft chain, M is the monomer unit, and $PM^{\bullet}_{n}$ and $PM^{\bullet}_{m}$ are the grafted growing chains. Changes in the grafting conditions may affect one or more of these three kinetic steps (eqs 3-5), leading to changes in the rate and overall degree of grafting.

It is known that gamma radiation onto polymeric materials produces free radicals, which can react for several ways modifying the morphology of the macromolecular chains. As a result of radiation process, long chain branches in PFA films can be formed. The styrene was chosen as a monomer with reactive sites to be introduced by the radiation process in the polymer matrix. The influence of ionizing radiation on the properties of the polymer depends on whether the polymer performs crosslinks or suffers degradation that causes changes in most of the valuable properties of polymers.

The films were weighted before and after the grafting process for DOG determination (eq 1). The highest results were achieved after 14 days of simultaneous radiation and grafting process. As a result, we concentrated our studies and analysis in the effect of total dose on the grafting of styrene in toluene solutions after 14 days from irradiation. The relationship between degree of grafting and the irradiation dose are shown in Figure 1. The degree of grafting was found to be dependent upon the irradiation dose. The degree of grafting

increases gradually with the increase in the radiation dose. This behaviour can be understood based on the fact that the increase in the dose leads to generation of more radicals in the grafting system, and as a result, more radicals contribute to grafting reaction. The radicals in fluorinated polymer backbone remain trap after radiation during several days. So, the grafting reaction continuous occurs while these radicals are accessible and recombining with the radicals of the monomer. This behaviour after of post-irradiation simultaneous process was analyzed in this work and it was verified that the degree of grafting did not change enough during the periods studied and the thermal properties of this grafted films, after each period, wasn't affected then it was chosen the highest DOG to carry on this work that is the sample kept at room temperature for 14 days.

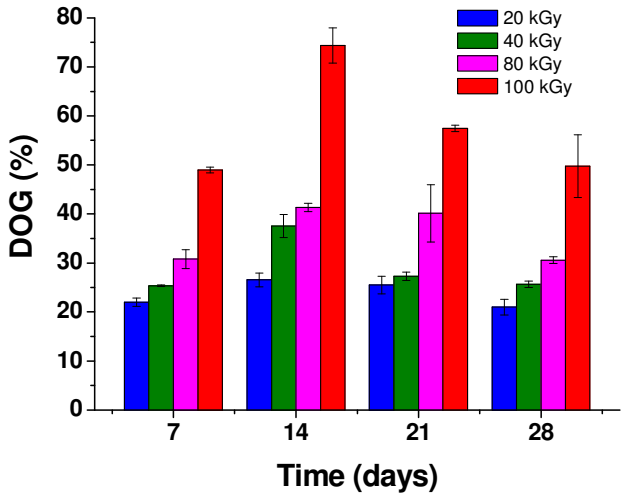


Figure 1. Relation between degree of grafting, DOG (%) and irradiation doses for PFA films.

To confirm the grafting of styrene in the grafted PFA films, FTIR spectra was conducted. In the FTIR spectra of the graft PFA films (Figure 2), new peaks appeared in the region 3100 to 3000 cm^{-1}, owing to =C-H stretching vibration of the styrene groups. The bands at 2920 cm^{-1} and 2850 cm^{-1} are asymmetric and symmetric stretching, respectively, that were attributed to the aliphatic CH_2 group of the styrene graft. The band at 1600 cm^{-1} is the skeletal C=C stretching vibration and 1490 and 1460 cm^{-1} are the skeletal C=C in plane deformation of styrene graft. C–H out of plane bending overtone and combination bands was in the region around 1660–2000 cm^{-1}. [6]

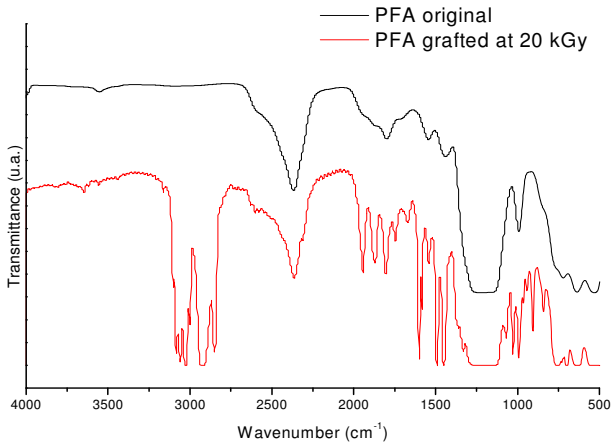


Figure 2. FTIR Spectra of PFA original film and grafted at 20 kGy dose.

The thermal results were shown in figure 3.

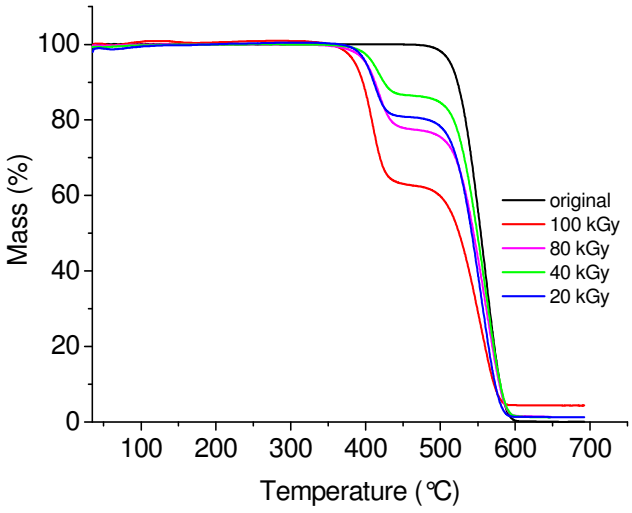


Figure 3. TG curves for original and grafted PFA films. Irradiation doses at 20, 40, 80 and 100 kGy.

The thermal stabilities of the PFA films were determined by TG, figure 3. The original PFA has only one sharp weight loss that was ascribed to the decomposition of polymer main chain, at 524 °C. For the grafted PFA there are two decomposition steps the first one is attributed to styrene grafted that begins the decomposition between 394 and 408 °C and the second is the decomposition of polymer chain (between 521 e 527 °C).

In Table 1, the original PFA melting temperature (T_m) was 313 °C and styrene side chain graft incorporation into PFA films was observed a little decrease in the values. The

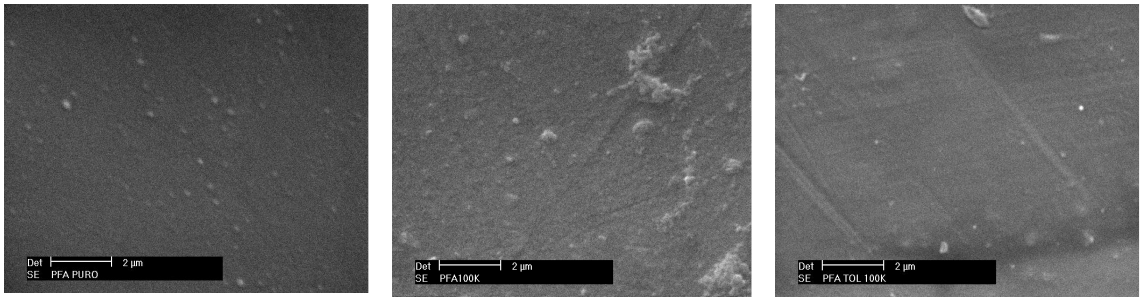
small variation in the T_m despite the increase in the degree of grafting suggests that the polystyrene grafts occurred mainly in the amorphous region, therefore the crystalline region was not affected or affected to only minor extension [8]. The effect of the radiation grafting is not effective to change the crystalline structure of the polymer matrix.

Table 1. Thermal data for PFA films.

Dose (kGy)	DOG (%)	T_m (°C)
original	-	313
20	26.5 ± 1.4	309
40	37.5 ± 2.4	310
80	41.3 ± 0.8	310
100	74.4 ± 3.6	308

DOG: degree of grafting; T_m: melting temperature.

The structural changes showed that irradiated PFA films at 100 kGy exhibited higher grafting degree. Surface analysis by SEM technique of irradiated, grafted and original films have presented a homogeneous surface according to figure 4.



original irradiated grafted

Figure 4. SEM images of original, irradiated at 100 kGy and grafted in styrene/toluene solutions.

4. CONCLUSIONS

Radiation-induced grafting of styrene onto PFA films was investigated after simultaneous irradiation (in post-irradiation condition) using a ^{60}Co source. We have examined the influence of radiation dose 20 to 100 kGy range by FTIR, TG, DSC and SEM techniques. These techniques showed evidences regarding the styrene graft.

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