

Cation Exchange Membranes by Radiation-Induced Graft Copolymerization of Styrene onto PFA Copolymer Films. III. Thermal Stability of the Membranes

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ABSTRACT: Thermal stability of cation exchange, PFA-g-polystyrene sulfonic acid membranes prepared by radiation-induced graft copolymerization of styrene onto PFA films followed by sulfonation was studied by thermal gravimetric analysis (TGA) and oven heat treatment. The tested samples included original and grafted PFA films as reference materials. All the membranes showed multistep decomposition patterns due to dehydration, desulfonation, dearomatization, and decomposition of the PFA matrix. Investigations of the individual decomposition behaviors showed that the weight loss strongly depends upon the degree of grafting. However, the decomposition temperatures were found to be independent of the degree of grafting. The loss in some selected membrane properties such as ion exchange capacity and water uptake was found to be function of the degree of grafting, temperature, and the time of heat treatment. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1877–1885, 2000

Key words: TGA; thermal stability; cation exchange membrane; radiation-induced graft copolymerization

INTRODUCTION

Radiation-grafted cation exchange membranes have shown the potential to be used as separators and proton conductors in water electrolyzers and SPE fuel cells.^{1–3} Considerable work has been recently devoted to develop new cation exchange membranes by radiation-induced graft copolymerization of styrene onto various fluorinated and partially fluorinated polymer films such as PTFE, FEP, PVDF, and ETFE using simultaneous and preirradiation techniques.^{4–10} However, such membranes have to meet combinations

of requirements to maintain good separation and electrochemical capabilities. These requirements include high ionic conductivity, defined swelling behavior, high chemical resistance, and mechanical integrity.¹¹ Thermal stability is one of the most important requirements that depends mainly on the chemical and physical nature of the membranes and determines their operational temperatures. Polyanskii and Tulupov earlier reported a detailed review on the thermal behavior of various ion exchange membranes.¹² Moreover, investigations of thermal stability of polystyrene radiation-grafted and sulfonated FEP membranes and identification of their degradation products formed at various temperatures have been carried out by Gupta et al.^{13,14} These membranes were found to show a multistep degradation pattern, which was attributed to dehydration, desulfonation, dearomatization, and degra-

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dation of FEP matrix.¹³ Hietala et al.¹⁵ has conducted similar investigations onto polystyrene radiation-grafted and sulfonated polyvinylidene fluoride (PVDF) membranes. In our previous studies we reported the preparation of cation exchange membranes by simultaneous radiation grafting of styrene onto PFA films and subsequent sulfonation.^{16,17} The physico-chemical properties such as water uptake, ion exchange capacity, and ionic conductivity of these membranes were found to be dependent mainly on the degree of grafting.

This article reports the results of the thermal stability investigation of PFA-*g*-polystyrene sulfonic acid membranes. The results were analyzed in correlation with the degree of grafting. The effect of heat treatment on some selected properties of the membranes such as ion exchange capacity as well water uptake was also studied.

MATERIAL AND EXPERIMENTAL

Membrane Preparation

PFA-*g*-polystyrene sulfonic acid membranes were prepared by simultaneous radiation-induced graft copolymerization of styrene of purity more than 99% (Fluka) onto PFA film of 120 μm thickness (Porghof, USA). The grafting was carried out using γ -rays from a ⁶⁰Co source under nitrogen atmosphere and at ambient temperature. Details of the grafting reaction and the effect of grafting conditions on the degree of grafting were published elsewhere.¹⁶ The degree of grafting was determined as the weight gain and was calculated using the following equation:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where, W_g and W_0 are the weights of grafted and original films, respectively.

The grafted films were sulfonated using a mixture of chlorosulfonic acid/1,1,2,2 tetrachloroethane (30 : 70) at a temperature of 90°C for 5 h. After completion of the reaction, the membranes were washed with methylene chloride and dried in the air. Finally, the membranes washed several times with deionized water. Details of sulfonation of the grafted films can be found elsewhere.¹⁷ The degree of sulfonation of the membranes was found to be in the range of 90–100%.

Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was performed on membranes having various degrees of grafting. Samples of original and grafted PFA films were included as references. The samples were dried under vacuum at 60°C for 24 h, then were stored under dessicator. TGA runs were carried out on samples having typical weight of 10–20 mg using a Perkin-Elmer TGA-7 in a temperature range of 50–700°C. All the heating runs were made at a constant heating rate of 20°C/min in nitrogen atmosphere. A minimum of three specimens was tested for each sample.

Oven-Heat Treatment

Heat treatment of the membranes is carried out in an oven (Heraeus, Germany) at various temperatures in the range of 50–400°C under nitrogen atmosphere. The time of heat treatment was varied from 0.33 to 4.0 h. The weight loss, water uptake, and ion exchange capacity of the membranes were determined in each experiment, and compared with the same data obtained before running the test.

Ion Exchange Capacity

Ion exchange capacity (IEC) of the membranes was determined by acid-base titration. The membrane samples in acid form were immersed into 0.5M KCl solution overnight at room temperature. The protons (H^+) released in the solution were titrated with standerlized 0.05M KOH solution by automatic titrator (Metrohom, 702 SM Titrimo) until pH 7 was reached. Membrane samples were regenerated into acid form again by boiling with 3.5M HCl for 3 h. From the volume of KOH consumed in titration, IEC per unit mass (meq/g) of the membrane was calculated.

Water Uptake

Water uptake measurements were carried out by immersing clean and vacuum dried membrane samples in deionized water and boiling them until swelling equilibrium is reached. The membrane samples were removed, the excess of water adhering to the surface was quickly wiped by absorbent paper and then the membrane samples were weighed. The membrane water uptake was calculated according to the following equation:

$$\text{Water uptake (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (2)$$

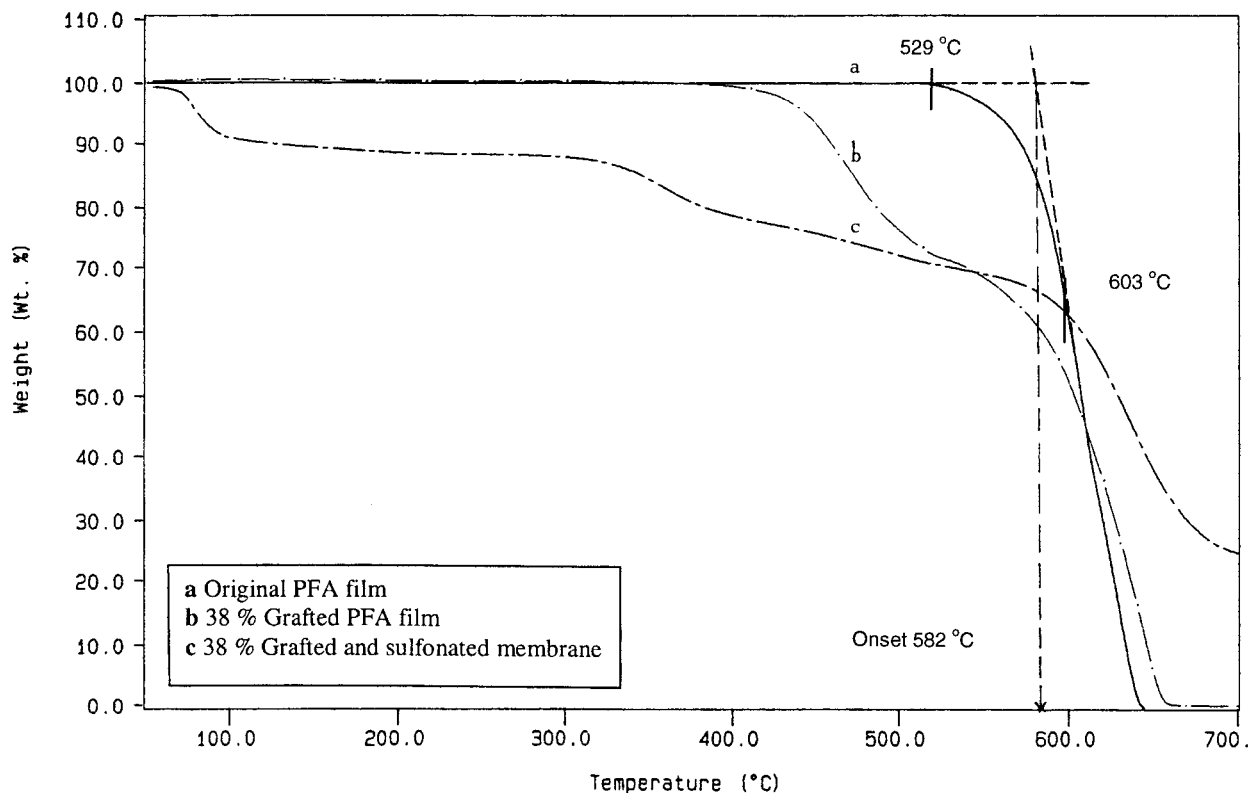


Figure 1 TGA thermograms of (a) original PFA film (b) 38% grafted PFA film, and (c) 38% grafted and sulfonated membrane.

where, W_w and W_d are the weights of wet and dried membranes, respectively.

RESULTS AND DISCUSSION

TGA thermograms of original PFA and 38% grafted PFA films as well as 38% grafted and sulfonated membrane are shown in Figure 1. As can be seen from thermogram "a", the original PFA film shows one-step decomposition pattern after being heated up to $\sim 530^\circ\text{C}$. Grafting of styrene onto PFA film results in PFA-g-polystyrene film having two-step decomposition patterns under the influence of TGA heat treatment as seen in thermogram "b". Both the incorporated polystyrene grafts and the PFA matrix undergo two distinct decomposition temperature starts at 420 and 530°C . It can be seen that the presence of polystyrene grafts in the grafted film does not bring any changes to the inherent decomposition temperature of the PFA matrix. These results are quite similar to those obtained by Gupta et al.¹³ and Hietala et al.¹⁵ upon studying the thermal decomposition of styrene grafted FEP and PVDF

films, respectively. It can be concluded that polystyrene grafts are incompatible with the PFA matrix. Such incompatibility arises from the difference in the nature and the structure of polystyrene grafts from that of PFA matrix. The former has an amorphous hydrocarbon structure, whereas the latter composed of crystalline fluorocarbon structure. As a result, phase-separated microdomains are formed in the grafted film. Similar conclusions have been drawn by Holmberg et al.⁹ and Hietala et al.¹⁸ for styrene-grafted PVDF films.

The sulfonation of the grafted films introduces three-step decomposition patterns as depicted from the three transitions shown in thermogram "c". The weight loss, which starts at a temperature below 100°C and continues to 200°C , is due to the removal of water bound to the hydrophilic sulfonic acid groups present in the membrane during the initial heating. The remaining of some water up to temperatures higher than 100°C is due to the strong hydrogen bonding between some water molecules and sulfonic acid groups. Similar behavior was observed for styrene-grafted and sulfonated FEP

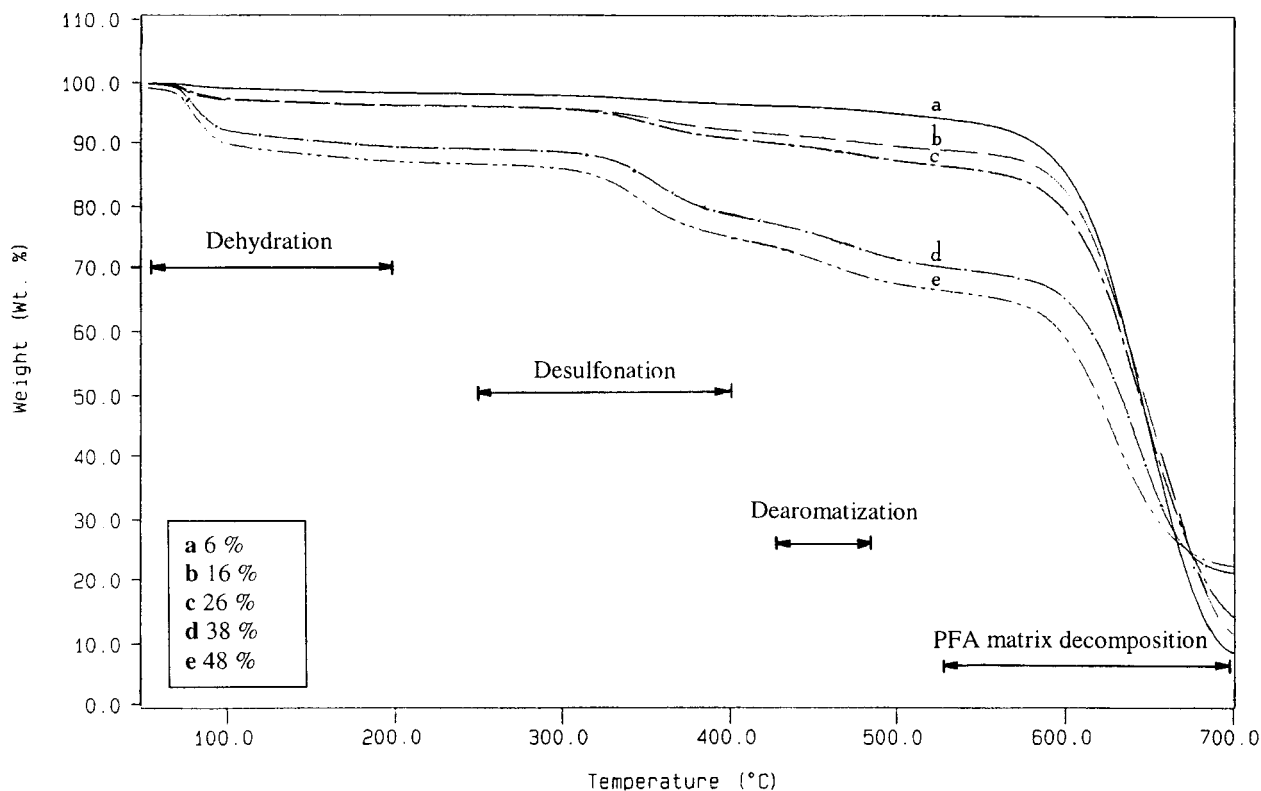


Figure 2 TGA thermograms of PFA-*g*-polystyrene sulfonic acid having various degrees of grafting: (a) 6%; (b) 16%; (c) 26%; (d) 38%; (e) 48%.

as well as PVDF proton exchange membranes. Commercial membranes such as Nafion 117 showed also a similar behavior.¹⁹

The initial decomposition of the sulfonated membrane almost starts at a temperature of $\sim 320^{\circ}\text{C}$ where the sulfonic acid groups degradation begins. The final decomposition pattern at a temperature of $\sim 530^{\circ}\text{C}$ is due the decomposition of PFA matrix. It can be observed that the decomposition region represented by the continuous weight loss in the range of $330\text{--}520^{\circ}\text{C}$ does not show clear discrimination between desulfonation and decomposition of polystyrene grafts. These observations suggest that the sulfonation of polystyrene-grafted PFA make the membrane more susceptible to thermal decomposition than only the grafted films. Based on the aforementioned results, it may be stated that the membranes are thermally stable to some degree up to $320 \pm 2^{\circ}\text{C}$ under the present experimental conditions.

The TGA thermograms of PFA-*g*-polystyrene sulfonic acid having various degrees of grafting are presented in Figure 2. All the membranes show multistep degradation patterns due to de-

hydration, desulfonation, decomposition of the polystyrene grafts (dearomatization), and PFA matrix. The initial weight loss due to dehydration takes place in a broad temperature range up to 200°C . The massive decomposition due to desulfonation is represented by the weight loss starts at a temperature about 320°C and continues to around 400°C . This was followed by the decomposition of polystyrene grafts in a temperature range of $420\text{--}490^{\circ}\text{C}$. The final decomposition pattern of PFA matrix occurs at a temperature around 530°C . It is found that the membranes do not undergo complete degradation, and some of the ashes are left behind at the end of the experiment. That result is in contrast to the original and grafted films, where no ashes are found at the end of the test. It is noticed that the weight of the formed ash increases with the increase in the degree of grafting. Such behavior is similar to that of styrene-grafted and sulfonated FEP as well as PVDF membranes.^{13,9} It can be suggested that the presence of sulfonic acid groups enhances the stability of the PFA matrix and the ash formation.

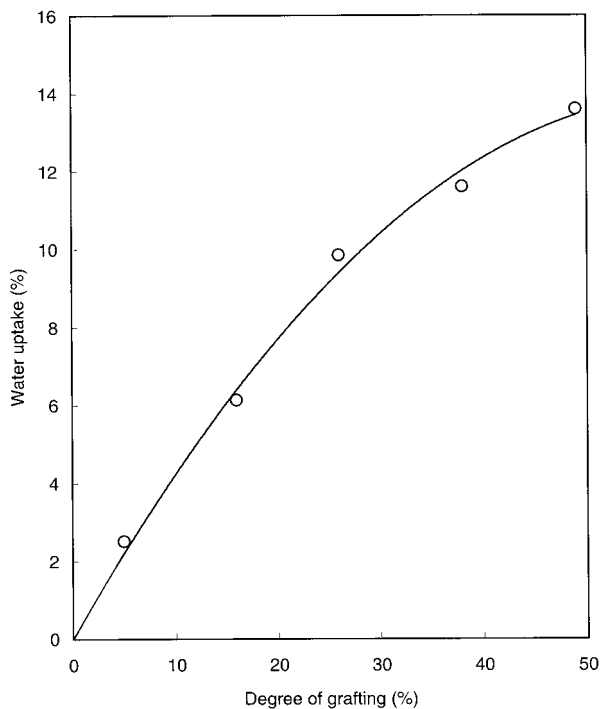


Figure 3 The variation of the water uptake with the degree of grafting at a temperature in the range of 50–200°C.

Behavior of the Individual Decomposition Steps Dehydration

To study the dehydration behavior of the membranes as a function of the degree of grafting, the loss in water uptake of the membranes is calculated from the weight loss recorded in the thermograms at a temperature range of 50–200°C. Figure 3 shows the variation of the water uptake with the degree of grafting at the temperature range of 50–200°C. It is found that the retained water uptake increases with the increase in the degree of grafting [calculated from eq. (1)]. The introduction of the hydrophilic sulfonic acid groups imparts a hygroscopic nature to the membranes. As the degree of grafting increases, the amount of sulfonic acid increases, and as a result, the membrane hydrophilicity increases. Therefore, membranes having high degrees of grafting retain more water than those having low degrees of grafting. These results are in a good agreement with those related to radiation-grafted polystyrene sulfonic acid membranes based on FEP and PVDF films.^{13,15}

Desulfonation

The desulfonation behavior of the membranes is investigated from the thermograms depicted in

Figure 2. The desulfonation temperature of all membranes was found to remain almost constant for all the membrane at about 320°C, regardless the degree of grafting. Such results suggest that the desulfonation is independent process, and does not interfere with the decomposition of both of polystyrene grafts and PFA matrix in all membranes. However, the weight loss during the desulfonation is found to be a function of the degree of grafting, as can be seen from Figure 4. This figure shows the variation of the weight loss due to desulfonation with the degree of grafting at a temperature range of 200–320°C. It is found that the weight loss due to desulfonation increases with the increase in the degree of grafting. This is attributed to the increase in the amount of sulfonated polystyrene grafts with the increase in the degree of grafting, which are susceptible to thermal decomposition. These results suggest that the amount of decomposition taking place in the membranes strongly depends upon the amount of sulfonated polystyrene grafts contained in the membrane, i.e., the degree of grafting. These results are in a complete agreement with those reported for styrene-grafted and sulfonated FEP as well as PVDF membranes.^{13,15} It can be con-

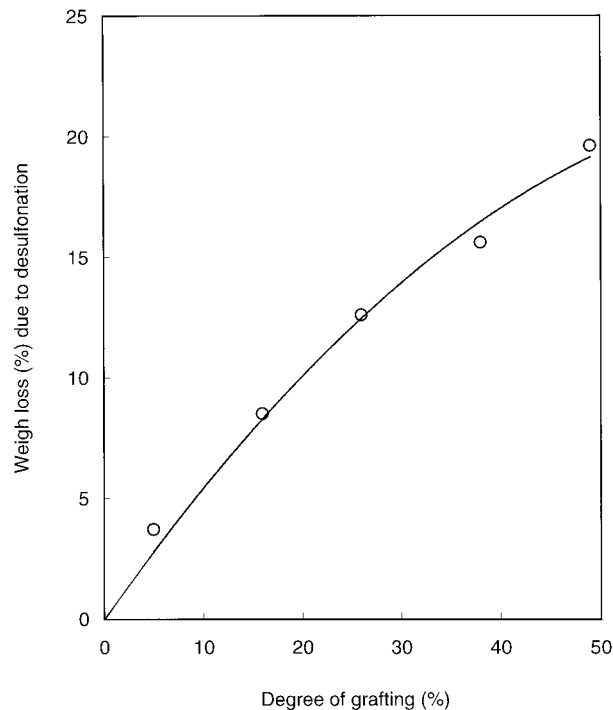


Figure 4 The variation of the weight loss due to desulfonation with the degree of grafting at a temperature in the range of 200–320°C.

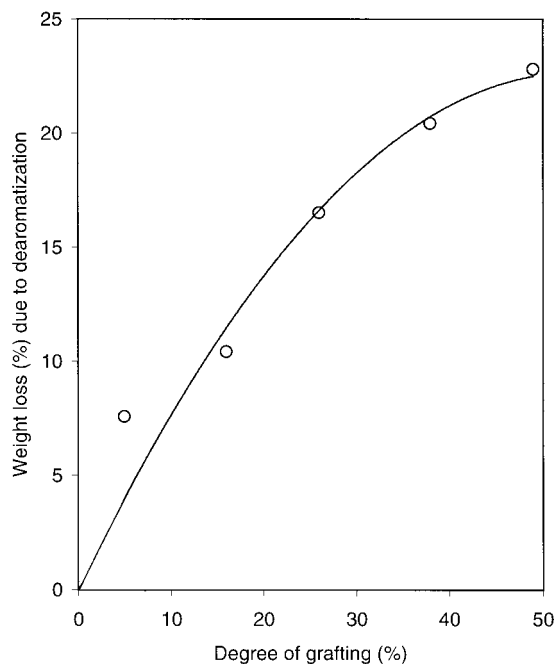


Figure 5 The variation of the weight loss due to the dearomatization with the degree of grafting at a temperature in the range of 350–490°C.

cluded that membranes having lower degrees of grafting are more thermally stable than those having higher degrees of grafting.

Dearomatization

The dearomatization (decomposition of polystyrene grafts) behavior of the membranes is investigated through the recorded weight loss in the TGA thermograms in the range of 350–490°C. Figure 5 shows the variation of the weight loss due to the dearomatization with the degree of grafting at the temperature range of 350–490°C. The weight loss is found to increase with the increase in the degree of grafting. This result suggests that the dearomatization is a function of the degree of grafting. However, it is important to mention that the dearomatization temperature ($420 \pm 2^\circ\text{C}$) remained almost constant for all the membrane, as can be seen from Figure 2. Therefore, it is independent of the degree of grafting.

PFA Matrix Decomposition

The polymer matrix degradation behavior represented by weight loss of the membranes is calculated from the weight loss recorded in the TGA thermograms in the range of 530–650°C. Figure 6 shows the variation of the weight loss during

the decomposition of PFA matrix and the degree of grafting at temperature in the range of 530–650°C. It is found that the weight loss decreases with the increase in the degree of grafting in the membranes. These results confirm the increase in the weight of the membrane ash with the increase in the degree of grafting. These results suggest that the incorporation of sulfonic acid groups induce the tendency of the char formation in the membrane, and this tendency increases with the increase in the degree of grafting. Similar conclusions were suggested for polystyrene sulfonic acid membranes that are based on FEP and PVDF films.^{13,15} The decomposition temperature of the PFA matrix of all membranes was found to be almost constant for all the membrane ($530 \pm 3^\circ\text{C}$), regardless the degree of grafting, as depicted in Figure 2. This indicates that the decomposition temperature of the PFA matrix is also independent of the degree of grafting.

Effect of Heat Treatment on the Membrane Properties

Ion Exchange Capacity

The correlation between the ion exchange capacity (IEC) retained in a membrane having a 38%

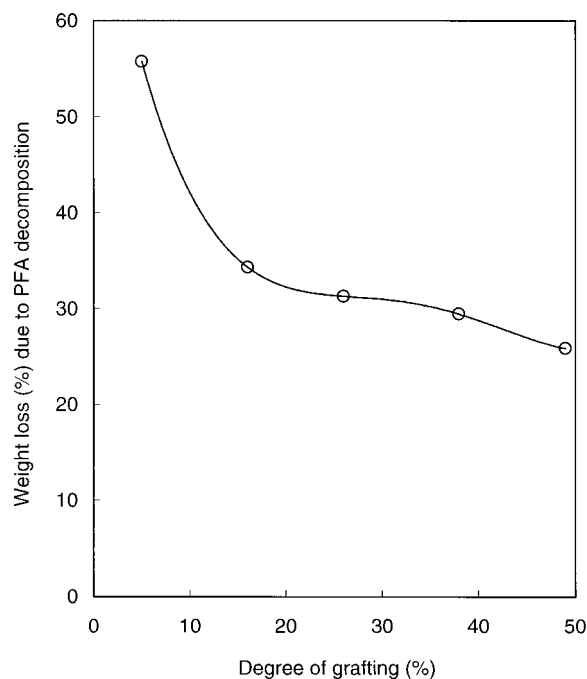


Figure 6 The variation of the weight loss during the decomposition of PFA matrix and the degree of grafting at temperature in the range of 530–650°C.

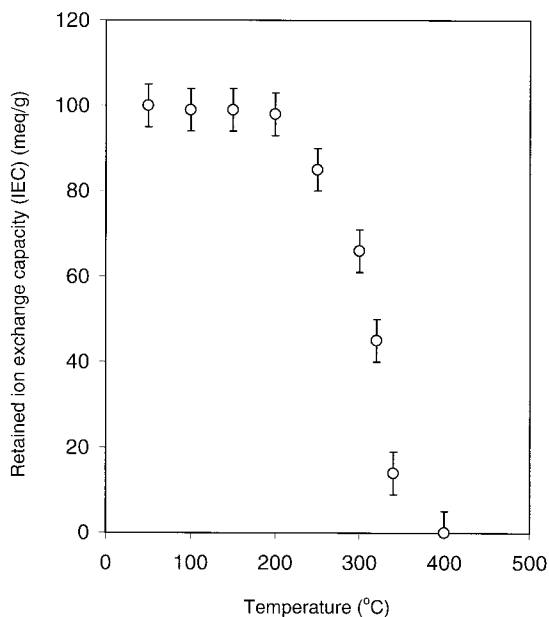


Figure 7 The correlation between the ion exchange capacity retained in a membrane having a 38% degree of grafting and the oven treatment temperature.

degree of grafting and the oven treatment temperature is shown in Figure 7. It is found that the IEC is nearly constant until a temperature as high as 200°C. However, further heating causes a sharp drop in the retained IEC until it completely vanishes at a temperature of ~400°C. Figure 8 depicts the correlation between the time of the heat treatment and IEC of a membrane having a 38% degree of grafting. As can be observed, the IEC decreases sharply in the first hour then gradually with the increase in the time of heat treatment and reaches zero after ~4 h. This result is in a complete agreement with that reported for FEP-g-polystyrene sulfonic acid membrane, having a degree of grafting of 40%.¹³ The sharp decrease in the IEC at the first hour is ascribed to the massive weight loss due to the decomposition of the sulfonic acid groups (desulfonation). Prolonging of heat treatment time brings further decomposition to the sulfonic acid groups (but at lower levels than decomposition at the first hour) until their complete removal from the membrane is reached at a temperature around 400°C. This result indicates that the loss in IEC (desulfonation) is a time-dependent process. A similar trend was reported for polystyrene/divinylbenzene sulfonic acid resin.²⁰

The variation of the IEC with the degree of grafting under the effect of heat treatment at a

temperature of 320°C for 20 min compared to untreated membranes is shown in Figure 9. It can be obviously seen that the heat-treated membranes show lower IEC compared to the untreated ones, and the amount of loss in IEC is found to be approximately equal to one-half of its original value. Moreover, the fraction of the retained IEC is almost constant for all the membranes. These results are in a good agreement with those related to styrene grafted and sulfonated FEP Membranes and polystyrene resins, which were obtained by Gupta et al and Karpov et al., respectively.^{13,21}

Water Uptake

The correlation between the water uptake retained in a membrane having a 38% degree of grafting and the oven treatment temperature is shown in Figure 10. The retained water uptake shows no significant change until 200°C. Further heating causes a sharp decrease in the retained water uptake until it completely vanishes at a temperature of ~400°C. This result shows a similar trend to that of the correlation between IEC

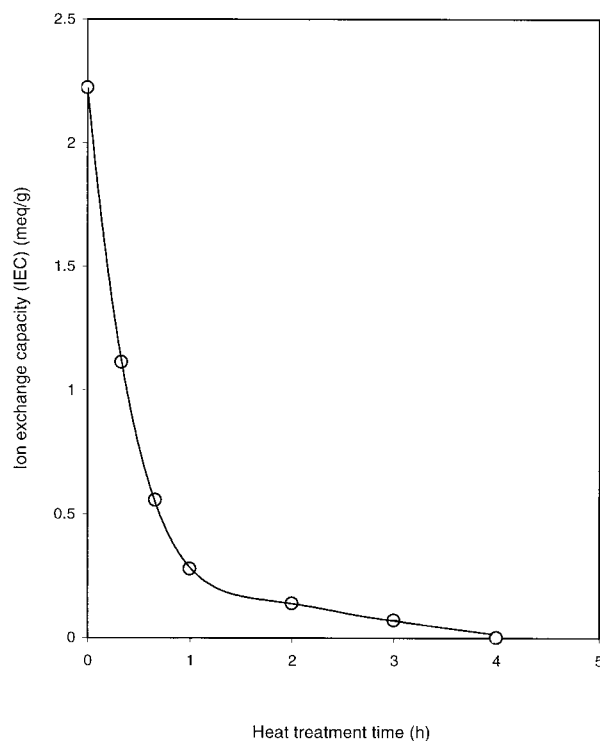


Figure 8 The correlation between the time of the heat treatment and the retained ion exchange capacity of a membrane having a 38% degree of grafting at a temperature of 330°C.

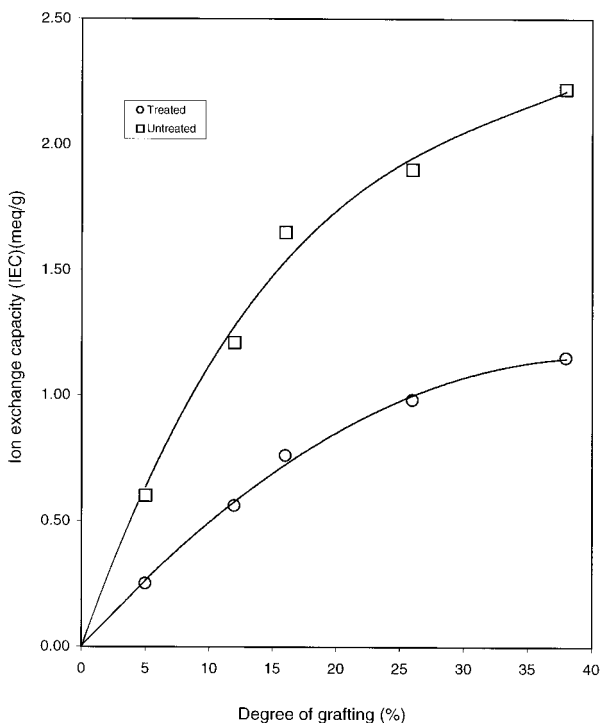


Figure 9 The variation of the ion exchange capacity with the degree of grafting under the effect of heat treatment at a temperature of 330°C for 20 min.

retained and the oven heat treatment temperature presented in Figure 7. This due to the interrelationship between the water uptake and the fraction of sulfonic acid groups controlling the IEC in the membrane. Higher IEC leads to higher water uptake and vice versa. However, the reduction in water uptake is found to be very high compared to that of IEC at the same experimental conditions.

The variation of the water uptake with the degree of grafting of the heat-treated membranes compared to untreated membranes is presented in Figure 11. It is found that the water uptake of the heat-treated membranes is drastically reduced compared to that of untreated membranes. Moreover, there is a similarity in trends between the effect of heat treatment on the water uptake of the membrane and that of the effect of the heat treatment on the IEC presented in Figure 9. However, the reduction in water uptake is found to be very high as compared to that of IEC at the same experimental conditions. The drastic decrease in water uptake of the heat-treated membranes is mostly due to the reduction in the imparted hydrophilicity of the membranes resulting from the decrease in the number of sulfonic acid groups.

The high loss in water uptake compared to IEC is attributed to the possible crosslinking of the molecular chains taking place during the desulfonation and involving two neighboring polystyrene grafts. Such possible crosslinking causes a hindrance in the mobility of the polystyrene side chains and subsequent restriction in the membrane water sorption. This resulted in a formation of rigid crosslinked structure in the membrane and, therefore, the water uptake was sharply decreased. This behavior is quite similar to that of styrene-grafted and sulfonated FEP membranes, and is explained on the same basis proposed by Gupta et al.^{13,14}

CONCLUSION

TGA thermal stability investigations showed that PFA-g-polystyrene sulfonic acid membranes undergo multistep degradation patterns due to dehydration, desulfonation, dearomatization, and decomposition of the PFA matrix. These membranes were found to be stable to around 320°C under nitrogen atmosphere. The desulfonation of the membranes was found to strongly affect their ion exchange capacity, and water uptake as re-

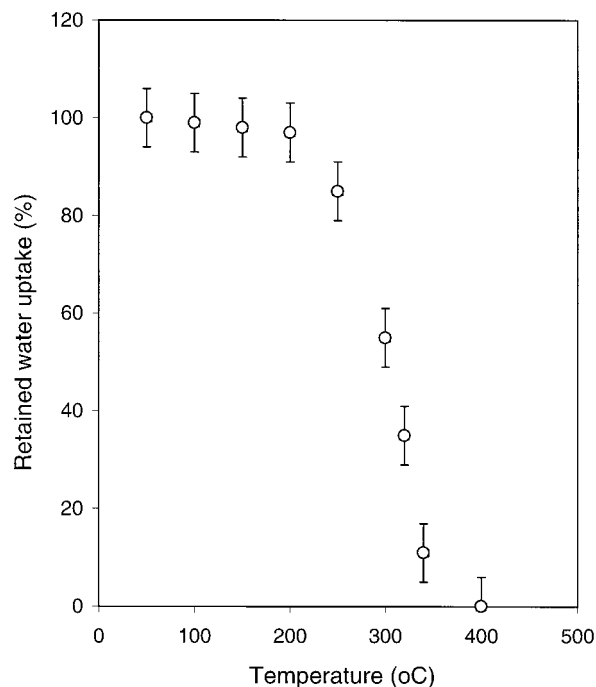


Figure 10 The correlation between the water uptake retained in a membrane having a 38% degree of grafting and the oven-treatment temperature.

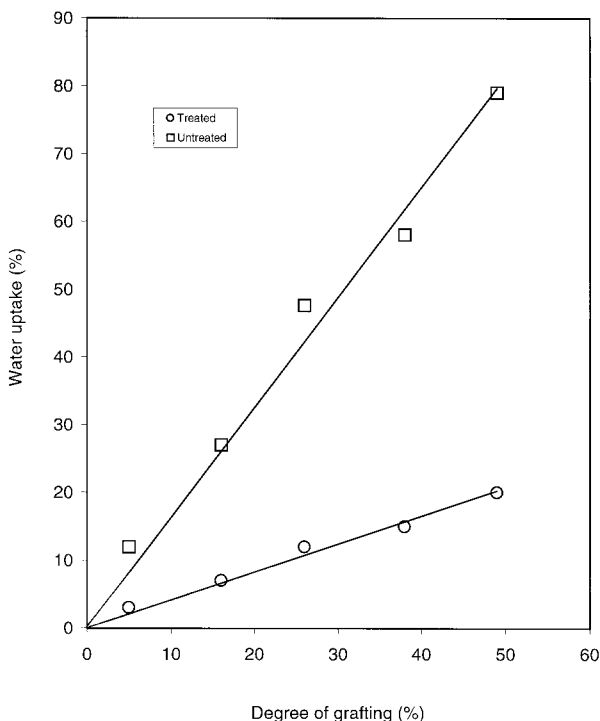


Figure 11 The variation of the water uptake with the degree of grafting of the heat-treated membranes compared to untreated membranes.

vealed from oven heat-treated samples. The water uptake of the heat-treated membranes was found to decrease to much higher levels compared to the decrease in the ion exchange capacity at the same experimental conditions. The desulfonation was suggested to leave the membranes rigid and crosslinked via interaction of two sulfonic acid groups from the same or adjacent polystyrene chains.

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