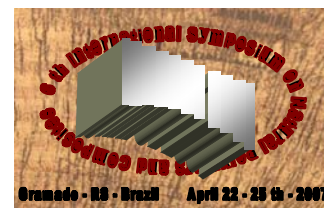




STUDY OF THE STYRENE GRAFTING ONTO PVDF AND PTFE FILMS



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Grafting of styrene onto polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE) was studied using styrene/toluene solutions. First, PTFE and PVDF films were prepared and the process was conducted by radiation-induced graft polymerization of styrene, by a Co^{60} source. Films of PTFE and PVDF were immersed in styrene/toluene at 1:4, 1:1 and 4:1 (vol/vol) concentration and then submitted to gamma radiation at 40 kGy dose. After irradiation, the samples were evaluated at the period of 21 days at room temperature in order to observe the behavior of grafting degree. Chemical changes in the PVDF and PTFE films after styrene grafting were monitored and the results were evaluated by FTIR, DSC, TGA. The degree of grafting (DOG) was determined gravimetrically. The structural changes showed that irradiated films exhibited the highest grafting degree at 1:1 concentration in both of films.

Introduction

There has been considerable interest in proton exchange membrane fuel cells (PEMFCs) 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[®] 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 solution and irradiated in the sequence.

The PEM have to attempt the requirements to maintain good separation and electrochemical capabilities. These include high ionic conductivity, defined swelling behaviour, high chemical resistance and mechanical integrity.

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.[1,2] The Scherer group intend to work on low-cost starting materials and offers the prospect of cost-competitive membranes for the polymer electrolyte fuel cell. [3]

Li et. al. have studied PTFE-g-PS (grafting polystyrene) and PTFE-g-AMS/STY (grafting α -methylstyrene/styrene) or PTFE-g-S/DVB (styrene/divinylbenzene) into radiation-crosslinked polytetrafluoroethylene (RX-PTFE) films and then sulfonated.[4-7]

Radiation-grafting with reactive styrene monomers in tetrafluoroethylene-co-hexafluoropropylene, PTFE/FEP polymer alloy have been examined by Asano et. al. using electron beam (EB) at room temperature.[8] Poly(vinylidene fluoride) (PVDF) based polymer membranes have also been prepared by Mokrini et. al. with blend styrene-(ethylene-butylene)-styrene block copolymer.[9] In addition, Kallio and a co-worker have studied different PVDF thick films by radiation grafting with styrene followed by sulfonation and compared to Nafion[®]. [10]

Among membrane properties, thermal stability is one of the most important characteristics, as it determines the operating temperature of the membrane in the electrochemical cell. Thermal stability of polystyrene grafted films prepared by radiation grafting onto poly(tetrafluoroethylene), PTFE [11-13], (tetrafluoroethylene-co-hexafluoropropylene), FEP [14], and polyvinylidene fluoride, PVDF [15,16], and poly(tetrafluoroethylene-co-perfluorovinyl ether) was studied using thermal gravimetric analysis (TGA) and

differential scanning calorimetry analysis (DSC) under nitrogen atmosphere.

In this work is used the simultaneous method, for PTFE and PVDF films consisting in the immersion on monomer solution and irradiation in the sequence, with variation of the monomer concentration. The graft and ungraft samples were characterized by TGA, DSC, FTIR and degree of grafting (DOG).

Experimental

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 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 1:4, 1:1 and 4:1 (v/v) concentrations and irradiated. In the sequence thermal treatment of the irradiated samples were made in vacuum oven for 8h, at 70 °C. After this procedure 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 in 8h. Irradiations were accomplished via Co⁶⁰ source (dose rate of 10 kGy h⁻¹) at 40 kGy dosis at room temperature in oxygen free atmosphere.

Following irradiation the samples were evaluated at room temperature for 21 days in order to observe the degree of grafting behavior. Mass 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 masses of the samples after and before grafting, respectively. All the degree of grafting (%) values at different experimental conditions correspond to the average value given by six samples for each case.

Instrumental analysis

The FTIR analyses were performed on Nexus 670 FT-IR Thermo Nicolet.

TGA technique was accomplished in a Mettler - Toledo TGA / SDTA 851 thermobalance, using inert atmosphere of N₂ from 25 to 750 °C at heating rate of 10 °C /min.

DSC curves were obtained in a Mettler-Toledo DSC 822, under nitrogen atmosphere, for PTFE from 0 to 400 °C at 20° C/min heating rate; keeping at 400 °C per 3 min; 400 to 0 °C at -50° C.min⁻¹ cooling rate; then kept at 0 °C per 3 min and reheated from 0 to 400 °C, at 10° C/min heating rate.

As for PVDF, the temperature ranged from -25 to 240°C at 10° C/min heating rate; then from 240 to -25 °C at 5 °C/min cooling rate; afterwards it was kept at -25 °C per 5 min and reheated from -25 to 300 °C at 10° C/min heating rate.

The overall degree of crystallinity of samples was calculated using the Equation (2).

$$X_c = (\Delta H_m / \Delta H_{m100}) \times 100 \quad (2)$$

where, ΔH_m is the heat of melting of PTFE or PVDF film and ΔH_{m100} is the enthalpy of the 100% crystalline. PTFE (92.9 J.g⁻¹ [8]) and PVDF (104.7 J.g⁻¹[9]) polymers.

Results and Discussion

The films were analyzed before and after the grafting process.

The relationship between degree of grafting and styrene monomer diluted in toluene at 1:4, 1:1 and 4:1 concentrations of styrene are shown in table 1.

Table 1: degree of grafting of PVDF and PTFE films at 1:4, 1:1 and 4:1 concentrations.

FILM	% STYRENE	DOG / %
PVDF	20 (1:4)	3,9
	50 (1:1)	13
	80 (4:1)	8,8
PTFE	20 (1:4)	5,8
	50 (1:1)	11
	80 (4:1)	6,6

The degree of grafting was found to be strongly dependent upon the concentration of styrene. Dilution of styrene at 1:1 concentration was found to enhance the degree of grafting in PVDF and PTFE films. This is due to the higher formation of free radicals in the grafting system, which subsequently leads to a higher amount of grafting. Since the monomer (styrene) is also being irradiated, significant homopolymer formation takes place in the grafting medium, which reduces the grafting yield to the large extent. This explains the DOG reduction of 13 to 8,8% in the PVDF films and 11 to 6,6% in the PTFE films.

The viscosity of the grafted layers controls the diffusion of the monomer to the grafting sites and that the solvent is basically used in grafting processes to induce swelling of the grafted layers, enhancing the degree of monomer accessibility to grafting sites[17,18]. The choice of solvent is one of the important factors in the radiation induced grafting processes. The better dissolution of the grafted polystyrene chains in the toluene/styrene solution enhances the diffusion of monomer through the grafted into film matrix and, as a result, leads to an increasing in the grafting yield.

In order to confirm the grafting of styrene in the grafted PVDF and PTFE films, FTIR spectra was conducted. The characteristic peaks in the PVDF base

polymer (Figure 1) are those near to 3000 cm^{-1} representing C-H stretching vibration. In infrared spectra of the graft PVDF films new peaks appeared in the region $3080 - 3010\text{ cm}^{-1}$ owing to aromatic C-H stretching vibrations; $2975 - 2840\text{ cm}^{-1}$, due to aliphatic C-H stretching vibration and $1601-1500\text{ cm}^{-1}$, attributed to aromatic C=C stretching vibrations [19]. In the FTIR spectra of the graft PTFE 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 band at 2920 cm^{-1} and 2850 cm^{-1} are the asymmetric and symmetric stretching, respectively, 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 e 1460 cm^{-1} are the skeletal C=C in plane deformation of styrene graft.[5]

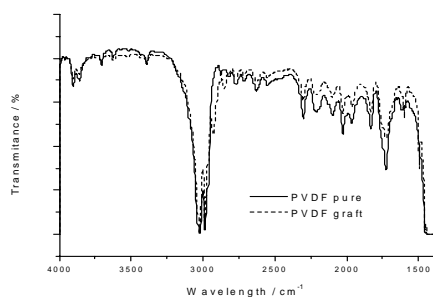


Figure 1: Infrared transmission spectra of PVDF in the region $4000-1500\text{ cm}^{-1}$, pure (unirradiated) and grafted films at 40 kGy dose.

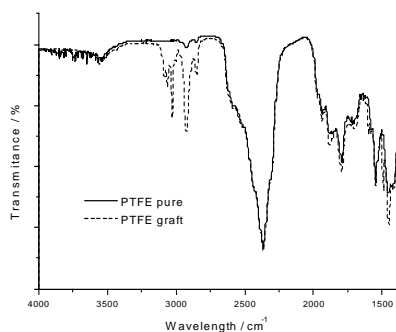


Figure 2: Infrared transmission spectra of PTFE in the region $4000-1500\text{ cm}^{-1}$, pure (unirradiated) and grafted films at 40 kGy dose.

It is known that gamma radiation onto polymeric materials produces free radicals, which can react during several ways modifying the morphology of the macropolymeric 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 to be introduced in the polymer matrix with reactive sites formed by the radiation process.

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.

Figures 3 and 4 shows the TGA curves of PVDF and PTFE films pure and grafted at 1:4, 1:1 and 4:1 concentrations of styrene respectively.

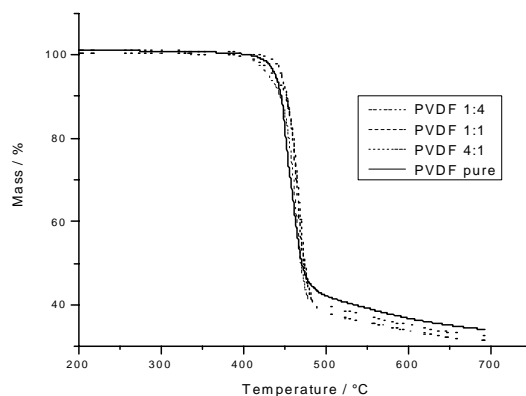


Figure 3: TGA curves for the thermal decomposition of PVDF films pure and grafted at 1:4, 1:1 and 4:1 concentrations of styrene under nitrogen atmosphere.

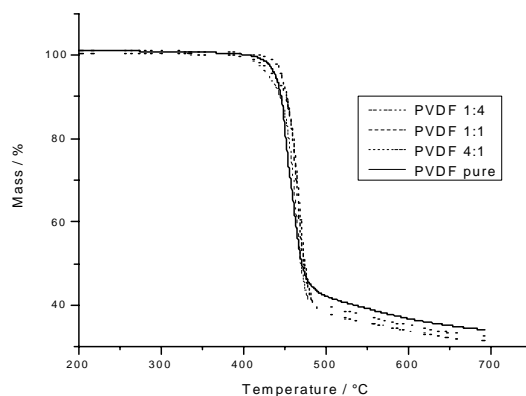


Figure 4: TGA curves for the thermal decomposition of PTFE films pure and grafted at 1:4, 1:1 and 4:1 concentrations of styrene under nitrogen atmosphere.

The T_{onset} and T_{endset} were shown in Tables 2 and 3 for PVDF and PTFE respectively.

Table 2: Experimental temperatures by TGA for PVDF films.

sample	T_{onset}	T_{endset}
PVDF pure	436.9	460.0
PVDF 1:4	448.8	474.1
PVDF 1:1	453.9	478.3
PVDF 4:1	451.0	481.3

T_{onset} =Initial degradation temperature; T_{endset} =Final degradation temperature / °C.

In TGA results, the initial degradation temperature (T_{onset}) for the non grafted PVDF film, was 436.9 °C and after grafting the values displaced to T_{onset} were

448.8; 453.9 and 451.0 °C, at 1:4, 1:1 and 4:1 concentrations of styrene respectively.

Table 3: Experimental temperatures by TGA for PTFE films.

sample	T _{onset}	T _{endset}
PTFE pure	555.4	594.9
PTFE 1:4	560.4	601.8
PTFE 1:1	562.7	603.7
PTFE 4:1	562.5	602.2

T_{onset}=Initial degradation temperature; T_{endset}=Final degradation temperature / °C.

In PTFE films, T_{onset} for the non grafted PTFE film was 555.4 °C and grafted films show chiefly two separated steps of degradation pattern in TGA: the first one presents the T_{onset} of 374.4, 384.3 and 384.0 °C; and the second one 560.4, 562.7 and 562.5 °C at 1:4, 1:1 and 4:1 concentrations respectively. The first degradation step can be attributed to the degradation of styrene graft and the second can be attributed to film matrix degradation.[5]

According to T_{onset} results the grafting films of PVDF and PTFE are more stable than the original films.

In table 4, the original PVDF melting temperature (T_m) was 170.1 °C and styrene side chain graft incorporation into PVDF films not caused change in T_m.

The original PTFE has T_m at 330.3 °C and styrene side chain graft incorporation into PTFE film has caused no significant change in T_m 327.0, 327.8 and 328.9 °C at 1:4, 1:1 and 4:1 concentrations respectively in agreement with the literature.[5]

Table 4 shows the effect of grafting on the heat of melting and degree of crystallinity of PTFE and PVDF films. The short changes in melting and crystallization temperatures (T_m and T_c) in both irradiated films are functions of the concentration of styrene. The degree of crystallinity (X_c) were found to decrease with the increase of DOG, in agreement with the literature [11,20]. In fact the graft produces irregularities that difficults the crystallization.

Table 4: The effect of grafting on the heat of melting and degree of crystallinity of PTFE and PVDF films.

sample	T _c	T _m	ΔH _m	X _c
PVDF pure	139.1	170.1	41.5	39.6
PVDF 1:4	138.1	169.0	43.6	42,9
PVDF 1:1	136.9	169.0	37.4	40.3
PVDF 4:1	138.1	170.1	39.2	39.2
PTFE pure	301.4	330.3	19.6	21.1
PTFE 1:4	299.5	327.0	27,3	44.2
PTFE 1:1	299.4	327.8	26.0	33.8

PTFE 4:1	295.6	328.9	29,9	36.2
T _m and T _c =	melting	and	crystallization	temperatures/°C;
X _c	= degree of crystallinity/%.			

The melting enthalpy (ΔH_m) and the degree of crystallinity (X_c) of PVDF films show changes with the styrene concentration used, whereas those of PTFE films, ΔH_m show no significant changes but the X_c decrease with the DOG.

In both films, the little variation in the T_m despite the increase in the degree of grafting suggest a tendency of the formed polystyrene grafts not to penetrate the crystalline structure. [2]

Conclusions

The overall results of this work suggest that the structural changes took place in PVDF and PTFE films during the preparation of this samples have a strong impact on their various properties.

To conclude, gamma radiation is therefore a satisfactory route to grafting of styrene in PVDF and PTFE films. Further studies will be performed to evaluate the behavior of these films under sulfonation.

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