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# Radiation-induced grafting of styrene into poly(vinylidene fluoride) film by simultaneous method with two different solvents

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## ABSTRACT

Radiation-induced grafting of styrene into poly(vinylidene fluoride) (PVDF) films with 0.125 mm thickness at doses of 1 and 2.5 kGy in the presence of a styrene/*N,N*-dimethylformamide (DMF) solution (1:1, v/v) and at doses of 20, 40 and 80 kGy in presence of a styrene/toluene solution (1:1, v/v) at dose rate of 5 kGy h<sup>-1</sup> was carried out by the simultaneous method under nitrogen atmosphere and room temperature, using gamma rays from a Co-60. The films were characterized before and after modification by calculated grafting yield (GY %), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG). GY results shows that grafting increases with dose, and the grafting of styrene was confirm by FT-IR due to the new characteristic peaks and by the TG and DSC attributed to changes in thermal behavior of the grafted material. Results showed that the system allows the controlled grafting of styrene into PVDF using gamma rays at doses as low as 1 kGy in DMF.

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## 1. Introduction

Grafting of monomers into polymers is frequently studied as polymer modifying process, usually as a first step and followed by some chemical reaction aiming certain properties for specific applications. Radiation-induced grafting copolymerization is a well established knowledge about producing grafted polymers. Fluoropolymers are studied as matrix for grafting due to their good thermal, chemical and mechanical properties and modified fluoropolymers are frequently used as ion exchange membranes for fuel cells, polymeric actuators, ultrafiltration membrane, waste treatment, in biomedical applications and they can be produced by different ways (Charlesby, 1991; Bhattacharya and Misra, 2004; Clochard et al., 2010; Gubler et al., 2005; Youcef et al., 2008).

Several methods are available to produce radiation induced grafted polymers. The simultaneous method consists of irradiating the polymeric matrix immersed in monomer or monomer solution at once, where graft reaction takes place almost instantaneously (Bhattacharya and Misra, 2004).

This paper presents results of radiation-induced grafting of styrene into poly(vinylidene fluoride) (PVDF) films with different doses with two different solvents, i.e., toluene and *N,N*-dimethylformamide (DMF).

Prior to irradiation, swelling behavior of the film on the solvents and monomer solutions was determined, and based on these results and on the differences between the solvents' behavior under irradiation (Sagert et al., 1991; Hayashi et al., 1971) the use of smaller

doses was proposed when DMF is used as solvent, since it swells the PVDF matrix much better than toluene and it can act as chain transfer agent.

## 2. Experimental

### 2.1. Membrane preparation

PVDF films with 0.125 mm thickness (purchased from Goodfellow) were immersed in styrene/toluene or styrene/*N,N*-dimethylformamide (DMF) solutions (1:1 (v/v)) in glass bottles and nitrogen gas was bubbled to ensure an inert atmosphere. The bottles were sealed and irradiated at room temperature at 1 and 2.5 kGy when DMF was used as a solvent and 20, 40 and 80 kGy with toluene as a solvent, by the simultaneous method at dose rate of 5 kGy h<sup>-1</sup> with gamma rays from a Co-60 source. After irradiation, washing overnight with toluene in Soxhlet system was made to remove solvent, un-reacted monomer and homopolymer. Films were dried in vacuum oven to eliminate residual solvents at 70 °C, until constant mass and characterized as described below. All products were used as received, without further purification.

### 2.2. Characterizations

Grafting yield (GY) was evaluated gravimetrically according to the Eq. (1) (Nasef, 2001):

$$GY(\%) = [(W_g - W_o) / W_o] \times 100 \quad (1)$$

where  $W_g$  and  $W_o$  are the weight of the samples after and before grafting, respectively.

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All GY values correspond to the average value given by nine samples. Infrared spectroscopy was performed at Thermo Nicolet 6700 by the direct method using ATR. Thermogravimetric measurement (TG/DTG) was recorded with a Mettler-Toledo TGA/SDTA 851 thermobalance in nitrogen atmosphere, from 25 up to 700 °C at a heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) was carried out in a 822 Mettler-Toledo under nitrogen atmosphere at a heating rate of 10 °C min<sup>-1</sup> in the temperature range of 30–250 °C, isotherm in 250 °C for 5 minutes, from 250 to –50 °C and a second heat from –50 to 250 °C. SEM images were obtained in a Phillips XL 30 microscope.

Swelling was determined by weighing samples after immersion in solvents without monomer and in styrene/toluene or styrene/DMF solutions at room temperature for up to 24 h (1440 min.). The liquid on the surface of wet films was mopped quickly with absorbent paper and mass increase attributed to solvents or solutions was calculated by Eq. (2), based on water uptake (Gubler et al., 2005):

$$S(\%) = [(w_s - w_o) / w_o] \times 100 \quad (2)$$

where  $w_o$  and  $w_s$  are the dry and swollen weight of used samples, respectively.

**Table 1**  
GY results for styrene into PVDF in different doses with toluene and DMF as solvents.

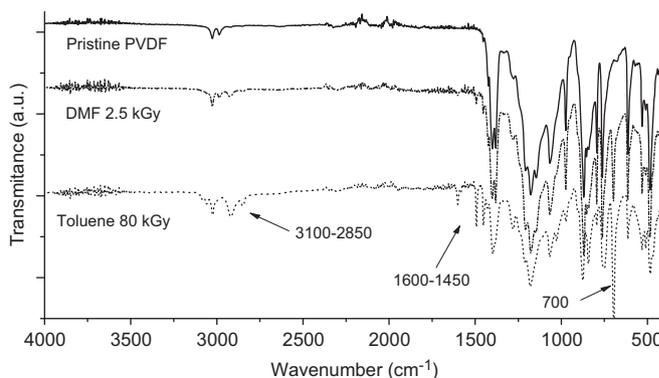
Dose (kGy)	GY (%)
<i>Toluene</i>	
20	2.4
40	3.8
80	4.1
<i>DMF</i>	
1	12.5
2.5	27.2

### 3. Results and discussion

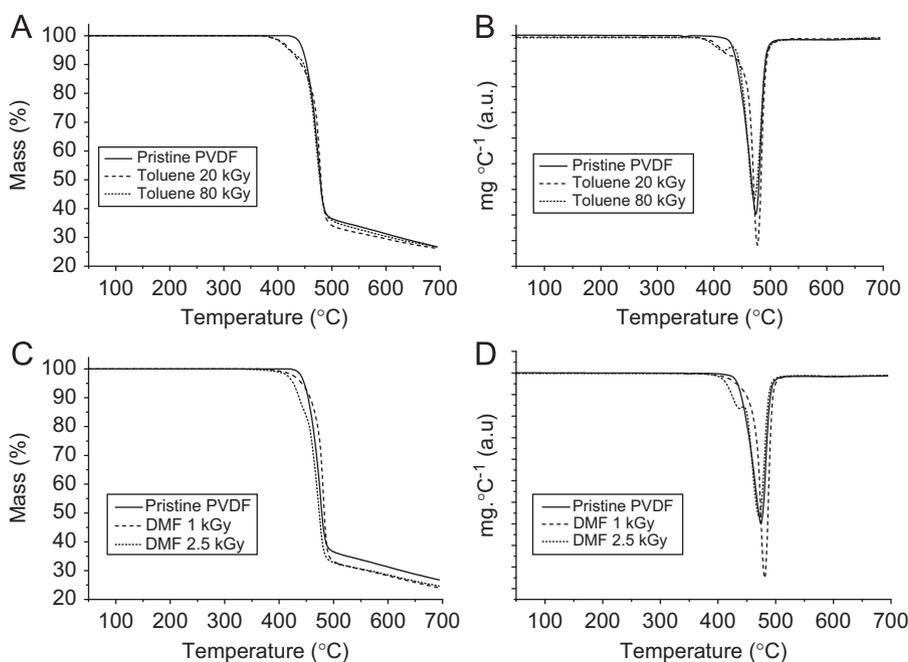
It was observed that DMF solution swells the matrix about 10 times compared to toluene solution. Based on that, one can say that the styrene/toluene solution rests only on the surface during the irradiation and grafting reaction, hindering the monomer penetration. However, DMF allows homogeneous penetration of the monomer through the polymer and with monomer available in the inner layers; it can react immediately with radicals formed on the bulk matrix, allowing greater grafting yields.

The relationship between GY and the dose is shown in Table 1 for the two styrene solutions. With toluene as solvent the results are very close to that obtained in previous work at similar conditions (Geraldés et al., 2008). GY results when DMF was used are much greater than that in toluene. It leads to conclude that DMF allows to greater grafting even with smaller doses. In both the cases, GY was found to be dose dependent. This behavior can be understood based on the fact that the higher dose leads to more radical generation in the grafting system.

As one can see, when DMF is used as solvent, GY increases greatly with the increase in dose; however, the doses used are much smaller than those commonly used with gamma rays or electron beam



**Fig. 1.** FTIR spectra for pristine PVDF and grafted in toluene solution with 80 kGy and in DMF solution with 2.5 kGy.



**Fig. 2.** TG and DTG of grafted PVDF in toluene (A and B) and DMF solutions (C and D), respectively.

(Nasef, 2001; Gursel et al., 2008). As an example, with the dose of 2.5 kGy it was possible to achieve GY values near to the referred as the optimum for fuel cell application, i.e., 30% (Youcef, et al., 2008).

IR spectra were conducted and confirmed the grafting of styrene in the grafted PVDF films (Fig. 1). The new peaks in the region 3100–3000  $\text{cm}^{-1}$  owing to =C–H stretching vibration of the styrene groups, the bands at 2920  $\text{cm}^{-1}$  and 2850  $\text{cm}^{-1}$  attributed to the asymmetric and symmetric stretching, respectively, of aliphatic  $\text{CH}_2$  group of the styrene graft. The band at 1600  $\text{cm}^{-1}$  is the skeletal C=C stretching vibration; 1490 and 1460  $\text{cm}^{-1}$  are the skeletal C=C in plane deformation of styrene; the C–H out of plane bending overtone and combination bands was in the region 1660–2000  $\text{cm}^{-1}$  and the band at 690–700  $\text{cm}^{-1}$  is the styrene ring out of plane deformation (Geraldies et al., 2008; Vien et al., 1991).

Thermal stability of the PVDF films was determined by TG/DTG (Fig. 2). The pristine PVDF has only one sharp weight loss, ascribed to the decomposition of polymer main chain around 475 °C, Fig. 2A. For the grafted PVDF, as clearly observed at the DTG curve Fig. 2B, there are two degradation steps, the first attributed to the grafted styrene degradation between 375 and 440 °C and the second to the PVDF matrix, between 440 and 475 °C. PVDF grafted in DMF solution, the step associated to the grafted styrene is intensified, Fig. 2C and D. By the initial degradation temperature it was observed that the polymeric matrix suffered no higher degradation.

Fig. 3 shows the DSC curves for pristine and grafted PVDF samples. One small endothermic region around 70–90 °C can be seen for the samples irradiated with DMF solution, event not well defined in samples irradiated in toluene solutions. This is attributed to the formation of small diffuse polystyrene regions through the matrix, once the polystyrene has glass transition temperature in that region (Pu, 1999). The melting temperature for the pristine PVDF is 168.9 °C and a very small decrease in the  $T_m$  is verified, in some cases, when the GY values are increased.  $T_m$  in toluene 40 kGy was observed at 167.5 °C; in 80 kGy at 166.4 °C while in DMF 2.5 kGy was 167.0 °C. This behavior confirms that crystalline region was not affected or affected in minor extension because the grafted polystyrene occurs only or mainly in the amorphous region (Gupta and Scherer, 1994).

Fig. 4 shows surface SEM images of the pristine (a) and grafted PVDF. It suggests that the grafted polystyrene is deposited mainly in the surface of the PVDF when toluene is used as a solvent, forming a new layer (Fig. 4b–d). As toluene is not a good solvent for PVDF, the styrene has no access to the radicals formed in the inner layers of the PVDF matrix and the grafting reaction takes place on the surface. It may be the reason for the small degrees of grafting even for a high dose and for the small change in thermal properties of the PVDF.

Otherwise, SEM images suggest that the graft of styrene in DMF solutions (Fig. 4e and f) forms homogeneously through the matrix. Samples grafted in styrene/DMF solutions show surface morphologies very similar to the pristine PVDF, even with

grafting yield between 12% and 27%, as opposed to less than 4.5% using toluene under high irradiation doses.

It can be explained by the solubility of the matrix in DMF, which allows the styrene to penetrate to the inner layers, achieving free radicals created in the bulk. Toluene allows the styrene to achieve just the radicals near the surface. Properties related to the solvents may interfere in the grafting too. One of these properties may be the solvent radiolysis, since the toluene produces less reactive radicals, as hydrogen and methyl groups and DMF may produce more reactive byproducts containing oxygen and nitrogen, i.e., radiolysis byproducts take different routes, interacting by different ways with the polymer, the monomer and the solvent itself (Sagert et al., 1991; Hayashi et al., 1971), resulting in different amounts of radicals in the system.

Another factor that deserves attention is the chain transfer constants for the monomer and solvents. These constant decrease in the order DMF > styrene > toluene (Harayma et al., 2003; Kim et al., 2010; Sugihara et al., 2011; Toohey and Weale, 1962) and we can deduce that the grafted chains formed in DMF solutions are shorter than those in toluene solutions but more numerous. Toluene probably leads to the formation of long chains but in small numbers.

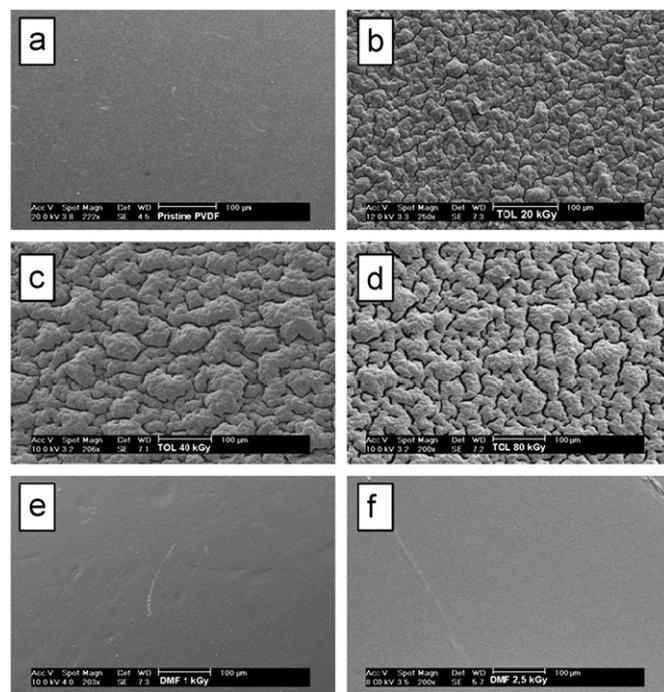


Fig. 4. SEM images of pristine PVDF (a) and grafted in toluene solution at 20 kGy (b), 40 kGy (c) and 80 kGy (d) and in DMF solution at 1 kGy (e) and 2.5 kGy.

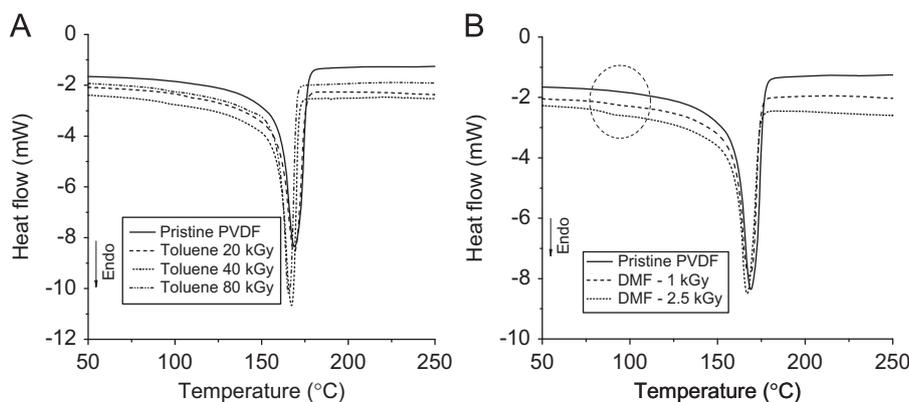


Fig. 3. DSC curves for grafted PVDF in toluene (A) and DMF solutions (B).

#### 4. Conclusions

Grafting takes place mainly on the surface and in small amounts when toluene is used as a solvent for styrene. When DMF is used, it is possible to achieve higher degrees of grafting even using small doses of 1 and 2.5 kGy, leading to greater and homogeneous distribution of grafted chains through the matrix (as SEM shown). This difference may be attributed to the PVDF swelling properties in solutions, the radiolysis byproducts during solvent irradiation and the chain transfer constants for the monomer and solvents, pointing out the importance of solvent properties and behaviors under irradiation on the grafting results. Thermal analysis showed differences in thermal behavior of grafted samples when DMF was used as solvent rather than toluene, leading to conclude that styrene, in DMF solution, penetrates in the inner layers of the polymeric matrix and forms small diffuse polystyrene regions as shown by the polystyrene glass transition, not visible in samples irradiated in toluene solution.

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