The Study on Radiation Grafting of Acrylic Acid onto Fluorine-Containing Polymers. IV. Properties of Membrane Obtained by Preirradiation Grafting onto Poly(tetrafluoroethylene–Hexafluoropropylene)

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Synopsis

Some properties of the membranes obtained by preirradiation grafting of acrylic acid onto poly(tetrafluoroethylene–hexafluoropropylene) (FEP) film have been investigated. Swelling behavior, dimensional change by grafting, electric conductivity, and mechanical properties of the grafted films were found to depend largely on the degree of grafting and to increase as the grafting proceeds. These properties were also found to be independent of the preparation conditions such as irradiation dose, grafting temperature, film thickness, and monomer concentration lower than 60 wt %. The electric conductivity of the membranes prepared at lower monomer concentration (lower than 60 wt %) is higher than that prepared at 80 wt % acrylic acid concentration. X-ray microscopy of the grafted film revealed that the grafting proceeds from both surfaces of the film to the direction of center to give finally homogeneous grafting through the whole bulk of film. At lower monomer concentration the homogeneous grafting was achieved at a degree of grafting around 18%, while at 80 wt % acrylic acid it was achieved at a degree of grafting higher than 70%. The homogeneously grafted membranes show good electrochemical and mechanical properties which make them acceptable for practical uses as cation-exchange membranes.

INTRODUCTION

Extension to our previous studies dealing with the preirradiation grafting of acrylic acid (AAc) onto polytetrafluoroethylene[1,2] (PTFE) and poly(tetrafluoroethylene–hexafluoropropylene)[3] (FEP) films, a study have been made on the properties of the grafted FEP films. In the preirradiation method, some of the free radicals trapped in the polymer matrix can react with the monomer, under the suitable conditions, to form a graft copolymer. It is well known that the preirradiation method is limited to the crystalline and semicrystalline polymers. However, with the amorphous polymers in the rubbery state, the radicals produced by the radiation do not survive long enough to subsequently initiate grafting due to the decay of free radicals in such structure. In general, the lifetime of the trapped radicals is higher at low temperatures. Accordingly, irradiation at low temperatures increases the grafting yield, as compared to irradiation at room temperature, if the grafting step is carried out within a short time

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after irradiation because the lifetime of trapped radicals is limited. The amount of grafting depends not only on the free radicals abundance but also on the availability of these trapped radicals to the monomer related to the diffusion of the monomer into the polymer matrix.

In the preceding studies[1-3] it was found that the grafting of AAc onto PTFE and FEP films proceeds successfully by using preirradiation technique under vacuum at −78°C. Meanwhile, it was observed that the lower the monomer concentration, the more deeply the grafting proceeds and it reaches the film center with homogeneous distribution of the grafted chains in the film. The grafted PTFE film shows a good electric conductivity and high permselectivity (ca. 90%),[2] as well as good mechanical properties, which made them acceptable for the practical use as a cation exchange membrane.

As reported on the grafting onto fluorine-containing polymers such as PTFE,[4-6] poly(vinyl fluoride),[7] and tetrafluoroethylene–ethylene copolymer,[7] the properties of these grafted copolymers made them extremely attractive as trunk polymers for permselective membranes preparation. Though copolymers like FEP exhibit similar good properties and offer advantages in processing, especially, the grafting on this trunk polymer for membrane preparation was not described in detail.

The intention of this study is to investigate the properties of the grafted FEP film, such as swelling behavior, homogeneity of grafting, electric conductivity, and mechanical properties. Also, the purpose of this study is to elucidate the grafting mechanism proposed in the previous study[3] and the possibility of their practical application as ion-exchange membrane.

EXPERIMENTAL

Materials and Methods. The FEP-*g*-AAc films were prepared by the preirradiation grafting method as described in the previous study.[3] The methods and apparatus used for the measurements of swelling behavior, dimensional change, electric resistance, distribution of grafting, and mechanical properties were the same as in the previous study on PTFE-*g*-AAc system.[2] Analysis by infrared spectroscopy was carried out by using a Diffraction Grating Infrared Spectrometer, A-302 (Japan Spectroscopic Co., Ltd.).

RESULTS AND DISCUSSION

Swelling Behavior

It is very important for the practical application of the membrane as an ion exchange membrane or a reverse osmosis one that the membrane must exhibit a suitable hydrophilicity as well as good electrochemical and mechanical properties. By introducing hydrophilic groups into the hydrophobic polymers by grafting of hydrophilic monomers such as acrylic acid, the graft copolymer will exhibit hydrophilic properties and swell in water. It is well known that fluorine containing polymers cannot swell in any monomer or solvent. The FEP film, however, becomes hydrophilic and swells in water by the grafting of acrylic acid.

Figures 1 and 2 show the swelling behavior of the grafted FEP film as a function

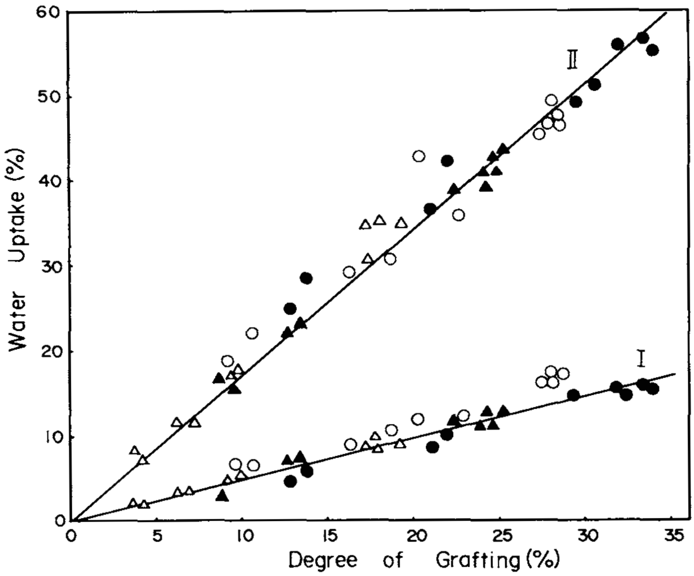


Fig. 1. Water uptake vs. degree of grafting for the grafted FEP films obtained at various preirradiation doses (Mrad): (△) 1; (▲) 3; (○) 5; (●) 10. Swelling temp = 25°C. Grafting conditions: acrylic acid concn = 40 wt %; grafting temp = 35°C; original film thickness = 75 μm.

of degree of grafting. Water uptake increases with degree of grafting (Fig. 1). Also, the volume change of the grafted film on wetting increases linearly with degree of grafting (Fig. 2). The conversion of the carboxylic acid groups into their potassium salt brought a higher hydrophilicity for the grafted film. The water uptake for the KOH-treated membrane, (II) in Figure 1, is approximately fourfold as compared with that for the untreated one, (I). On the one hand, the percent increases of volume of the wet membrane is remarkably enhanced by

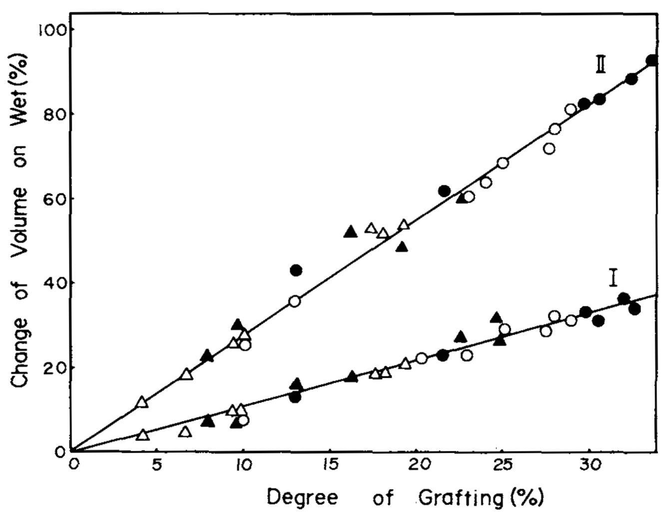


Fig. 2. Percent change of volume on wetting as a function of degree of grafting at various preirradiation doses (Mrad): (△) 1; (▲) 3; (○) 5; (●) 10. Swelling temp = 25°C. Grafting conditions are the same as in Figure 1.

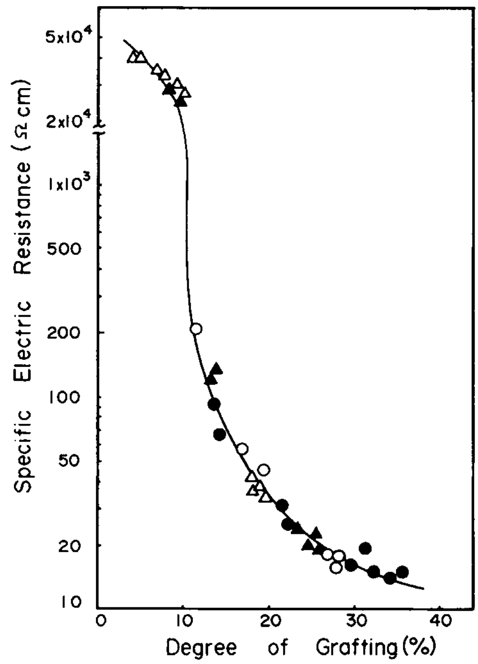


Fig. 3. Logarithmic plots of the specific electric resistance vs. degree of grafting for the grafted FEP films obtained at various preirradiation doses (Mrad): (△) 1; (▲) 3; (○) 5; (●) 10. Grafting conditions are the same as in Figure 1.

such alkali treatment and reaches almost 100% at a degree of grafting of 32%, as can be seen in Figure 2. This means that the grafted FEP film becomes highly hydrophilic by the grafting with AAc, followed by alkali treatment.

Investigation of the effects of grafting conditions, such as preirradiation dose, grafting temperature, monomer concentration, and film thickness on the swelling behavior of the grafted film shows that no effect of such conditions is observed. Results suggest that the degree of swelling depends mainly on the degree of grafting, i.e., on the amount of the hydrophilic groups in the film, and also on the form of electrolyte, (—COOH) or (—COOK). These results coincide with those obtained for the grafted PTFE film in the previous study.[2]

Electric Resistance

It is well known that among the fundamentals of ion exchange membrane is a lower electric resistance. In this study, the electric resistance of KOH-treated membrane was measured and the effect of preparation conditions was investigated. Figure 3 shows the relationship between the specific electric resistance and the degree of grafting for the membranes obtained at various preirradiation doses. It is obvious that the electric resistance decreases as the degree of grafting increases and falls down sharply at a degree of grafting ranging from 10–15%. At a higher degree of grafting, the electric resistance becomes very low (ca. 15 Ω·cm). On the other hand, it can be seen that the preirradiation dose have no influence on the electric resistance within the range of dose examined here (1–10

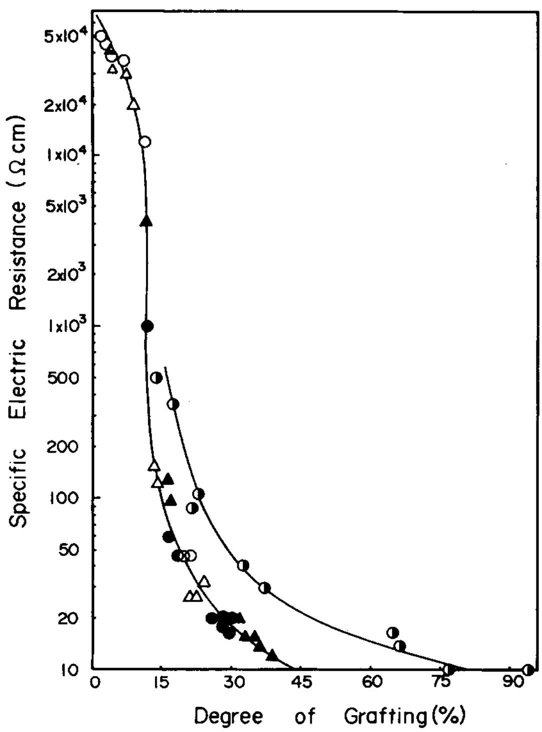


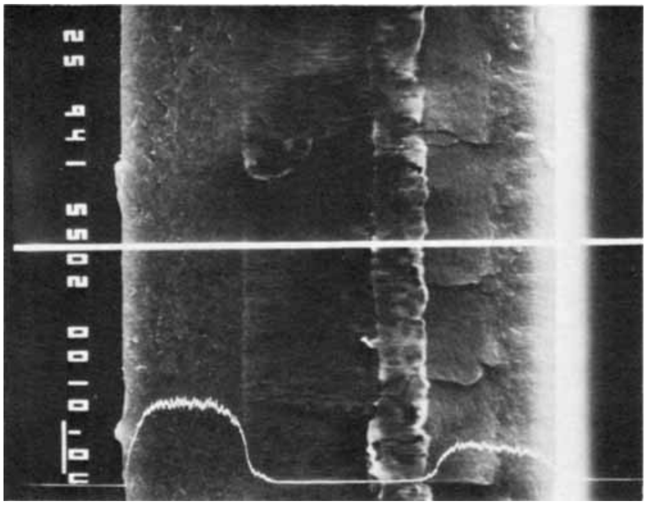
Fig. 4. Logarithmic plots of the specific electric resistance vs. degree of grafting for the grafted FEP films obtained at various acrylic acid concentrations (wt %): (○) 10; (△) 20; (●) 40; (▲) 60; (◑) 80. Grafting conditions, except preirradiation dose (5 Mrad), are the same as in Figure 1.

Mrad). It was also observed that the grafting temperature and the film thickness have no effect on the electric resistance of the grafted film.

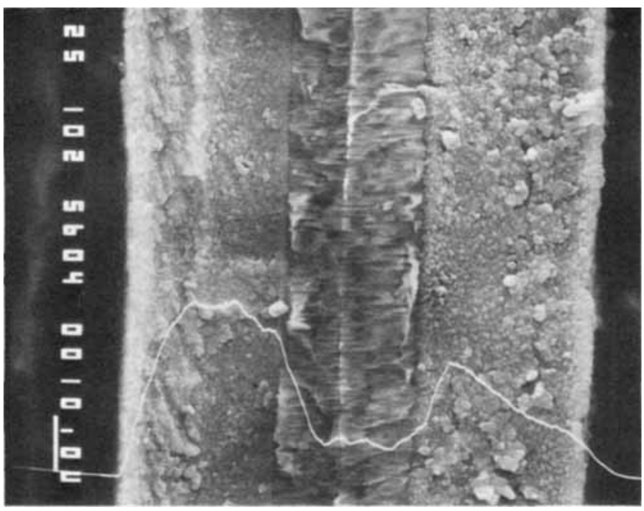
At these experimental conditions, the specific electric resistance depends mainly on the amount and distribution of the electrolytes in the grafted film, and is independent of the preirradiation dose. These results can be reasonably understood by assuming that the grafting proceeds from both surfaces of film to the center part with progressive diffusion of monomer. It is suggested that the grafting does not proceed deeply through the film matrix in the region where the grafted film has a higher electric resistance.

The effect of monomer concentration on the specific electric resistance of the membrane was investigated and is shown in Figure 4. It can be seen that the specific electric resistance decreases with increasing the degree of grafting at any monomer concentration. Meanwhile, the specific electric resistance of the membrane obtained at 80% AAc deviates to a higher value to give finally, above 70% grafting, a very low value (10 Ω·cm).

As reported previously,[3] the rate of grafting of AAc onto FEP film is lower at low AAc concentration as compared with that at higher ones. This may result in the homogeneity of grafting at lower AAc concentrations ranging from 10%–60%; however, some heterogeneity of grafting may occur at higher ones. Accordingly, the specific electric resistance is independent of AAc concentration in the range of 10%–60%, at which the grafting proceeds more deeply through



(a)



(b)

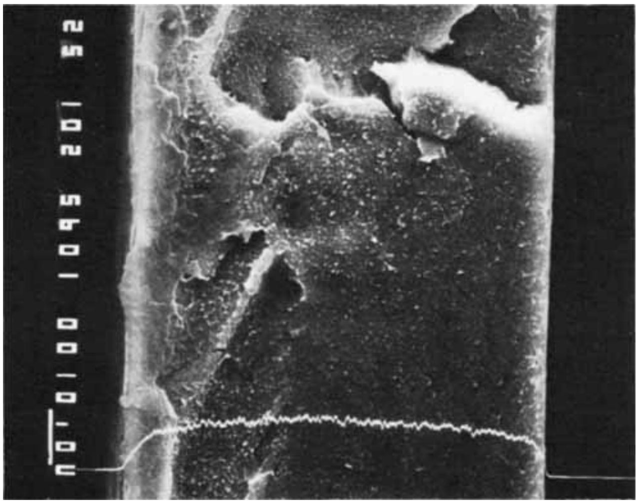
Fig. 5. XMA micrograph of the grafted FEP film. Grafting conditions: preirradiation dose = 5 Mrad; acrylic acid concn = 40 wt %; original film thickness = 75 μm; grafting temp = 35°C: (a) degree of grafting 10.7%; specific electric resistance = 213 Ω·cm; K_α intensity, ×1/5; (b) degree of grafting 13.1%, specific electric resistance = 139.7 Ω·cm; K_α intensity, ×1; (c) degree of grafting 22.3%, specific electric resistance = 24.1 Ω·cm; K_α intensity, ×1/5.

the film with homogeneous distribution of the electrolytes at a degree of grafting above 18%. The homogeneity of grafting, for the membrane obtained at 80% AAc, may be achieved at a higher degree of grafting more than 40%.

As a matter of fact, the behavior of electric resistance for the grafted FEP film coincides with that obtained for the PTFE-*g*-AAc.[2]

Distribution of Grafting

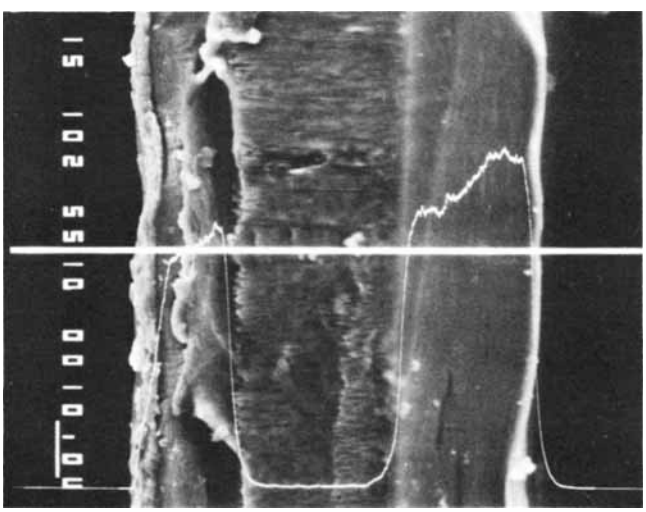
An important parameter for membrane preparation is the suitable conditions necessary to achieve the grafting through the film. Only film with completely



(c)

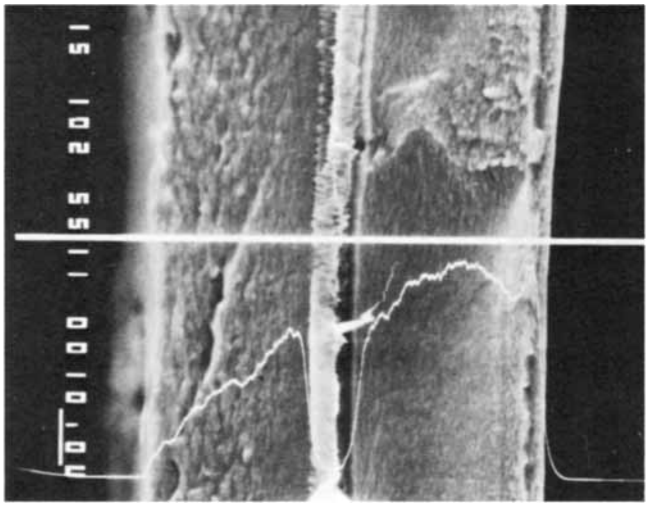
Fig. 5 (*Continued from the previous page.*)

grafted cross section will exhibit suitable qualities as an ion exchange membrane. We observed the distribution of the grafting in the trunk polymer film by X-ray microanalyzer (XMA). Figure 5 shows the change of the grafted layer for the membranes obtained at a constant AAc concentration (40%). It is obvious that the grafting proceeds from both surfaces of the film into the direction of center part. At a lower degree of grafting [Figs. 5(a) and 5(b)], the nongrafted layer still remains in the middle part of film, which disappears as the grafting proceeds, to give, finally, a membrane with homogeneous distribution of the grafted chains [Fig. 5(c)]. On the other hand, the membrane prepared at a higher AAc concentration (80%) still have a large nongrafted layer even at a degree of grafting



(a)

Fig. 6. XMA micrograph of the grafted FEP film. Grafting conditions: preirradiation dose = 5 Mrad; acrylic acid concn = 80 wt %; original film thickness = 75 μm; grafting temp = 35°C. (a) degree of grafting 32.6%; specific electric resistance = 40 Ω·cm; K_α intensity, ×1; (b) degree of grafting 76.3%; specific electric resistance = 8.1 Ω·cm; K_α intensity, ×1.



(b)

Fig. 6 (*Continued from the previous page.*)

more than 30% [Fig. 6(a)]. The nongrafted layer decreased to a narrow zone by increasing the degree of grafting [Fig. 6(b)].

The thickness of the grafted layer was calculated from XMA and plotted as a function of degree of grafting and is shown in Figure 7. It can be seen that the thickness of the grafted layer increases linearly with degree of grafting at a lower AAc concentration, 40%, (I), and the grafting proceeds thoroughly into the film center at a degree of grafting around 18%. However, at a higher AAc concentration (80%), the thickness of the grafted layer is smaller than that obtained at a lower one, and it increases gradually with degree of grafting (II).

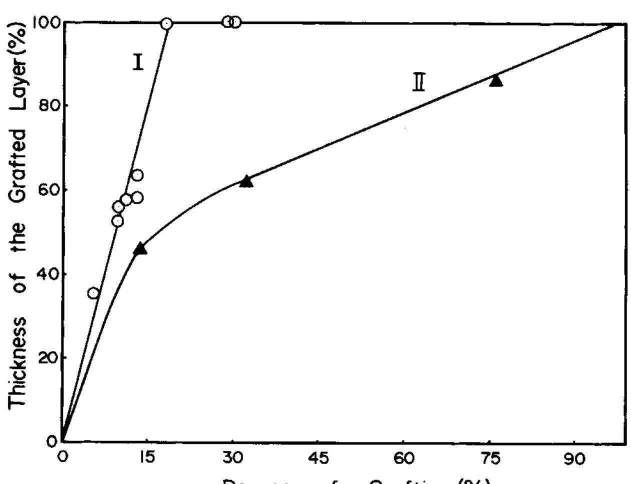


Fig. 7. Percent thickness of the grafted layer vs. degree of grafting for the membranes obtained at various monomer concentrations: (I) 40 wt % AAc; (II) 80 wt % AAc.

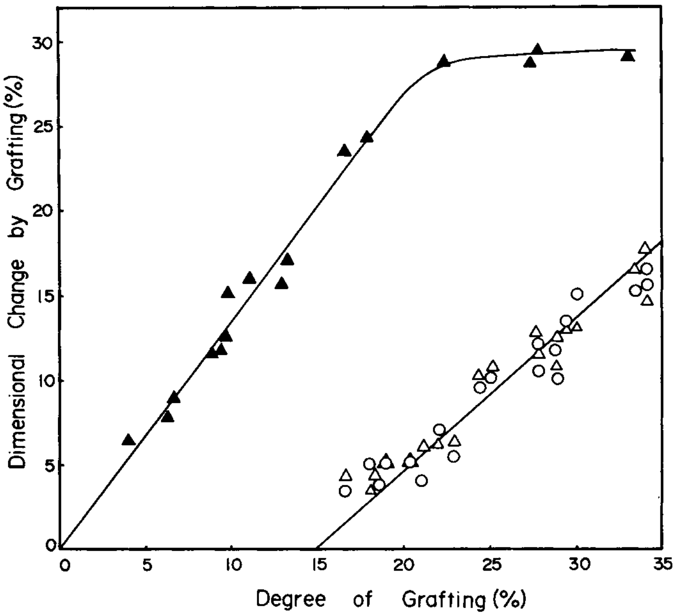


Fig. 8. Dimensional changes [(○) width; (△) length; (▲) thickness] of the grafted FEP films on dry state as a function of degree of grafting. Grafting conditions: preirradiation dose = 5 Mrad; acrylic acid concn = 40 wt %; grafting temp = 35°C; original film thickness = 75 μm.

Analysis of these diagrams at various grafting conditions leads to the following conclusions:

1. The penetration rate of the grafting front decreases with increasing monomer concentration higher than 60%.

2. To achieve the grafting through the film at a lower degree of grafting, a lower monomer concentration is more suitable than higher one.

In the previous study[2] dealing with the properties of the PTFE-*g*-AAc membrane, it was found that the grafting reaches to the center part of film at a degree of grafting above 9% for the membrane obtained at 40% AAc concentration. It was also observed that the grafting time necessary to achieve the saturation of grafting on PTFE[1] is less than that for FEP film.[3] By comparison between the behavior of grafting on PTFE and that of FEP, one can assume that the rate of monomer diffusion into FEP matrix is less than that in the case of PTFE, despite the higher degree of grafting obtained on FEP film. As is well known, PTFE is a typical degradable polymer upon irradiation; however, no extensive damage was observed for FEP.[8] Degradation of polymer matrix may facilitate the diffusion of monomer through the film, and, consequently, the higher rate of monomer diffusion can be expected for PTFE film more than for FEP. This may be one of the reasons why PTFE gives a homogeneous distribution of grafting even at a lower degree of grafting as compared with FEP. The other reason may be attributed to the different morphology of these polymer films which depends largely on the method of making film. PTFE and FEP films used here were ones prepared by skieving a sintered rod and by using an extruder, respectively. The monomer penetrations into these films, therefore, may be quite different from each other. As a matter of fact, at a given degree of grafting the specific electric resistance of the grafted PTFE film is lower than that of the grafted FEP, as reported previously.[2]

The dimensional changes caused by grafting were measured for the dry membrane obtained at a lower AAc concentration (40%) are shown in Figure 8. It is obvious that the film thickness increases as the grafting starts. The rate of increase in film thickness is directly proportional to the degree of grafting, and it tends to level off after the grafting has been reached to the film center at ca. 18% grafting. On the other hand, an induction period was observed in the changes of width and length. Then they begin to increase after the grafting reaches the film center.

This result suggests that the nongrafted layer prevents the dimensional change in directions of width and length, but not in thickness which is in close agreement with that observed for PTFE-*g*-AAc.[2]

The grafting mechanism which was proposed from the behavior of electric resistance of the grafted film is reasonable with the results obtained for the distribution of grafting and dimensional change of the membrane. This may confirm that the grafting proceeds from both surfaces of film into the center part to give finally a highly homogeneous distribution of the grafted chains.

Mechanical Properties

One of the necessities for the membrane properties is to exhibit mechanical properties acceptable for the practical uses. In this study, the mechanical properties of the original and grafted FEP films were investigated. Figure 9 shows the changes of tensile strength (T_b) and percent elongation (E_b) at break point for the original FEP film which was irradiated at various doses in air and *in vacuo* at room temperature. It can be seen that at both irradiation conditions T_b and E_b decrease with increasing the dose. The decrease in T_b and E_b upon irradiation under vacuum, however, is small compared with that irradiated in air. It is well known that the degradation of polymers during irradiation is enhanced by the presence of oxygen. The extensive damage for the FEP film irradiated in air may be due to the oxidative degradation.

The changes in T_b and E_b of the dry membrane irradiated at various doses were measured as a function of degree of grafting and are shown in Figure 10. No significant changes of T_b and E_b occurred by grafting at low doses. At a higher dose (10 Mrad), however, they decrease and thereafter increase gradually with degree of grafting to reach finally almost the same value observed at low doses.

From the practical point of view, as the membrane will be used on wetting, T_b and E_b were measured after the grafted film was soaked in distilled water for 24 h at room temperature. The changes of T_b and E_b for the wet membranes obtained at various doses are shown in Figure 11 as a function of degree of grafting. It is obvious that the absolute values of T_b and E_b for wet membranes are smaller as compared with those for dry ones at a given degree of grafting and irradiation dose. In general, almost the same tendencies of T_b and E_b for the wet membrane as those for the dry one were also observed.

The behavior of mechanical properties of the membrane obtained at 10 Mrad, which decrease sharply at a lower degree of grafting and then increase at a higher one, may be due to some effects caused by crosslinking in the graft copolymer. Such crosslinking structure may be formed by acrylic acid, which easily forms

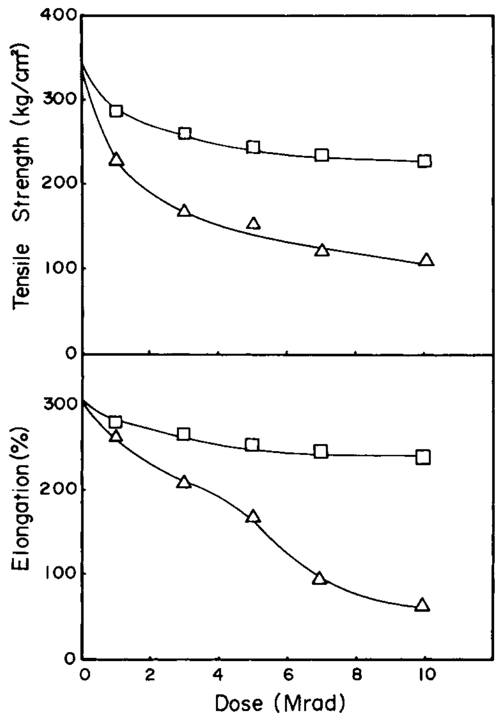


Fig. 9. The change of mechanical properties of the original FEP films caused by γ-rays irradiation *in vacuo* (□) and in air (△) at room temperature.

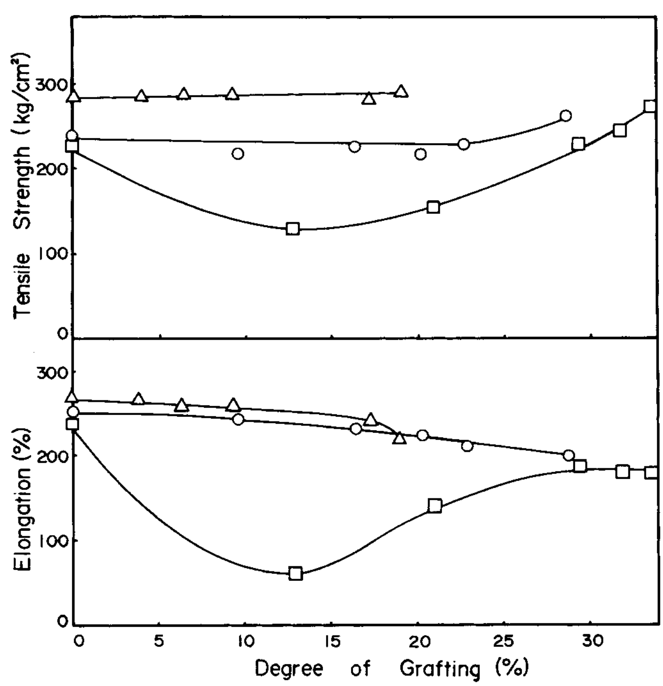


Fig. 10. The change of mechanical properties of the grafted FEP films on dry as a function of degree of grafting. Grafting conditions are the same as in Figure 1. Doses (Mrad): (△) 1; (○) 5; (□) 10.

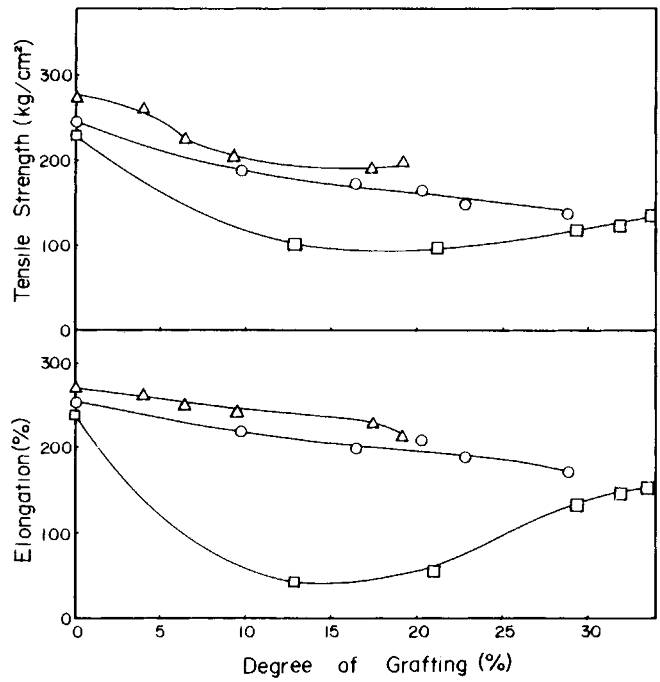


Fig. 11. The change of mechanical properties of the grafted FEP films on wetting as a function of degree of grafting. Grafting conditions are the same as in Figure 1. Doses (Mrad): (△) 1; (○) 5; (□) 10.

cyclic dimer bridged by hydrogen bonds, and enhanced at a higher dose. At a lower degree of grafting the crosslinking network structure is located close to the film surface; however, at a higher one the whole bulk of the polymer matrix becomes crosslinked, and, consequently, the mechanical properties increase. On the other hand, the mechanical properties of the wet membrane are lower than those of the dry one because of their high swelling behavior in water. The occluded water in polymer matrix may facilitate the loosening and slipping of the molecules on strain. It was reported in the previous study[2] that the heterogeneity of grafting leads to a decrease in the mechanical properties of the PTFE-*g*-AAc film due to some stresses occuring on the polymer matrix, which is enhanced on wetting.

These results show that the mechanical properties of the grafted FEP film are good and may make them acceptable for practical uses. Results show also that T_b and E_b are dependent on the preirradiation dose and degree of grafting. The membrane obtained at a lower dose does not show a remarkable decrease in their mechanical properties. From this point of view, it is preferable that the preparation of these membranes must be carried out at a lower dose as much as possible to reduce the expected degradation.

Analysis by Infrared Spectroscopy

Infrared analysis was made for the original and grafted FEP films to confirm the formation of graft copolymer. It is well known that acrylic acid easily forms

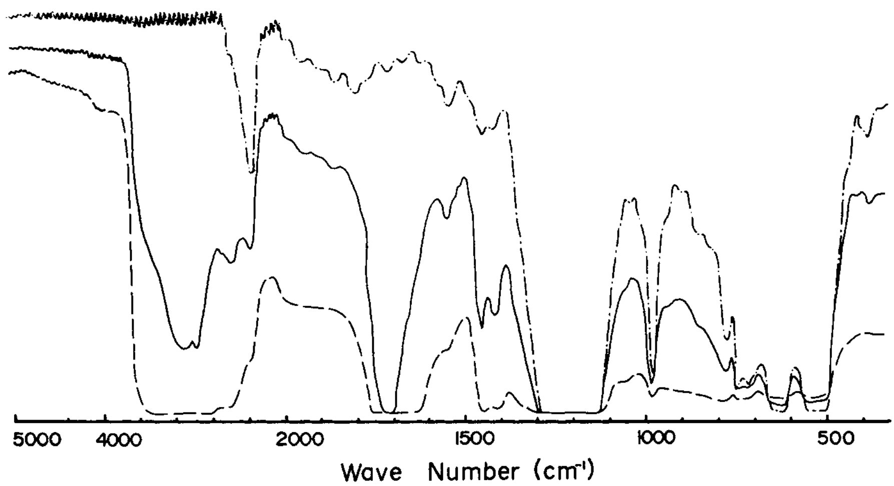


Fig. 12. IR spectra of the original FEP and FEP-grafted AAc films: (- • -) original FEP film of thickness = 75 μm; (—) degree of grafting 5.5%; (- - -) degree of grafting 26.9%.

cyclic dimer bridged by hydrogen bonds, especially in nonpolar solvents. The abnormally strong hydrogen bonding in the carboxylic acids is an advantage in one way, as the OH stretching vibrations are so distorted from the normal as to be relatively characteristic, so that observations in this region give a valuable indication of the presence of carboxylic acids.[9]

Figure 12 shows the spectra of the original FEP film and the FEP-*g*-AAc having different degrees of grafting, 5.5% and 26.5%, respectively. The characteristic bands of FEP and poly(acrylic acid) graft chains appear clearly in the graft copolymer. Peaks appeared around 1700, 2600, and 2770 cm^{-1}, and the strong broad band appearing around 3000 cm^{-1} are characteristic for poly(acrylic acid) structure. The intensity of the band near 1460 cm^{-1}, which comes from FEP structure, increases in the grafted film because of acrylic acid. The peak appeared around 1700 cm^{-1} confirms the existence of carbonyl groups and in-

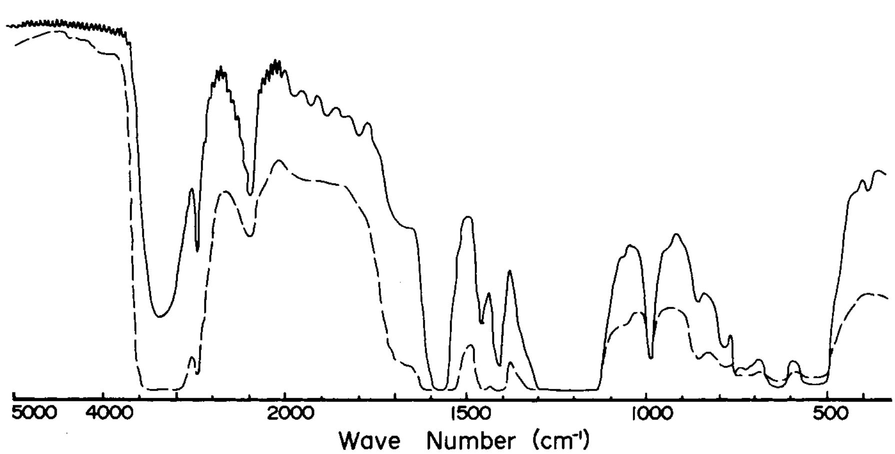


Fig. 13. IR spectra of the FEP-grafted AAc and KOH-treated: (—) degree of grafting 4.1%; (- - -) degree of grafting 26.4%.

creases as the degree of grafting increases. The absorption at 2970 cm^{-1} is assigned to —CH_2— asymetric stretching groups. At a lower degree of grafting, the absorption at 3000–3300 cm^{-1} is due to the hydrogen bonding and hydroxyl groups. This absorption becomes very broad and strong as the degree of grafting increases. The absorption between 2500 and 2700 cm^{-1} is indicative of a strongly hydrogen-bonded OH groups.[9]

Figure 13 shows the spectra of KOH-treated membranes having degree of grafting, 4.1% and 26.4%. The intensity of absorption of the characteristic bands increases with degree of grafting. Ionization of carboxylic groups by alkali treatment results in equilibration of two oxygen atoms attached to the carbon with the disappearance of the carbonyl absorption and the appearance of two new bands near 1550 and 1400 cm^{-1} arising from symmetrical and antisymmetrical vibrations of COO^- ionic groups.

CONCLUSIONS

Investigation of the properties of the FEP-*g*-AAc film such as swelling behavior, electric conductivity, distribution of the grafted chains, and mechanical properties was carried out and it can be concluded that:

1. The KOH-treated membrane shows a higher swelling in water, i.e., its water uptake is fourfold that of the untreated.
2. The specific electric resistance of the membrane is largely dependent on degree of grafting and to somewhat on the higher monomer concentration above 60%. However, it is independent of other preparation conditions such as preirradiation dose, grafting temperature, and film thickness.
3. Distribution of grafting was observed by X-ray microanalyzer and confirmed that the grafting proceeds from both surfaces of film with progressive diffusion of monomer, and reached the center to give finally a homogeneous distribution of grafted chains in the film. The dependence of the specific electric resistance and the grafting distribution on the grafting conditions was also observed by XMA. At a lower monomer concentration (less than 80%) the grafting proceeds more deeply to give a homogeneous distribution even at a lower degree of grafting as compared with that obtained at a higher monomer concentration (80%).
4. The grafted film was found to have almost the same mechanical properties as those of the original one which was irradiated at the same dose, especially at a lower dose. However, the wet membranes showed somewhat lower mechanical properties because of their high swelling.
5. Analysis by infrared spectroscopy of the membrane confirmed the existence of poly(acrylic acid) structure in the graft copolymer. It was also suggested that hydrogen bonding and crosslinking structure are present in the graft copolymer.

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