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SOLVENT AND IRRADIATION DOSES EFFECTS ON THE ION EXCHANGE CAPACITY OF SULFONATED STYRENE GRAFTED PVDF

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ABSTRACT

Polymers exhibiting ion exchange capacity are studied for many years due to their application in several fields, such as membranes for proton exchange fuel cells, filtration membranes, heavy ions recovery and artificial muscles and sensors. Radiation induced grafting followed by sulfonation is a well-known way to obtain ion exchange polymers. Fluorinated polymers are frequently used as polymeric matrix for grafting due to their excellent physicochemical properties. Radiation induced grafting of styrene into poly(vinylidene fluoride) (PVDF) by simultaneous method in 1:1 styrene/toluene or styrene/*N,N*-dimethylformamide solutions was studied. Irradiations were performed under nitrogen atmosphere, room temperature and at doses of 5, 10 and 20 kGy with dose rate of 5 kGy.h^{-1} from a ^{60}Co gamma source. After washing, grafted materials were sulfonated in 10% chlorosulfonic acid/1,2-dichloroethane solutions for 4 h at room temperature. Characterization shows that increasing irradiation dose corresponds to increases in the grafting yield (GY %) gravimetrically calculated and these different solvents shows different grafting behaviors. Toluene allows no more than 3 % of grafting while DMF allows up to 55 % of grafting in the same condition. Grafting in toluene solution occurs on the surface and in DMF solution it occurs in the bulk, as confirmed by SEM. Both irradiation doses and solvent used have direct effects in the ion exchange capacities (calculated after titrations). FT-IR spectra exhibit new peaks after grafting and after sulfonation, attributed to grafted monomer and sulfonic groups attached to the styrene. DSC shows differences in thermal behavior of the polymer before and after each step.

1. INTRODUCTION

The irradiation processing of polymers is a well-established way to modify some properties of polymers, due to the irradiation effects on the polymeric chains, especially by chain scission, crosslink and grafting [1 2]. Grafting of monomers in fluorinated polymers has been the object of study in the last few decades because it let to produce different materials with modified properties and radiation-induced graft copolymerization is a well-established knowledge which dating back almost 50 years [1]. Fluoropolymers are studied due to their excellent thermal, chemical and mechanical properties [2]. Modified fluoropolymers may find applications as ion exchange membranes for fuel cells, polymeric actuators, ultrafiltration membrane, and waste treatment and in biomedical applications [2,3]. In all cases it is important to know and to control the morphology of the obtained polymer, in order to maintain useful polymers [3,4,6]. The advantage of the Radiation-induced graft copolymerization technique is that during the ionization process, any compound absorbs sufficient energy to break some covalent bonds producing free radicals or excited molecules that can initiate the polymerization of most kind of monomers [5]. In the radiation technique the presence of an initiator is not necessary and the chemical nature of the monomer or polymer is not so important like conventional chemical reactions [2]. 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 [2,7,9]. 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 two different solvents to styrene (toluene or *N,N*-dimethylformamide) and the sulfonation of the obtained grafted polymers with chlorosulfonic acid to compare the influence of dose and solvent on the ion exchange capacities.

2. EXPERIMENTAL

2.1. Preparation Procedure

Commercial PVDF films with 0.125 mm thickness (Goodfellow) were immersed in styrene solution with toluene 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^{-1} with gamma rays from a ^{60}Co source. After irradiation, washing was made overnight with toluene in Sohxlet system to remove the solvent/monomer solution and the ungrafted homopolymer formed in solution. Films were dried in vacuum oven to eliminate residual solvents at 70 °C, until constant mass and then characterized.

Sulfonation was carried out immersing the grafted films in 10% chlorosulfonic acid/1,2-dichloroethane solutions for 4 h under room temperature. After sulfonation the films were washed with deionized water until neutral pH and were also characterized. All products were used as received, without further purification.

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 case;

$$GY\ (\%) = [(W_g - W_o)/W_o)]x100 \qquad (1)$$

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 with samples of the films analyzed 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^{-1} 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. Swelling was determined prior the irradiation, weighing samples after determined periods immersed in the solutions of styrene/toluene and styrene/DMF 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 wather uptake [3,8].

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

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

Ion exchange capacity (IEC) of the sulfonated membranes were calculated according to the equation (3) [3] after immersing sulfonated samples in a 3 $Mol.l^{-1}$ NaCl solution overnight [9] for exchange of H^+ to Na^+ and then titrating the solution with NaOH (0.05 $Mol.l^{-1}$).

$$IEC_E\ (meq.g^{-1}) = (C_{NaOH} \times V_{NaOH})/M_{pol} \qquad (3)$$

where C_{NaOH} and V_{NaOH} are the concentration and the volume of the NaOH solution used for titration, respectively and M_{pol} is the dry mass of the sulfonated samples.

The theoretical IEC values were obtained according to the equation (4) [10], where G is the grafting yield.

$$IEC_T = (9{,}62 x G)/(100+[1{,}77 x G]) \qquad (4)$$

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 toluene/styrene and styrene/DMF solutions are shown in fig. 1:

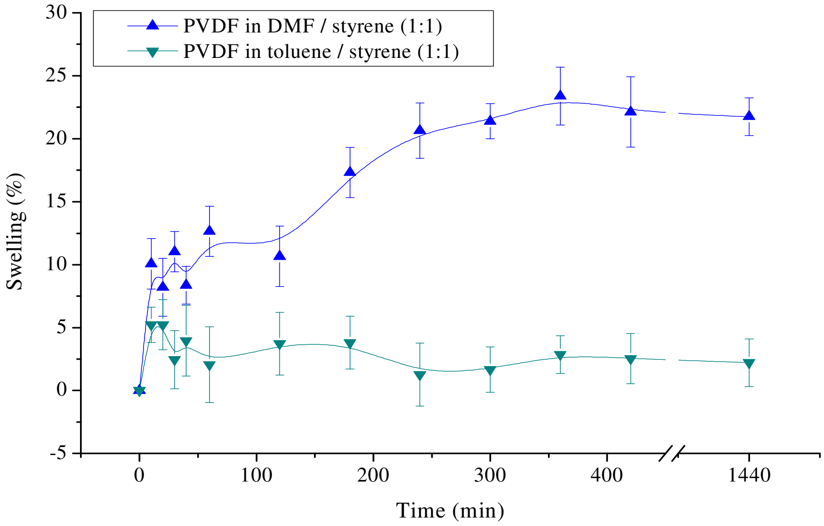

Figure 1. Swelling of the PVDF film in the grafting solutions

As one can see from the fig. 1, PVDF swells much more in the solutions containing DMF as solvent, 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 DMF 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 two solvents.

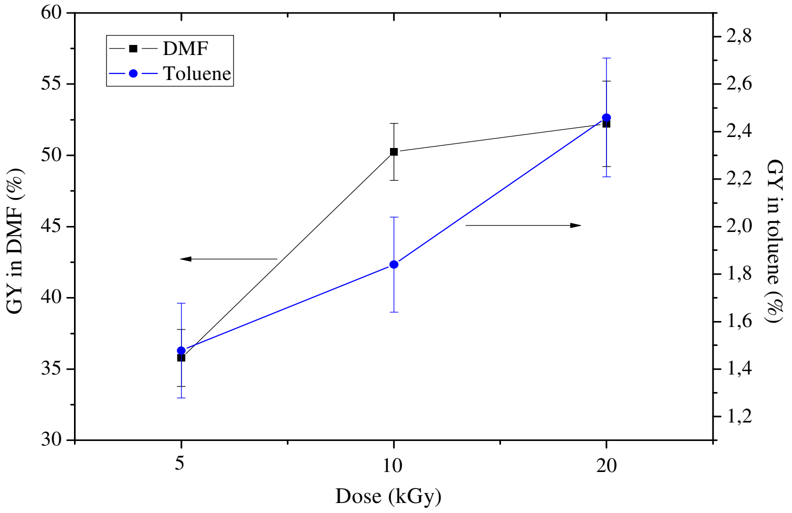

Figure 2. Grafting yield obtained with DMF and toluene as solvents for styrene.

As shown in fig. 2, grafting results are strongly dependent of the solvent nature, and the results obtained using DMF as solvent are almost 20 times greater than the grafting obtained with toluene. 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 DMF irradiation [11, 12, 13, 14]. 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 and DMF solutions, as shown in fig. 3:

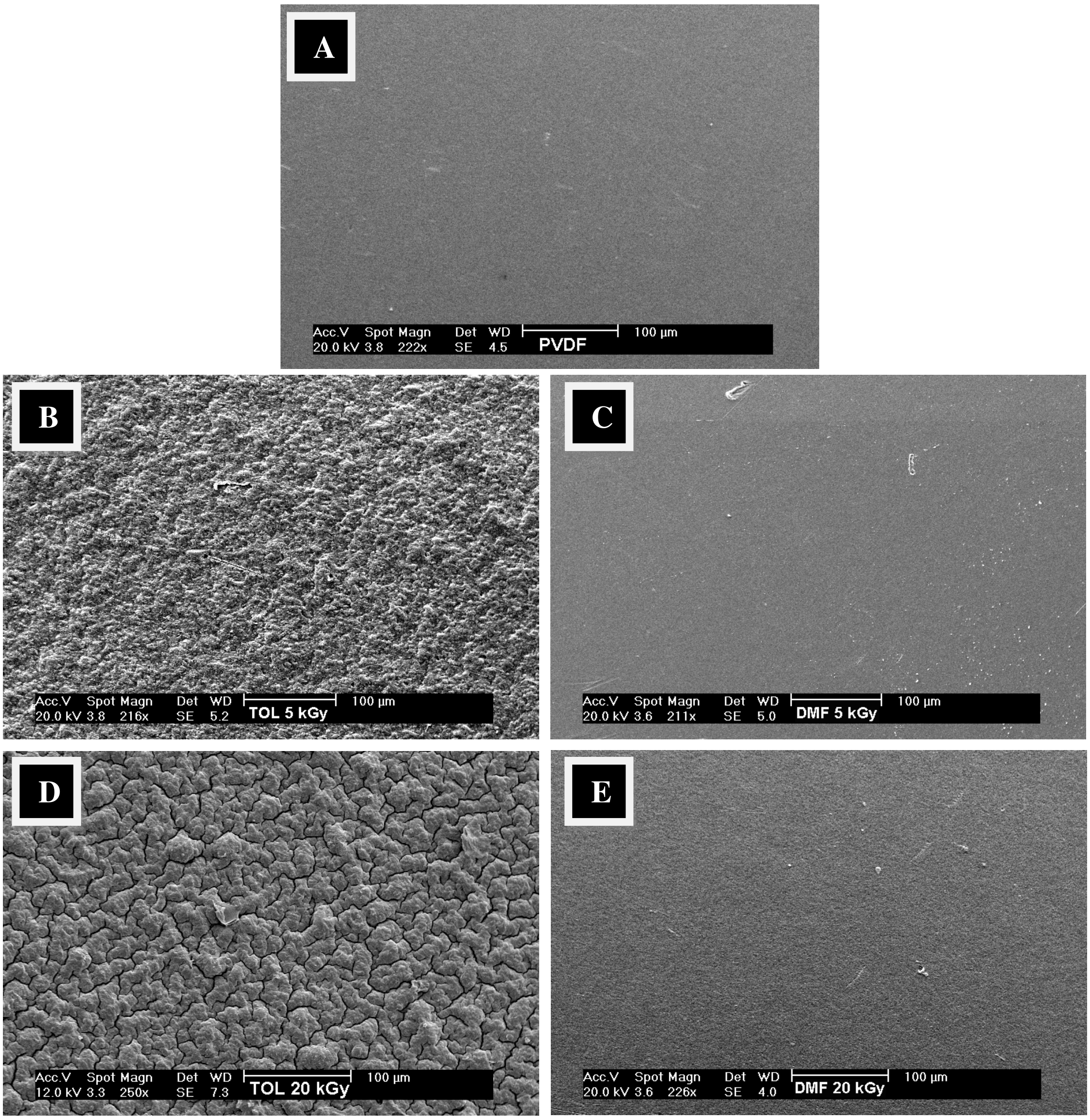

Figure 3. SEM images of pristine (A) and grafted PVDF in toluene (B and D) and DMF (C and E) with doses of 5 and 20 kGy, respectively.

As seen from fig. 3, the surfaces of the samples irradiated with 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 55%).

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 > styrene > toluene [15, 16 - 21] and it means that the styrene grafted chains should be smaller and more numerous using DMF 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 as solvent, with the appearance of a new event, attributed to the glass transition of the PS, between 75 and 90 °C [22].

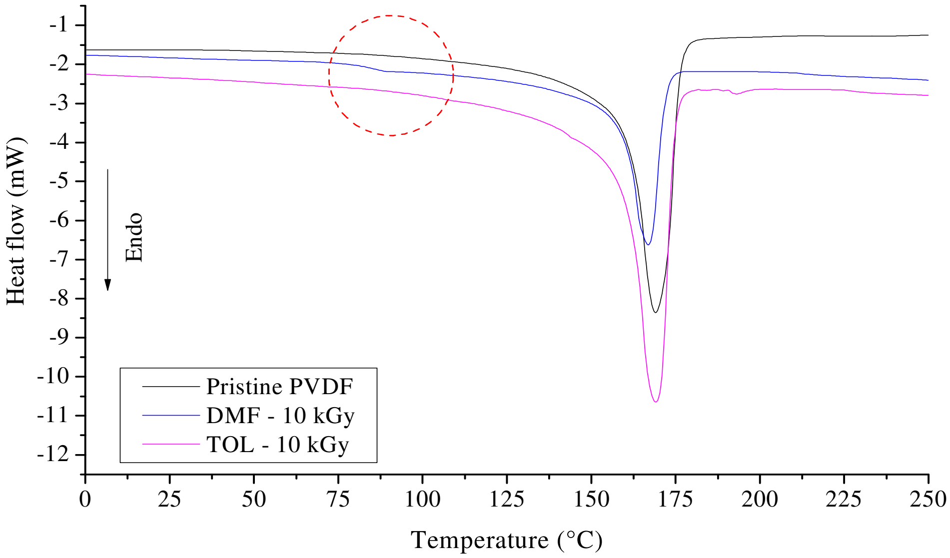

Figure 4. DSC spectra of pristine PVDF and grafted in toluene and DMF as solvent with 10 kGy.

This new peak cannot be 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 change in the PVDF behavior, and DMF solution allows 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.

FT-IR spectra allows to conclude that styrene has been grafted due to the new characteristics peaks appearance, as shown in figure 5

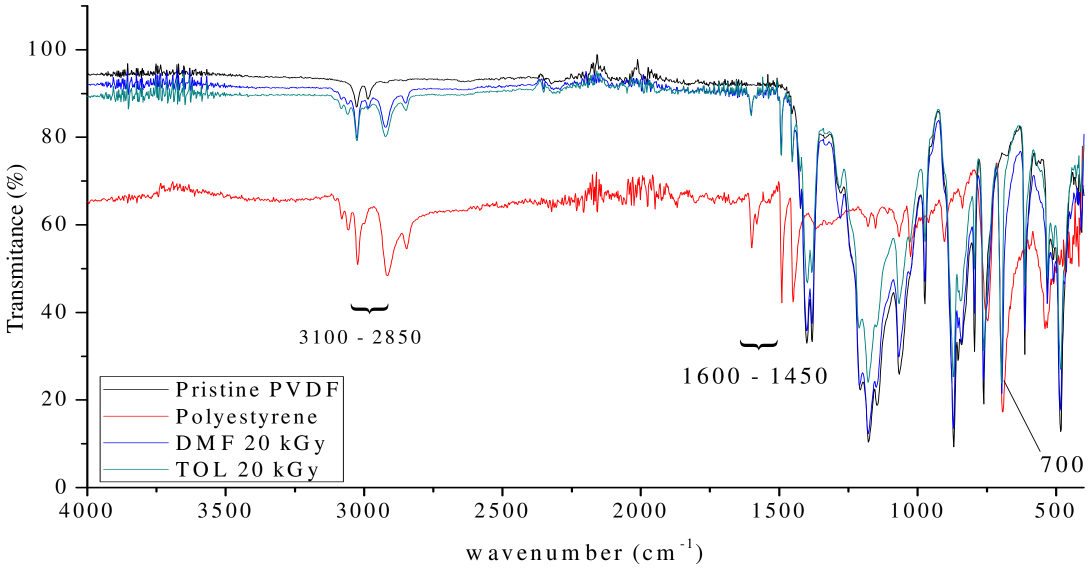

Figure 5. FT-IR spectra of pristine PVDF, polystyrene and PVDF-g-PS grafted in toluene and DMF as solvent with 20 kGy.

New characteristics bands can be seen in the grafted (fig. 5) polymer around 3100 cm^{-1} and 2850 cm^{-1} from polystyrene, attributed to the stretching of the aromatic C-H bond, between 1600 and 1450 cm^{-1} due to the ring C=C bond stretching, 695-705 cm^{-1} due to the out of plane C-H vibration and the 700 cm^{-1} due to the out of plane ring deformation [4, 23].

Fig. 6 and fig. 7 presents the theoretical and experimental IEC values (IEC T and IEC E, respectively) obtained after grafted samples sulfonation, in toluene and in DMF solutions respectively.

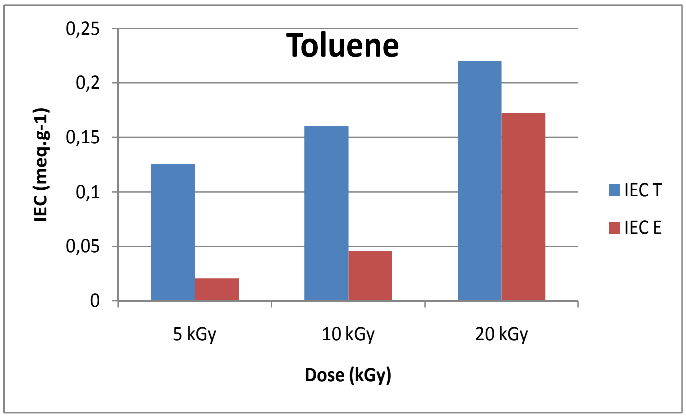

Figure 6. IEC values for samples grafted in toluene solutions after sulfonation.

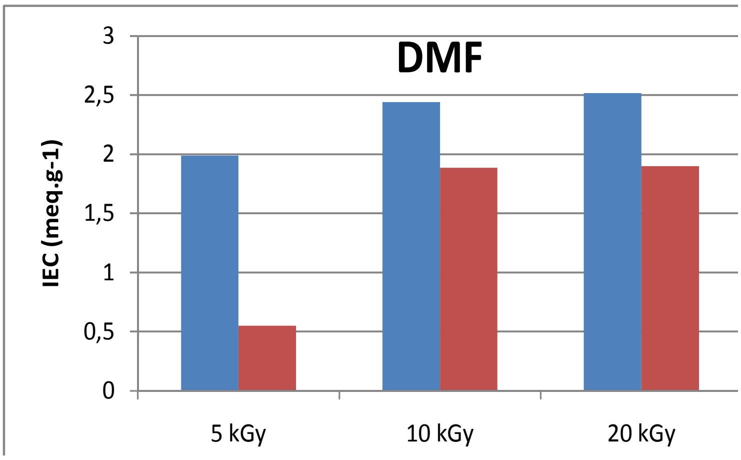

Figure 7. IEC values for samples grafted in DMF solutions after sulfonation.

As demonstrated, the surface deposited PS layer do not reach great IEC values, due to the small amount of styrene available to be sulfonated. The samples grafted in DMF solutions, on the other hand allows IEC values at least 10 times greater than toluene. It is clearly related to the grafting yield, since increasing the grafting there is more styrene rings to be sulfonated. The differences between theoretical and experimental IEC allows to conclude that there are some unsulfonated styrene rings, i.e., without at least one sulfonic group attached.

Sulfonated samples show a few differences from the grafted ones. These grafted in toluene solutions does not shows significant difference, due to the small amount of grafted styrene and IEC, whereas the samples grafted in DMF solutions show a clear difference, with the formation of a heterogeneous surface, even for the samples with the lowest grafting yield, as shown in fig. 8.

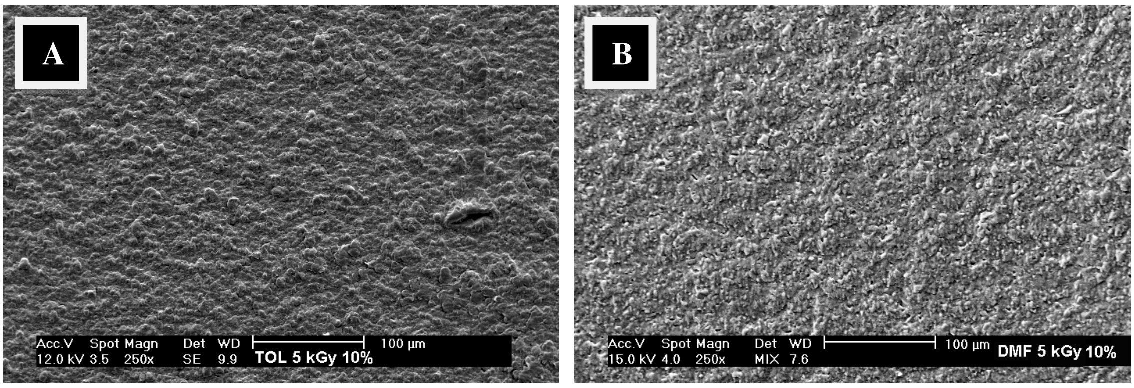

Figure 8. SEM images of sulfonated PVDF-g-PS grafted in toluene (A) and in DMF (B) solutions using 5 kGy.

The surface roughness seem on the sample grafted in DMF solution can be explained by the formation of pores, due to the repulsion of the sulfonic groups, forming “holes” through the polymer. Based on the IEC results it is possible to infer that those holes are present through the entire matrix.

The thermal behavior after sulfonation shows the difference of the samples in fig. 9. There is a significant reduction on the melting point in the sample grafted in DMF with the highest GY values after sulfonation. It can be explained due to the more present styrene and the repulsion of the sulfonic groups, that seems to interfere on the PVDF crystal formation and the glass transition event of the PS disappear, probably due to the same reason.

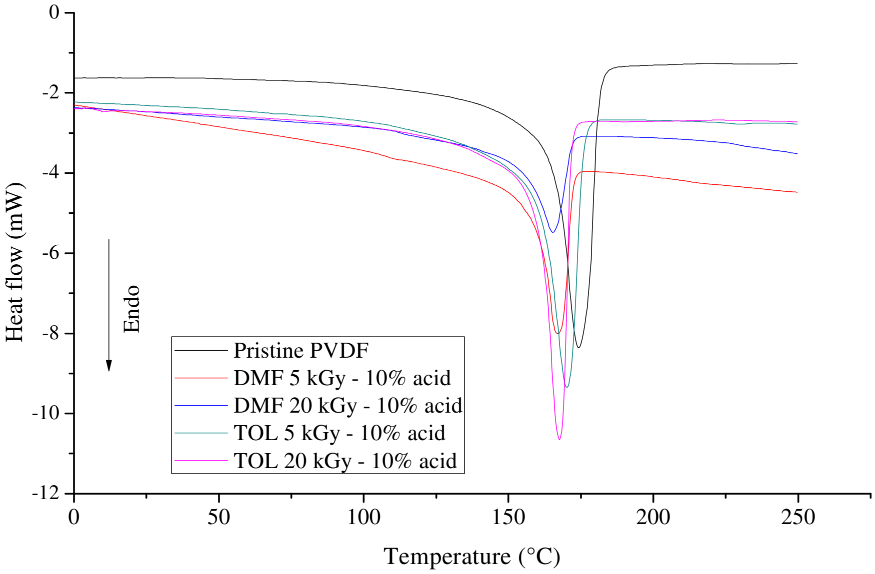

Figure 9. DSC spectra of pristine PVDF and sulfonated samples grafted in toluene and DMF solutions irradiated with 5 and 20 kGy.

Fig. 10 shows the FT-IR spectra of the sulfonated samples, and one can see the new peaks from the sulfonic groups in 580 cm^{-1} from the scissor deformation of the sulfonic groups, in 1030 cm^{-1} attributed to the symmetric stretching of the sulfonic group, in 1000 and 838 cm^{-1} due to the para-substituted rings. The peak in 673 cm^{-1} can be due to the ring C-S bond stretching and 1121 cm^{-1} to the antisymmetric stretching of the group SO2 in the hydrated sulfonic group [4, 23, 24].

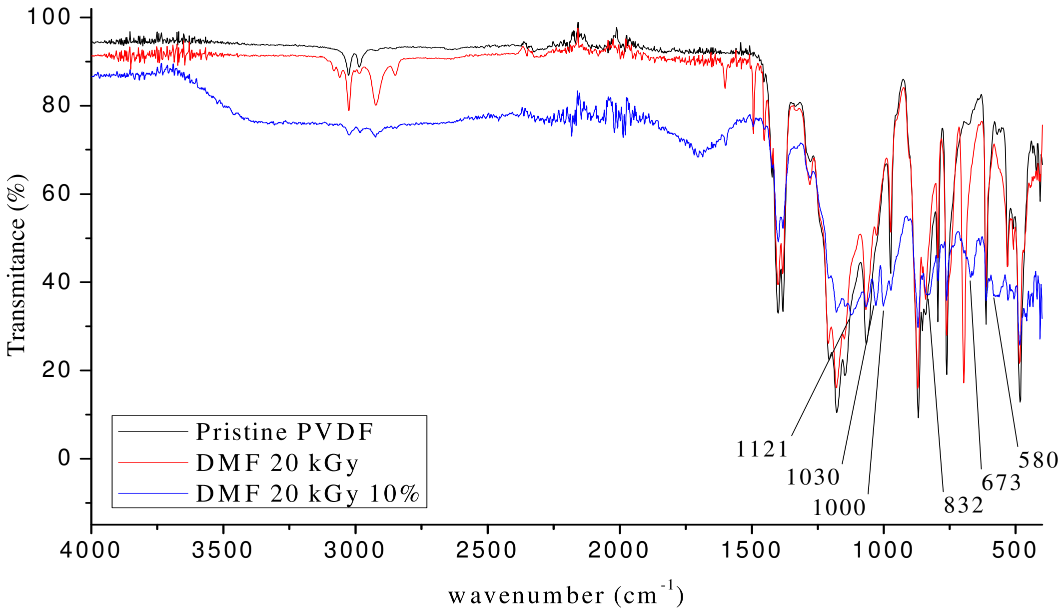

Figure 10. FT-IR spectra of pristine PVDF, grafted PVDF in DMF as solvent and sulfonated, both with 20 kGy.

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 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 and the sulfonic groups due to the new characteristics bands on the spectra due to the monomer and sulfonic groups' characteristics bands. Thermal behavior of the pristine, grafted and sulfonated polymers shows different behaviors attributed to the grafted monomer and the sulfonic groups of the films. Thermal analysis shown small changes in thermal behavior of grafted samples when DMF is used as solvent compared to the pristine PVDF that may let to conclude that styrene penetrates in the inner layers of the polymeric matrix and can form small diffuses polystyrene regions region as shown by DSC

IEC seems to be directly related to the grafting yields and consequently to the solvent used during irradiation, and irradiation conditions take important roles on the IEC results, since the increasing on the grafting allows increase the IEC and the way the monomer is grafted change the morphology and properties of the resultant polymer.

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