

Proton-Exchange Membranes via the Grafting of Styrene and Acrylic Acid onto Fluorinated Ethylene Propylene Copolymer by a Preirradiation Technique. IV. Dynamic Mechanical Analysis, X-Ray Diffraction, and Scanning Electron Microscopy Studies of Grafted and Sulfonated Membranes

S. Phadnis, M. Patri, B. C. Chakraborty, P. K. Singh, P. C. Deb

Naval Materials Research Laboratory, Additional Ambernath 421506, India

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ABSTRACT: The grafting of styrene and acrylic acid onto fluorinated ethylene propylene copolymer was carried out by a preirradiation technique. The resulting membranes were sulfonated with concentrated sulfuric acid. The effects of the degree of grafting and sulfonation on the structure of the membranes were studied by X-ray diffraction and scanning electron microscopy. The crystallinity percentage decreased with increasing grafting. Scanning electron microscopy studies confirmed that grafting took place by a front

mechanism, by which grafting started at the surface and slowly proceeded inwards. The dynamic mechanical properties of the membranes and their sulfonated derivatives were also investigated. The storage modulus at room temperature increased with grafting and increased further with sulfonation. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1426–1431, 2005

Key words: morphology; radiation; grafting; crystallinity

INTRODUCTION

Radiation-grafted membranes have gained much importance in recent years because of their wide range of applications^{1–4} and ease of synthesis.⁵ Fluoropolymers have been mainly used to synthesize these membranes as they are thermally and mechanically stable. A good amount of information is available on the radiation grafting of polytetrafluoroethylene (PTFE), fluorinated ethylene propylene copolymer (FEP), poly(ethylene-co-tetrafluoroethylene) (ETFE), and poly(vinylidene difluoride) (PVDF).^{6–9} However, among fluoropolymers, FEP has drawn more attention because its radiation stability is better than that of Teflon. Various monomers such as styrene, acrylic acid, and other vinyl monomers have been grafted onto FEP to develop membranes for various applications.¹⁰ These membranes have shown the potential to replace presently available membranes, which are expensive.

The grafting of vinyl monomers onto fluoropolymers results in copolymers with properties different from those of the virgin fluorinated polymers because the

grafted chains are different in their chemical nature and structural changes occur during the grafting. Upon chemical modification such as sulfonation, the properties are expected to change further. One such property is the crystallinity of the polymer matrix. Structural changes occurring during grafting and sulfonation need to be studied because they influence the overall performance of membranes. Studies have shown that the addition of a hydrocarbon moiety leads to changes in the thermal and mechanical properties.^{11,12} This has been explained by many workers researching the formation of microdomains in a fluoropolymer matrix.¹²

We grafted styrene and acrylic acid onto FEP by a preirradiation technique. The degree of grafting was strongly dependent on the reaction parameters, including the total radiation dose, monomer concentration, time, and temperature.¹³ The physicochemical properties of the membranes were studied and found to be dependent on the degree of grafting.¹⁴ The thermal and mechanical properties were also studied and found to be strongly influenced by the graft content in the membranes.¹⁵ As reported by many workers, grafting is known to take place through a front mechanism.⁵ However, this was not studied by us earlier for this system. This article deals with the morphological and dynamic properties of the grafted and sulfonated membranes.

Correspondence to: M. Patri (mrpatri@rediffmail.com).

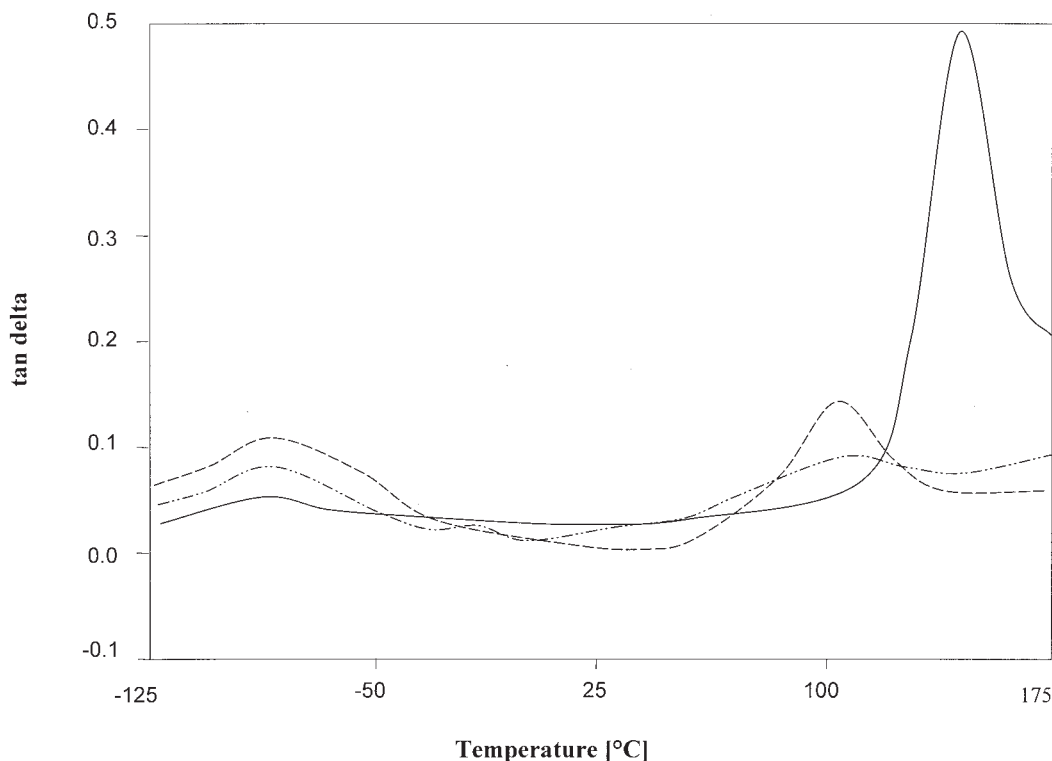


Figure 1 DMA plot of (---) FEP, (—) FEP-g-STAA, and (- · -) sulfonated FEP-g-STAA membranes (24% grafting).

EXPERIMENTAL

Grafting and sulfonation

The grafting of FEP with the styrene/acrylic acid monomer pair was carried out in two steps. First, the FEP film (75 μm thick) was irradiated with γ -rays from a ^{60}Co source. Styrene (Fluka, Switzerland) and acrylic acid (Fluka, Switzerland) were purified by distillation under reduced pressure. Grafting was then carried out in a glass ampule, which was vacuum-sealed after freeze thawing. Membranes with different degrees of grafting were obtained with various reaction parameters.¹³ The grafted films were freed from the homopolymer and ungrafted copolymers by extraction with toluene and methanol in a Soxhlet apparatus for 24 h in each solvent.

Sulfonation was carried out in concentrated sulfuric acid at room temperature for 2 h. The membranes were washed with distilled water until they were acid-free and were stored in distilled water for further use.

Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of the grafted and sulfonated membranes were determined at 1 Hz on a Rheometric Scientific dynamic mechanical thermal analyzer (UK) from -125 to 200°C at a heating rate of $5^\circ\text{C}/\text{min}$. The measurements were carried out in the tensile mode, and the storage modulus and glass-

transition temperature (T_g) were determined. The temperature at the maximum loss factor ($\tan \delta_{\text{max}}$) was taken to be T_g .

X-ray diffraction (XRD) analysis

The XRD analysis was carried out at the ambient temperature on a Philips X-ray PW 1730/10 diffractometer (the Netherlands) equipped with a scintillation counter. The scanning rate was 10 mm/s. The extent of crystallinity was calculated by the measurement of the area of the crystalline region and the total area obtained from the XRD analysis:

Degree of crystallinity(%) =

$$\frac{\text{Area of crystalline region}}{\text{Total area}} \times 100 \quad (1)$$

Scanning electron microscopy (SEM)

The samples were dried under reduced pressure at 80°C for 24 h before scanning. The grafted samples to be analyzed were first stained with copper by the placement of the membranes in a saturated solution of copper chloride overnight. The films were then washed thoroughly with distilled water to remove excess copper chloride. The SEM analysis was carried out on a Leo 1450 SEM instrument (UK). The distri-

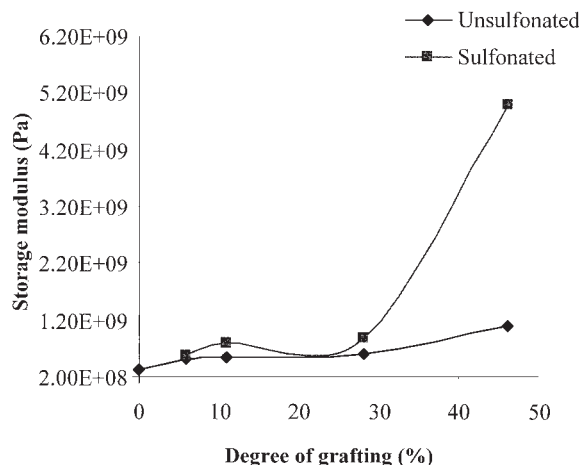


Figure 2 Variation of the storage modulus with the degree of grafting.

bution of copper across the membrane was determined by X-ray mapping. For the sulfonated membranes, the distribution of sulfur across the membranes was investigated. All the samples were coated with gold by a sputtering technique before the scanning.

RESULTS AND DISCUSSION

The grafting of styrene-*co*-acrylic acid onto FEP and its subsequent sulfonation were expected to bring about some changes in the structure of FEP films, as the same resulted in changes in the physicochemical, thermal, and mechanical properties^{14,15} of the membranes. These changes in the properties was expected to be a function of the change in the structure of the original FEP films.

DMA

The dynamic mechanical properties of FEP grafted with styrene and acrylic acid and its sulfonated deriv-

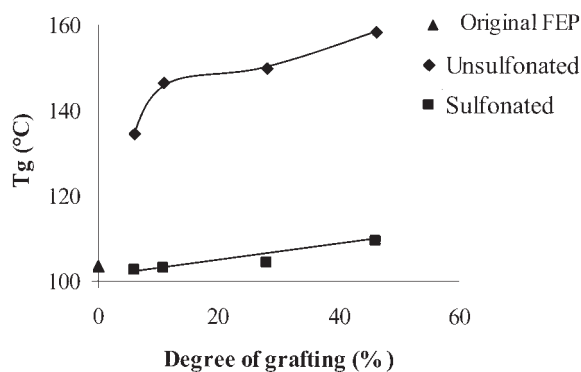


Figure 3 Variation of T_g (temperature at $\tan \delta_{\max}$) with the degree of grafting.

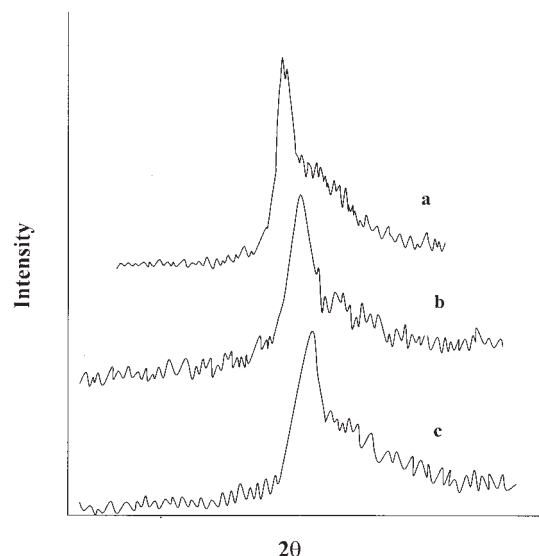


Figure 4 XRD graph of (a) FEP, (b) FEP-g-STAA, and (c) sulfonated FEP-g-STAA membranes (46% grafting).

atives were investigated (Fig. 1). Figure 2 shows the changes in the storage modulus as a function of the degree of grafting of grafted (with styrene and acrylic acid) and sulfonated FEP membranes. Upon the grafting of FEP, the modulus at room temperature increased because of the addition of a hard segment [$T_g = 148^\circ\text{C}$ according to differential scanning calorimetry (DSC)]. This trend continued as the grafting increased and was further enhanced upon sulfonation.

FEP showed multiple transitions at -85 and 103.5°C (Fig. 1). Upon grafting, the relaxation temperature of FEP at 103.5°C shifted to a higher temperature because of the incorporation of the styrene/acrylic acid copolymer, as shown in Figure 1. The relaxation temperature for all the grafted membranes showed a single peak, which indicated no phase separation. Upon sul-

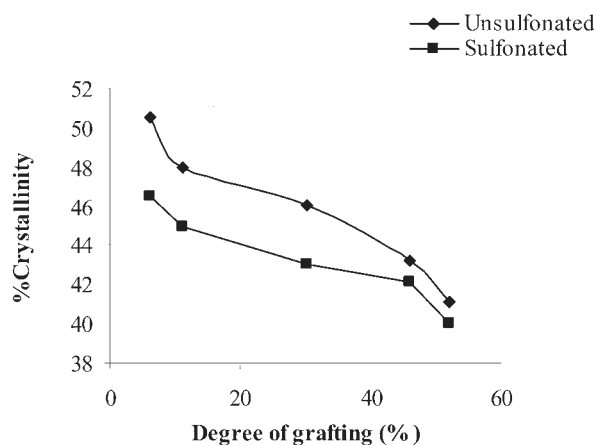


Figure 5 Variation of the crystallinity with the degree of grafting.

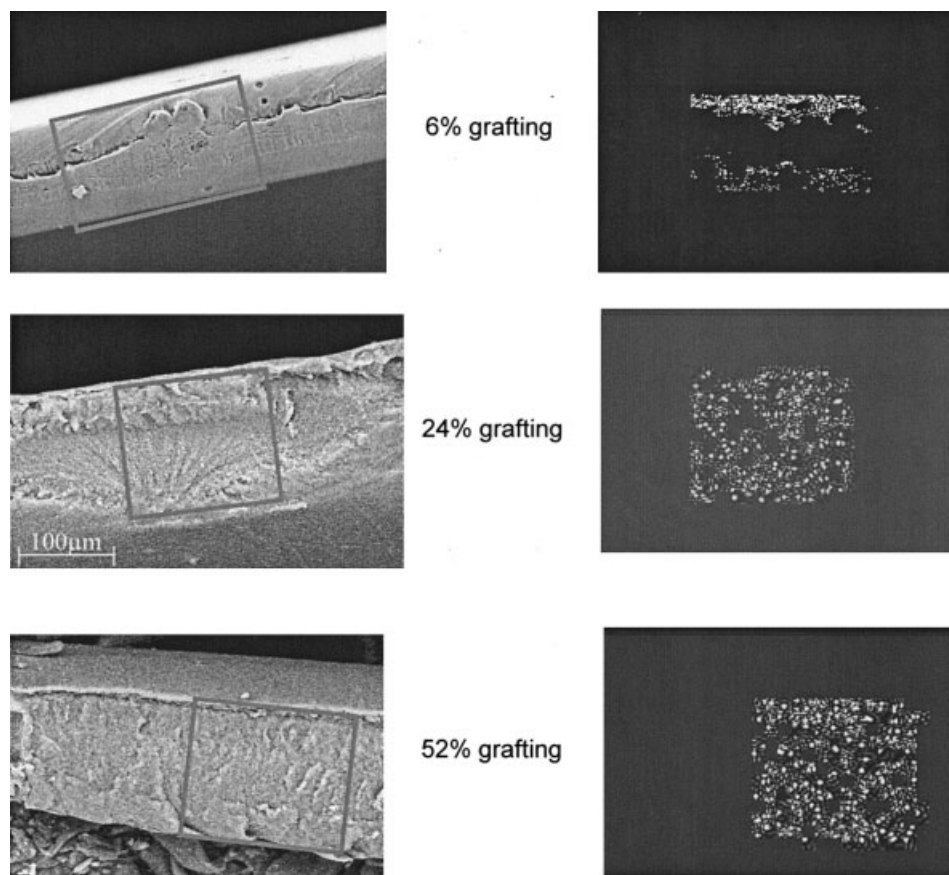


Figure 6 SEM images showing the distribution of copper in FEP-g-STAA membranes.

fonation, the loss factor ($\tan \delta$) appeared at a lower temperature (Fig. 1). In fact, the addition of the bulkier $-\text{SO}_3\text{H}$ group should have shifted this peak to a higher temperature. Although the samples were dried at 80°C *in vacuo* for 7 days, because of the strongly hydrophilic nature of the $-\text{SO}_3\text{H}$ group, the sample absorbed moisture from the environment, and this resulted in a lower peak temperature for $\tan \delta$. Moreover, $\tan \delta$ further increased with an increase in the temperature. This indicated that the trend observed for the relaxation temperature in DMA could be due to a slow degradation pattern of the membranes, as found by thermogravimetric analysis. Also, no defined peak was noticed. DSC studies have shown that T_g 's of sulfonated membranes are higher than T_g 's of unsulfonated membranes.¹⁴ The variation of T_g ($\tan \delta_{\max}$) with the degree of grafting is shown in Figure 3. The T_g values increased with the degree of grafting. A similar trend was observed via DSC. However, the T_g values obtained from DMA studies were different from those obtained from DSC studies because the mode of analysis differed for the measurements.

XRD analysis

The crystallinity of styrene/acrylic acid grafted FEP and its sulfonated derivatives was calculated from an

XRD plot (Fig. 4) and is presented in Figure 5. Figure 4 shows that the intensity of the diffractogram, representing the crystallinity, decreased upon grafting and further decreased upon sulfonation. The decrease in the crystallinity (Fig. 5) upon grafting and subsequent sulfonation was due to the dilution effect of crystallites due to the incorporation of styrene-*co*-acrylic acid into the amorphous region of the FEP matrix and was also due to crystal disruption, which was explained via DSC in our earlier studies.¹⁵

The crystallinity of the membranes was determined by two methods: DSC¹⁴ and XRD. Although the changes in the crystallinity showed the same trend in both studies, the values from the DSC studies differed from those obtained from XRD analysis. This discrepancy was explained by the fact that the X-ray scattering originated from highly ordered and crystalline regions of the FEP membranes. Grafting is known to cause changes in the lamellar thickness. Although the chain ends and loops were not ordered enough to contribute to the melting enthalpy obtained in the DSC studies, they could be detected by XRD. We concluded that grafting occurred in the amorphous region of FEP and in some areas very close to the surfaces of the crystallites, and this broke up partly ordered chain structures of the FEP matrix. Similar observations were made by Hietala et al.¹⁶

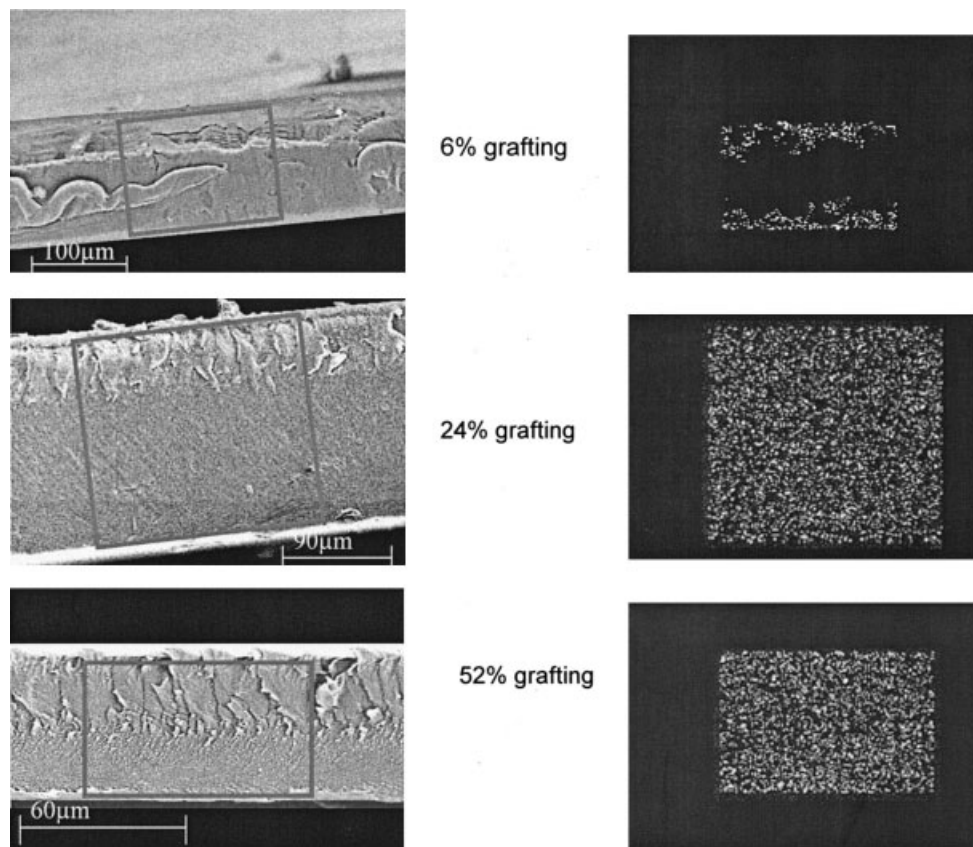


Figure 7 SEM images showing the distribution of sulfur in sulfonated FEP-g-STAA membranes.

SEM

Cross-sectional views of fractured samples of the grafted and sulfonated membranes were obtained with a scanning electron microscope. Figure 6 shows X-ray mapping images of copper-stained FEP-g-(styrene-co-acrylic acid) membranes with different degrees of grafting. For the membrane with a 6% degree of grafting, the distribution of copper was greater at the surface than at the core. With 24 or 52% grafting, the copper was uniformly distributed across the membranes. This confirmed that the grafting took place by a front mechanism. Grafting started at the surface and proceeded toward the interior via the diffusion of the monomer. Therefore, the membranes with a higher degree of grafting had a uniform distribution of copper because at a higher degree of grafting, the grafting fronts met at the center, and this led to homogeneity. Similar observations were made for sulfonated membranes, for which at a lower degree of grafting, sulfur was distributed at the surface, as Figure 7 shows. This was reflected in the conductivity measurements of the membranes: membranes with a higher degree of grafting had higher through-through conductivity than those with a lower degree of grafting.¹⁴ Hegazy et al.¹⁷ determined the distribution of grafts across PTFE and FEP membranes grafted with acrylic acid by X-ray

microscopy. They confirmed that grafting proceeded from both surfaces with progressive diffusion of the monomer and reached the center to finally yield a homogeneous distribution of grafted chains in the films. Gupta et al.¹⁸ studied the distribution of ionic sites by microprobe measurements. The results of the analysis showed that at a lower degree of grafting, the distribution of sulfur was less across the membranes and greater at the surface. As the grafting proceeded, the grafted polymer was uniformly distributed across the membrane. A similar mechanism of grafting was applicable in this case.

CONCLUSIONS

Grafting styrene and acrylic acid is known to cause changes in the structure of the FEP matrix in the form of dilution of crystallites and to some extent in the form of crystal distortion. The dynamic mechanical properties of the membranes and their sulfonated derivatives were found to depend on the degree of grafting. The storage modulus and relaxation temperature increased with an increase in the degree of grafting, and this was further enhanced by sulfonation. SEM analysis confirmed that grafting took place by a front mechanism: the grafting

started at the surface and slowly proceeded to the interior with the diffusion of the monomer from both surfaces.

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