

## GRAFTING OF STYRENE ONTO FLUOROPOLYMERS FILMS

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### ABSTRACT

Grafting of styrene onto poly(vinylidene fluoride) (PVDF) and poly(tetrafluoroethylene) (PTFE) films was studied for the synthesis of ion exchange membranes. Radiation-induced grafting of styrene onto PVDF and PTFE films was investigated by simultaneous method using a  $\text{Co}^{60}$  source. The films of PVDF and PTFE were irradiated at total dose of 20 to 120 kGy and chemical changes were monitored after contact with styrene. Films of PTFE and PVDF were immersed in styrene/toluene 1:1 and were submitted to gamma radiation. After irradiation the samples were evaluated at periods of 0, 7, 14, 21 and 28 days, at room temperature in order to measure the grafting degree. Results of infrared spectroscopic analysis (FTIR), differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and the degree of grafting (DOG) were evaluated. The characterization techniques showed that irradiated PVDF and PTFE films exhibited a much higher grafting degree at 120 kGy.

### 1. INTRODUCTION

The development of proton exchange membrane fuel cells (PEMFCs) has been considerable interest for their applications to electric utility, portable power and transportation. The proton exchange membrane (PEM) is a vital component in this type of fuel cell; it acts as a separator to prevent mixing of the reactant gases and as an electrolyte for transporting protons from the anode to the cathode. Nafion<sup>®</sup> by DuPont is the most frequently used PEM material because of its chemical stability and commercial availability. However much effort is being focused on the development of low cost membrane materials. Radiation induced grafting of functional monomers into fluorinated membranes was designed as an alternative route to gain the proton conduction membranes for PEMFCs applications. Among those functional monomers, styrene was the most widely used. Generally, there are two methods for the irradiation induced grafting. One is pre-irradiation method, concerning of irradiation of fluorinated polymer and subsequent styrene monomer addition for grafting. The other is the simultaneous irradiation method, where the fluorinated polymer films is soaked in the styrene monomer solution and irradiated in the sequence. 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. Novel proton-conducting membranes for hydrogen and methanol fuel cells by the radiation grafting of monomers onto various trunk polymers (e.g., FEP, ETFE etc.) and subsequent sulfonation of the grafted side chains have been studied by G. G. Scherer group in Paul Scherer Institute [1-4]. The Scherer group intends to work on low-cost starting materials and offers the prospect of cost-competitive membranes for the polymer electrolyte fuel cell [5]. In this work was used the simultaneous method, for PTFE and PVDF films consisting in the immersion on monomer solution and irradiation in the sequence, with variation of dose. The

graft and ungraft samples were characterized by TGA, DSC, FTIR and degree of grafting (DOG).

## 2. EXPERIMENTAL

### 2.1. Prepared films

The styrene was supplied by Maxepoxi Ind. Com. and toluene from Merck. PTFE was used in the form of 0.2 mm thick film and was obtained from ULTRAHI PLÁSTICOS. PVDF was supplied in the form of pellets by ARKEMA GROUP. Films are made by pressing samples between two finely polished inox steel plates and through this process, films of PVDF of 0.12mm. Films of PTFE and PVDF were immersed in styrene/toluene at 1:1 (v/v) concentration and irradiated. Several samples were prepared. In the sequence thermal treatment of the irradiated samples were made in vacuum oven for 8h at 70 °C. After this the films were washed with toluene in soxhlet extractor and then dried in vacuum oven until constant weight. The extraction to remove the remaining homopolymer was effective after 8h. Irradiations were accomplished via Co<sup>60</sup> source (dose rate of 10 kGy h<sup>-1</sup>) at 20 to 120 kGy dose at room temperature in oxygen free atmosphere. The gamma ray radiation was the first chosen to do this experiment, in the future different dose rate and graft polymerization will be studied. Following irradiation the samples were evaluated at room temperature for 0, 7, 14 and 21 days in order to observe the degree of grafting behavior. Weights increasing of the samples were measured to determine the degree of grafting (DOG) according to the equation (1);

$$\text{DOG (\%)} = [(w_g - w_o)/w_o] \times 100 \quad (1)$$

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.

### 2.2. Instrumental analysis

The infrared analyses were performed on Nexus 670 Thermo Nicolet, MID - FTIR with films cut into pieces and analyzed them. TGA technique was accomplished in a Mettler - Toledo TGA / SDTA 851 thermobalance, using inert atmosphere of N<sub>2</sub> from 25 to 750 °C at heating rate of 10 °C min<sup>-1</sup>. DSC curves were obtained in a Mettler-Toledo DSC 822, under nitrogen atmosphere, for PTFE from 0 to 400 °C at 20 °C min<sup>-1</sup> heating rate; keeping at 400 °C per 3 min; 400 to 0 °C at 50 °C min<sup>-1</sup> cooling rate; then kept at 0 °C per 3 min and reheated from 0 to 400 °C, at 10 °C min<sup>-1</sup> heating rate. As for PVDF, the temperature ranged from -25 to 240 °C at 10 °C min<sup>-1</sup> heating rate; then from 240 to -25 °C at 5 °C min<sup>-1</sup> cooling rate; afterwards it was kept at -25 °C per 5 min and reheated from -25 to 300 °C at 10° C min<sup>-1</sup> heating rate.

## 3. RESULTS AND DISCUSSION

The overall graft copolymerization process [6] involves three kinetic steps, which may be represented as follows:

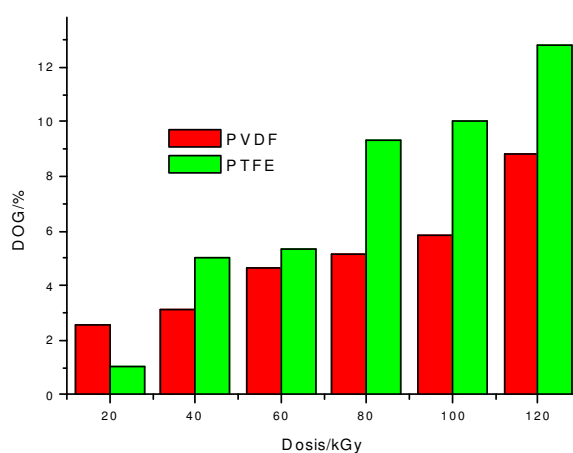


termination:



where P is the polymer substrate, P<sup>\*</sup> is the primary radical site formed on the substrate, PM<sup>\*</sup> is the initiated graft chain, M is the monomer unit, and PM<sup>\*</sup><sub>n</sub> and PM<sup>\*</sup><sub>m</sub> 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.

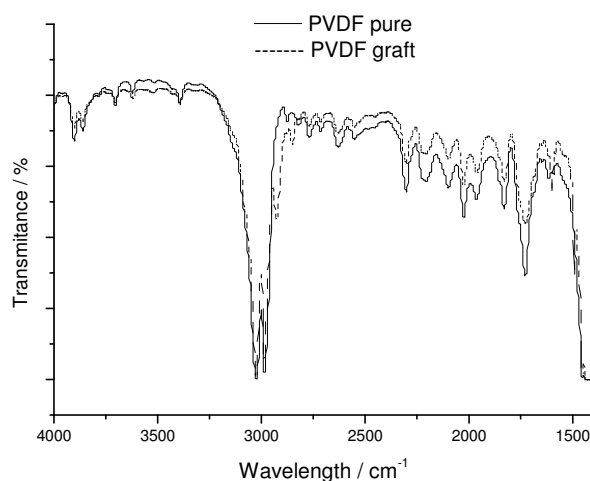
The films were weighted before and after the grafting process for DOG determination. The highest results were achieved after 21 days of simultaneous radiation and grafting process. As a result, we concentrated our studies and analysis in the effect of total dose on the grafting of styrene in toluene solutions after 21 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.



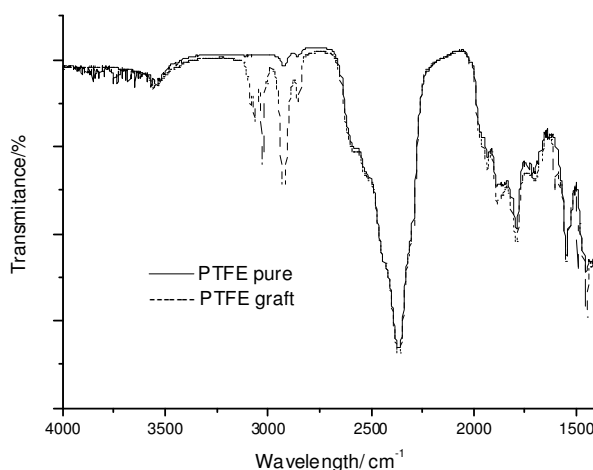
**Figure 1– Relation between degree of grafting, DOG (%) and irradiation dosis for PVDF and PTFE films.**

To confirm the grafting of styrene in the grafted PVDF and PTFE films, FTIR spectra was conducted. The characteristic peaks in the PVDF based polymer (Figure 2) are those near to 3000 cm<sup>-1</sup> representing C-H stretching vibration. In infrared spectra of the graft PVDF films new peaks appeared in the region 3080 - 3010 cm<sup>-1</sup> owing to aromatic C-H stretching vibrations; 2975 - 2840 cm<sup>-1</sup>, due to aliphatic C-H stretching vibration and 1601-1500 cm<sup>-1</sup>, attributed to aromatic C=C stretching vibrations [7]. In the FTIR spectra of the graft PTFE

films (Figure 3), new peaks appeared in the region 3100 to 3000  $\text{cm}^{-1}$ , owing to =C-H stretching vibration of the styrene groups. The bands at 2920  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  are asymmetric and symmetric stretching, respectively, that were attributed to the aliphatic  $\text{CH}_2$  group of the styrene graft. The band at 1600  $\text{cm}^{-1}$  is the skeletal C=C stretching vibration and 1490 and 1460  $\text{cm}^{-1}$  are the skeletal C=C in plane deformation of styrene graft.[8]



**Figure 2: FTIR Spectra of PVDF film pure and graft in the region 4000-1500  $\text{cm}^{-1}$  at 100 kGy dose (DOG = 5.9%).**



**Figure 3: FTIR Spectra of PTFE film pure and graft in the region 4000-1500  $\text{cm}^{-1}$  at 100 kGy dose (DOG = 10.0%).**

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 PVDF and PTFE 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. Radiation degradation always causes changes in most of the valuable properties of polymers. The thermal data were shown in tables 1 and 2 for PVDF and PTFE respectively.

**Table 1: Thermal data for PVDF films.**

<b>Dose</b>	<b>DOG</b>	<b>T<sub>onset</sub></b>	<b>T<sub>c</sub></b>	<b>T<sub>m</sub></b>
<b>20</b>	2.6	437.9	139.1	169.0
<b>40</b>	3.1	453.9	136.9	169.0
<b>60</b>	4.6	435.0	145.9	169.0
<b>80</b>	5.1	438.0	142.3	168.0
<b>100</b>	5.9	440.2	136.6	167.2
<b>120</b>	8.8	439.6	137.2	167.7
<b>pure</b>	-	436.9	139.1	170.1

Dose = irradiation dose/kGy; DOG = degree of grafting/%; T<sub>onset</sub> = Initial degradation temperature/°C; T<sub>m</sub> and T<sub>c</sub>= melting and crystallization temperatures/°C.

**Table 2: Thermal data for PTFE films.**

<b>Dose</b>	<b>DOG</b>	<b>T<sub>onset</sub></b>	<b>T<sub>c</sub></b>	<b>T<sub>m</sub></b>
<b>20</b>	2.6	553.0	301.3	327.2
<b>40</b>	3.1	560.4	301.1	328.8
<b>60</b>	4.6	553.4	303.5	326.8
<b>80</b>	5.1	545.8	297.7	328.2
<b>100</b>	5.9	548.7	300.3	326.9
<b>120</b>	8.8	548.1	301.1	326.8
<b>pure</b>	-	555.4	301.4	330.3

Dose = irradiation dose/kGy; DOG = degree of grafting/%; T<sub>onset</sub> = Initial degradation temperature/°C; T<sub>m</sub> and T<sub>c</sub>= melting and crystallization temperatures/°C.

According to T<sub>onset</sub> results, in this study, the grafting films of PVDF and PTFE are nearly from the original films. In Table 1, the original PVDF melting temperature (T<sub>m</sub>) was 170.1 °C and styrene side chain graft incorporation into PVDF films not caused significant change in T<sub>m</sub> values. For PTFE (table 2) the T<sub>m</sub> for ungraft film was 330.3 °C and the grafted films

was observed a little decrease in the values. The small changes in melting and crystallization temperatures ( $T_m$  and  $T_c$ ) in both irradiated films are functions of the dose of irradiation. In both films, the small variation in the  $T_m$  despite the increase in the degree of grafting suggests that the polystyrene grafts occurred only in the amorphous region, therefore the crystalline region was not affected or affected to only minor extension [2].

#### 4. CONCLUSIONS

Radiation inducing grafting of styrene onto PVDF and PTFE films was investigated using the simultaneous radiation method in presence of monomer. We have examined the influence of radiation dose 20 -120 kGy range by FTIR, TGA and DSC techniques. These techniques showed evidences regarding the styrene graft. Further studies will be performed to evaluate the behaviour of these films under sulfonation.

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