Proton-Exchange Membranes via the Grafting of Styrene and Acrylic Acid onto Fluorinated Ethylene Propylene Copolymer by a Preirradiation Technique. III. Thermal and Mechanical Properties of the Membranes and Their Sulfonated Derivatives

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ABSTRACT: Polymer electrolyte membranes were prepared via the grafting of styrene and acrylic acid onto fluorinated ethylene propylene copolymer with a preirradiation technique and subsequent sulfonation. The thermal and mechanical properties of the grafted membranes and their sulfonated derivatives were dependent on the degree of grafting. The grafted membranes showed a two-step degradation pattern, whereas their sulfonated derivatives showed a three-step degradation pattern. The glass-transition temperature and crystallinity percentage of the membranes were determined with differential scanning calorimetry. With an increase in the degree of grafting and sulfonation, the glass-transition temperature increased, whereas the crystallinity percentage decreased. The tensile strength and elongation decreased with the degree of grafting and sulfonation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1418–1425, 2005

Key words: glass transition; radiation grafting; crystallinity

INTRODUCTION

Radiation-induced graft copolymerization is an easy method for synthesizing membranes with desired properties for various applications.[1–4] Depending on the polymers used and the conditions of polymerization, grafting imprints the properties of the resultant grafts on the backbone material. Fluorinated polymers are suitable starting materials for synthesizing membranes because they possess excellent thermal, mechanical, and chemical stability. Through the grafting of specific monomers onto fluorinated polymers, membranes with desired properties can be obtained. Radiation-induced graft copolymerization on different fluoropolymers such as polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF), fluorinated ethylene propylene copolymer (FEP), and poly(ethylene-co-tetrafluoroethylene) (ETFE) has been widely studied.[5–9] However, among fluoropolymers, FEP has drawn the most attention because its radiation stability is better than that of other fluoropolymers.

The performance of these grafted membranes depends on their thermal and mechanical stability. The sulfonation of the grafted membranes is further known to change the overall structures of the membranes. These structural changes may be evident from the crystalline–amorphous ratio, lamellar defects, and the domain formation of the grafted component in the membranes,[10] and these lead to changes in the thermal and mechanical properties.[11,12]

In a previous study, we carried out the grafting of styrene and acrylic acid onto FEP by a preirradiation technique, and the effects of the reaction conditions on the degree of grafting were studied.[13] The physicochemical properties of the membranes were evaluated and found to be strongly dependent on the grafting and sulfonation.[14]

In this study, we evaluated the thermal and mechanical properties of styrene-*co*-acrylic acid grafted FEP films and their sulfonated derivatives as a function of the degree of grafting. The degradation pattern was studied, and the mechanism of degradation was proposed from the ion-exchange capacity (IEC) of the degraded membranes. The variation of the glass-transition temperature (T_g) with the degree of grafting was evaluated with differential scanning calorimetry (DSC). The changes in the crystallinity of the original film upon grafting and sulfonation were studied from the melting thermograms obtained from DSC studies. An attempt was made to explain the properties of the grafted membranes by changes occurring in the structure and microstructure of the original membrane because of chemical and physical changes.

EXPERIMENTAL

Grafting and sulfonation

Grafting was carried out according to a procedure given in an earlier article.[13] An FEP film (75 μm thick; DuPont) was irradiated with a ^{60}Co radiation source and grafted with the monomer pair styrene (Fluka) and acrylic acid (Fluka) in the molar ratio of 52:48 in benzene (60:40 v/v). The membranes were grafted for the desired time at 70°C. The grafted membranes were freed from the homopolymer by repeated washing separately in methanol and toluene in a Soxhlet apparatus and were dried at reduced pressure at 80°C to a constant weight. The degree of grafting was calculated as follows:

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

where W_g is the weight of the grafted membrane and W_0 is the weight of the ungrafted FEP film.

The membranes were then sulfonated in concentrated sulfuric acid at room temperature for 2 h.

Thermogravimetric analysis (TGA)

The thermal stability and degradation pattern of the membranes were measured with a Hi-Res TGA 2950 thermogravimetric analyzer from TA Instruments. The membranes were dried under reduced pressure at 80°C for 7 days before all thermal measurements. Samples weighing 8–10 mg were heated from the ambient temperature to 800°C at a heating rate of 20°C/min in a nitrogen atmosphere.

Heat treatment

Sulfonated membranes with different degrees of grafting were subjected to heat treatment in a tubular furnace in an inert atmosphere at various temperatures (from 180 to 450°C). This treatment was carried out to determine the pattern of degradation occurring in sulfonated membranes when they were subjected to heat treatment.

IEC

The IEC of the sulfonated membranes before and after heat treatment was measured by the placement of the membranes in NaOH solutions of known concentrations for a period of 24 h. The strength of NaOH was measured by titration with 0.1N oxalic acid with phenolphthalein as an indicator. The IEC was calculated as follows:

$$\text{IEC(mequiv/g)} = \frac{V(N_1 - N_2)}{W}$$

where V is the volume of NaOH (mL), N_1 is the initial normality of NaOH, N_2 is the normality after exchange, and W is the weight of the sample (g).

DSC

The DSC analysis of the unsulfonated and sulfonated grafted samples was carried out on a TA Instruments Q600 DSC instrument. A sample weighing 8–10 mg was placed in an aluminum pan, and the DSC thermogram was obtained from the ambient temperature to 300°C at a constant heating rate of 5°C/min. From the DSC scan, T_g, the heat of fusion, and the crystallization were obtained. The degree of crystallinity was calculated as follows:

$$X_{\text{mem}}(\%) = \frac{\Delta H_{\text{mem}}}{\Delta H_{\text{FEP}}} \times 100$$

where X_{mem} is the total crystallinity, ΔH_{mem} is the heat of fusion of the grafted membrane, and ΔH_{FEP} is the heat of fusion of a 100% crystalline FEP film (87.9 J/g).[15]

The crystallinity of the FEP fraction (X_{FEP}) was calculated from the weight fraction of FEP in the grafted and sulfonated membranes with the following formula:

$$W = m_{\text{FEP}}/m_{\text{FEP}} + m_{\text{STAA}}$$

where m_{FEP} is the mass of FEP in the grafted membrane and m_{STAA} is the mass of the grafted copolymer.

For sulfonated membranes, the weight fraction of FEP was calculated as follows:

$$W = m_{\text{FEP}}/m_{\text{FEP}} + m_{\text{STAA}} + m_{\text{SO3H}}$$

where m_{SO3H} is the mass of the SO_3H group.

X_{FEP} of the membrane was calculated as follows:

$$X_{\text{FEP}}(\%) = \frac{\Delta H_{\text{mem}}}{W} \times 100$$

Mechanical properties

The tensile strength and elongation of FEP, grafted FEP, and its sulfonated derivative (both wet and dry samples) were determined with a Hounsfield model 50K-S universal testing machine. Test specimens 10 cm long and 10 mm wide were cut with a standard die. The clamping distance was 5 cm, and the crosshead speed was 100 mm/min.
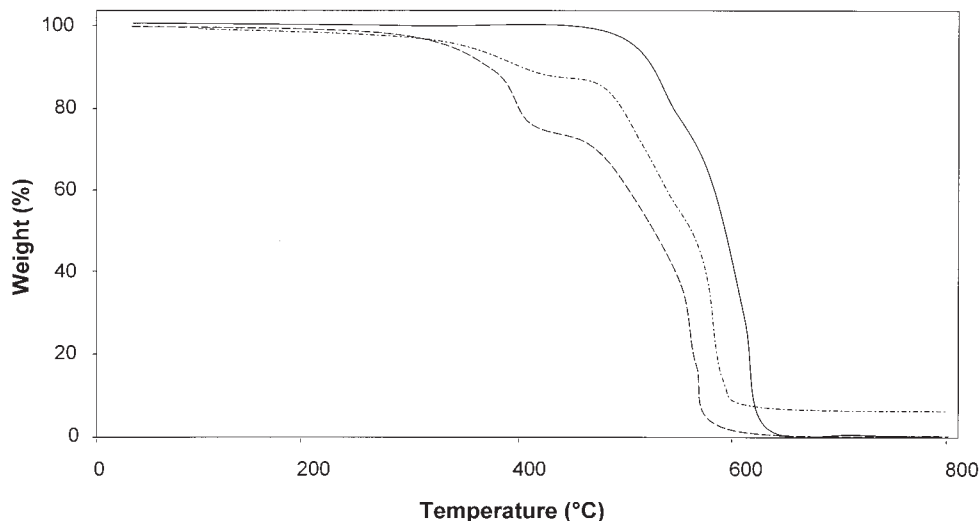
Figure 1 TGA plot of (—) FEP, (- - -) FEP-*g*-STAA, and (- · -) sulfonated FEP-*g*-STAA membranes (46% grafting).

RESULTS AND DISCUSSION

The preirradiation grafting of styrene and acrylic acid onto FEP was carried out, and the resultant membranes were sulfonated. Membranes with different degrees of grafting were obtained with various reaction conditions.[13] The properties of the membranes were strongly influenced by the amount of the grafted copolymer present in the membrane. Furthermore, upon sulfonation, the acrylic acid components of the grafted chain underwent intramolecular cyclization with the benzene ring of the styrene moiety. The mechanism and influence of this phenomenon on the physicochemical behavior of the membrane was also explained.[14] The effect of the change in the structure of the membranes upon grafting and sulfonation on the thermal and mechanical properties was studied in this work.

TGA

The thermograms of the original FEP, FEP grafted with styrene and acrylic acid (46% grafting), and its sulfonated derivative are shown in Figure 1. Ungrafted FEP underwent single-step degradation, which started at 490°C. The grafted membrane showed a two-step degradation pattern, at 304 and 490°C. The addition of styrene and acrylic acid to FEP induced two-step degradation without altering the degradation temperature of FEP (490°C). This showed that the grafted styrene-*co*-acrylic acid degraded earlier than the FEP matrix. A similar trend has been observed for other grafted systems,[16] for which it has been reported that the grafted monomers form microdomains in the FEP matrix.

The sulfonation of these grafted membranes resulted in a three-step degradation pattern. The first step started below 100°C and continued up to 180°C, the second one started at about 292°C, and the third one started at 490°C. The initial weight loss below 100°C was due to the loss of water molecules associated with the sulfonic acid groups in the membrane. Further weight loss up to 180°C was due to the removal of water molecules that were strongly hydrogen bonded to the sulfonic acid groups. The degradation at 292°C was probably due to desulfonation. Gupta et al.[17] extensively studied the degradation of FEP-*g*-styrene–SO_3H and reported that degradation around 300°C was due to desulfonation. This weight loss continued up to 438°C. A distinction between desulfonation and degradation of the grafted membrane could not be made.

The occurrence of desulfonation was confirmed by the measurement of the IEC of the membranes after degradation. The membranes were heated at 320°C for
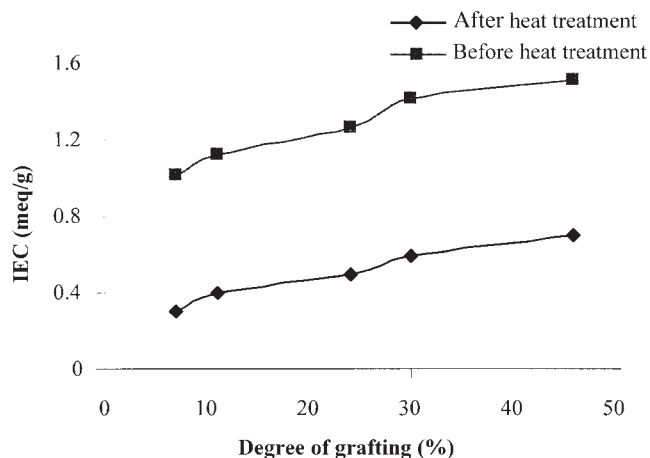

Figure 2 Variation of IEC of sulfonated membranes before and after heat treatment.

TABLE 1
Weight Losses at Different Temperatures for FEP-*g*-STAA Membranes and Their Sulfonated Derivatives with Different Degrees of Grafting

Degree of grafting (%)	Weight loss (%) at different temperatures (°C)					Residue (%)
	300	350	400	450	500	
6	0.6 (1.3)	1.1 (1.9)	3.3 (3.1)	7.6 (4.1)	14.4 (11.3)	0 (2.9)
11	1.1 (1.3)	1.9 (2.5)	6.5 (4.6)	10.4 (6.4)	20 (19.5)	0 (3.8)
24	2.3 (2.7)	4.3 (4.4)	10.7 (8.5)	18.5 (11)	27.5 (21.9)	0 (6.7)
30	2.8 (4.1)	4.5 (7.6)	11.2 (13.6)	28.2 (17.3)	36.7 (31.3)	0 (7.1)
46	3.4 (4.3)	8.1 (10.1)	22 (15.5)	32.7 (19.7)	50 (37.6)	0 (10)

Values in parentheses are for sulfonated membranes.

30 min, and the IEC was measured. A plot of the IEC versus the degree of grafting is shown in Figure 2. The IEC dropped to less than half the initial value. This confirmed that degradation around 300°C was due to desulfonation.

Table I shows the weight loss from 300 to 500°C for membranes with different degrees of grafting. Although the membranes had the same initial degradation temperature, the weight loss increased with an increase in the degree of grafting because of the increase in the amount of thermally degradable grafting.

Also, Figure 1 shows that the sulfonated membranes did not undergo complete degradation, unlike the FEP and grafted FEP membranes (Table I). The results may be explained in terms of a crosslinking reaction occurring between the adjacent styrene sulfonic acid groups in the membrane matrix during the desulfonation process, which imparted rigidity to the membrane matrix. Also, the grafted copolymer underwent cyclization during sulfonation, and this resulted

in a condensed ring structure.[18] Thus, as degradation proceeded, there was a loss of sulfonic acid groups, which left behind a hydrocarbon-based cyclized structure that did not degrade even at 800°C. To understand the mechanism of degradation, we heat-treated sulfonated membranes with a 46% degree of grafting at different temperatures, and the Fourier transform infrared (FTIR) spectra of the degraded films were recorded (Fig. 3). The FTIR spectra showed that at 180°C there was a decrease in the intensity of the peak around 3400 cm^{-1}, which represented the presence of water molecules. As the temperature increased from 250 to 450°C, the intensity of the peaks around 1040 and 1700 cm^{-1}, due to —SO$_3$H and —COOH groups, respectively, decreased considerably, and this indicated desulfonation and decarboxylation. A new peak appeared at 1760 cm^{-1}, indicating the formation of anhydride. At 450°C, the peak for the —COOH group disappeared completely, and the peak at 1760 cm^{-1} became prominent; this indicated the stability of the
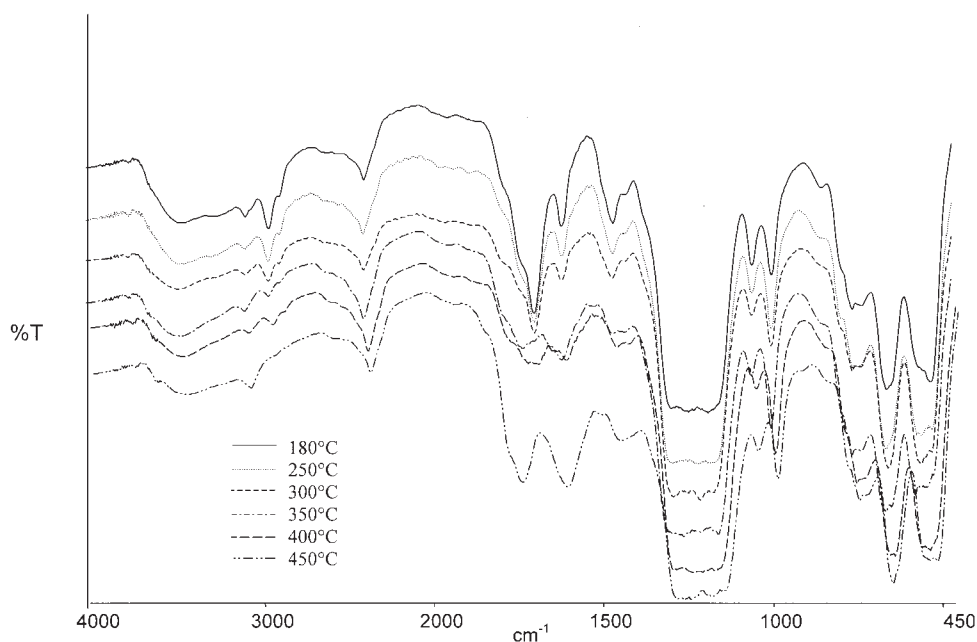

Figure 3 FTIR spectra of a sulfonated FEP-*g*-STAA membrane (46% grafting) heat-treated at various temperatures (*T*).

Temperature (°C)	Mode of degradation
180–250	Dehydration
300–400	Desulfonation and decarboxylation, anhydride formation was initiated
450	Complete desulfonation and decarboxylation formed anhydride was stable

anhydride group. Furthermore, because of these structural changes, the weight loss of the sulfonated membranes was less than that of the corresponding unsulfonated ones (Table I). Also, as mentioned earlier, these membranes did not undergo complete degradation, leaving behind some char. Table II lists the possible degradation steps involved during the heat treatment of the sulfonated membranes from 180 to 450°C.

Based on these observations, a plausible mechanism of degradation has been proposed and is shown in Figures 4 and 5. In Figure 4, both intramolecular and intermolecular cyclization involving COOH and SO_3H groups can result in a condensed structure. This upon heating may release $O=S=O$, providing a more stable condensed cyclized structure. This route is possible

only when styrene and acrylic acid moieties are alternating. In Figure 5, in which the styrene and acrylic acid units are not alternating, the loss of water involving two adjacent —COOH groups may result in the formation of an anhydride, which was found to be stable even at 450°C. However, regardless of the mode of degradation, the end product was char.

DSC

T_g of styrene/acrylic acid grafted FEP and its sulfonated derivative at various degrees of grafting is given in Table III. T_g increased with grafting and further with sulfonation. This increase in T_g was due to the nature of the grafted styrene and acrylic acid. The copolymer of styrene and acrylic acid was amorphous and had a T_g of 148°C; the chemical attachment of styrene/acrylic acid increased the amorphous content of the FEP film. Because T_g of the styrene/acrylic acid part was higher, the increase in the graft content offered a greater restriction on the main-chain mobility, and this resulted in an increase in T_g. The addition of sulfonic acid groups further hindered the chain mobility, and the membrane matrix became more rigid; this increased T_g. During this study, we observed that a correct T_g was obtained only when the membranes
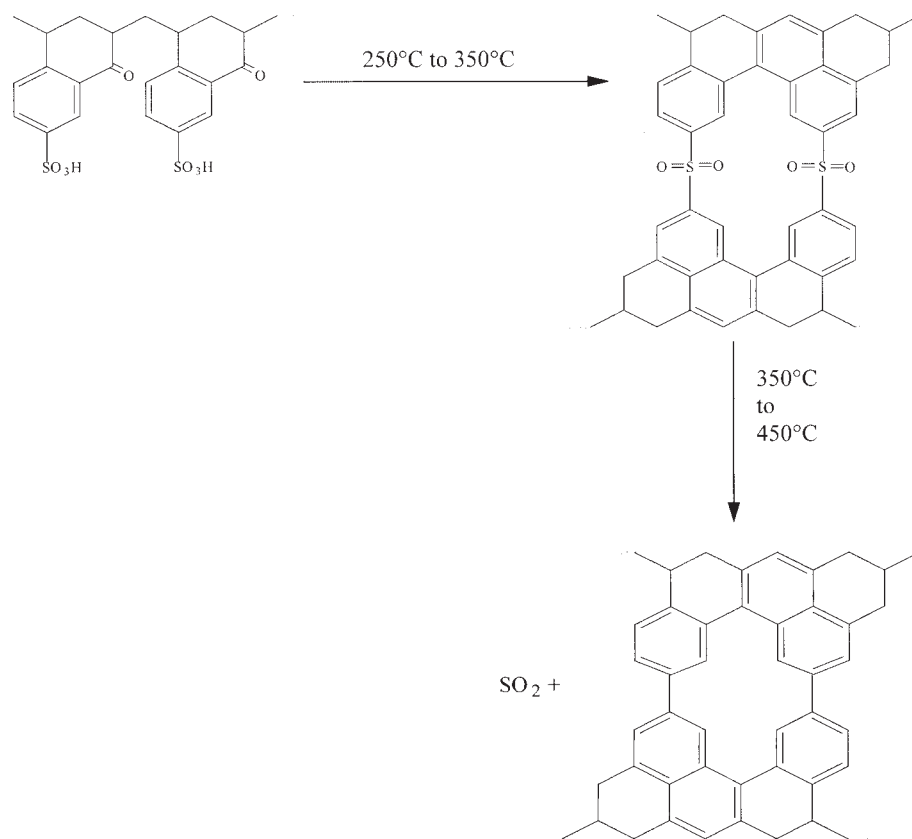

Figure 4 Mechanism of degradation when styrene and acrylic acid groups are alternating.
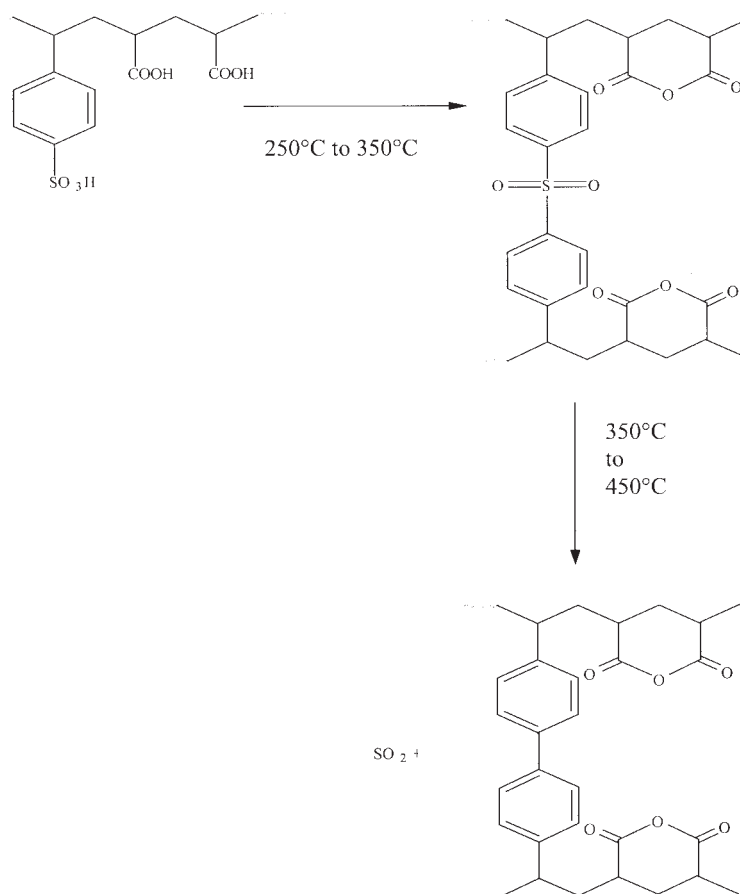
Figure 5 Mechanism of degradation when styrene and acrylic acid are randomly placed.

were subjected to stringent drying conditions. Similar results were also reported by Gupta et al.[10]

From the thermograms (Fig. 6) *obtained from the DSC studies of FEP, FEP-g-*(styrene-co-acrylic acid), sulfonated FEP-g-(styrene-co-acrylic acid), and their sulfonated derivatives, the values of the melting temperature (T_m), enthalpy of fusion (ΔH_f), and crystallinity percentage were determined (Tables III and IV). T_m of a polymer material is indicative of its crystal structure. Thus, the marginal changes in T_m indicated that the original crystal structure was not affected during grafting and sulfonation. Because T_m of FEP was much

higher than the reaction temperature, it was assumed that the graft monomers did not swell the crystallites or penetrate the crystal structure. This result also substantiated that the grafting took place in the amorphous region of FEP.

ΔH_f was measured from the area under the melting curves. The crystallinity percentages for the membranes were calculated from the corresponding values of ΔH_f (Table IV). Although T_m (Table III) did not change much upon grafting and sulfonation, the area under the melting curve (i.e., ΔH_f) and, therefore, the crystallinity percentage decreased with an increase in

TABLE III
Variation of T_g and T_m with Degree of Grafting

Degree of grafting (%)	T_g (°C)		T_m (°C)	
	Unsulfonated	Sulfonated	Unsulfonated	Sulfonated
6	140.12	140.62	269.96	269.14
11	143.76	144.16	269.01	268.87
24	144.91	146.43	268.33	267.92
30	151.16	160.33	267.64	266.69
46	160.79	164.72	266.83	265.60

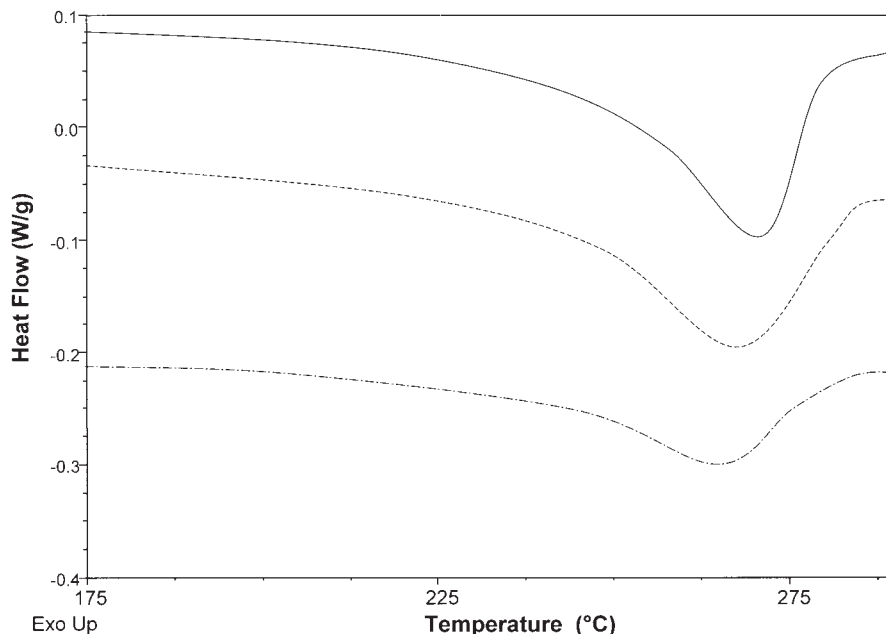T_g of FEP = 103°C; T_m = 270.51°C.

Figure 6 DSC thermogram of (—) FEP, (- - -) FEP-g-STAA, and (- · -) sulfonated FEP-g-STAA membranes (46% grafting).

the degree of grafting and subsequent sulfonation. To determine the extent of variation in the crystallinity upon grafting and upon sulfonation, we had to correct ΔH_{mem} with the weight fraction of FEP in the membranes.

The observed decrease in ΔH_f illustrated a reduction in the crystallinity upon grafting and subsequent sulfonation (Table IV). This reduction was explained by a dilution of the crystalline region of the FEP matrix due to the incorporation of amorphous styrene/acrylic acid graft content. However, upon the correction of ΔH_{mem} with the weight fraction of FEP in the membranes, we found that the crystallinity of the virgin FEP membrane was marginally different from the crystallinity of the FEP fraction in the grafted copolymer. This suggested that there was some amount of crystal distortion also occurring during grafting and upon sulfonation. Thus, the change in the heat of fusion of the grafted and sulfonated membranes was due to the cumulative effect of crystal dilution and crystal distortion; this was also mentioned by Hietala

et al.[19] From these observations, it may be understood that radicals were generated both in the amorphous and crystalline regions of FEP, and upon grafting, some of the grafted chains were attached to the crystalline region, developing a certain stress at the graft–lamella junction. This, in turn, ruptured the crystallites.

The crystallinity was also measured by X-ray diffraction, and the results will be presented in conjunction with SEM studies in subsequent publications.

Tensile properties

The tensile strength and elongation at break of both wet and dry grafted FEP samples are given in Table V. As the degree of grafting increased, both the tensile strength and elongation decreased. The grafting of styrene and acrylic acid resulted in the introduction of bulkier groups to the FEP matrix, and this reduced the interaction between the FEP chains, as a result of which the tensile strength and elongation at break

TABLE IV
Variation of ΔH_{mem} and Degree of Crystallinity (χ) with the Degree of Grafting

Degree of grafting (%)	ΔH_{mem} (J/g)		χ_{mem} (%)		χ_{FEP} (%)	
	Unsulfonated	Sulfonated	Unsulfonated	Sulfonated	Unsulfonated	Sulfonated
6	19.89	18.51	22.62	21.06	21.15	19.97
11	17.57	16.54	19.98	18.82	19.74	19.13
24	14.03	13.51	15.96	15.36	18.46	19.06
30	12.17	10.75	13.84	12.23	17.38	16.91
46	9	7.42	10.23	8.44	16.67	16.06

Heat of fusion of virgin FEP = 21.32J/g; % crystallinity calculated = 24.25.

TABLE V
Tensile Strength and Elongation at Break

Degree of grafting (%)	Tensile strength (MPa)				Elongation (%)			
	Unsulfonated		Sulfonated		Unsulfonated		Sulfonated	
	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry
6	15.53	19.49	14.69	16.2	169	107.15	56	52.2
11	12.33	19.41	14.31	15.6	166.15	43.2	50.06	29.27
24	11.64	18.84	13.41	14.9	154.9	24.4	42.6	14.43
30	10.34	17.8	12.57	14.3	146.35	23.8	39.12	12.19
46	8.4	13.23	10.69	12.5	120.4	4.98	31.13	4.01

Tensile strength of FEP = 21 MPa; elongation at break = 310%.

decreased. Also, the membranes under the wet condition had lower strength and higher elongation at break. Water molecules attached to the ionic sites possibly reduced the interaction between the chains and also induced a plasticizing effect that led to a loss in the tensile strength and an increase in the elongation at break. A similar trend was found for the sulfonated derivatives (Table V). However, the values were lower than those of the corresponding unsulfonated grafted membrane. The SO$_3$H group being more hydrophilic, more water molecules were associated with the sulfonic acid groups in the wet membranes and were responsible for the reduction in the strength of the membranes. Furthermore, we observed in earlier studies[18] that styrene-*co*-acrylic acid upon sulfonation yielded a condensed ring structure. However, this possibility was restricted to the presence of styrene and acrylic acid alternating with each other along the chain.

CONCLUSIONS

Considerable changes in the properties of FEP took place upon the grafting of styrene and acrylic acid and the subsequent sulfonation of the membranes. The grafted membranes underwent two-step degradation because of the difference in the nature of the degradation of the grafted chains and backbone polymer. A three-step degradation pattern was observed for the sulfonated membranes because of the incorporation of sulfonic acid groups. Sulfonation of the membranes introduced the tendency of char formation. From the FTIR spectra of the heat-treated samples, we observed that both desulfonation and decarboxylation took place during degradation. On the basis of these observations, a tentative mechanism for the degradation of

sulfonated membranes was proposed. T_g increased upon grafting and upon sulfonation. A reduction of the crystallinity upon grafting and sulfonation could be attributed to the cumulative effect of the dilution of crystallites and crystal distortion.

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