

Synthesis and Characterization of Acrylic Acid-Grafted Hydrocarbon and Fluorocarbon Polymers with the Simultaneous or Mutual Grafting Technique

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ABSTRACT: Radiation-induced graft copolymerization has been used extensively to modify polymers with acrylic acid to impart some properties of the monomer but still maintain the strength and stability of the polymer chain. This article describes the process of the simultaneous graft copolymerization reaction for the modification of hydrocarbon- and fluorine-containing polymers to produce hydrophilic membranes. The effects of the conditions of grafting, such as the radiation dose rate, the total dose, and the

monomer concentration on the resulting graft copolymers are discussed in detail. The characterization of the grafted membranes is described in terms of their composition, ion-exchange capacity, equilibrium water content, and electrolytic resistivity. It has been shown that some of these properties can be predicted from the degree of grafting. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 230–243, 2003

Key words: radiation; membranes; fluoropolymers

INTRODUCTION

Membranes used in electrochemical applications must have high stability under very harsh media and possess appropriate electrical properties. Fluoropolymers such as poly(tetrafluoroethylene) (PTFE) are known for their high stability,¹ but they are unsuitable for such applications because they are hydrophobic and not ionically conducting. A solution to this problem is to modify the structure of the polymer to convey the necessary functional properties but retain the durability of the original polymer backbone.

One technique that can be used to bring about such a structural change is radiation grafting. This method has been known and used for polymer modification for many years.^{2–4} Basically, a polymer is irradiated with high-energy photons in the presence of a monomer. If the conditions are appropriate, a graft copolymer is formed that has a combination of the properties of the backbone polymer and the monomer.

In this article, the preparation of a number of graft copolymers is described. The effect of various conditions was investigated for the grafting of acrylic acid onto fluorocarbon and hydrocarbon polymer films of different thicknesses. The method employed was mutual (or simultaneous) grafting; that is, both the poly-

mer and monomer were irradiated simultaneously³ with a cobalt 60 γ source.

The polymers chosen for this study included low-density polyethylene (LDPE), ethylene–tetrafluoroethylene (ETFE), perfluoroalkoxy vinyl ether (PFA), fluorinated ethylene–propylene (FEP), PTFE, and poly(vinylidene fluoride) (PVDF). A comparison of different sources for the same polymer with respect to the grafting procedure is also reported.

To produce a selection of graft copolymers with different properties, we investigated the effects of the radiation total dose, the dose rate (grafting time), and the monomer concentration. These are all important parameters in mutual grafting because they can markedly influence the composition of the resulting copolymer. Once grafted, the materials were characterized by the ion-exchange capacity (IEC), the equilibrium water content (EWC), and the electrolytic resistivity.

In all the grafting reactions described, 8 g/dm³ iron(II) sulfate was used as an homopolymerization inhibitor [to discourage the formation of poly(acrylic acid)].

EXPERIMENTAL

Materials

All the polymers and reagents were used as received. The polymer suppliers are shown in Table I.

Acrylic acid (99%) was supplied by Aldrich, and it was inhibited with 200 ppm monomethyl ether hydroquinone. Iron(II) sulfate (FeSO₄ · 7H₂O) was supplied by BDH Merck, Ltd. (Analar-grade). Demineralized

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TABLE I
List of Polymer Suppliers

Polymer type	Supplier	Nominal thickness (μm)	Method of film formation
PTFE	De Wal	50, 150, 250	Skived
PTFE	De Wal	50, 125	Skived + tensilized
PTFE	Fluorocarbon	50, 150, 250	Skived
PTFE	Chemfab	50	Cast
FEP	Ensinger	50, 125, 250	Extruded
FEP	DuPont	50	Extruded
PVDF	Nowofol	50	Extruded
PFA	Chemfab	50	Extruded
ETFE	DuPont	50	Extruded
LDPE	Transatlantic Plastics	125	Blown

water was supplied from an Elgastat mixed-bed demineralizer (High Wycombe, UK) with a conductivity of less than $50 \mu\text{S}$.

Hydrochloric acid (0.1M) and sodium hydroxide (0.1M), with factor limits of 0.9995–1.0005, were supplied by Fisher Scientific UK (Loughborough, UK) and were analytical-grade. Phenolphthalein, bis(4-hydroxyphenyl)-(3H)-isobenzofuranone, and [3,3-bis-(4-hydroxyphenyl-phthalide)] as a 5 wt % solution in 50/50 (w/w) ethanol/water, with a transition interval of pH 8.0 (colorless) to pH 10 (red), were supplied by Aldrich.

Grafting procedure

Pieces of polymer films were interleaved with a non-woven interlayer and placed in a glass grafting tube, which was filled with an aqueous acrylic acid solution until the roll was saturated and covered. Any oxygen present was removed by a nitrogen purge, and the vessel was sealed. It was then irradiated at $23 \pm 1^\circ\text{C}$ in a cobalt 60 γ source for a predetermined time at a known dose rate. The grafted films were removed from the spent monomer solution and were washed repeatedly in demineralized water until neutrality was achieved. Any acrylic acid homopolymer present within the polymer matrix was removed by Soxhlet extraction with methanol for 48 h. It was then washed in demineralized water and dried to a constant weight.

The degree of grafting (DOG) of the membranes was calculated with the following formula:

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

where W_0 is the weight of the polymer film before grafting and W_g is the weight of the grafted polymer. Therefore, the DOG represents the proportion of the copolymer that is grafted material and has an upper limit of 100%. Therefore, a copolymer with a 50% DOG is 50% original polymer and 50% grafted monomer.

Effect of the grafting time (dose rate)

A 25 vol % acrylic acid/75 vol % demineralized water grafting solution was used. The reaction vessel was purged with nitrogen for 2 h for the removal of oxygen and was then irradiated at dose rates of 500, 166, 100, and 50 Gy h^{-1} for a total of 20, 60, 100, and 200 h, respectively, to a total dose of 10 kGy.

Effect of the total dose

These reactions were carried out with a 25 vol % acrylic acid/75 vol % demineralized water grafting solution. The reaction vessel was purged with nitrogen for 2 h and irradiated at 166, 333, and 500 Gy h^{-1} for 60 h to give total doses of 10, 20, and 30 kGy, respectively.

Effect of the acrylic acid concentration

The grafting solutions were made with different concentrations of acrylic acid (10, 20, and 30 vol %) with demineralized water as a diluent. The grafting solution was purged with nitrogen, and the samples were irradiated at 166 Gy h^{-1} for 60 h to a total dose of 10 kGy.

Heat treatment

After the grafting reaction and before further characterization, all the materials reported were subjected to a thermal treatment. The method used was similar to one that has been used to prepare graft copolymer separators for the battery industry.⁵ The grafted membranes were heated in a 5% (w/v) aqueous sodium hydroxide solution for 5 min at 95°C , washed to neutrality in demineralized water, and dried in an oven at 40°C . The process has been found to increase the hydrophilicity of grafted membranes, possibly by allowing the acidic groups to realign themselves within the polymer structure.

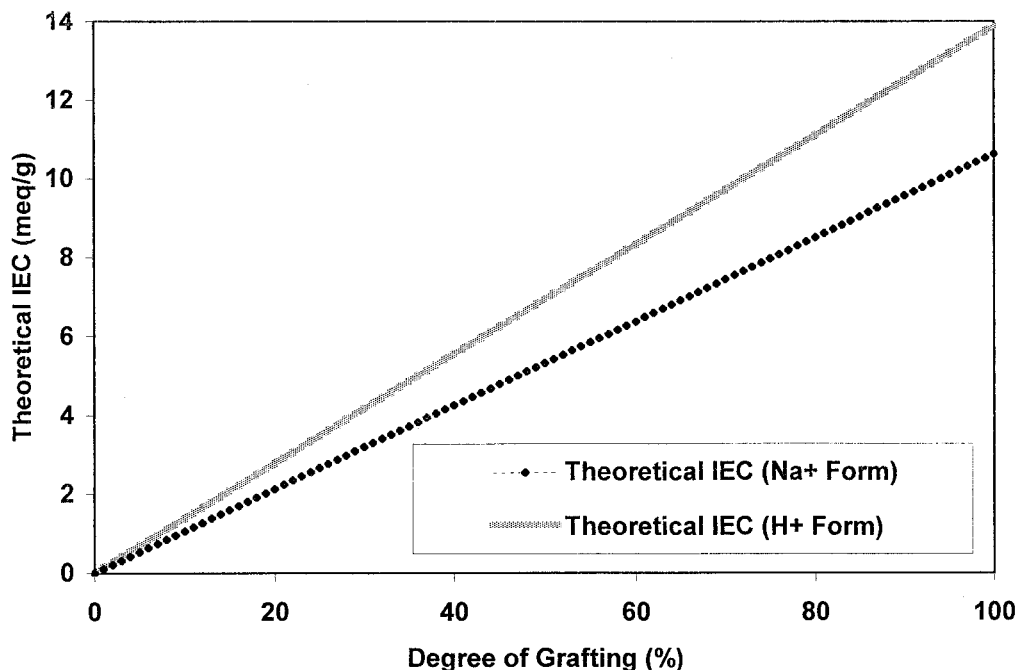


Figure 1 Theoretical IEC versus the DOG for the acrylic acid-grafted membranes in both sodium and hydrogen forms.

Characterization techniques

The membranes were characterized with complementary techniques. Although the DOG gives an indication of the composition of the copolymer in terms of the quantity of acrylic acid present, it does not show

where the graft resides in the polymer. A high DOG does not necessarily mean that the polymer is grafted through the thickness of the polymer film; it may be highly grafted at the film surface, with little or no grafting at its center.

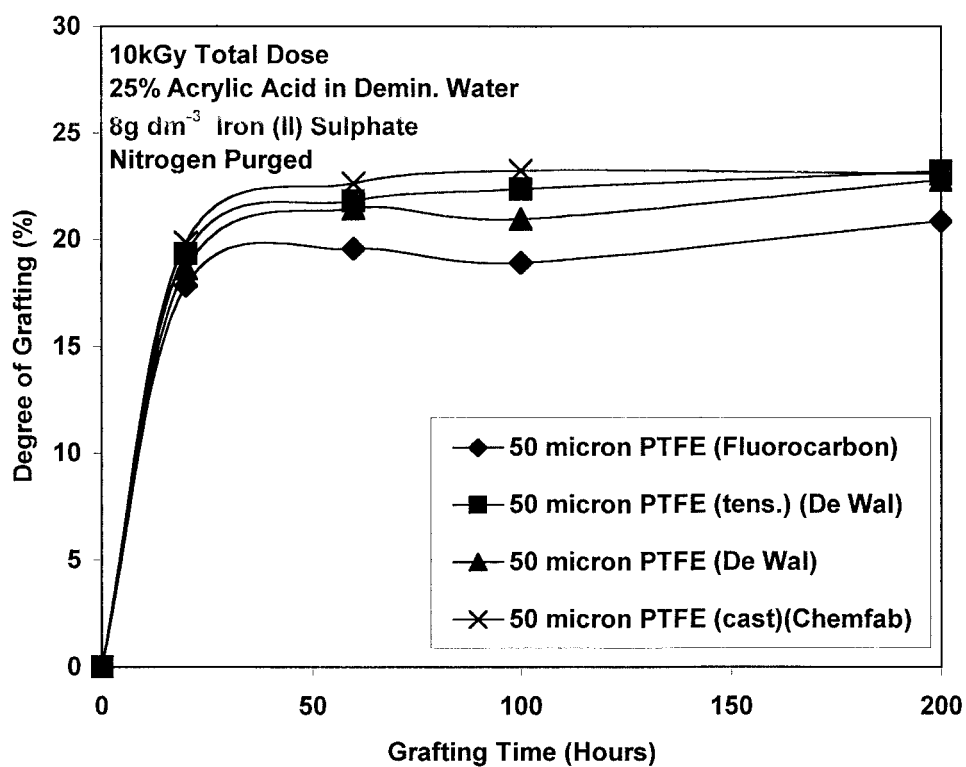


Figure 2 Effect of the irradiation time (dose rate) on the DOG for selected 50- μ m PTFE films.

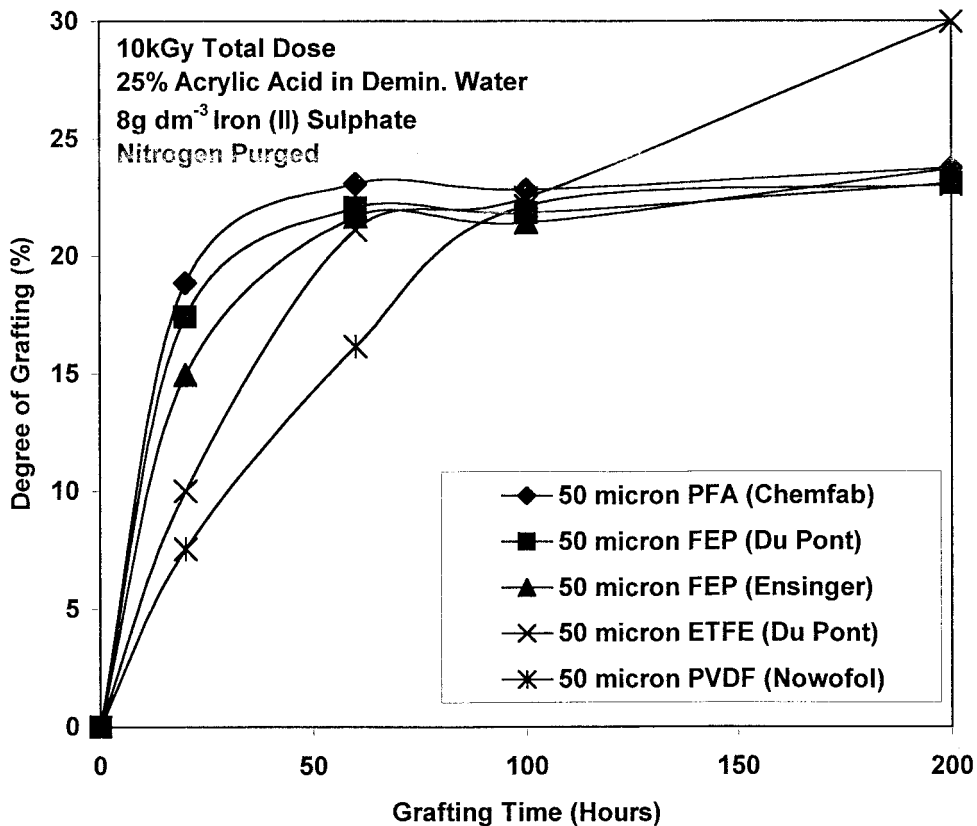


Figure 3 Effect of the irradiation time (dose rate) on the DOG for the 50- μ m polymer films.

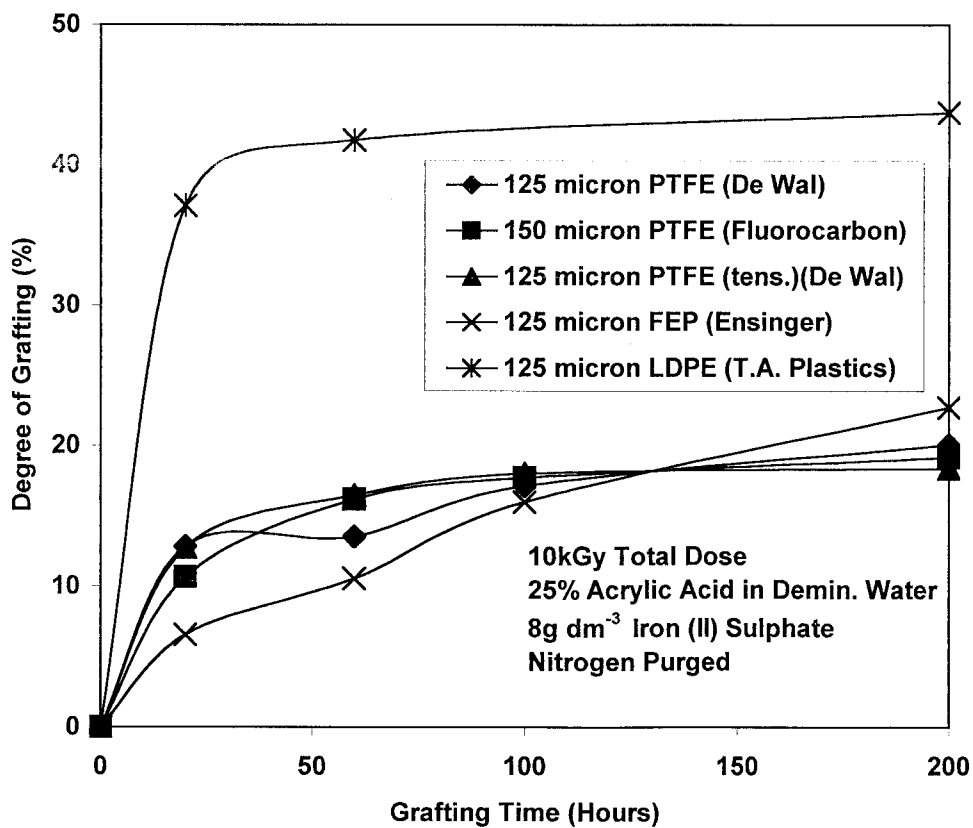


Figure 4 Effect of the irradiation time (dose rate) on the DOG for the 125- μ m polymer films.

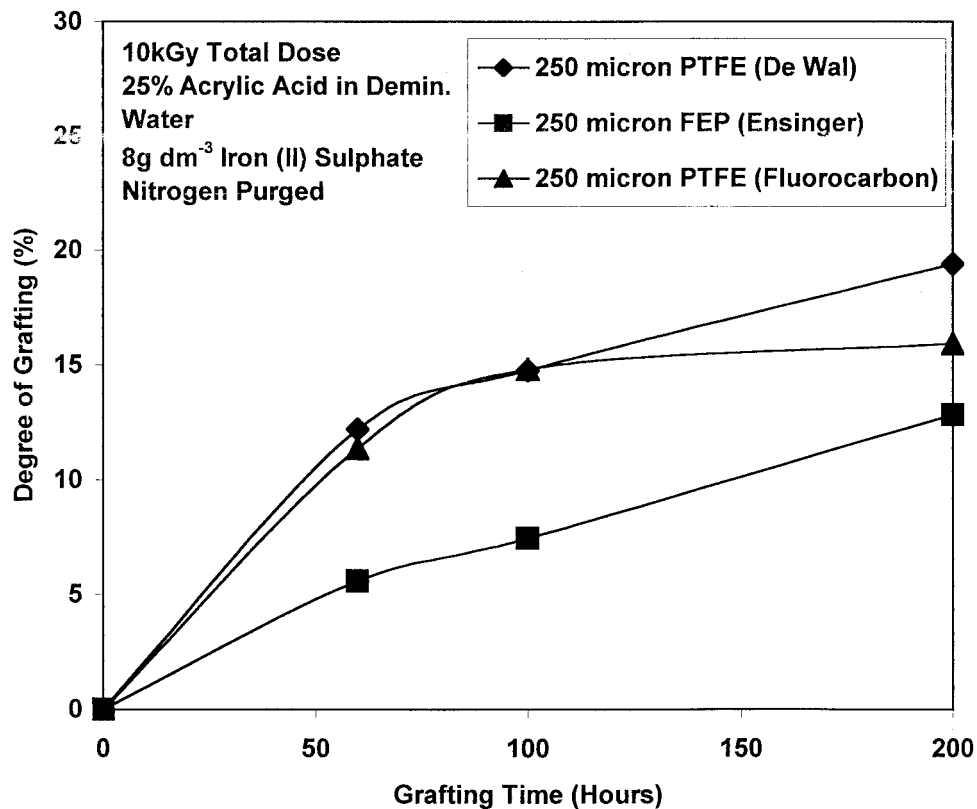


Figure 5 Effect of the irradiation time (dose rate) on the DOG for the 250- μ m polymer films.

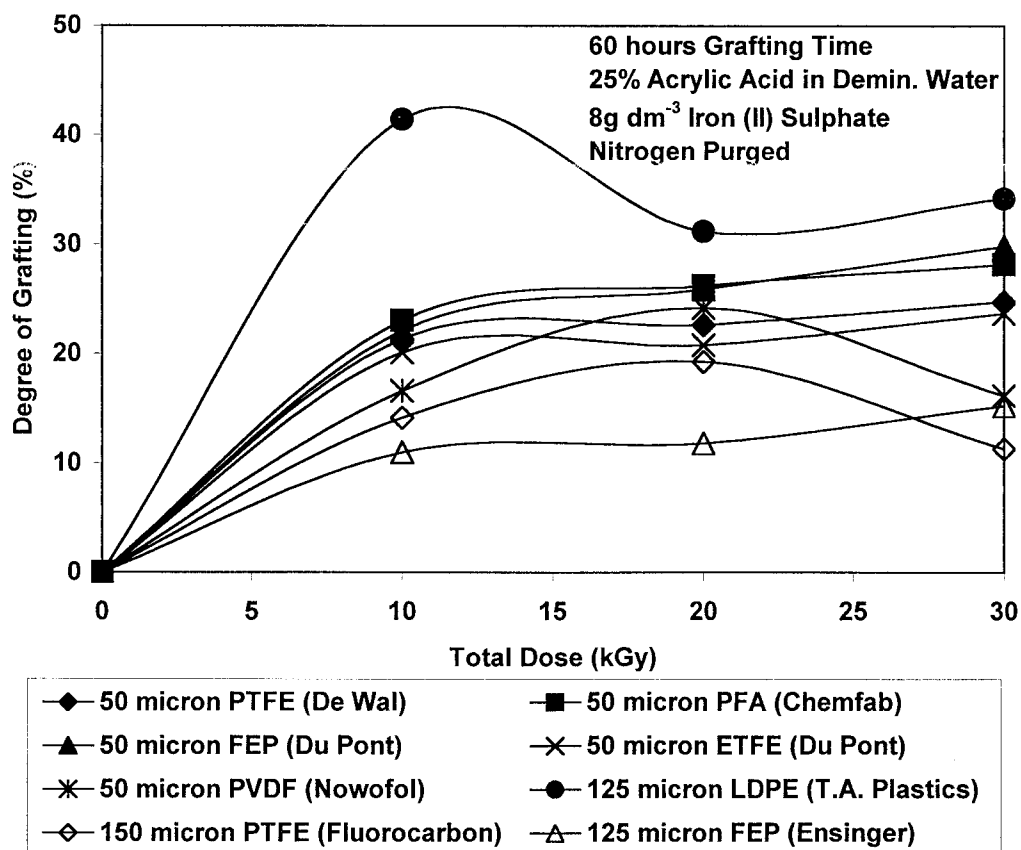


Figure 6 Effect of the total dose on the DOG.

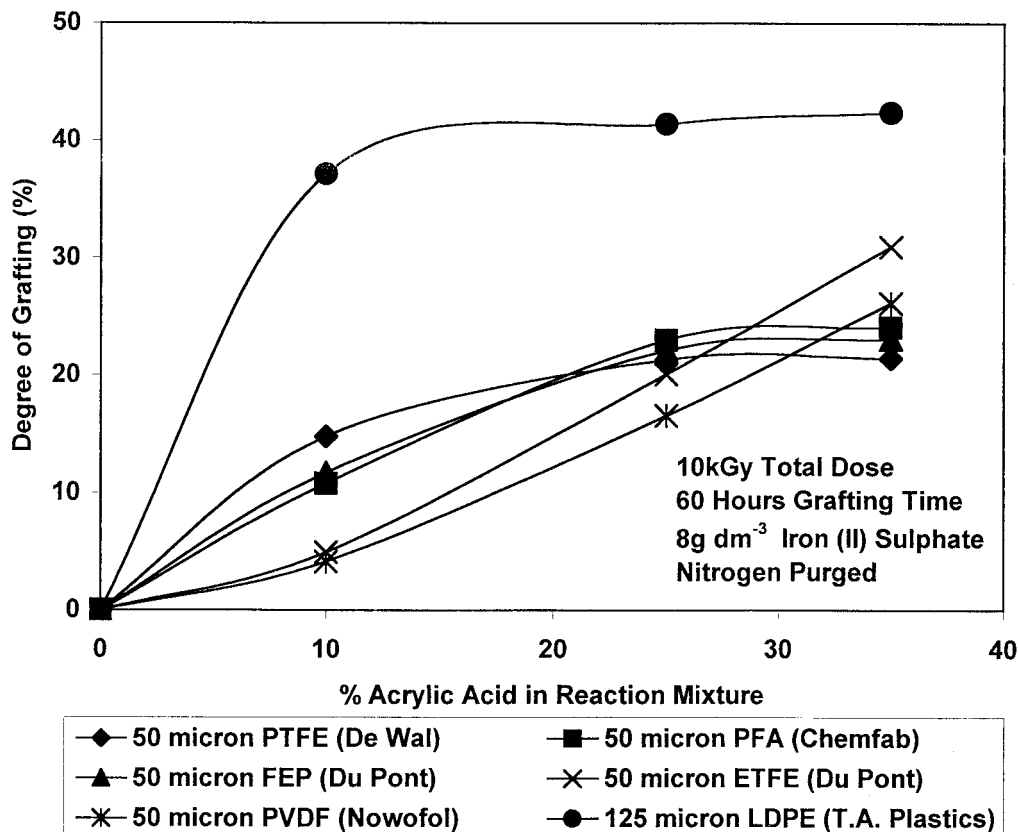


Figure 7 Effect of the monomer concentration on the DOG.

For specific applications, such as battery separators, it is necessary to use additional methods of characterization. The electrolytic resistivity of the membrane gives an indication of the homogeneity of the graft through the membrane. A high resistivity is an indication that the membrane is not fully grafted throughout its thickness. As the DOG increases, a dramatic decrease in resistivity can be expected when grafting throughout the membrane is established.

The IEC is also not a positive indication of homogeneous grafting. It is a measure of the availability of protons able to exchange ions with an outside medium. For ionic conduction, as required in an electrochemical cell, the IEC becomes an important parameter that limits the maximum current able to pass through the membrane. The IEC, for acrylic acid copolymers, is a measure of the ability of the protons to exchange cations with an outside medium (i.e., millimoles of acid present per gram of dry membrane).

A theoretical value for the IEC based on the DOG of acrylic acid can be calculated if assumptions about the grafted membrane are made. These include the gravimetric DOG being purely due to the addition of the monomer and no other reactions, such as crosslinking or scission of the polymer caused by the radiation, taking place. It can be calculated with respect to the membrane in its dry hydrogen form or dry sodium

form; Figure 1 shows the theoretical IEC versus the DOG of acrylic acid in the sodium and hydrogen forms.

The EWC influences the electrolytic resistivity, IEC, and dimensional changes that occur in the material with hydration.

Areal electrolytic resistivity

The electrolytic resistivity of the membranes was measured with a technique similar to that employed by Salkind and Kelly.⁶ The membrane was placed in a thermostatically controlled cell at a temperature of $25 \pm 1^\circ\text{C}$. An external torque clamp was used to ensure that the membranes were not compressed during testing. The membrane samples were equilibrated in the electrolyte (0.1M HCl or 0.1M NaOH) for a minimum of 16 h before being measured. The resistivity measurements were taken with a Wayne Kerr universal bridge (Bognor Regis, UK) (model B642) at a frequency of 1591.5 Hz over a known test area. The resistivity value of the electrolyte pathway was measured with a polymer blank with a thickness comparable to that of the membrane, with a hole cut in the test area. The blank measurement was then subtracted from the sample measurement. For each membrane, two samples were tested, and the results were aver-

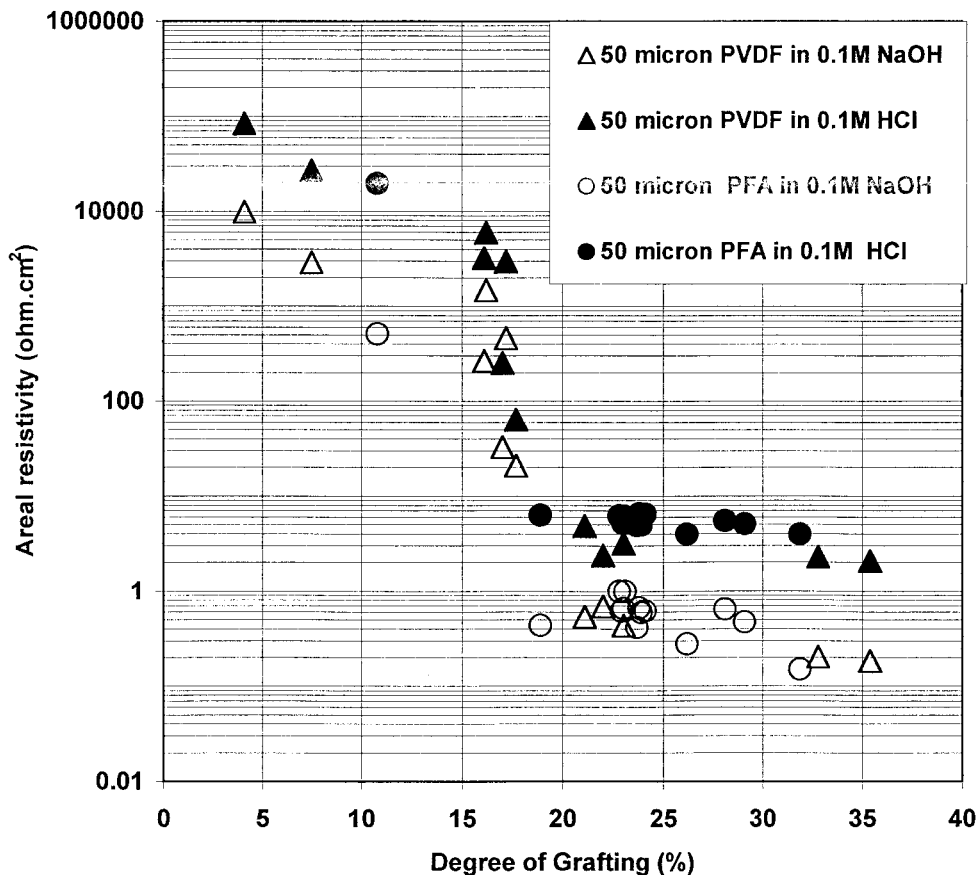


Figure 8 Areal resistivity versus the DOG for selected 50- μm acrylic acid-grafted membranes in acidic and alkaline electrolytes.

aged. The membrane resistivity was then calculated, with the area of the sample taken into account.

IEC

The method used to measure the IEC was developed from procedures described in the literature.^{7,8} Approximately 0.5 g of the membrane was equilibrated in a 0.1M HCl solution for at least 24 h at ambient temperature. The sample was then blotted dry, placed in 50 mL of a sodium hydroxide solution of known molarity (nominally 0.1M), and allowed to exchange for 24 h more at ambient temperature with occasional swirling. Aliquots of the exchanged NaOH solution were titrated to a phenolphthalein end point against an HCl solution of known molarity. The procedure was carried out in triplicate, and the results were averaged. The sample pieces in the exchange were blotted dry, placed in a vacuum oven at $105 \pm 5^\circ\text{C}$, and weighed to a constant weight.

The value obtained with this method is related to the sodium form of the membrane.

EWC

The EWC of the membranes was measured by the immersion of a piece of a membrane (at least 0.1 m \times

0.15 m) in demineralized water for a minimum of 16 h at ambient temperature. The hydrated membrane was blotted dry, weighed, measured, and dried to a constant weight. The dry membrane was then weighed and measured. The EWC was calculated as a function of the hydrated state:

$$\frac{(\text{Hydrated Weight}) - (\text{Dry Weight})}{(\text{Hydrated Weight})} \times 100 = \text{Equilibrium Water Content (\%)}$$

RESULTS AND DISCUSSION

This work has shown that the mutual method is suitable for grafting all the polymers used with acrylic acid.

The use of a nonwoven interlayer between layers of a polymer film was found to be highly desirable. It enabled the monomer solution to be in close contact with the polymer film, replenishing the solution at the radical sites during the grafting reaction via a wicking effect. This led to uniform grafting throughout the thickness and across the area of the sample. Failure to use an interlayer resulted in noticeably patchy grafts, as evidenced by their appearance after equilibration in water during the washing procedure.

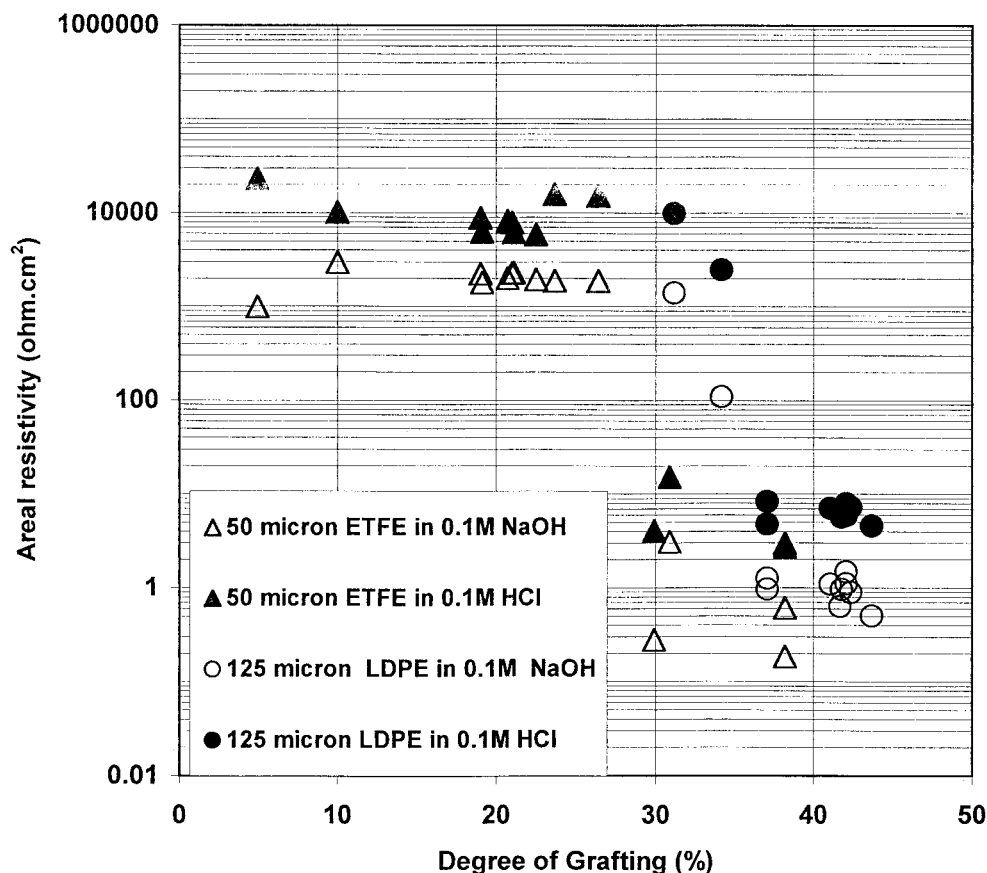


Figure 9 Areal resistivity versus the DOG for selected acrylic acid-grafted membranes in acidic and alkaline electrolytes.

Effect of the grafting time (dose rate)

In mutual grafting, this work has shown that the dose rate, for a given total dose, is an important parameter. In Figures 2–5, it can be seen that the DOG steadily increases as the grafting time increases (i.e., the dose rate decreases). This is entirely consistent with a diffusion-controlled grafting reaction, in which, for the initial period of approximately 20 h, grafting is facilitated by the availability of the monomer at the grafting front within the thickness of the polymer film. It is well documented² that monomer diffusion and, therefore, grafting take place predominantly in the amorphous regions of the polymer. As the reaction proceeds and these regions become filled with grafted monomer, the rate of grafting slows. Therefore, for most of the 50- μm polymer films, once this point is reached, typically at 40 h, no further increase in grafting is observed. The exceptions are the polymers ETFE and PVDF, for which, in Figure 3, it can be seen that the grafting rate is slower and the plateau is not reached until after 60 h. For the thicker films for which diffusion throughout the thickness takes longer, it can be predicted that the time to the maximum grafting level will be longer. This is seen in Figure 4 for the 125- μm films and in Figure 5 for the 250- μm films, for

which the times are increased to approximately 60 h and more than 100 h, respectively.

It was originally thought that the origin and type of the polymer film might influence the grafting properties by virtue of the differences in morphology arising from different production methods. However, in Figure 2, it can be seen that this is not necessarily the case. The tensilized and cast PTFE films show substantially the same behavior as the two skived materials. Furthermore, notionally the same, PTFE films from two different suppliers also showed similar DOGs and grafting rates. In this work, therefore, for a given polymer, the reaction chemistry did not appear to depend on a particular manufacturer's product.

Effect of the total dose

The effect of the total dose on the mutual grafting of acrylic acid can be seen in Figure 6. With the 50- μm polymer films, there appears to be only a gradual increase in the DOG as the total dose is increased from 10 to 30 kGy, with the exception of PVDF, for which the DOG decreases above 20 kGy. For the thicker films, an increase in the total dose for PTFE and LDPE also appears to be detrimental to the grafting yield. In

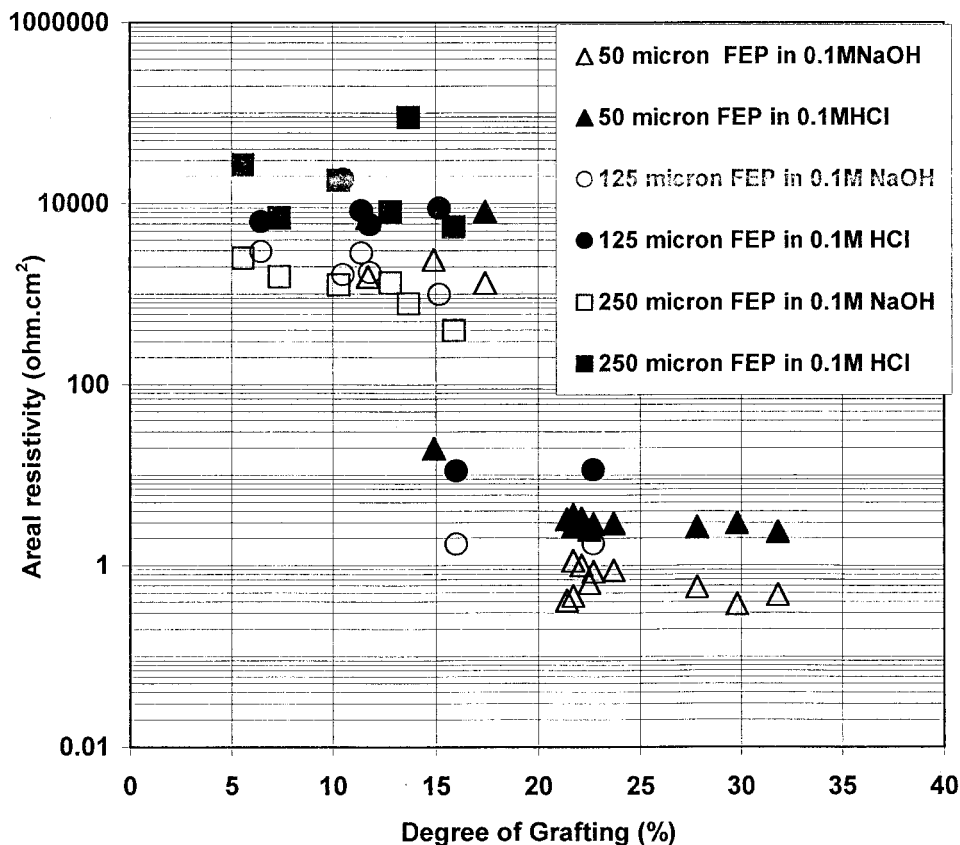


Figure 10 Areal resistivity versus the DOG for various acrylic acid-grafted FEP membranes in acidic and alkaline electrolytes.

PTFE, this may be due to the high dose causing degradation of the polymer backbone in preference to the grafting reaction. It is also known that LDPE² and PVDF⁹ crosslink when irradiated in an inert atmosphere, and it has been found by many workers² that it is not the dose rate that affects the crosslinking reaction, but the total dose. Therefore, at higher total doses, the crosslinking of the polymer may inhibit the ability of the acrylic acid monomer to access the radical sites formed in the polymer; therefore, especially for the thicker films, the DOG is reduced.

Effect of the acrylic acid concentration

The effect of varying the monomer concentration at a constant dose, dose rate, and reaction atmosphere can be seen in Figure 7. The general trend is that the DOG increases as the monomer concentration increases. For most of the polymers, a plateau is reached with a monomer concentration of around 25 vol %. Raising the concentration further does not lead to a higher DOG. It is thought that the monomer becomes unable to reach radical sites in the polymer because of the increasing viscosity of the grafting solution due to some homopolymerization of the acrylic acid.

The exceptions to this are ETFE and PVDF, for which a significantly different grafting profile is seen, with no evidence of a plateau even at a monomer concentration as high as 35%.

The ease with which the LDPE film grafts, in comparison with the fluorocarbon films, is clearly demonstrated and is attributed to the much higher diffusion and solubility of the monomer in the hydrocarbon polymer.

Effect of the DOG on the areal resistivity of the membranes

The areal resistivity of the membranes was measured in both 0.1M NaOH and 0.1M HCl electrolytes. The results are given in Figures 8–10, which show the areal resistivities plotted against the respective DOGs. The general trend is that the resistivity decreases as the DOG increases. Of more interest is that for each membrane there is a value of the graft weight above which the resistivity of the membrane falls sharply. This is attributed to the point at which the graft penetrates through to the center of the film from both sides, creating a pathway by which the conducting species can travel through the thickness of the copolymer. The

TABLE II
Breakthrough Grafting Points Compared to the Degree of Crystallinity of the Different Polymers

Film	Thickness (μm)	DOG at breakthrough point (%)	Degree of crystallinity (%)
PTFE (cast)	50	<20	93–98 ¹
PTFE	50	<17	93–98
FEP	50	17–20	70 ¹¹
PFA	50	12–18	65–75 ¹¹
PVDF	50	18–22	41–50 ^{12,13}
ETFE	50	25–30	30–37 ¹²
PTFE	125	15–17	93–98
FEP	125	15–20	70
LDPE	125	34–37	31–35 ^{14,15}
PTFE	150	13–16	93–98
PTFE	250	13–15	93–98
FEP	250	>17	70

results support the accepted stepwise grafting front theory¹⁰ for the formation of this class of copolymers.

It can be seen from the figures that the breakthrough grafting point is dependent more on the chemical nature of the polymer film (whether fluorocarbon or hydrocarbon) than on its thickness. For clarity, these approximate breakthrough points are summarized in Table II. The data show that, for the fluoropolymers (PTFE, FEP, and PFA), the DOG for penetration is broadly in the same range (15–20%) and is not related to the precise chemical nature of the fluoropolymer. For the hybrid (partially fluorinated) polymers (PVDF

and ETFE), the breakthrough point is slightly higher (~18–30%), and for the hydrocarbon polymer (LDPE), it is even higher (~34–37%).

The explanation for this may lie in the degrees of crystallinity of the respective polymers. As previously stated, grafting predominantly takes place in the amorphous part of the polymer, and in a high-crystallinity polymer, such as a fluoropolymer, the amorphous regions will fill more quickly as grafting proceeds.

It is also noted that the areal resistivity of the copolymer membranes is lower in the alkaline electrolyte than in the acidic electrolyte. Acrylic acid is a weak acid group and in acidic media is less likely to dissociate; therefore, the number of ions available to take part in conduction is less than that in an alkaline environment, in which the carboxylic group is normally considered to be fully dissociated.

Effect of the DOG on the IEC

As discussed previously, the theoretical IEC of the membranes can be calculated with the DOG alone. This takes into account the reaction of the monomer grafting onto the polymer and assumes that any weight gain in the polymer is due solely to the addition of acrylic acid and that no parasitic reactions, such as crosslinking, take place. Plotting the measured IEC values against the DOG and against theoretical IEC values for the same polymer can, therefore, provide an indication of the existence of parasitic reactions.

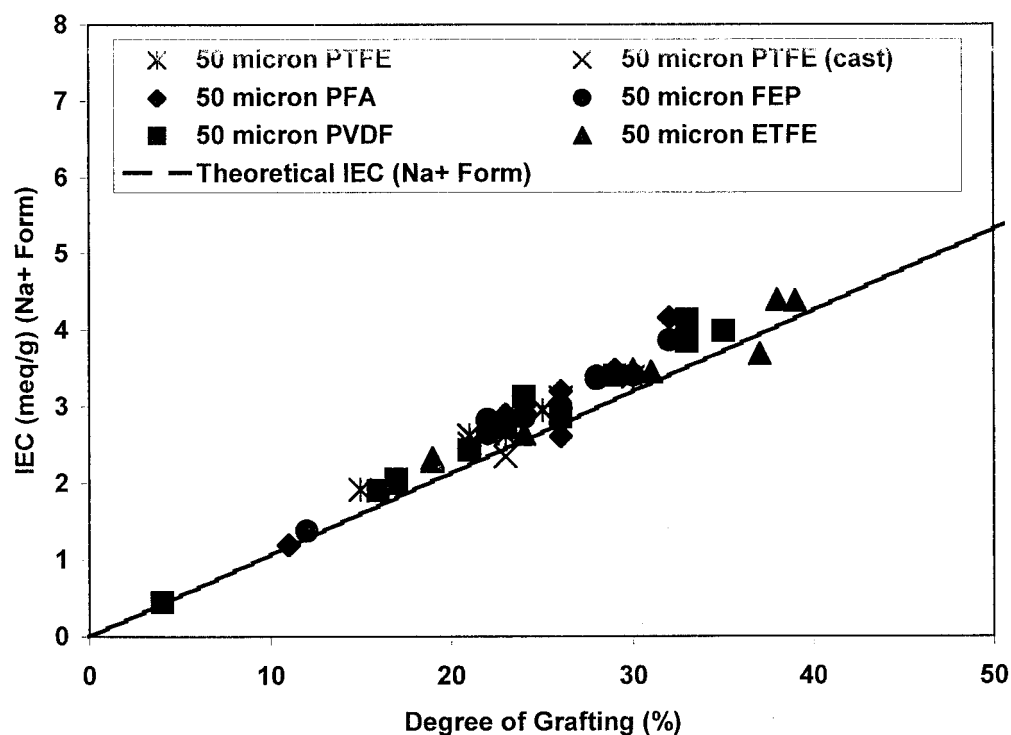


Figure 11 Theoretical and measured IEC versus the DOG for the 50- μm acrylic acid-grafted membranes.

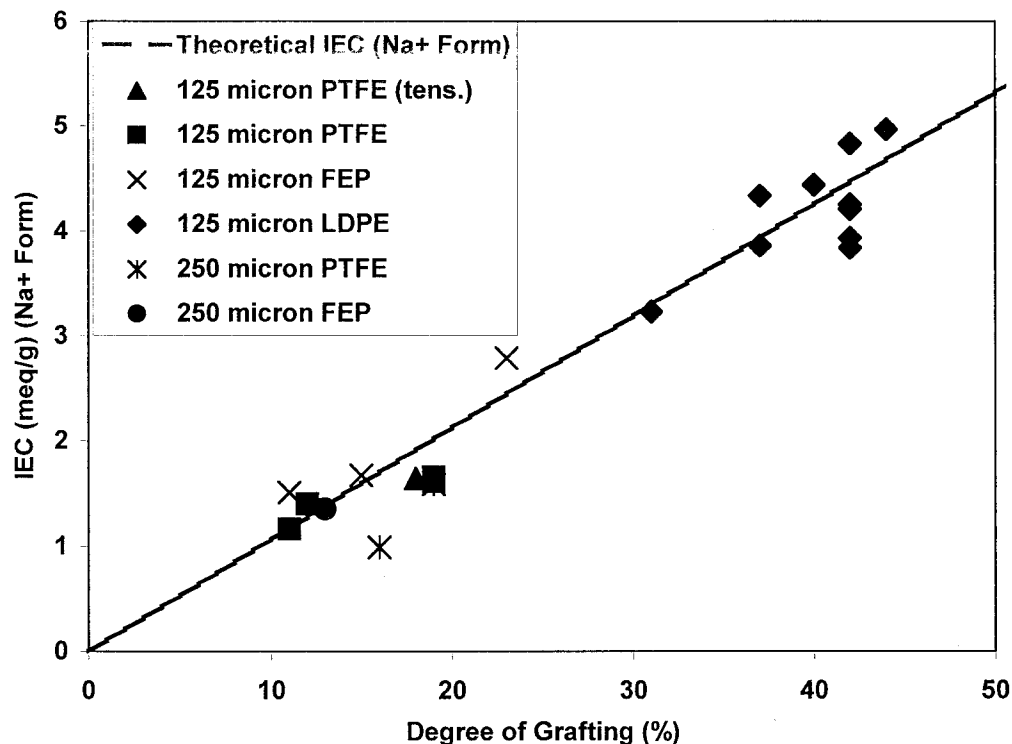


Figure 12 Theoretical and measured IEC versus the DOG for the thicker acrylic acid-grafted membranes.

In Figures 11 and 12, the theoretical values correlate well with the measured values and are shown to be independent of the backbone polymer, grafting conditions, and membrane thickness. This sole dependence on

the DOG is evidence that, for all the copolymers analyzed, the acid groups grafted to the polymer film are all accessible and able to take place in ion-exchange processes. It also suggests that the precise structure of the

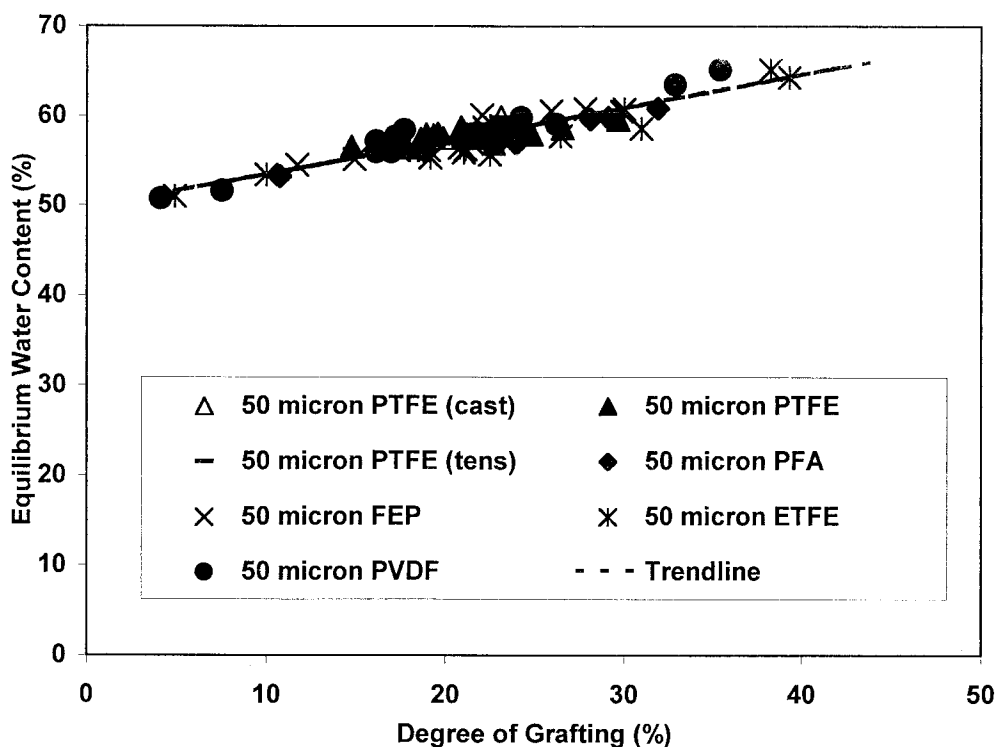


Figure 13 DOG versus the EWC for the 50- μ m acrylic acid-grafted membranes.

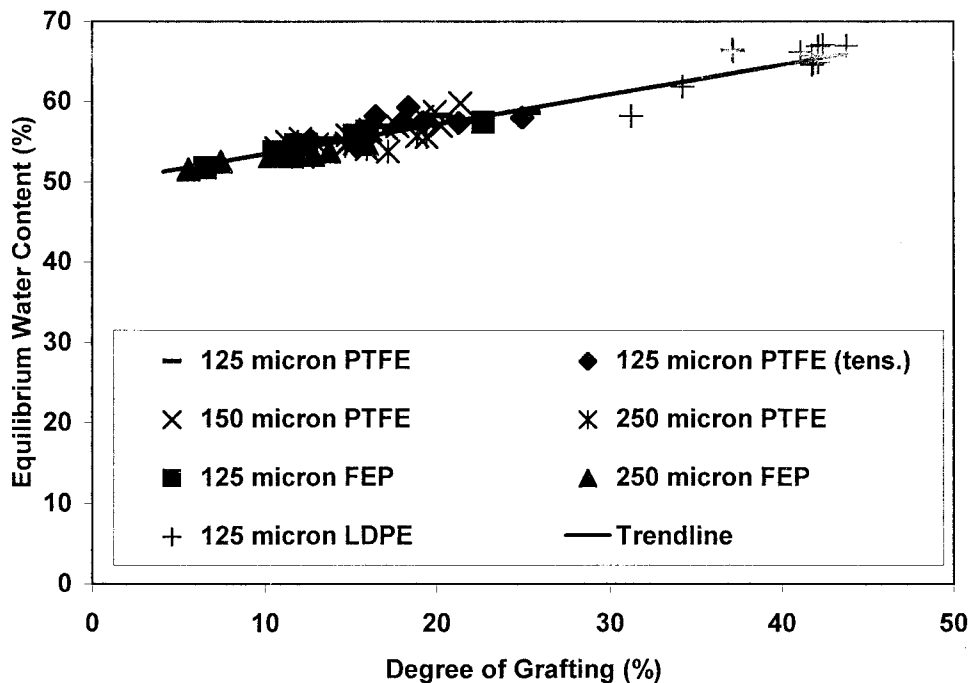


Figure 14 DOG versus the EWC for the thicker acrylic acid-grafted membranes.

host polymer is not important in determining the ionic properties of the resultant copolymer. It could simply be considered a scaffold onto which the ionomeric graft is attached. This is very important because it means that the polymer backbone can be chosen for its superior grafting qualities, overall chemical stability, or low cost.

Effect of the DOG on the EWC

The relationship between the EWC and DOG is shown in Figures 13 and 14. The EWC of the membranes is directly proportional to the graft and, like the resistivity and IEC measurements, is independent of the base polymer film (both type and thickness) and the grafting conditions used to prepare the polymer.

It is clear that the EWC must rise sharply between zero grafting (i.e., the hydrophobic base polymer film) and the copolymer containing 5% acrylic acid, which has an EWC of approximately 50%. Moreover, the EWC only varies by approximately 15% for the DOG between 5 and approximately 45%. The quantity of water absorbed at the 5% DOG equates to each acid group being associated with approximately 40 molecules of water, whereas at the 36% DOG, this falls to approximately 7 molecules of water. This may be explained by the assumption that at the low grafting level, a significant proportion of the amorphous part of the polymer remains unfilled but, because of the hydrophilic nature of the newly formed copolymer, is able to absorb water. As the DOG increases, the regions available for water become increasingly filled with the grafted acrylic acid.

Although it is evident that the acrylic acid functional group is very hydrophilic and has a great capacity for attracting and associating with water, the limiting EWC is reached when the hydrostatic forces within the material due to water absorption are balanced by the intramolecular and intermolecular forces maintaining the integrity of the film.

Both the IEC and EWC have been shown to be functions of the DOG, and Figures 15 and 16 confirm the linear relationship between these two parameters for the copolymers tested.

CONCLUSIONS

Homogeneous and reproducible copolymers of a number of fluoropolymers and a hydrocarbon polymer with acrylic acid have been prepared with the mutual grafting technique. The technique reported is suitable for preparing membranes up to 250 μm thick (at least).

The DOG has been shown to be a function of the radiation total dose, the grafting time (radiation dose rate), and the monomer concentration in the grafting solution. Increasing the radiation total dose and monomer concentration in the grafting solution leads to an increase in the yield, but limits have been established beyond which no further increase is observed. The DOG is inversely related to the radiation dose rate.

This study has shown that, for the polymers used, although for each polymer type a set of optimum conditions can be determined to give the required DOG, for polymers of the same generic formula, the

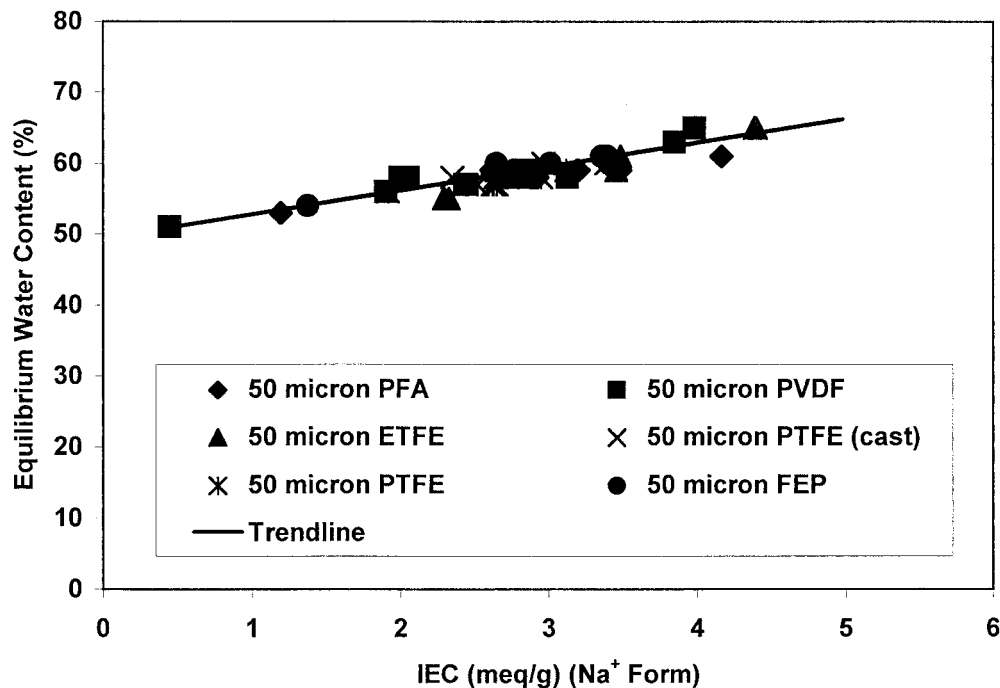


Figure 15 IEC versus the EWC for the 50- μ m acrylic acid-grafted membranes.

DOG can be relatively insensitive to their previous processing history.

The most important property determining the characteristics of acrylic acid-grafted copolymers is the DOG, that is, the percentage of ionomer in the copol-

mer. However, this parameter alone cannot describe the homogeneity of the graft.

The electrolytic resistivity, IEC, and EWC of the copolymers have all been shown to be functions of the DOG.

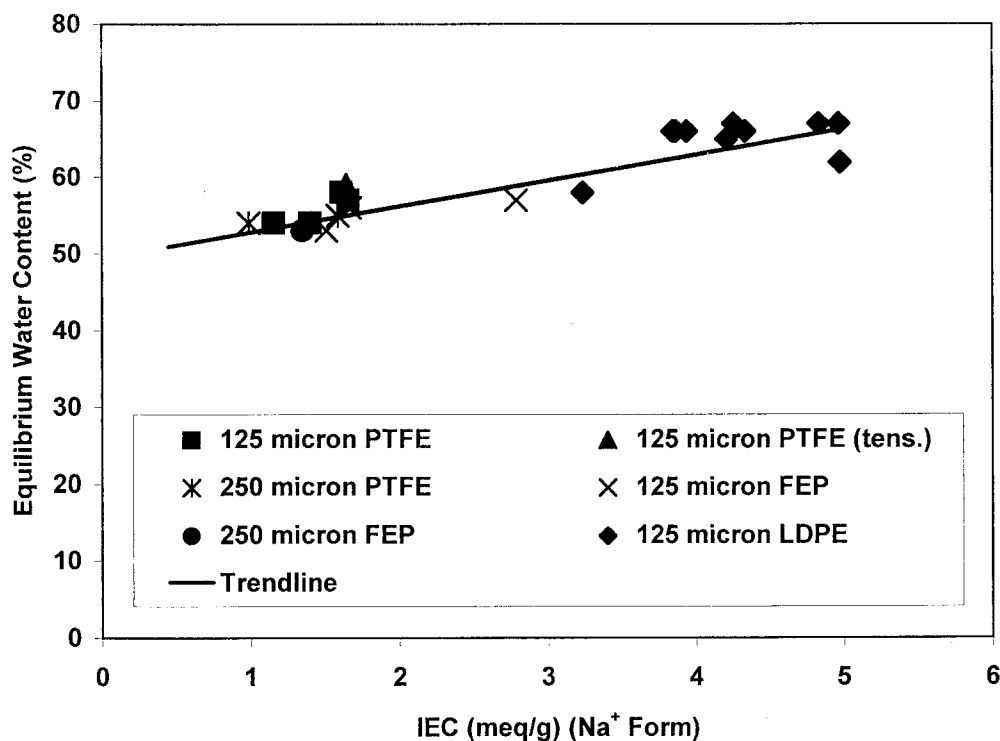


Figure 16 IEC versus the EWC for the thicker acrylic acid-grafted membranes.

For low-resistivity membranes, a certain minimum ionomer content is required. This varies with the type of host polymer and appears to be less dependent on the membrane thickness. A breakthrough value of the grafting level has been established for the materials tested, and the presence of such a value is consistent with the well-documented stepwise grafting procedure.

Amorphous polymer films require a higher DOG to reach the breakthrough point for electrolytic conductivity than more crystalline materials.

The measured IEC values confirm that the acidic groups are fully dissociated in alkaline media and are therefore available to contribute to ionic conduction.

Correlations have been made between the DOG, IEC, and EWC. These correlations have been shown to be independent of the chemical nature of the host polymer or its thickness.

The EWC is proportional to the DOG, and even very low DOGs can produce copolymers able to hold large amounts of water.

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