

## SOLVENT INFLUENCE DURING RADIATION INDUCED GRAFTING OF STYRENE IN PVDF

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### ABSTRACT

Radiation-induced grafting was studied to produce styrene grafted poly(vinylidene fluoride) (PVDF) membranes. PVDF films with 0.125 mm thickness were irradiated at doses between 5 and 20 kGy in the presence of styrene/N,N-dimethylformamide (DMF), styrene/acetone or styrene/toluene solutions (1:1, v/v) at dose rate of 5 kGy h<sup>-1</sup> by simultaneous method, using gamma rays from a Co-60, under nitrogen atmosphere and at room temperature. The films were characterized before and after modification by grafting yield (GY %), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM and EDS), differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG). GY results shows that grafting increases with dose and toluene hinders the grafting, leading to a small GY comparing to DMF and acetone. It was possible to confirm the grafting of styrene by FT-IR due to the new characteristics peaks and by the TG and DSC due to changes in thermal behavior of the grafted material. SEM and EDS show surface and cross-section distribution of the grafting, which takes place on the surface and heterogeneously with toluene as solvent and homogeneously and penetrating into the inner layers of the matrix using DMF and acetone as solvent.

### 1. INTRODUCTION

Irradiation polymer processing or modification is a well-established way to modify some properties of polymers or to create new material, due to the irradiation effects on polymers, i.e. by chain scission, crosslink or grafting [1, 2]. Among different methods of modifying polymers, radiation-induced graft copolymerization is a well-established knowledge which dating back almost 5 decades [1]. Fluoropolymers are studied due to their excellent chemical and thermo-mechanical properties [2]. Modified fluoropolymers may be applied in ion exchange membranes, polymeric actuators, filtration membranes, waste treatment and biomedical applications [2,3]. In all these cases, it is important to know and to control the morphology of the obtained polymer, in order to obtain useful materials [3,4,6]. The advantage of the Radiation-induced graft copolymerization technique is that during the ionization process, the radicals created can react with the monomers and start the copolymerization reaction without chemical initiators or catalysts [5]. Several methods are available to produce radiation induced grafted polymers [1]. One of these is known as simultaneous method, consisting in the irradiation of polymer matrix immersed in monomer or monomer solution, but homopolymer may be formed and must to be removed [2,7]. It is known that Poly(vinylidene fluoride) (PVDF) presents negligible damages on its properties when irradiated with doses up to 100 kGy under inert atmosphere, but the presence of

solvents may change its behavior [1] and the solvent can have an important rule on the grafting process [6]. This paper aims to present results of radiation-induced grafting of styrene onto PVDF films with different doses using different solvents to styrene, i.e. toluene, acetone and *N,N*-dimethylformamide

## 2. EXPERIMENTAL

### 2.1. Preparation Procedure

Commercial PVDF films with 0.125 mm thickness (Goodfellow) were immersed in styrene solution with toluene, acetone or *N,N*-dimethylformamide (DMF) in concentrations of 1:1 (v/v) in glass bottles. Nitrogen gas was bubbled to ensure inert atmosphere and the bottles were sealed and irradiated at room temperature at 5, 10 and 20 kGy, by the simultaneous method at dose rate of 5 kGy h<sup>-1</sup> with gamma rays from a <sup>60</sup>Co source. After irradiation, the polymer washing was made during 15 hours with hot toluene in Soxhlet system to remove the solvent/monomer solution and the homopolymer formed in solution. Films were dried in vacuum oven to eliminate residual solvents at 70 °C, until constant mass and then characterized.

### 2.2. Characterization

Sample mass increase was measured to determine the grafting yield (GY) according to the equation (1) [7] and all GY values corresponds to the average value given by nine samples for each irradiation condition;

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

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

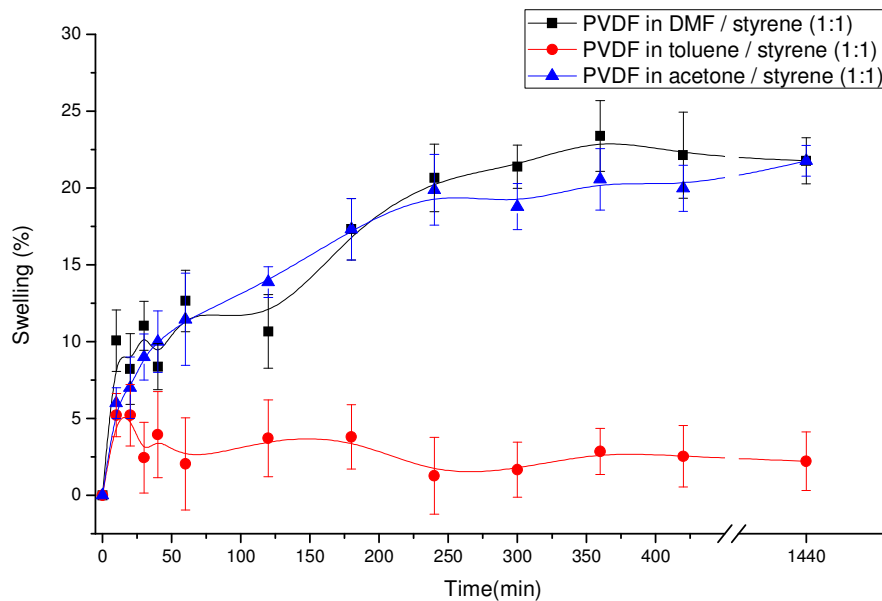
Infrared spectroscopy (FT-IR) was performed at Thermo Nicolet 6700 by the ATR method. Differential Scanning Calorimeter (DSC) was carried out in a 822 Mettler-Toledo under nitrogen atmosphere, at a heating rate of 10 °C min<sup>-1</sup> in the temperature range of 30 to 250 °C, isotherm in 250°C for 5 minutes, from 250 to -50 °C and a second heat from -50 to 250 °C. Scanning electron microscopy (SEM) images were obtained in a Phillips XL 30 microscope. The swelling of the PVDF film in the studied solutions was determined prior the irradiation, weighing PVDF samples periodically, after immersed in the solutions at room temperature for up to 24 h (1440 min.). The liquid on the surface of wet membranes was mopped quickly with absorbent paper and mass increase attributed to the solutions was calculated by equation (2), based on water uptake [3,8].

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

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

### 3. RESULTS AND DISCUSSION

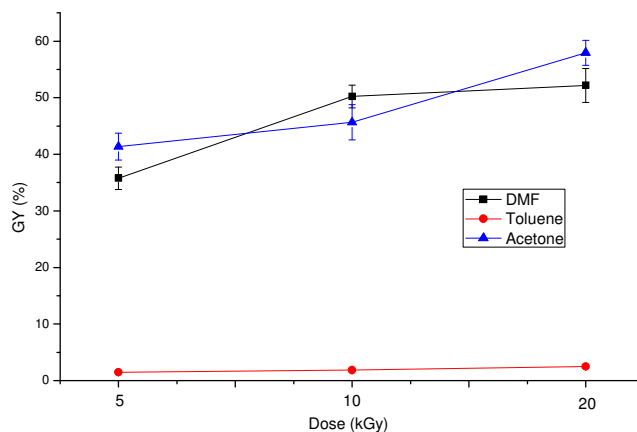
The swelling behavior of PVDF films in grafting solutions were measured to determine how the monomer can penetrate into the bulk matrix depending on the solvent nature since the nature of the solvent can determine the resultant morphology of the grafted polymer [1, 2, 7]. The swelling results for PVDF using the monomer solutions are shown in fig. 1.



**Figure 1. Swelling of the PVDF film in the grafting solutions**

As one can see from fig. 1, PVDF swells much more in the solutions containing DMF and acetone as solvents, whereas the toluene allows only a very small swelling, mainly due to the formation of a liquid film on the polymer surfaces. Based on that, it can be deduced that both DMF and acetone allows the penetration of the monomer into the inner layers of the bulk matrix instead the superficial layer formed using toluene.

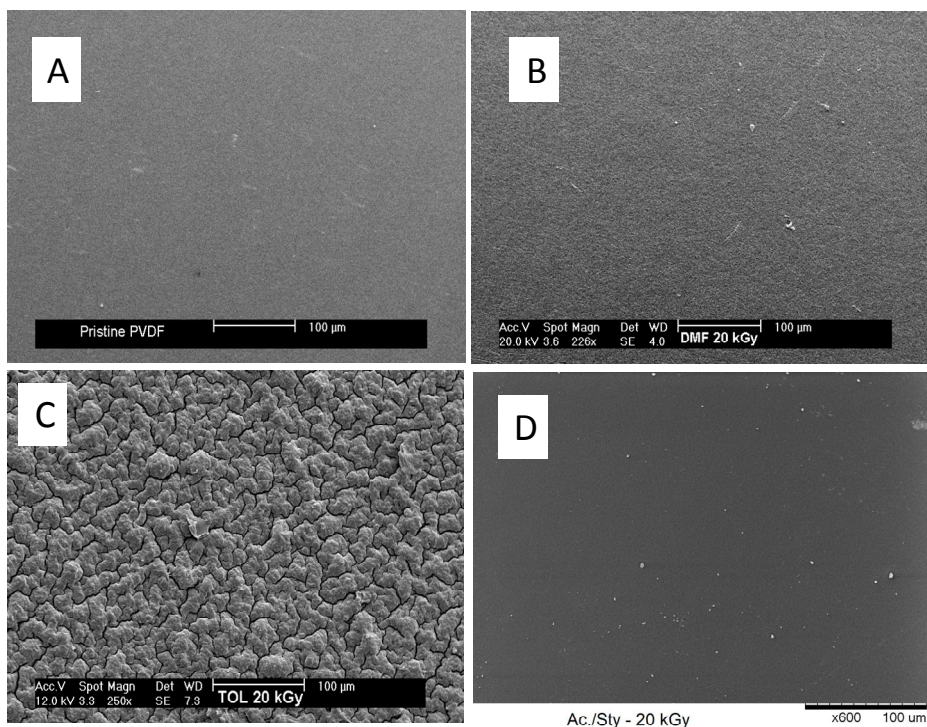
Then, it can be expected great differences on the grafting results, as the radicals formed in the inner layers can easily react with penetrated monomer or not, reaching different grafting yields. Fig. 2 shows the grafting results obtained for these different solvents according to the irradiation doses.



**Figure 2. Grafting yield obtained with the styrene/solvent solutions, from 5 to 20 kGy.**

As shown in fig. 2, grafting results are strongly dependent of the solvent nature, and the results obtained using DMF or acetone as solvent are almost ten to fifteen times greater than the grafting obtained with toluene, that barely reaches 5%. It can be due to the different swelling behavior, as explained above, but just the swelling cannot explain these enormous differences. The radiolysis of the solvent probably takes an important role in the reaction, since the byproducts generated during the irradiation of the toluene are mainly hydrogen and methyl instead the most reactive byproducts containing oxygen and nitrogen formed during acetone or DMF irradiation [9, 10, 11, 12]. These radiolysis byproducts can react with the matrix and the monomer, creating more radical sites and enhancing the grafting yield.

Since the styrene/toluene solutions practically do not swells the polymer, superficial deposition of the polystyrene (PS) can be expected, confirmed by the surface SEM images obtained for the pristine PVDF and for grafted samples in toluene, acetone and DMF solutions, as shown in fig. 3:



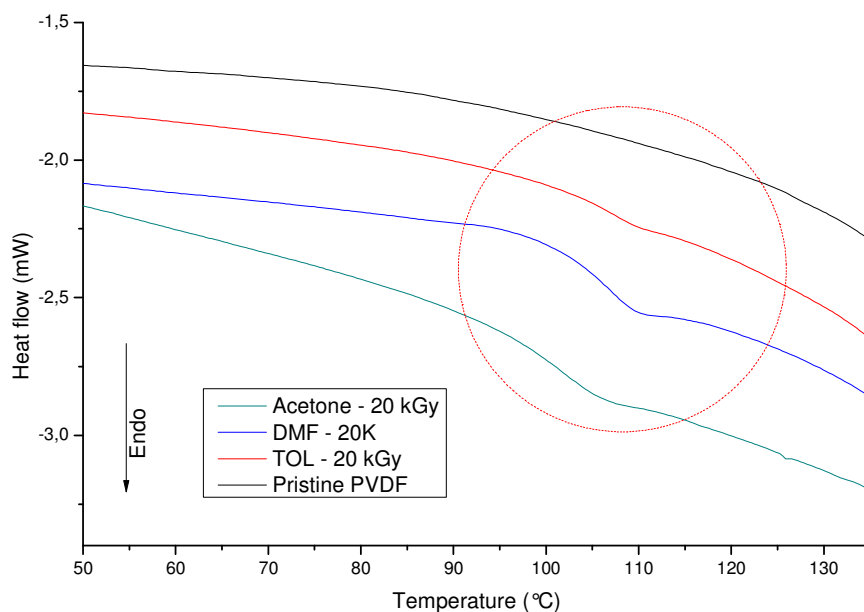
**Figure 3. SEM images of pristine (A) and styrene grafted PVDF in DMF , toluene and acetone solutions (B, C and D) respectively, with 20 kGy,.**

As seen from fig. 3, the surfaces of the samples irradiated with acetone or DMF as solvent maintain the morphology very close to the pristine matrix even with larger styrene grafting. Toluene, on the other hand, shows an irregular surface, attributed to the deposition of an external PS layer. This layer seems to be superficial since the grafting results for toluene are much smaller (less than 3%) than those allowed by the DMF (between 30 and 60%).

Another factor that must to be considered is the chain transfer constant to the monomer and to the solvents. These constant decrease in the order DMF and acetone > styrene > toluene [13, 14 - 19] and it means that the styrene grafted chains should be smaller and more numerous using DMF or acetone as solvent than using toluene.

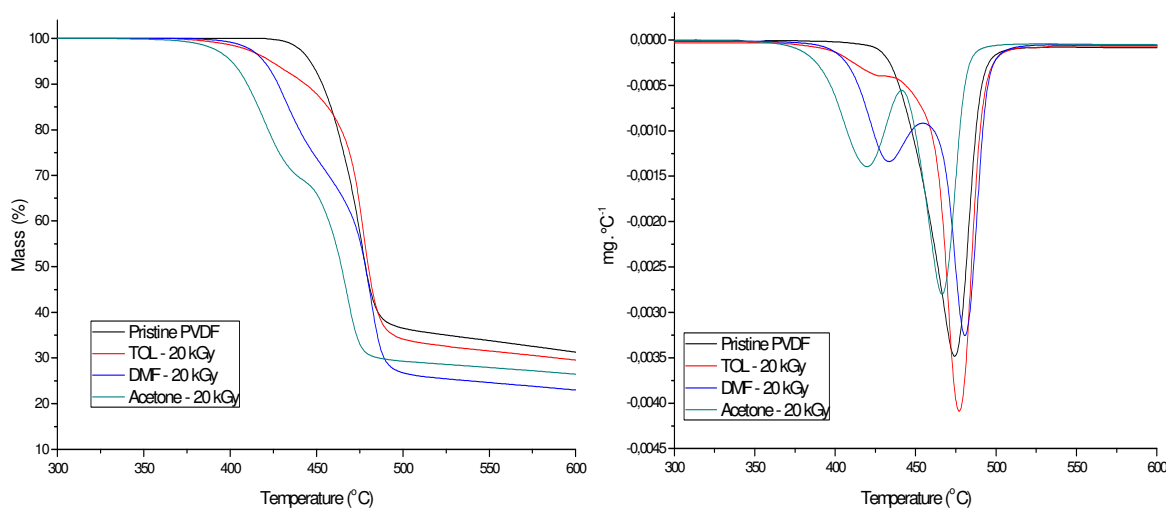
Thermal behavior can be seen in the figure 4, that show the DSC of the pristine and grafted materials. As one can see in fig. 4 the DSC behavior changes for the samples grafted in DMF and acetone as solvent, with the appearance of a new event, attributed to the glass transition of the PS, between 75 and 90 °C [20].

This new peak cannot be clearly seen in the samples grafted in toluene, since the amount of grafted styrene is very small. Due to its surface deposition, the grafted PS layer obtained with toluene solutions seems to have almost no influence in the PVDF behavior, and acetone or DMF solutions allow the obtaining of a homogeneous grafted material, with a small reduction on the melting point of about 3 °C, allowing to say that the styrene forms domains in the amorphous PVDF region, not changing too much the crystalline regions.



**Figure 4. DSC spectra of pristine PVDF and grafted in toluene and DMF as solvent with 10 kGy.**

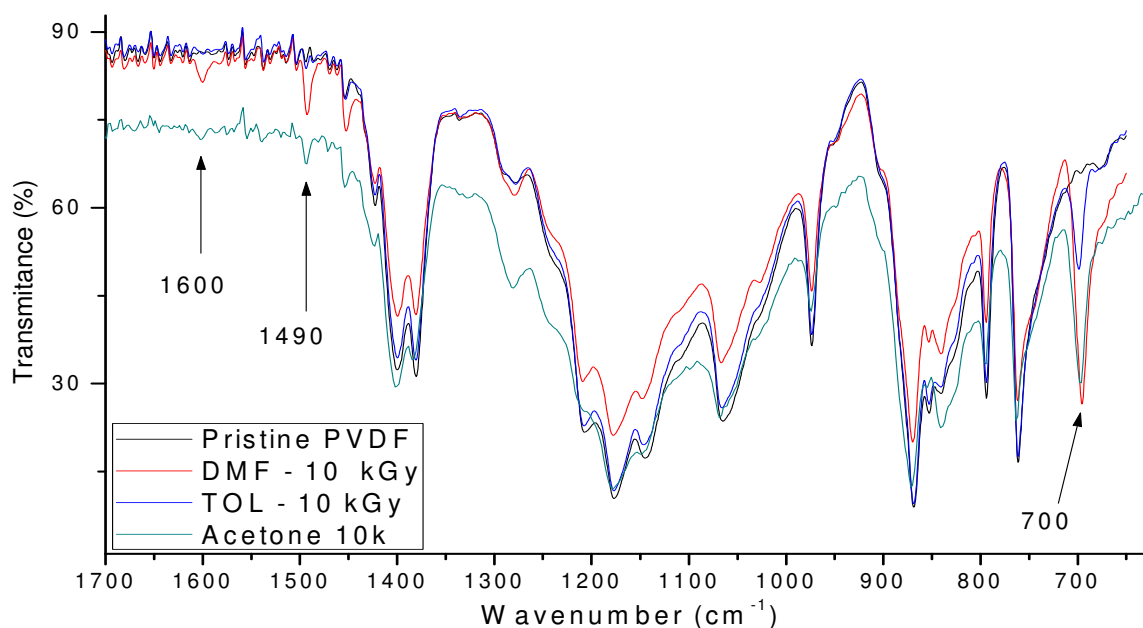
Thermo gravimetric analysis was done to evaluate the amount of styrene grafted in the PVDF according to the solvent and its influence on the matrix thermal behavior and the results can be seen in fig. 5:



**Figure 5. TG and DTG of PVDF, pristine and grafted in studied solutions with 10 kGy.**

As one can see, toluene allows only a small styrene grafting, acetone and DMF on the other hand allow a great quantity of styrene penetrates on the matrix, leading to great GY% and the higher thermal stability reduction, with a first event of decomposition due to grafted styrene.

FT-IR spectra allows to conclude that styrene has been grafted due to the new characteristics peaks appearance, as shown in fig. 6:



**Figure 6. FT-IR spectra of pristine PVDF, polystyrene and PVDF-g-PS grafted in toluene and DMF as solvent with 20 kGy.**

New characteristics bands can be seen in the grafted (fig. 5) polymer around  $3100\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  from polystyrene, attributed to the stretching of the aromatic C-H bond, between  $1600$  and  $1450\text{ cm}^{-1}$  due to the ring C=C bond stretching,  $695\text{-}705\text{ cm}^{-1}$  due to the out of plane C-H vibration and the  $700\text{ cm}^{-1}$  due to the out of plane ring deformation [4, 21]. Due to the small amount of styrene grafted in toluene solutions, the intensity of the characteristic peaks is reduced comparing to the acetone or DMF solutions.

#### 4. CONCLUSIONS

Graft copolymerization in the present system depend not only upon the efficiency of the radicals initiating due to the used dose but also upon the availability of the monomer molecules in the grafting layers. This availability is strongly dependent on the solvent nature, properties and its behavior during irradiation.

Radiation induced grafting of styrene onto PVDF is possible at the studied conditions, and both irradiation doses and solvent shows to play important roles on the ion exchange capacity results. As SEM images suggest, the grafting takes place mainly on the surface and in small amount when toluene is used as solvent. When DMF or acetone is used, it is possible to obtain higher grafting results, leading to greater and homogeneous distribution through the

matrix, evidencing the importance of the solvent properties and behavior under simultaneous irradiation method. In studied conditions, the solvent affect more significantly the grafting than the irradiation dose.

FTIR confirms the presence of the grafted monomer due to the new characteristics bands on the spectra. Thermal behavior of the pristine and grafted polymers shows different behaviors attributed to the grafted monomer on the films. Thermal analysis shown small changes in thermal behavior of grafted samples when toluene is used as solvent compared to the pristine PVDF, that may let to conclude that styrene do not penetrates in the inner layers of the polymeric matrix. Acetone and DMF as solvents may form small diffuses polystyrene regions through the amorphous region containing large amount of polystyrene, as shown by DSC and TG.

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