Thermal Properties of Proton-Conducting Radiation-Grafted Membranes

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ABSTRACT: Proton-exchange membranes are required to exhibit chemical, mechanical, and thermal stability for fuel cell applications. The present investigation has been carried out to explore the thermal behavior of poly(ethylene-alt-tetrafluoroethylene) (ETFE)-based proton-conducting membranes, both uncrosslinked and crosslinked, prepared by radiation grafting and subsequent sulfonation. The influence of preparation steps (irradiation, grafting, sulfonation, crosslinking) on the thermal degradation, crystallinity, and melting behavior of membranes with varying degree of grafting was examined. ETFE base film and grafted films were studied as the reference materials. Furthermore, poly(tetrafluoroethylene-co-hexafluoropropylene)-based grafted films and membranes were investigated as well for comparison. Membrane preparation steps, degree of grafting, crosslinking, type of base polymer have considerable influence on the thermal properties of membranes. The crystallinity of the films decreases slightly by grafting, while a significant decrease was observed after sulfonation. For instance, crystallinity decreased from 37% (pristine ETFE) to 36% (uncrosslinked grafted film) and 23% (uncrosslinked ETFE-based membrane). On the other hand, the melting temperature of the base polymer was almost unaffected by irradiation and grafting. The crosslinked ETFE-based membranes exhibit a slightly higher melting temperature (262.5 °C) than their corresponding grafted films (261.3 °C) and the base film (260.6 °C). © 2008 Wiley Periodicals, Inc.

Key words: thermal properties; membranes; irradiation; differential scanning calorimetry; thermogravimetric analysis

INTRODUCTION

Polymer electrolyte membranes used in low temperature fuels have a dual function, to provide proton transfer between the anode and the cathode and to separate these compartments. Radiation-induced grafting, including the subsequent sulfonation reaction, has been used to develop proton-conducting membranes, which are considered to be low-cost replacements for Nafion membranes for low-temperature fuel cells. Our laboratory prepared polymer electrolyte membranes using styrene as the monomer and poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) as the base polymer film and divinyl benzene (DVB) as the crosslinker by radiation-induced grafting followed by subsequent sulfonation. These membranes were evaluated in low temperature fuel cells and the performance, in terms of current–voltage properties of these membranes, comparable to commercially available Nafion membranes and durability of several thousand hours have been demonstrated.1,2

Later, we used substituted styrene monomers with protected α-position, α-methylstyrene/methacrylonitrile, and α,β,γ-trifluorostyrene derivatives to enhance the durability.3,4 Recently, we revisited the synthesis and characterization of radiation-grafted membranes using poly (ethylene-alt-tetrafluoroethylene) (ETFE) as the base material, because of its higher radiation stability and superior mechanical properties as compared with FEP. Previously, we reported on radiation-initiated grafting of styrene onto ETFE in the presence of DVB as the crosslinker, characterization of fuel cell relevant properties, and cell performance of the resultant membranes.5 Subsequently, a detailed study on the influence of grafting parameters and reaction kinetics were performed for the combination of styrene/ETFE.6 The desired high operating temperatures (up to 100 °C) and the aggressive chemical environment of fuel cells require excellent mechanical and thermal properties for the membranes. Thermal stability of membranes strongly depends on the chemical and physical properties of the materials. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are fast and reliable methods to determine material properties such as crystallinity,
glass transition, melting, and decomposition behavior. The investigation of thermal stability and melting behavior of styrene-grafted FEP-based films and membranes have been performed by Gupta et al.\textsuperscript{7–9} Moreover, authors carried out the identification of degradation products formed to understand the possible degradation mechanisms.\textsuperscript{10,11} The thermal stability, phase separation, and crystallinity of styrene-grafted poly(vinylidene fluoride) (PVDF) membranes have been investigated in detail by Hietala et al.\textsuperscript{12,13} Nasel et al. studied the thermal properties of styrene-grafted FEP,\textsuperscript{14,15} poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA),\textsuperscript{16,17} poly(tetrafluoroethylene) (PTFE),\textsuperscript{18} PVDF\textsuperscript{19} based membranes.

As aforementioned, much previous work was oriented toward thermal characterization of styrene-grafted FEP-, PTFE-, PFA-, PVDF-based films and membranes, and however, there is only little quantitative data on ETFE-based materials. Characterization of ETFE base polymer films by various techniques including DSC was reported earlier; yet, the authors mainly focused on the effect of base film properties and irradiation method.\textsuperscript{20} In a previous work, we examined the thermal properties of the radiation-grafted films based on FEP, ETFE, and PVDF.\textsuperscript{21} We reported on the influence of irradiation and grafting procedures on crystallinity and thermal degradation of ETFE-based grafted films in detail, whereas ETFE-based membranes were not studied.

Compared with previous work on thermal properties performed in our laboratory or by other research groups, we currently use a quite different membrane preparation method by radiation grafting. To begin with, we perform electron beam irradiation instead of γ-irradiation and we use the preirradiation method instead of simultaneous irradiation with very low irradiation doses (1.5 kGy). Then, grafting is carried out using nonsolvents, a mixture of isopropanol and water, instead of bulk styrene grafting. Moreover, mild sulfonation conditions (low concentration of chlorosulfonic acid, room temperature reaction) are used. Consequently, the resultant ETFE-based membranes exhibit different ex situ properties; therefore, it is desirable to characterize the resultant ETFE-based membranes.

The present investigation has been carried out to study the thermal behavior of mainly ETFE-based proton-conducting membranes, both uncrosslinked and crosslinked, prepared by the preirradiation grafting method and subsequent sulfonation. Melting behavior and crystallinity of the ETFE-based membranes have been investigated by DSC and thermal stability and degradation behavior of the membranes have been studied by TGA. In addition, ETFE-based grafted films have been examined to understand the influence of grafting procedures. Furthermore, FEP-based membranes have been analyzed as the reference materials for the investigation of melting and thermal stability.

**EXPERIMENTAL**

**Materials**

Tefzel® ETFE 100LZ film, having a thickness of 25 μm was purchased from DuPont, Circleville, OH, USA. The average molar weight ($M_w$) is 1,200,000 Da. Teflon-FEP® 100A film with a thickness of 25 μm was purchased from the same supplier. The average molar weight ($M_w$) of the FEP 100 is 325,000 Da.

The reagents used during membrane preparation are isopropanol (analytical grade; Fisher Scientific, Wohlen, Switzerland), styrene (purum grade; Fluka, Buchs, Switzerland), and DVB (technical grade, ~80%, mixture with isomers 3- and 4-ethylvinylbenzene; Fluka), dichloromethane (Fluka), chlorosulfonic acid (Fluka).

**Membrane preparation**

Both ETFE and FEP base films were preirradiated in an air atmosphere with an electron beam source. The total irradiation dose was 1.5 kGy for ETFE and 3 kGy for FEP films (1 Gy = 1 J/g energy absorbed). The samples were stored at −80°C after irradiation. The irradiated base films were grafted using a solution of styrene and DVB (styrene:DVB, 9 : 1 (v/v)) in an 11 : 5 (v/v) isopropanol/water. Grafting reactions were performed at 60°C for grafting times varying between 15 min to 24 h under inert atmosphere. The irradiated film samples were thoroughly washed with toluene after grafting and then dried at 80°C overnight. The graft levels (GL) of the samples were determined by the difference between the weight of the base polymer film (initial weight) and the weight of the grafted sample divided by the initial weight.

Sulfonation of grafted films were performed with chlorosulfonic acid in dichloromethane (2% (v/v)) for 5 h at room temperature and then the introduced functional groups were hydrolyzed and ion-exchanged using sodium hydroxide and treated with hydrochloric acid to regenerate the acid form of the membrane. Finally, the resultant membranes were immersed in deionized water for 2 h at 80°C to obtain the water-swollen membranes.

**Differential scanning calorimetry**

DSC measurements were performed on a Perkin–Elmer DSC7 instrument under N₂ atmosphere. Indium ($T_m = 156.6°C$) and lead ($T_m = 327.5°C$) standards were employed for the temperature and energy calibration.
The membranes were converted to salt form and then dried at 50°C in an oven for at least 6 h. Single heating curves were obtained at a constant heating rate of 20°C/min over a range of 30–300°C using a constant nitrogen flow. Prior to measurements, the probes were flooded with nitrogen for at least 10 min inside the sample holder. The following integration limits were chosen for the measurement of the heat of fusion (ΔHf): 210–272°C for ETFE and 220–288°C for FEP.

The degree of crystallinity of the base polymer film was calculated according to the following equation:

\[
\text{Crystallinity (\%)} = \frac{\Delta H_f}{\Delta H_0} \times 100
\]

where ΔHf is the heat of fusion determined from the peak area of the melting and ΔH0 is the reported value of heat of fusion for 100% crystalline polymer (113.4 J/g for ETFE and 87.9 J/g for FEP, respectively). A correction was applied for the dilution of the base polymer by grafted polystyrene and sulfonic acid group (in salt form) for the determination of the inherent (intrinsic) crystallinity.

Thermogravimetric analysis

TGA measurements were carried out on a Perkin-Elmer TGA7 instrument under nitrogen atmosphere. The temperature calibration was performed according to the Curie point of alumel and perkalloy as calibration standards. Single heating curves were obtained at a constant heating rate of 20°C/min over a range of 50–650°C. Films were purged with a nitrogen flow in the TGA chamber for at least 10 min prior to measurement and membranes were heated to 100°C and hold at this temperature for 10 min to remove excess water prior to TGA measurements.

The relative thermal stability of the films and membranes was evaluated in terms of the initial decomposition temperature (IDT) at which the first 2% mass loss had occurred. The TGA curves were differentiated to determine the maximum rate decomposition temperature (MRDT), selecting the minima of the first derivative. The specific weight loss of a decomposition feature was determined by the local maxima of the first derivative.

RESULTS AND DISCUSSION

Melting behavior and crystallinity by DSC

The melting points and heats of fusion of ETFE- and FEP-based membranes and their respective base films and grafted films were determined from single heating (melting) curves of DSC thermograms. The melting endotherms of these materials were generally increasing slightly over a broad temperature range before reaching the maximum and then decreasing sharply to the baseline value. This can be explained by a big range of small crystallites melting at lower temperatures.

It was reported previously that the polymer melting behavior and crystallinity were influenced by radiation processing.22 Pristine ETFE films, electron beam irradiated with 1.5–30 kGy in air, were investigated by DSC as depicted in Figure 1. A broad single melting peak is present for all doses and it is clear that melting behavior is not affected by irradiation dose in this range. The inset shows the influence of irradiation dose on crystallinity and melting temperature (Tm). It is observed that a preirradiation step (within the limits of irradiation dose used in this study) does not yield significant changes in melting and crystallinity of pristine ETFE films. That is to say, the melting temperature (average crystallite size) is almost constant with increasing irradiation dose, whereas a slight increase in crystallinity of the base film upon irradiation is determined. This may be attributed to the crystallization of mobile short-chain segments formed due to chain scission reactions. A similar behavior was reported previously for FEP, ETFE, PVDF films even with the use of different irradiation procedures (irradiation by γ-rays or inert atmosphere, etc.).20,21 Nasef et al.23 reported an initial increase in crystallinity of ETFE base films after electron beam irradiation up to 100 kGy, beyond which it decreased gradually as the dose increased (up to 1200 kGy), due to the growing crystalline defects at high doses. These authors also observed a significant decrease in Tm with irradiation in this dose range.
The water in the membranes produces a broad endothermic peak at around 50–150°C, and consequently influences the baseline up to 170°C (Fig. 2). Several drying procedures were investigated to minimize the interference of water. It was found that drying the acid form of the membrane at 50°C with or without vacuum did not yield an improvement, whereas drying the membrane (acid form) at 100°C diminished the water effect to some extent. However, a membrane again quickly absorbed water. The removal of water was accomplished by converting the acid form of the membrane to the salt form and subsequent drying at 50°C for at least 6 h. This conversion did not cause the change of the measured values of $\Delta H_f$ and $T_m$ offering a stable measurement process. Moreover, it is not required to proceed the tedious drying procedures (drying for several days) prior to DSC measurements, unlike as described in previous publications.\textsuperscript{14,19}

DSC thermograms of the ETFE base film, ETFE-$g$-PS (grafted film, crosslinked), and ETFE-$g$-SPS (membrane, crosslinked), both with GLs of 21%, are shown in Figure 3(a). Although the radiation grafting of styrene and subsequent sulfonation induce some structural changes in base polymer film, the melting behavior of the grafted film and membrane is found to be similar to that of the base film. The crosslinked ETFE-based membranes exhibit a slightly higher melting temperature (262.5°C) than their corresponding grafted films (261.3°C) and the base film (260.6°C) [Fig. 3(a)]. Uncrosslinked ETFE-based membranes behave in the same manner (data not shown).

The DSC thermograms of crosslinked ETFE-based membranes with varying graft levels (GL: 4–55%) (membrane, crosslinked, GL: 21%) are compared in Figure 3(b). The melting temperature of the membrane (273.8°C) is marginally higher than those of the base film (268.7°C) and of the grafted film (269.6°C). The perfluorinated FEP films and membranes have higher melting temperatures than the partially fluorinated ETFE-based samples. Furthermore, the much higher and narrower endotherms for ETFE-based materials compared with those for FEP offer more accurate results for $\Delta H_f$ and $T_m$. Interestingly, while the peak shapes for ETFE membranes are rather broadened compared with those of the base film and the grafted film, FEP membranes have an even more pronounced melting maximum than their corresponding films, similar to the earlier findings of Gupta and coworkers\textsuperscript{7,9} On the contrary, previously Nasef et al.\textsuperscript{19} reported a remarkable decrease in melting temperature of PVDF films (167.9°C) after sulfonation (160.4°C) and it was attributed to the deterioration, which occurred in the crystallites due to sulfonation.

The DSC thermograms of ETFE of base film, grafted film (crosslinked), and membrane (crosslinked). (b) DSC thermograms of FEP of base film, grafted film (crosslinked), and membrane (crosslinked).
are depicted in Figure 4. It is observed that the shape of the thermograms under the melting peak changed with GL. Consequently, the peak height and the area under the thermograms, corresponding to the heat of fusion, decrease with GL. This may be attributed to the deterioration in the crystalline structure of pristine polymer by the grafting and sulfonation procedures. Moreover, $T_m$ remains almost constant with graft level ($\sim 261^\circ C$). FEP-based membranes investigated under the same conditions exhibited a similar trend (data not shown). Moreover, there was no significant difference in terms of melting behavior between crosslinked and uncrosslinked materials, based either on ETFE or FEP. These results are in agreement with those reported for other grafted films and membranes based on FEP,\textsuperscript{7,9,21} ETFE,\textsuperscript{21} PVDF,\textsuperscript{21} poly(ethylene terephthalate),\textsuperscript{24} and high-density polyethylene.\textsuperscript{25}

DSC is a versatile method to determine the crystallinity of polymers. The variation of crystallinity of both grafted films and membranes based on ETFE is shown in Figure 5. In the case of grafted films, the measured $\Delta H_f$ values decrease by increasing GL. Previously, it was reported that the measured $\Delta H_f$ of the grafted films was truly the heat of fusion of the backbone component, whereas the polystyrene fraction did not contribute at all.\textsuperscript{7} Therefore, the decrease in heat of fusion by grafting is predominantly caused by the dilution of inherent crystallites of the backbone by the incorporation of amorphous polystyrene moiety in the grafted films. It is known that grafting occurs preferentially in the amorphous phase of the semicrystalline polymer, since the monomer diffusion is slow and radicals are less reactive in the crystalline phase. The inherent crystallinity can be determined from the corresponding heat of fusion values after correcting for the weight fraction. The inherent crystallinity of the grafted films drops only slightly as a function of GL. Although, the reduction in crystallinity follows a similar trend for crosslinked and uncrosslinked samples, the decrease in crystallinity is more significant in the case of crosslinked films. This can be attributed to some stress, introduced to the base material produced by the rigid crosslinked polystyrene domains.

The decrease in inherent crystallinity is more pronounced in the case of membranes. Once the films are sulfonated, the hydrophilic polystyrene sulfonic acid domains, which absorb water within the hydrophobic polymer matrix, lead to strong hydrophilic-hydrophobic stress in the membrane. Consequently, distortion of the crystallites occurs. Therefore, the decrease of inherent crystallinity for the membranes is due to the cumulative influence of the dilution effect and crystal disruption.

Moreover, the difference between the crosslinked and uncrosslinked membranes in terms of inherent crystallinity is not substantial. The probably greater stress in the more rigid crosslinked samples upon swelling might be balanced by the lower swelling value itself.

Although FEP-based grafted films and membranes, measured under the same conditions, followed a similar trend, some differences were detected as well (data not shown). Besides their different initial crystallinities, the crystallinity of ETFE decreased more rapidly upon grafting and sulfonation, compared with that of FEP. For instance, crystallinity decreased from 37% (pristine ETFE) to 23% (highly grafted ETFE-based membrane) and from 22% (pristine FEP) to 17% (highly grafted FEP-based membrane). In our earlier study, we determined that ETFE-based membranes exhibited a lower water content compared with FEP-based membranes, while both have a similar GL and the same DVB concentration in the initial grafting solution.\textsuperscript{5} For instance,
hydration numbers (number of water molecules per sulfonic acid group) were typically 6 and 9 for ETFE- and FEP-based membranes, respectively. Such a difference may be resulting from many factors. One factor can be the different crystallinity of the base materials. It is known for a polymer material, which exhibits low crystallinity, that water penetration into the matrix will be facilitated. Because the crystalline regions are impermeable to water, water molecules can approach ionic sites in the unordered (amorphous) region more easily. Consequently, the water content will be higher.

The variation of crystallinity of FEP-based grafted films and membranes with graft level was previously investigated in detail by Gupta et al. These authors reported almost no change in crystallinity by grafting and a considerable decrease in crystallinity by sulfonation. Similar results were published for PFA based grafted films and membranes. However, in a recent investigation, the influence of the irradiation and grafting processes on the crystallinity was investigated for FEP, ETFE, PVDF polymers by DSC. The grafting process was found to have the largest effect on base polymer crystallinity and resulted in a reduction of crystallinity in all cases. In fact, these authors used different grafting conditions (irradiation in inert atmosphere, high doses, styrene in toluene, etc) when compared with our study. Similarly, Hietala et al. also reported a significant decrease in crystallinity of PVDF films because of grafting.

Thermal stability and degradation behavior by TGA

Thermal stability and degradation behavior of radiation-grafted films and membranes were determined by TGA. Typical TGA results for the comparison of the base film, grafted film, and membranes are shown for ETFE- and FEP-based materials in Figures 6(a,b), respectively. In both cases the grafted film and the membrane have a GL of 21%. It is observed that the partially fluorinated ETFE is stable up to ~ 440°C, while perfluorinated FEP stays stable up to ~ 470°C, beyond which a smooth decrease in weight is detected. One weight loss step for pristine ETFE film and two poorly resolved weight loss steps for pristine FEP film are determined. The two step behavior of FEP can be explained by the loss of C3F6 first, followed by C2F4 fragments.

Upon grafting an additional decomposition step is introduced starting at about 380°C due to the degradation of grafted polystyrene. This is followed by the degradation of the backbone. The presence of polystyrene grafts does not change the decomposition temperature of the base polymer matrix. Polystyrene is composed of an amorphous hydrocarbon structure, while ETFE or FEP have a crystalline fluoro- carbon structure and as previously stated the polystyrene-grafted copolymer films behave as a two-phase system, where the polystyrene moiety forms a separate microdomain in the base polymer matrix. Similar behavior was published for the polystyrene-grafted ETFE, FEP, PVDF films, and PVDF films.

The specific weight loss due to the degradation of polystyrene grafts, determined by the local maxima of the first derivative of the TGA scans, as a function of polystyrene content of the ETFE- and FEP-based films, is presented in Figure 7. The situation in which the thermal degradation of the grafted polystyrene is independent of the degradation of the backbone is regarded as ideal behavior (slope = 1). It is clear that FEP-g-PS films, both crosslinked and uncrosslinked, exhibit almost ideal behavior. On the contrary, ETFE-g-PS films, especially the uncrosslinked samples, have data points well above this ideal line. Brack et al. observed a similar behavior for ETFE-based grafted films in an earlier investiga-
tion. These authors explained the less independent nature of the polystyrene degradation in the ETFE films by having the weaker C-H bonds in ETFE, which lead to easier abstraction reactions and better miscibility of polystyrene with the amorphous regions of the backbone.

It was determined that the degradation pattern of the membranes was dependent on the drying procedure prior to TGA measurements. To avoid the water interference, the membranes were converted to salt form and then dried according to the procedure described in the DSC section. Although similar thermograms were obtained for both the acid form and the salt form of the membranes up to 300°C, considerable difference in terms of decomposition of these two forms beyond that temperature was observed. Therefore, the acid form of the membranes was heated to 100°C in the TGA and hold at this temperature for 10 min to remove the excess water, before starting the weight loss analysis.

TGA thermograms of crosslinked ETFE-based membranes with various GLs are presented in Figure 8. The weight loss in the case of membranes takes place in several stages. A slight change in weight starting from below 100°C up to 200°C can be seen, which presents most probably the evolution of water that was bound to sulfonic acid groups of the membranes. Then, the second decomposition starts at ~280°C, due to degradation of sulfonic acid groups (desulfonation), and finally the degradation of ETFE backbone, which starts at ~460°C. However, desulfonation could not be observed as a separate step for all membranes, because it smoothly merged into the decomposition of the graft component (dearomatization) step (~280–460°C). In addition, it is observed that the GL had a strong influence on the weight loss of the membranes. To begin with, the weight loss due to the dehydration is slightly influenced by the GL, although the hydrophilicity of the membranes increases with GL. However, the weight loss due to the desulfonation increases with increasing GL, since the amount of sulfonated polystyrene grafts increases with GL. Similarly, the weight loss increases with GL, because of the aromatization, whereas the weight loss due to the backbone degradation decreases as the GL increases. On the other hand, the degradation temperatures are independent on the GL. It was found that FEP-based membranes analyzed at the same conditions yielded a similar degradation pattern. Moreover, our results for ETFE- and FEP-based membranes are in a complete agreement with the previous investigations for FEP,8,10 PVDF,12 and PFA15,16,17 based membranes.

The effect of crosslinking on the thermal stability of membranes was pronounced. Although crosslinking stabilize the polymer structure,12 thermal stability of the crosslinked ETFE-g-SPS membranes were lower compared with their uncrosslinked counterparts. It was found that that first degradation in crosslinked samples occurs at 10–15°C lower than the uncrosslinked samples, since the chemical crosslinkers may act as an impurity, which reduces the thermal stability. Previously, the influence of crosslinking on the degradation of the FEP-based grafted films and membranes were studied using TGA coupled to FTIR.11 It was found that crosslinking caused the shift of dearomatization reaction to higher temperatures; however, the desulfonation reaction was shifted to lower temperatures.

The variation of IDT, MRDT, and the residue as a function of GL for the crosslinked ETFE-based membranes is presented in Figure 9. The IDT and MDRT of the membranes decrease substantially up to a GL of 20%, beyond which no appreciable change is observed. Interestingly, the decomposition tempera-

Figure 7 Polystyrene loss as a function of polystyrene content of the ETFE- and FEP-based grafted films.

Figure 8 TGA thermograms of ETFE-based crosslinked membranes with varying graft levels (GL).
Features are generally slightly higher for the uncrosslinked samples. The lower IDT of the crosslinked samples may be due to the evaporation of unreacted DVB at around 200°C. The significantly higher MRDT of the uncrosslinked ETFE films is related to its completely different decomposition behavior of the styrenic compound, up to GLs at around 20%. Although FEP-based membranes exhibit a similar trend, the decomposition temperatures IDT and MDRT are higher in the FEP case. The membranes did not undergo complete degradation, in contrast to the non sulfonated counterparts. Instead, some residue was left behind at the end of the thermogram. The results depicted in Figure 9 show that the higher GL, the higher the residue is. This may be attributed to the increase of char formation of the polystyrene grafts in the presence of sulfur dioxide and water during degradation. The values for the ash increase with increasing grafting level (Fig. 9). Furthermore, a higher amount of residue is detected in the case of crosslinked membranes, for instance, the membranes with a high GL (55%) have 27 and 20% residue, for the crosslinked and uncrosslinked membranes, respectively. It was also proposed previously that different species were likely to be formed in sulfonated membranes during degradation and therefore stabilize the material, and their amount increased with GL.10,12

CONCLUSIONS
Proton-conducting membranes were synthesized by radiation grafting of styrene and styrene/DVB into partially fluorinated ETFE films, followed by sulfonation. Thermal properties of ETFE-based membranes were examined by DSC and TGA. Moreover, ETFE-based grafted films, FEP-based grafted films, FEP-based membranes, and their respective pristine films were also investigated. The main focus of this investigation is to understand the influence of irradiation, grafting, and sulfonation procedures on melting behavior and crystallinity of the materials. \( T_m \) was almost constant with increasing irradiation dose, whereas crystallinity increased slightly with dose. After grafting, \( T_m \) remained unchanged and a slight decrease in crystallinity with GL was observed. We determined that converting the acid form of the membrane to the salt form, then drying for a reasonable time, yielded reliable and reproducible results for membranes. Crystallinity of membranes decreased systematically with GL. Thermal stability of ETFE-based membranes was also investigated and compared with that of FEP-based membranes. The membranes were found to have a three-step degradation pattern, because of the removal of water, elimination of sulfonic acid groups, and finally degradation of the backbone. It was determined that the GL had a strong effect on the weight loss of the membranes, yet, the degradation temperatures were independent on GL. The IDT and MDRT of the membranes decrease considerably up to a GL 20%, beyond which no appreciable change is observed. Moreover, the residue increased with GL.

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