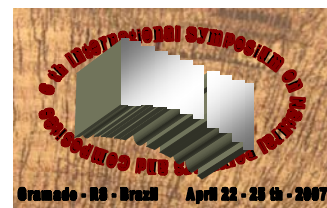




GRAFTING OF STYRENE ONTO FLUOROPOLYMERS FILMS VIA GAMMA RADIATION



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Grafting of styrene onto polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE) was studied using two different solvents. 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 1:4 or styrene/methanol 1:4 and then submitted to gamma radiation at 40 and 80 kGy doses. After irradiation, the samples were evaluated at time 0, 7, 14, 21 and 28 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 and also by SEM. The degree of grafting (DOG) was determined gravimetrically. The structural changes showed that irradiated PTFE films exhibited for the most samples the highest grafting degree to styrene/toluene whereas the irradiated PVDF films exhibited the highest grafting degree to styrene/methanol for both of dosis. Surface analysis of the grafted films by SEM technique has presented a strong effect from the solvents.

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 Nafion[®] is very expensive and much effort is being focused on the development of lower 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 to be grafted and after that promote polymer sulfonation. Generally, there are two methods for the irradiation induced grafting. One is pre-irradiation method, that is the fluorinated base polymer films were irradiated by gamma rays and then styrene monomer is added and grafted. The other is simultaneous irradiation method, that is, the fluorinated base polymer films are soaked in the styrene solution and then irradiated together.

The PEM have to meet a combination of requirements in order 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. 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.[1-4]

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.[5] Poly(vinylidene fluoride) (PVDF) based polymer membranes have also been prepared by Mokriani et. al. with blend styrene-(ethylene-butylene)-styrene block copolymer.[6] In addition, Kallio and a co-worker studied different PVDF thick films by radiation grafting with styrene followed by sulfonation and compared to Nafion[®]. [7]

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.[8,9]

Among membrane properties, thermal stability is one of the most important, as it determines the operating temperature of the membrane electrochemical cell. Thermal stability of polystyrene grafted films prepared by radiation grafting onto poly(tetrafluoroethylene), PTFE [10-12], (tetrafluoroethylene-co-hexafluoropropylene), FEP [13], and polyvinylidene fluoride, PVDF [14,15], and poly(tetrafluoroethylene-co-perfluorovinyl ether) was studied using thermal

gravimetric analysis (TGA) and differential scanning calorimeter analysis (DSC) under nitrogen atmosphere. Scanning electron microscope (SEM) studies can yield information on the morphology of graft copolymer systems.[16]

In this work is used the simultaneous method, which means that the PTFE and PVDF films are immersed in the monomer then exposed to ionizing radiation. Both the polymer and the monomer are exposed to radiation. The graft and ungraft samples were characterized by TGA, DSC, FTIR, SEM and degree of grafting (DOG).

Experimental

Prepared films

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. It was pressed between two finely polished inox steel plates and through this process, films of PVDF of 0.12mm have been made. The styrene was supplied by Maxepoxi Ind. Com. and toluene and methanol from Merck.

Films of PTFE and PVDF were immersed in styrene/toluene and styrene/methanol 1:4 and irradiated. 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 in 8h. Irradiations were accomplished via Co⁶⁰ source (dose rate of 10 kGy h⁻¹) at 40 and 80 kGy doses at room temperature at oxygen free atmosphere.

Following irradiation the samples were evaluated at room temperature for 0, 7, 14, 21 and 28 days in order to observe the degree of grafting behavior. Mass increase 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.

Instrumental analysis

The FTIR analyses were performed on Nexus 670 FT-IR Thermo Nicolet. The SEM images were run in a Phillips XL 30 Microscope, providing magnifications up to 40,000 times, with samples analyzed being covered with gold in a Sputter Coater BAL-TEC SCD 050. The images were amplified to 10,000X.

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

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

As for PVDF, the temperature ranged from -25 to 240°C at 10° C/minute heating rate; then from 240 to -25 °C at 5 °C/minute heating rate; afterwards it was

kept at -25 °C per 5 minutes and reheated from -25 to 300 °C at heating rate of 10° C/minute.

The overall degree of crystallinity of samples was calculated using 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 heat of melting 100% crystalline PTFE or PVDF polymer which equals 92.9 J.g⁻¹ [8] for PTFE and 104.7 J.g⁻¹ [9] for PVDF.

Results and Discussion

The films were analyzed before and after the grafting process. The highest results were achieved after 21 days of simultaneous radiation and grafting process. Because of this, we concentrated our study and analysis in the effect of solvents on the grafting of styrene in solutions prepared using the methanol or toluene as solvent.

The DOG in the grafted films has varied from 1.9 to 2.1% in methanol and 6.1 to 11.6% in toluene at 40 and 80 kGy respectively. As far as PTFE grafted films are concerned, the DOG varied 6.7% to 8.8% in methanol and 3.9 to 4.6% in toluene for PVDF films at 40 and 80 kGy respectively.

The degree of grafting was found to be strongly dependent upon the type of solvent. Dilution of styrene with methanol was found to enhance the degree of grafting in PVDF films when compared with toluene dilution. In the other hand, dilution of styrene with toluene was found to enhance the degree of grafting in PTFE films when compared with methanol dilution. Results were observed in PFA films like in PTFE for Cardona et al. and Nasef et al.[17,18] 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]

The choice of solvent is one of the main factors in the radiation induced grafting processes. Methanol, which has a higher chain transfer constant than toluene, caused faster termination of the graft growing polystyrene chains, leading to lower degree of grafting in methanol. It also induces a reduction in the monomer diffusion during irradiation due to the increase in the viscosity of grafting solution enhanced by the insolubility of the polystyrene homopolymer in methanol.

The better dissolution of the grafted polystyrene chains in the toluene/styrene solution enhances the diffusion of monomer through the grafted into PTFE matrix and, as a result, leads to an increasing in the grafting yield for the PTFE films. The results observed to graft in PVDF films suggested the importance of the structural reactivity of the polymer matrix. So, PVDF showed higher graft level than PTFE, the grafting yield results in increase in both of solvents, except for the sample in toluene at 80kGy dosis, this fact is not clear and suggested that polymer matrix viscosity other than polymer chain transfer constants as well as the solvent are important parameters.

The degree of grafting increases with the increase in the irradiation dose (40 and 80 kGy). This is due to the higher formation of free radicals in the grafting system, which subsequently leads to a higher amount of grafting.

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 $3100\text{ to }3000\text{ cm}^{-1}$, because of =C-H stretching vibration of the styrene groups. The band at 2920 cm^{-1} is the asymmetric stretching and 2850 cm^{-1} (symmetric stretching) were credited to the aliphatic CH_2 group of the styrene graft. The band at 1600 cm^{-1} is the skeletal C=C stretching vibration and $1490\text{ e }1460\text{ cm}^{-1}$ are the skeletal C=C in plane deformation of styrene graft.[4]

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.

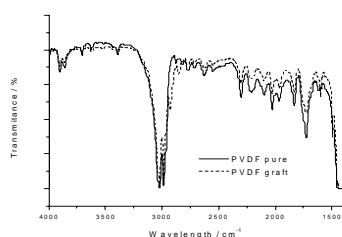


Figure 1: Infrared transmission spectra of PVDF in the region $4000-1500\text{ cm}^{-1}$, pure (unirradiated) and grafted films at 80 kGy dose.

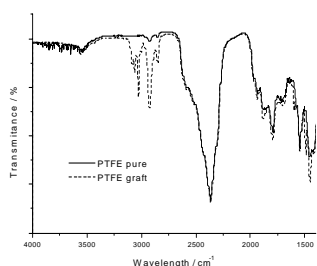


Figure 2: Infrared transmission spectra of PTFE in the region $4000-1500\text{ cm}^{-1}$, pure (unirradiated) and grafted films at 80 kGy dose.

The difference $T_{\text{endset}} - T_{\text{onset}}$, as shown in Tables 1 and 2 for PVDF and PTFE respectively, is called reaction interval. How smaller this interval is more stable is the material under thermal degradation; however this was not observed in these films.

Table 1: Experimental temperatures by TGA for PVDF films.

Film	Dose	T_{onset}	T_{endset}	$T_{\text{end}} - T_{\text{on}}$
PVDF/pure	-	436.9	460.0	23
PVDF/meth	40	443.7	477.6	34
PVDF/meth	80	448.1	475.1	27
PVDF/tol	40	449.4	474.2	25
PVDF/tol	80	436.8	464.8	28

T_{onset} =Initial degradation temperature; T_{endset} =Final degradation temperature; Dose/kGy; T_{onset} , T_{endset} and $T_{\text{end}} - T_{\text{on}}$ /°C; meth = in methanol; tol = in toluene

On the other hand, as for TGA results, the initial degradation temperature (T_{onset}) for the non grafted PVDF film, was $436.9\text{ }^{\circ}\text{C}$ and after grafting the values displaced to T_{onset} were 443.7°C and 448.1°C , at 40 and 80 kGy respectively, which indicated a modification to more stable films in the initiation of the degradation.

Table 2: Experimental temperatures by TGA for PTFE films.

Film	Dose	T_{onset}	T_{endset}	$T_{\text{end}} - T_{\text{on}}$
PTFE/pure	-	555.4	594.9	39
PTFE/meth	40	561.9	602.5	41
PTFE/meth	80	561.4	605.7	44
PTFE/tol	40	559.7	604.9	45
PTFE/tol	80	554.8	597.2	42

T_{onset} =Initial degradation temperature; T_{endset} =Final degradation temperature; Dose/kGy; T_{onset} , T_{endset} and $T_{\text{end}} - T_{\text{on}}$ /°C; meth = in methanol; tol = in toluene

The original PVDF melting temperature (T_m) was $172.3\text{ }^{\circ}\text{C}$ and styrene side chain graft incorporation into PVDF films caused decrease in T_m at 161.1°C to 40 kGy and 159.6°C to 80 kGy in agreement with the literature [10]. In PTFE films, T_{onset} for the non grafted PTFE film was $555.4\text{ }^{\circ}\text{C}$ and grafted films show chiefly two separated steps of degradation pattern in TGA: the first one presents the T_{onset} from $561.9\text{ }^{\circ}\text{C}$ to 561.4°C ; and the second one from $559.7\text{ }^{\circ}\text{C}$ to $554.8\text{ }^{\circ}\text{C}$ at 40 and 80 kGy respectively. The first degradation step can be attributed to the degradation of styrene graft and the second can be attributed to film matrix degradation.[4] Finally, the original PTFE has T_m at $322.9\text{ }^{\circ}\text{C}$ and styrene side chain graft incorporation into PTFE film has caused no significant change in T_m ($323.0\text{ }^{\circ}\text{C}$ for 40 kGy and $321.0\text{ }^{\circ}\text{C}$ for 80 kGy).[9]

Table 3 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 dose and reflect the disorder in the chemical structure caused by the competition between crosslinking and chain scission.

Table 3: 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
PTFEpure	301.4	330.3	19.6	21.1
PTFEmeth 40kGy	295.3	331.2	30.4	32.7
PTFEmeth 80 kGy	290.3	332.7	39.8	42.9
PTFEtol 40 kGy	299.5	326.9	27.3	29.4
PTFEtol 80 kGy	293.1	328.7	29.7	32.1
PVDFpure	139.1	170.1	41.5	39.6
PVDFmeth 40 kGy	136.9	166.8	40.0	38.2
PVDFmeth 80 kGy	136.4	167.5	36.6	35.0
PVDFtol 40 kGy	138.1	168.9	43.6	41.7
PVDFtol 80 kGy	137.5	167.2	39.6	37.8

T_m and T_c = melting and crystallization temperatures/ $^{\circ}$ C; X_c = degree of crystallinity/%; meth = in methanol; tol = in toluene.

The heat of melting (ΔH_m) and the degree of crystallinity (X_c) of PVDF films show no significant changes with the dose and solvent used, whereas those of PTFE films increase with the dose increase in both solvents. This indicated the transition to a more ordered material with crystallization induced by irradiation while to graft.

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. [9]

The morphological changes in the films with the variation of solvent were also monitored in surface (figure 3). The images were amplified to 10,000X. In the figures 3c to 3f, the surfaces are almost totally covered with the polystyrene layer if compared with figures 3a (PTFE pure) and 3b (PVDF pure).

Surface analysis of the grafted films by SEM technique have shown a strong effect from the solvents. The PVDF-g-PS in styrene/methanol films (figure 3c) showed the higher DOG but the surface showed small cavities and discontinuities. The surface of PTFE-g-PS in styrene/toluene (figure 3f) presents a more homogeneous surface. The behavior of polystyrene layer in presence of methanol and toluene are also evident, in methanol is observed cavities and holes

(figures 3c, e,) while in toluene, the surface of films is more homogeneous (figures 3d, f,) for both of films.

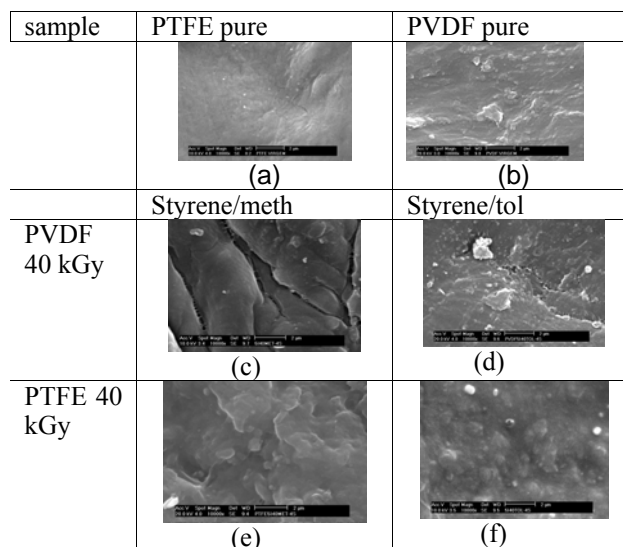


Figure 3: SEM images of a surface in: PTFE (a) and PVDF (b) pure; PVDF-g-PS (c) and PTFE-g-PS (e) in styrene/methanol; PVDF-g-PS (d) and PTFE-g-PS (f) in styrene/toluene solutions.

Conclusions

Radiation inducing grafting of styrene onto PVDF and PTFE films was investigated using the simultaneous method of irradiation in presence of monomer. We have examined the influence of radiation dose (40 and 80 kGy) in the period of 0 to 28 days after radiation, by FTIR, TGA, DSC techniques. The surface and morphology of non grafted and grafted films were analyzed by SEM. The DOG was also calculated. Eventually all the techniques showed changes in the polymers.

The structural changes were observed by FTIR due to the appearance of new peaks characteristics of styrene grafting. The irradiated PTFE films exhibited a much higher grafting degree at toluene solvent compared to the PVDF films, at methanol solvent.

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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