Radiation Grafting of Acrylic and Methacrylic Acids onto Poly(tetrafluoroethylene–hexafluoropropylene–vinylidene fluoride) TFB Films

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SYNOPSIS

A study has been made for the preparation of membranes by the direct radiation grafting of acrylic and methacrylic acids onto poly(tetrafluoroethylene–hexafluoropropylene–vinylidene fluoride) TFB films. The appropriate reaction conditions were selected under which the graft polymerization was carried out successfully. In this grafting system, ammonium ferrous sulfate (Mohr's salt), ferric chloride, and cuppric chloride were used as inhibitors to minimize the homopolymerization of acrylic acid and methacrylic acid. Also, the effect of monomer concentration on the rate of grafting was investigated. The dependence of the grafting rate on monomer concentration was found to be of the order of 1.1 and 1.0 for acrylic acid and methacrylic acid, respectively. This grafting system was proceeded by a front mechanism. Some selected properties of the grafted films such as swelling behavior, dimensional change, and mechanical and electrical properties were investigated. It was found that the grafted membranes possess good hydrophilic properties that may make them promising in some practical applications.

INTRODUCTION

Fluorine-containing polymers are appropriate in preparing membranes for separation processes because of their good thermal, mechanical, and chemical resistance. The hydrophobic character of the fluoropolymers can be overcome by radiation-initiated grafting of hydrophilic monomers onto these polymers.[1-11] The nature and morphological peculiarities of the trunk polymers as well as the grafting reaction parameters affect the membrane properties of the grafted films. The most important applications of these synthetic membranes are in industrial mass separation processes such as micro-, ultra-, and hyperfiltration, electrodialysis, and gas separation. However, a considerable amount of research is being conducted to develop membranes for many other uses such as enzyme reactors, electrochemical power sources, and ion-selective electrodes and for the controlled release of active agents in the medical and biomedical field. The goal of all membrane research is to develop structures with transport properties and chemical and mechanical stability tailor-made for their specific application.

Many studies were carried out in our laboratories devoted to the search for new and improved membrane compositions using almost every available polymeric material.[12-23] The preparation and selected properties of neutral, cationic, and anionic membranes obtained by radiation-initiated grafting of hydrophilic monomers onto different trunk polymers using the direct and postradiation techniques were investigated. These grafted membranes showed great promise for practical applications.

In the present study, the preparation and properties of membranes obtained by direct radiation-induced graft polymerization of acrylic and methacrylic acid solutions onto TFB films were investigated. The effect of grafting conditions on the grafting process and inhibition of homopolymerization was investigated. Some selected properties of the graft films such as water uptake, dimensional changes, electrical conductivity, and mechanical properties were investigated.

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Journal of Applied Polymer Science, Vol. 48, 1249–1257 (1993)
 CCC 0021-8995/93/071249-09

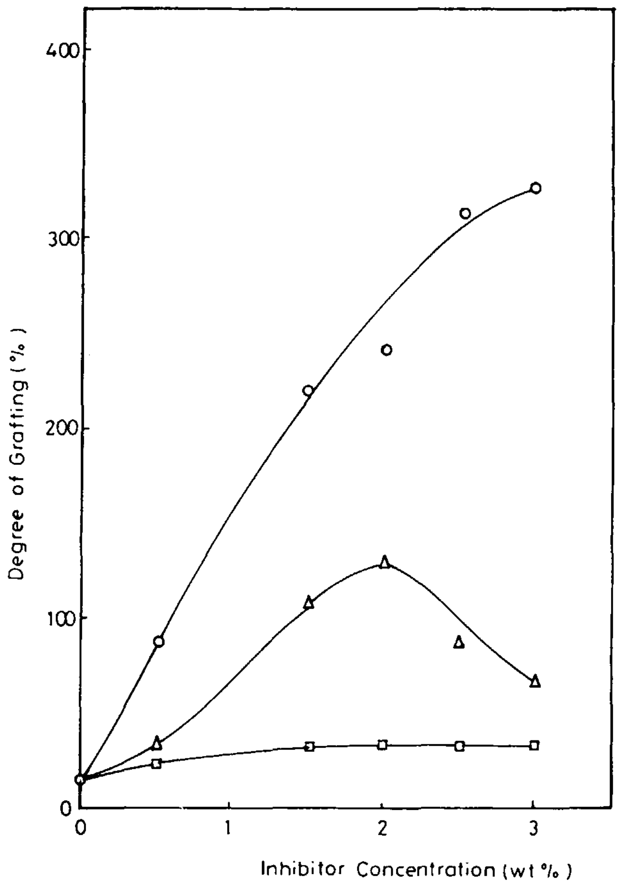

Figure 1 Effect of inhibitor concentration on the grafting yield of aqueous MAA (50% wt %) onto TFB films in N_2 gas at irradiation dose of 20 kGy: (□) Mohr's salt; (○) ferric chloride; (△) $CuCl_2$.

EXPERIMENTAL

Materials and Grafting Method

Poly(tetrafluoroethylene–hexafluoropropylene–vinylidene fluoride) TFB films, 100 μm, supplied by Hoechst-Germany, were washed with acetone and dried at room temperature. All chemicals were reagent grade and were used without further purification.

Graft Polymerization[15-17]

The direct radiation grafting method was used as a technique in which the polymer and monomer solution were subjected simultaneously to ionizing radiation. The inhibitor was added to minimize the homopolymerization of the monomer during irradiation. The glass ampule containing the monomer solution and films was deaerated by bubbling nitrogen for 6–8 min and then sealed. The glass ampules were then subjected to Co-60 γ-rays at a dose rate that ranged from 0.07 to 0.31 Gy/s. The grafted films were washed thoroughly with hot distilled water and soaked overnight in water to extract the residual monomer and the homopolymer occluded in the film. The films were then dried in a vacuum oven at 60°C for 24 h and weighed. The degree of grafting was determined by the percentage increase in weight as follows:

$$\text{Degree of grafting (\%)} = \frac{w_g - w_0}{w_0} \times 100$$

where w_0 and w_g represent the weights of initial and grafted films, respectively.

Water-uptake Measurements

Known weights of the clean and dry grafted films were immersed in distilled water at room temperature until equilibrium was reached (48 h in most cases). Then, the films were removed, blotted quickly with absorbent paper to remove the water

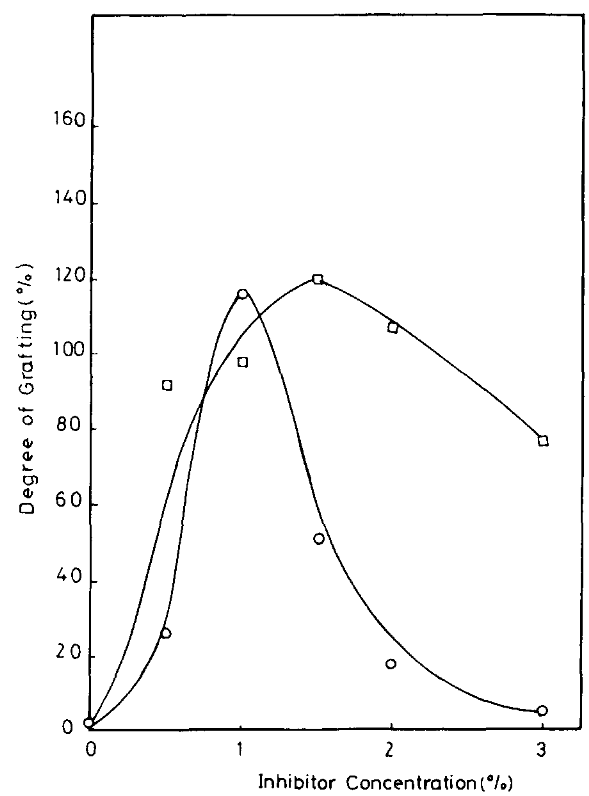

Figure 2 Effect of inhibitor concentration on the grafting yield of aqueous AAc (50% wt %) onto TFB films in N_2 gas at irradiation dose 20 kGy: (○) $FeCl_3$; (□) Mohr's salt.

attached on their surface, and weighed. The water-uptake percent was calculated as follows:

$$\text{Water-uptake (\%)} = \frac{w_s - w_g}{w_g} \times 100$$

where w_s and w_g represent the weights of wet and grafted films, respectively.

Electrical Conductivity Measurements

Conductivity measurements were carried out using a multi-Mega ohm-meter-MOM 11 (WTW Instruments, Germany). The electrical conductivity of the sample (σ) was determined by measuring the electrical resistance and the following equation was used:

$$\sigma = 1/R \cdot L/a \text{ ohm}^{-1} \text{ cm}^{-1}$$

where L = the thickness of specimen (cm), $a = (\pi r^2)$ is the area of the sample surface (cm^2) and R = ohmic resistance (ohm).

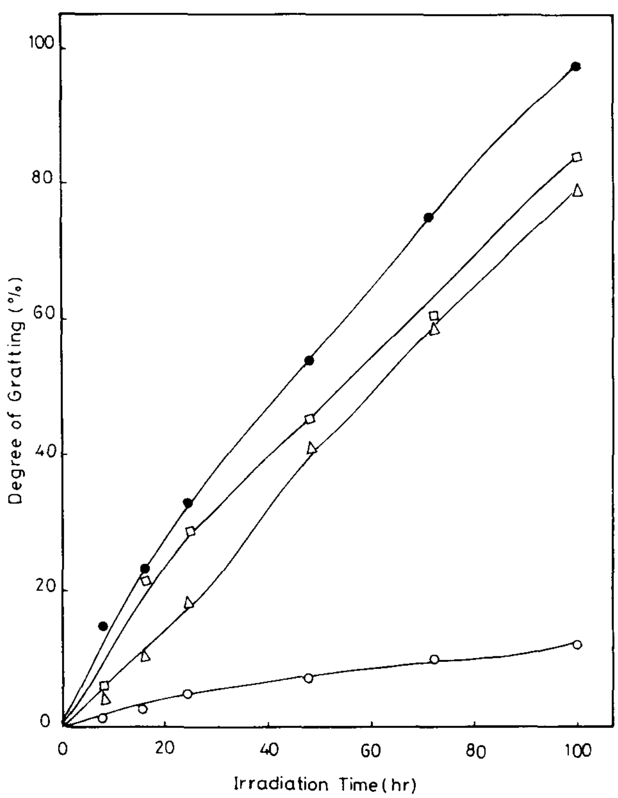

Figure 3 Degree of grafting vs. irradiation time in nitrogen atmosphere for grafting onto TFB films at various AAc concentration (wt %): (○) 10; (△) 30; (□) 50; (●) 70. Inhibitor concentration 1.5 wt %; film thickness 100 μm.

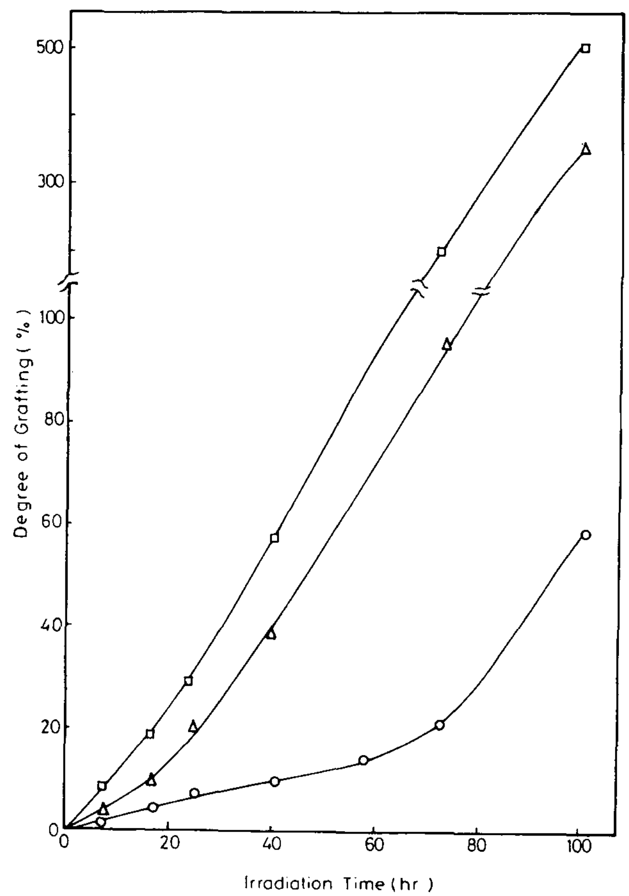

Figure 4 Degree of grafting vs. irradiation time in nitrogen atmosphere for grafting onto TFB films at various MAA concentrations (wt %): (○) 10; (△) 30; (□) 50. Inhibitor concentration 1.5 wt %; film thickness 100 μm.

Measurements of Mechanical Properties

The dumbbell-shaped samples 50 mm long with a neck of 28 and 4 mm wide were used. The measurements of tensile strength (T_b) and elongation percent (E_b) at break were carried out using an Instron (Model 1195, England) at a crosshead speed of 50 mm/min. The tensile strength and percent elongation were calculated as follows:

$$T_b = \frac{\text{load at break (kg)}}{\text{cross-sectional area of the dumbbell shape (cm}^2\text{)}}$$

$$E_b(\%) = \frac{L - L_0}{L_0} \times 100$$

where L is the length of the sample at the moment of rupture, and L_0, the distance between the two jaws, i.e., the length of the necked part.

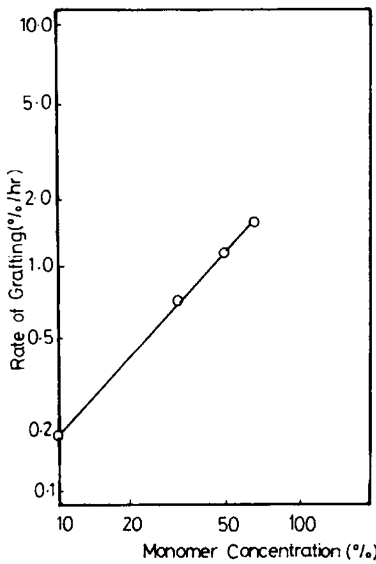

Figure 5 Logarithmic plots of the initial grafting rate vs. AAc concentration.

RESULTS AND DISCUSSION

Membrane Preparation

The direct radiation grafting of acrylic (AAc) and methacrylic acid (MAA) onto poly(tetrafluoroethylene–hexafluoropropylene–vinylidene fluoride) TFB films was studied.

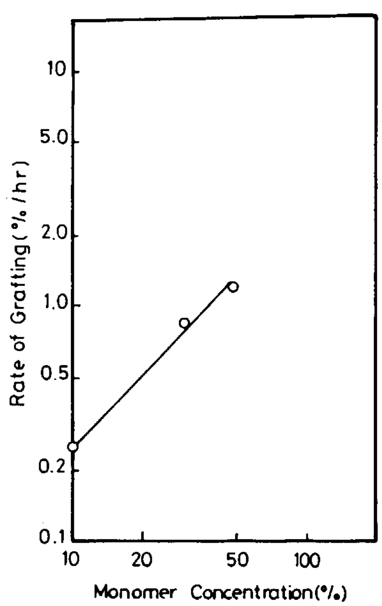

Figure 6 Logarithmic plots of the initial grafting rate vs. MAA concentration.

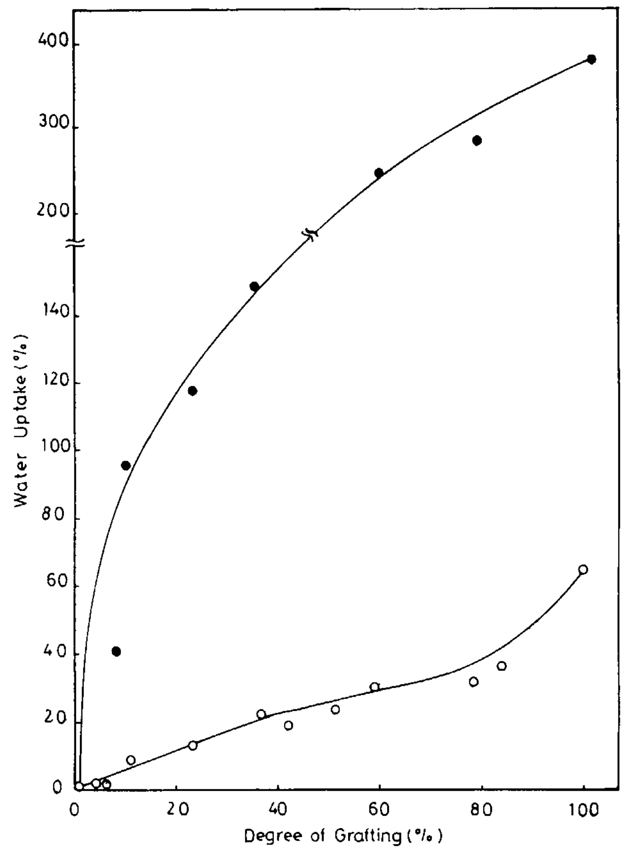

Figure 7 The water-uptake percent vs. degree of grafting of AAc onto TFB for (●) KOH-treated and (○) KOH-untreated films.

Effect of Inhibitor

It is well known that most water-soluble monomers such as AAc and MAA homopolymerize during ra-

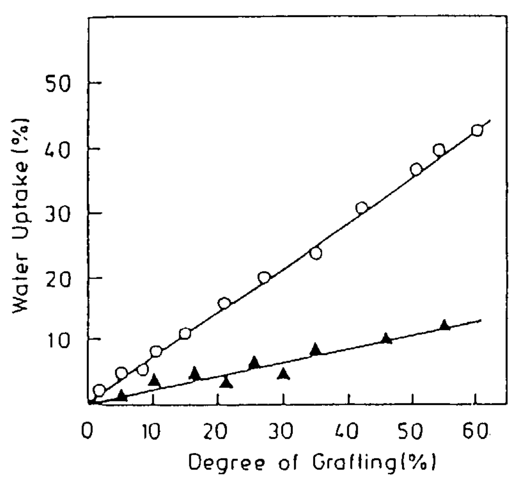

Figure 8 The water uptake percent vs. degree of grafting of MAA onto TFB for (○) KOH-treated and (▲) KOH-untreated films.

diation grafting. This is a disadvantage of the direct radiation technique, in which the polymer and monomer solutions are subjected to γ-irradiation simultaneously. Therefore, the addition of an inhibitor is required to prevent such homopolymerization. Figures 1 and 2 show the effect of inhibitor concentration on the grafting yield of aqueous AAc and MAA 50 wt % onto TFB films at an irradiation dose 20 kGy. Three inhibitors were used: Mohr's salt, ferric chloride, and cuppric chloride. It is obvious that the degree of grafting increases with inhibitor concentration to reach a maximum at 1.5 and 1.0 wt % of Mohr's salt and ferric chloride, respectively. At higher concentrations, however, the degree of grafting declines to somewhat lower values, as can be seen in Figure 1.

Figure 2 shows that the maximum inhibitor concentration at which there is no homopolymer formed is 2 wt % for all the inhibitor concentration used. The aforementioned results suggest that the inhibition of homopolymerization of AAc and MAA results in enhancing the diffusion of aqueous monomer into the interior regions of the film, leading to an interaction between the free radicals and monomer molecules. The grafted layers close to the film surface swell in the aqueous solution and progressively more diffusion of monomer occurred. As a consequence, higher degrees of grafting were obtained. It is probable that at higher inhibitor concentrations some of the inhibitors may diffuse into the polymer matrix. This may result in the addition of the homopolymerization of AAc inside the swollen film and the inhibitor itself may also interact with the formed free radicals during the radiation grafting process. Consequently, a decrease in the degree of grafting and inhibition of homopolymerization are expected at such high inhibitor concentrations.

Kabanov[24] reported a study of the radiation grafting of AAc by the direct method in the presence of Mohr's salt and absence of oxygen onto low-density polyethylene film (60–100 mm thickness) and at a dose rate of 0.088–0.51 Gy/s. He reported that

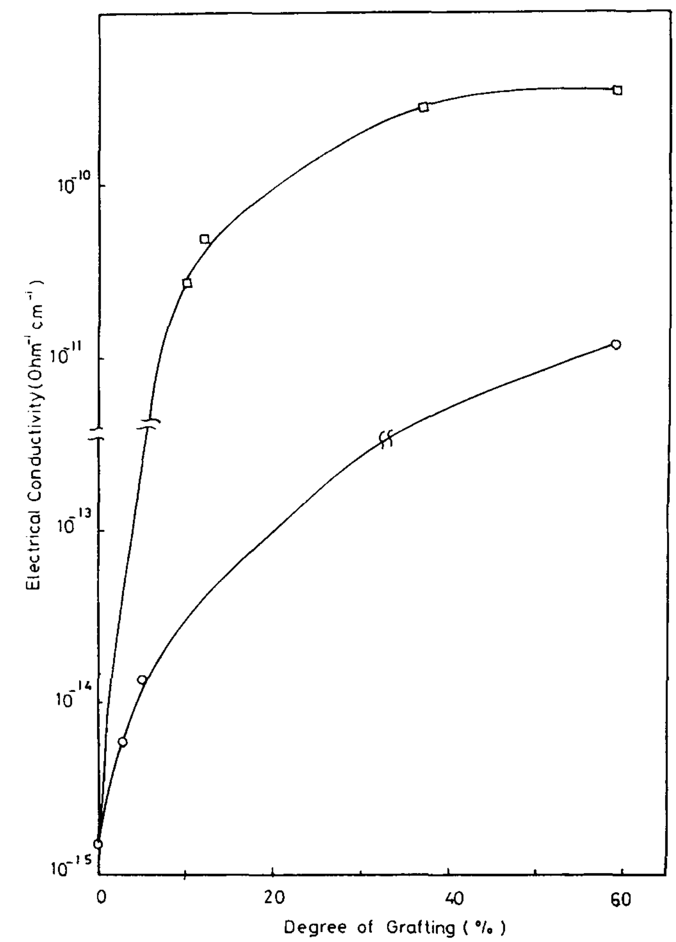

Figure 9 Electrical conductivity for the grafted TFB films (with AAc) as a function of degree of grafting: (□) KOH-treated and (○) untreated films.

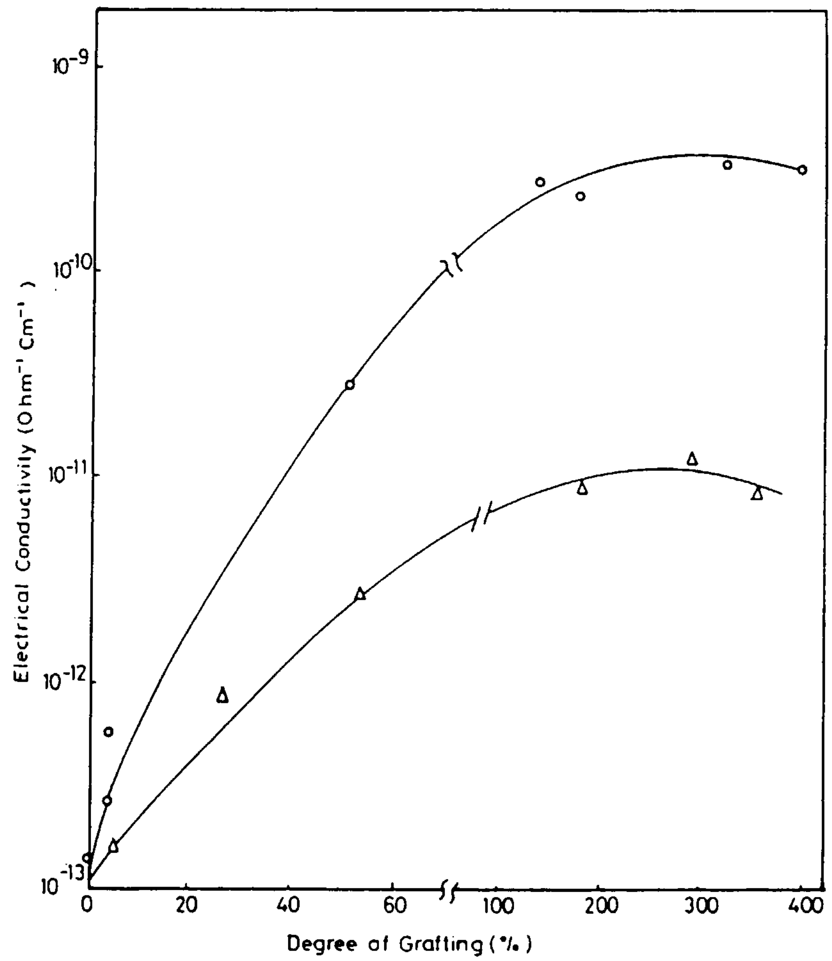

Figure 10 Electrical conductivity for the grafted TFB films (with MAA) as a function of degree of grafting: (○) KOH-treated and (△) untreated films.

the grafting rate depends greatly on the concentration of Mohr's salt. At first, the rate increases because of more active suppression of homopolymerization as compared with graft polymerization since the concentration of Mohr's salt in the solution is higher than in the graft layer. This difference in concentration is explained by the fact that poly(acrylic acid) (PAAc) forms complexes with the Fe^{3+} ions, whose diffusion is difficult in the graft layer. When the concentration of Mohr's salt is increased, the process of inhibition of graft polymerization increases as well.

Effect of Monomer Concentration

Diffusibility of the monomer diluent into the polymer matrix has a great influence on the grafting process and also on the grafting yield. Addition of 1.5 and 2 wt % Mohr's salt and $FeCl_3$ were effective in inhibiting the homopolymerization of aqueous AAc and MAA, respectively. Figures 3 and 4 show the relationship between the degree of grafting and irradiation time for various monomer concentrations in nitrogen atmosphere. It can be seen that the degree of grafting increases with irradiation time for all monomer concentrations. Meanwhile, at low monomer concentrations, the rate of grafting is lower than that at higher ones. Figures 5 and 6 show the logarithmic relationship between the initial rate of grafting and monomer concentration. Such plots give a linear relationship and the dependence of the grafting rate on monomer concentration was found to be of the order of 1.1 and 1.0 for AAc and MAA, respectively. It may be concluded that the diffusivity of the monomer into the polymer matrix is enhanced at higher concentrations, leading to much higher degrees of grafting. The grafted layers close to the film surface swell in the aqueous monomer and progressive diffusion of monomer into the center part of film is achieved.

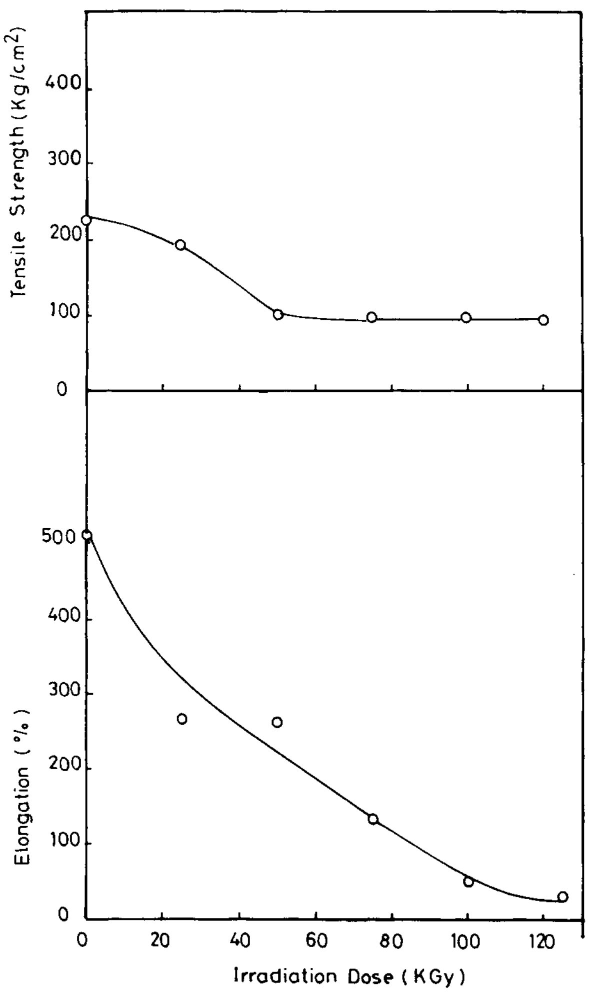

Figure 11 Change in tensile strength and elongation percent with irradiation dose (kGy) for TFB films.

Membrane Properties

Swelling Behavior

It is well known that fluorine-containing polymers cannot swell in any monomer or solvent. By the grafting of a hydrophilic monomer such as AAc and MAA onto TFB, the graft copolymer exhibits hydrophilic properties and swells in water. Figures 7 and 8 show the swelling behavior of the grafted TFB films as a function of degree of grafting. The water-uptake percent increases with the degree of grafting, for both the alkali-untreated and alkali-treated grafted films. However, the alkali-treated films possess much higher water uptake. The conversion of free carboxylic acid groups of grafted chains into their K-salt introduces electrolytic groups that confer an ion-character in the grafted films. These results suggest that the degree of swelling depends mainly on the amount of the hydrophilic groups in the film, i.e., on the degree of grafting and also on the form of electrolyte. Such treatment improves the hydrophilic properties and an increase in electric conductivity is expected as well.

Electrical Conductivity

Figures 9 and 10 show the semilogarithmic relationship between electric conductivity and degree of grafting for the grafted films. An improvement in the electric properties of the grafted film before and after refluxing with KOH solutions was observed. It is clear from Figure 9 that the conductivity of the KOH-treated grafted films is considerably greater than that of the untreated samples at any grafting percentage. This effect may be attributed to the fact that the electrolytic groups introduced by the alkaline treatment result in an increase of the mobility

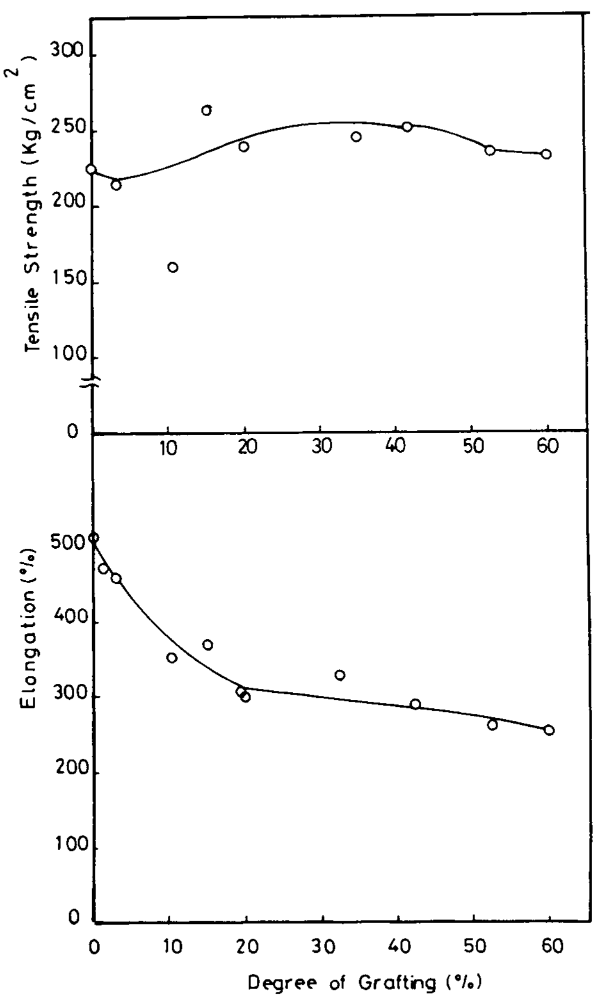

Figure 12 Change in tensile strength and elongation percent with degree of grafting for the grafted TFB films with AAc acid.

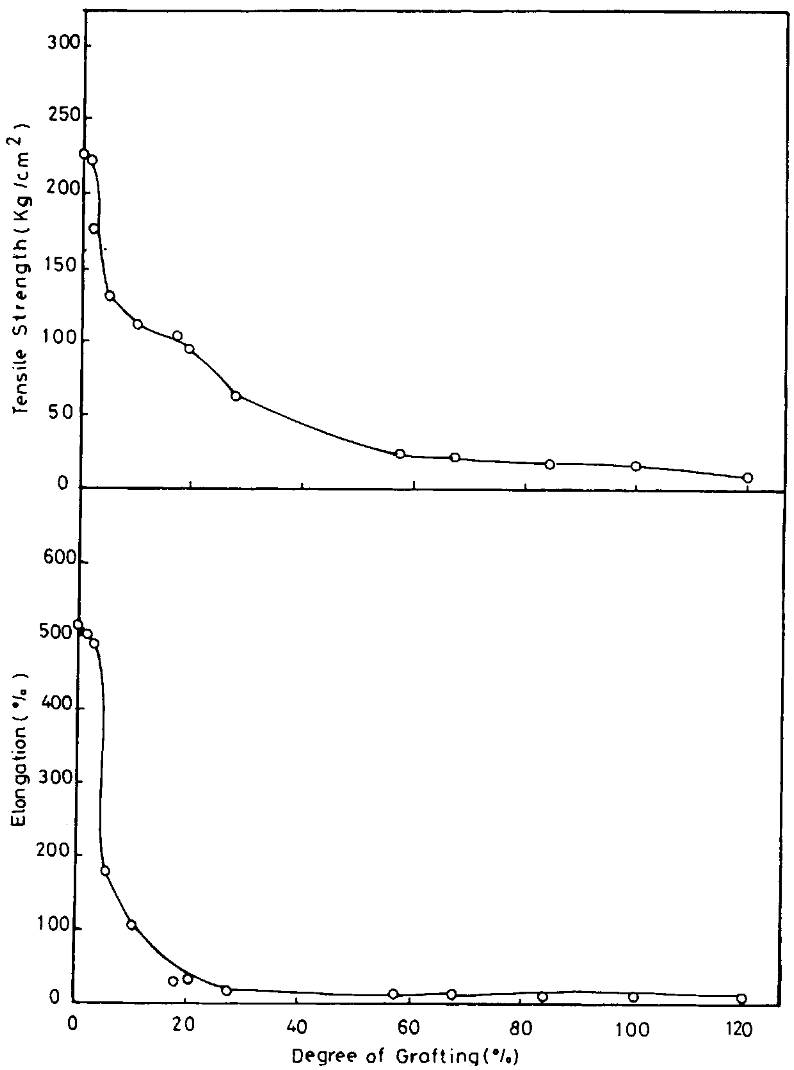

Figure 13 Change in tensile strength and elongation percent with degree of grafting for the grafted TFB films with MAA acid.

and freedom of the ionic species, leading to an increase in the electrical conductivity.

Mechanical Properties

Figure 11 shows the effect of irradiation dose on the elongation percent at break, E_b, and tensile strength, T_b, for the irradiated films. It is obvious that E_b and T_b decrease as the irradiation dose increases. The irradiated films became brittle and stiff. Also, the changes in T_b and E_b at break for the grafted TFB films are shown in Figures 12 and 13. It may be seen that there is no significant change in T_b, whereas E_b decreases as the degree of grafting increases (Fig. 12). However, when MAA was used as the grafting monomer, both T_b and E_b decreased sharply (Fig. 13). It seems that the introduction of the methyl group into AAc plays an important role in the mechanical properties.

It can be concluded that the grafted membranes obtained by the direct radiation grafting of AAc and MAA onto TFB films showed no deterioration in their chemical and thermal stability, good electrical and mechanical properties, and good swelling behavior, which make them very promising in some practical applications.

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Received January 7, 1992
Accepted August 7, 1992