

[ENE05] sulfonated polystyrene pore-filled electrolytes membranes by electrons induced grafting of styrene into PVDF films: thermal stability and structural investigation

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Introduction

There is considerable interest currently in pore-filled electrolyte membranes (Mika *et al.*, 1995, Yamaguchi *et al.*, 2003). These membranes have a variety of potential applications such as temperature and pH (ionic strength) sensors (Childs *et al.*, 2002), dialysis (Stachera *et al.*, 1998), proton exchange membrane (Bae and Kim., 2003, Yamaguchi *et al.*, 2003;) and so on. Efforts have been made in order to study and correlate the performance of such membranes with the grafting yield in these systems. The various steps which involved during the membranes preparation process is predicted to influence the overall structure of the membranes that depends upon the nature, amount and distribution of the grafted components (Gupta *et al.*, 1994).

The preparation of pore-filled electrolyte membranes for the fuel cell applications has been investigated by several workers recently (Yamaguchi *et al.*, 2003, Nasef *et al.*, 2003, Bae and Kim., 2003, Zubir *et al.*, 2004). However, an extensive study concerning to investigate the influence of the grafting upon the thermal stability as well as the structural changes in the resulting membranes has not been made.

The introduction of the polystyrene grafts and of the hydrophilic sulfonic acid groups into the hydrophobic PVDF matrix produces a very complex structure, which has different natures (hydrocarbon and ionic group) from the pristine (fluorocarbon) matrix. Thus, in the present investigation, we study the influence of the grafting yield and also the membrane

preparation procedures on the thermal degradation and structure properties of the sulfonated polystyrene pore-filled electrolyte PVDF membranes, which were prepared by the simultaneous grafting method and followed by a sulfonation reaction.

Materials and Methods

The sulfonated pore-filled PVDF membranes were prepared by the simultaneous method. The materials, such as monomer (styrene) and polymer substrate (PVDF film: 90 μ m thickness, density of 0.72 g/cm³, average pore size of 0.22 μ m) and the grafting and sulfonation procedures were described in detail in the previous study (Zubir *et al.*, 2004). The other chemicals were reagent grade and used without further purification.

Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis was carried out in order to study the thermal stability in term of the weight loss of the membranes samples during the experiment. The changes of weight throughout the TGA runs indicate the structure changes in the membranes. The TGA studies on membranes were carried out using Perkin-Elmer TGA-6. The membrane samples were initially dried under vacuum at 60°C for 24 hrs and stored in a dessicator over silica gel. The samples were typically used 10 – 20 mg for the measurements. Analysis was carried out at a constant heating rate of 10.00°C/min under N₂ atmosphere in the temperature range of 50-650°C for PVDF samples.

Differential Scanning Calorimetry (DSC)

Membranes with grafting yields in the range of (10% - 33%) were investigated for their thermal

properties and structural changes in correlation with the sulfonation process. Thermograms of samples were measured with a Mettler Toledo Star DSC instrument.

Prior to the DSC measurements, the sulfonated membrane samples were dried at 80°C in vacuum oven (1 torr) for 7 days. The drying of the samples were necessary in order to eliminate the possible interference of moisture on the melting thermograms which is normally appear in the form of strong endothermic peak at 60 – 160°C. After drying, the membranes were kept in a desiccator at ambient temperature over fresh silica gel. Typical samples having weight in the range of 5 – 10 mg were used. Pristine and grafted PVDF films were used as reference materials. The thermograms were studied in the temperature range of 50°C – 300°C for sulfonated PVDF membranes. The sulfonated PVDF samples were then cooled down to 50°C after holding for 5 minutes isothermally at 300°C. The heating rate during the runs was kept constant at 10°Cmin⁻¹ under nitrogen atmosphere. T_m was obtained from various points i.e. onset, the peak maximum and tail ends of the peak. The heat of fusion of the crystals was calculated from the peak area in the thermograms using Mettler Toledo Star system software.

The overall percentage crystallinity of the sample (X_c) was evaluated from the heat of fusion values of the corresponding membranes according to the following equation:

$$\text{Crystallinity} = \frac{\Delta H_{f(\text{mem})}}{\Delta H_{f(\text{crys})}} \times 100\%$$

where $\Delta H_{f(\text{mem})}$ is the heat of fusion measured for the membrane and $\Delta H_{f(\text{crys})}$ is the heat of fusion for totally crystalline PVDF, which were taken 104.7 J/g (Hietala *et al.*, 1997). The heat of fusion values of the membranes $\Delta H_{f(\text{mem})}$ were obtained from the area under the melting thermograms.

Results and Discussion

Thermal Stability

Figure 1 depicts the TGA thermograms of pristine porous PVDF films, polystyrene pore-filled PVDF films and sulfonated polystyrene pore-filled electrolyte PVDF membranes for PVDF1. The grafting yield for pore-filled PVDF1 film and sulfonated pore-filled electrolyte PVDF1 membranes are 10.62%. It was found that the pristine PVDF films are very stable approximately at 420°C. The degradation occurs with one-step behavior as presented in thermogram 'A' in Figure 1.

The incorporation of polystyrene grafts into PVDF matrix produced an additional degradation step due to the degradation of polystyrene grafts (dearomatization). The first degradation is initiated at ~350°C due to the dearomatization and followed by degradation of PVDF matrix, which occurs at ~430°C as depicted in thermogram 'B' in Figure 1. It is observed that the presence of polystyrene grafts in the PVDF matrix does not affect much alteration to the inherent degradation of the PVDF matrix. These behaviors indicate the incompatibility of the polystyrene grafts with PVDF matrix and leads to the formation of a phase separated microdomains in pore-filled PVDF films. Similar behaviors were also observed for styrene grafted PVDF (Hietala *et al.*, 1998), FEP (Gupta and Scherer, 1993; Gupta *et al.*, 1998; Nasef and Saidi, 2000 b); PTFE (Nasef, 2000 a); PFA (Nasef *et al.*, 2000 d) films, respectively.

The thermal degradation pattern of the sulfonated polystyrene pore-filled electrolyte PVDF1 membranes are rather more complex than that of the foregoing precursor samples but can still be divided into three steps (thermogram 'C' in Figure 2). The weight loss starts at a temperature below ~100°C and proceeds up to ~200°C due to the loss of bound water in the membranes. The amalgamation of the strong hydrophilic sulfonic acid groups in the membrane makes it hygroscopic. This is followed by another degradation starts at ~250°C, which is attributed to the desulfonation. In the final steps, the degradation begins at ~450°C due to the degradation of PVDF matrix. Similar to styrene grafted and sulfonated PVDF (Hietala *et al.*, 1998), FEP (Gupta and Scherer, 1993; Gupta *et*

al., 1998; Nasef and Saidi, 2000 b); PTFE (Nasef, 2000 a); PFA (Nasef *et al.*, 2000 d) membranes, there is a continuous weight loss between the two regions representing by the desulfonation and the degradation of the polystyrene grafts in a temperature interval of 250 °C – 450°C. Hence, these results suggest that the incorporation of sulfonic acid groups to the pore-filled PVDF films increase the membrane's susceptibility to thermal degradation in contrast to the pristine and pore-filled films. Based on the aforementioned results, it may be avowed that both sulfonated polystyrene pore-filled electrolyte PVDF membranes are thermally stable up to ~250°C under the present experimental conditions.

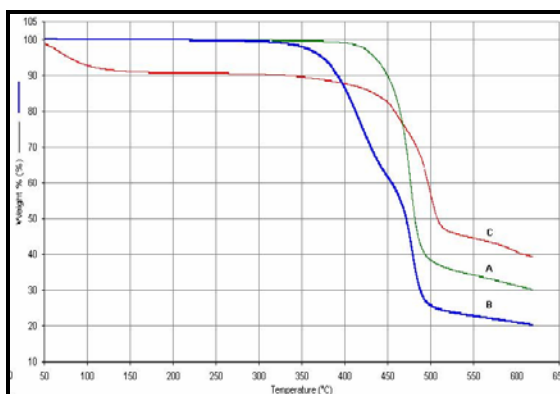


FIGURE 1 TGA thermograms of (A) pristine porous PVDF film; (B) polystyrene pore-filled PVDF film, grafting yield of 10.62% and (C) sulfonated polystyrene pore-filled electrolyte PVDF membrane, grafting yield of 10.62%.

The radiation grafting of styrene into both porous PVDF films followed by the sulfonation process produce membranes that exhibit similar degradation patterns for the whole range of grafting yield, 10.62% – 33.42% as depict in Figure 2. These degradation patterns are attributable to a sequence of dehydration, desulfonation or dearomatization and PVDF matrixes degradation, respectively.

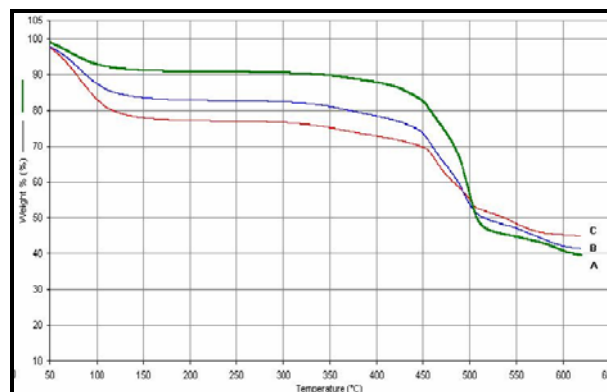


FIGURE 2 TGA thermograms of sulfonated polystyrene pore-filled electrolyte PVDF membranes having various grafting yields (A) 10.62%; (B) 21.62% and (C) 33.42%.

The degradation reaction for sulfonated polystyrene pore-filled electrolyte PVDF membranes are in contrast with the polystyrene pore-filled PVDF films since the residue weight at 650°C increases with increasing grafting yield. This assumption is supported by the data obtained in Table 4.8 that illustrates the variation in residual weight percentage as a function of grafting yield after completing TGA run. These behaviors are probably due to an increase in char formation of the polystyrene grafts in the presence of acidic fragmentation product originating from the sulfonic acid groups and water during the thermal degradation as reported by Hietala *et al.* (1998). Hence, it can be suggested that the presence of sulfonic acid groups enhances the thermal stability of the both PVDF matrixes and the ash formation. Similar conclusions have been drawn with those reported for styrene grafted and sulfonated PVDF (Hietala *et al.*, 1998), FEP (Gupta and Scherer, 1993; Nasef and Saidi, 2000 b), PTFE (Nasef, 2000 a) and PFA (Nasef *et al.*, 2000 d) membranes.

TABLE 1 Variation of the sulfonated polystyrene pore-filled electrolyte PVDF membranes residues with the grafting yield after a complete TGA heating run (650°C)

Grafting Yield, Y (%)	Weight of Residue (%)
<i>Sulfonated polystyrene pore-filled electrolyte PVDF membrane</i>	
10.62	39.73
21.62	41.43
33.42	44.86

Thermal Properties

The melting thermograms for pristine porous PVDF film, polystyrene pore-filled PVDF film and sulfonated polystyrene pore-filled electrolyte PVDF membranes that have various grafting yields are each presented in Figure 3. It can be seen that, all the sulfonated membranes show fairly significant increased in T_m which in turn depending on the membrane's grafting yield. This behavior can be explained on the basis of the incorporation of more amorphous polystyrene grafts that increase the amorphous fraction, which led to the reduction in the membrane's crystallinity. Moreover, the form of the melting endotherm peak differs significantly after grafting and sulfonating the pristine films. The intensity of the melting peaks of the sulfonated polystyrene pore-filled electrolyte PVDF membranes was observed to decrease considerably compared with the polystyrene pore-filled PVDF films as a consequent of sulfonating the polystyrene grafts. Further decreased in the intensity of the melting peaks for sulfonated PVDF membranes as well as the heat of melting (ΔH_m) that obtained from the area under the melting peak are distinguished in the function of increasing grafting yield.

Figure 4 shows the cooling thermograms of pristine porous PVDF film, polystyrene pore-filled PVDF film and sulfonated polystyrene pore-filled electrolyte PVDF membranes with various grafting yields. The sulfonated polystyrene pore-filled electrolyte PVDF membranes are exhibiting a declining trend in the crystallization temperature with increasing grafting yield, which summarized

in Table 2. This indicates the formation of the restrictive impact of the sulfonated polystyrene grafts on the mobility and ability to crystallize the PVDF residue. Similar observations have been made by Hietala *et al.* (1997), who investigated the structural investigation of radiation grafted and sulfonated PVDF membranes.

In the thermal analysis, the crystallinity of the membranes was calculated from the enthalpies of fusion, which was obtained from the area under the crystallization exotherm peak in cooling thermograms. From Table 2, it can be noted that the relatively rapid decrease in membrane's crystallinity is observed after the pristine film is being grafted and followed by sulfonation. All the sulfonated membranes show a decreasing trend as the grafting yield increases. These decreases are mostly governed not only by the dilution effect by the amorphous polystyrene grafts but also by the disruption of the PVDF crystals formed during the grafting and sulfonation processes, respectively.

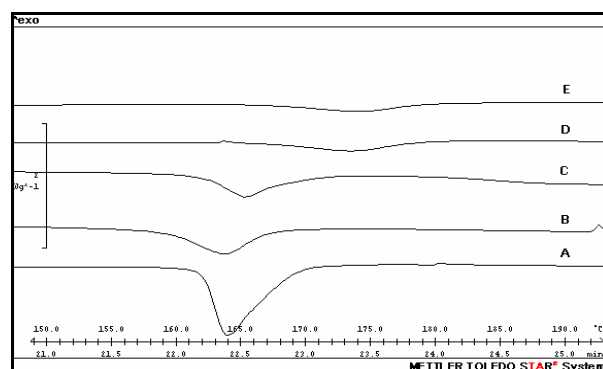


FIGURE 3 Melting thermograms of pristine porous PVDF film (A), polystyrene pore-filled PVDF film with a grafting yield of 10.62% (B) and sulfonated polystyrene pore-filled electrolyte PVDF membranes with various grafting yields of: (C) 10.62%; (D) 21.62%; (E) 33.42%.

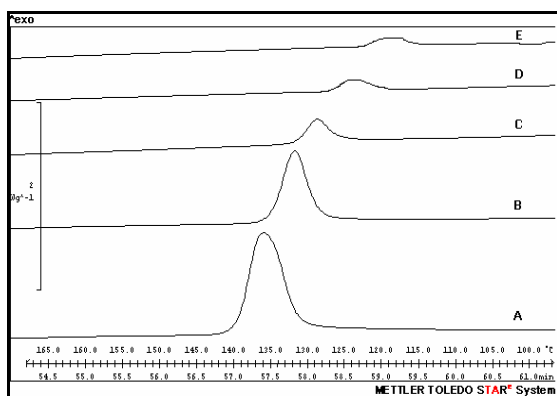


FIGURE 4 Cooling thermograms of pristine porous PVDF film (A), polystyrene pore-filled PVDF film with a grafting yield of 10.62% (B) and sulfonated polystyrene pore-filled electrolyte PVDF membranes with various grafting yields of: (C) 10.62%; (D) 21.62%; (E) 33.42%.

This dilution effect is formed from the incorporation of grafted amorphous polystyrene grafts at the non-crystalline region and pores of the PVDF matrix, which increase gradually with the grafting yield. Meanwhile, the crystallites disruption takes place probably due to the strong interaction between the hydrophilic sulfonic acid groups and the hydrophobic PVDF matrix under the influence of the sulfonation of polystyrene grafts. The extent of the influence of both effects in the resulting membrane is evident from the fact that the membrane's crystallinity at 33.42% of grafting yield decreases to nearly one-eighth of its pristine value. Similar results were also discussed by Gupta *et al.* (1994), Hietala *et al.* (1997; 1999 b) and Nasef (2002) for styrene grafted and sulfonated FEP, PVDF and PTFE membranes, respectively. Thus, based on the aforementioned discussion, it may be concluded that the grafting yield and the two-step membrane preparation procedure that is grafting and sulfonation were found to have an effect on the thermal and structural properties (i.e T_m and crystallinity) of the resulting membranes.

TABLE 4 Thermal and structural properties of pristine, polystyrene pore-filled PVDF film and sulfonated polystyrene pore-filled electrolyte PVDF membranes with various grafting yields.

Membrane	T _m (°C)	T _c (°C)	X _c (%)
A	163.7	136.3	37.1
B	163.4	132.0	10.4
C	165.1	128.8	7.0
D	173.3	123.7	6.5
E	173.8	118.1	5.1

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