Preparation and Some Properties of Hydrophilic Membranes Obtained by Radiation Grafting of Methacrylic Acid onto Fluorinated Polymers

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Synopsis

Hydrophilic membranes were prepared by direct radiation grafting of methacrylic acid (MAA) onto poly(tetrafluoroethylene-perfluorovinylether) copolymer (PFA) and poly(tetrafluoroethylene-hexafluoropropylene) copolymer (FEP) films followed by alkaline treatment to confer ionic character in the graft copolymer. Addition of 0.5 wt % $FeCl_3$ to the monomer solution effectively inhibited the homopolymerization process and higher grafting yield was obtained. The graft copolymerization of MAA was carried out in presence of methanol/water mixture (30/70 wt %) in nitrogen atmosphere irradiation. The dependence of the grafting rate on MAA concentration was found to be 0.63 and 0.94 order for PFA and FEP films, respectively. This grafting system proceeds by the front mechanism in which the monomer diffuses through the already grafted layer formed initially. Some selected properties of the graft copolymers were investigated. It was found that the grafted membranes possess good mechanical, electrical, and hydrophilic properties which may make them promising in some practical applications.

INTRODUCTION

Fluorine-containing polymers have drawn much attention in the past and gained wide practical use because of their excellent thermal, chemical stability, and mechanical properties. Recently many studies have been devoted to the study of preparation of hydrophilic membranes by radiation grafting of different hydrophilic monomers onto different polymeric substrates.[1-12]

Hegazy et al. investigated the preparation and some selected properties of cationic and neutral membranes by the postradiation grafting of acrylic acid[13-16] and N-vinylpyrolidone[17] onto fluorinated polymers.

In the present study, fluorinated membranes were prepared by direct radiation-induced graft polymerization of MAA solution onto PFA and FEP films. Some selected properties of the grafted polymers such as water uptake, electrical

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conductivity, and mechanical properties were also investigated. The possibility of their practical uses was discussed.

EXPERIMENTAL

Materials

1. Poly(tetrafluoroethylene-perfluoroethylether) (PFA) copolymer and poly(tetrafluoroethylene-hexafluoropropylene) (FEP) copolymer films (Mitsui Fluoro Chemical Co. Ltd., Japan) were washed with acetone and dried in a vacuum oven at 50°C.
2. Methacrylic acid (MAA) of purity 99%, (Merck), stabilized with 200 ppm hydroquinone, was used without further purification. The other chemicals were reagent grade and used as received.

Graft Polymerization

Graft polymerization was carried out in N_2 atmosphere, the glass ampoules that contain the films and monomer solution were deaerated by bubbling nitrogen gas for 5 to 7 min, sealed, and then subjected to ^{60}Co γ-rays at a dose rate of 0.1 Gy/s. The grafted films, thus obtained, were washed thoroughly with hot distilled water and soaked overnight in distilled water to extract the residual monomer and homopolymer which may have occluded in the films. The films were then dried in a vacuum oven at 50 to 60°C for 16 h and weighed.
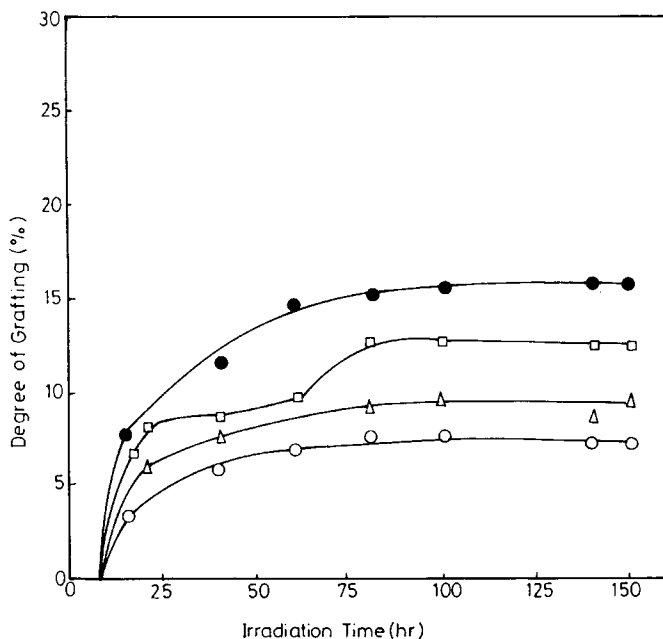

Fig. 1.   Degree of grafting onto 125 μm-thick PFA films as a function of irradiation time at various MAA concentrations (wt %); (○) 20; (△) 40; (□) 60; (●) 75.

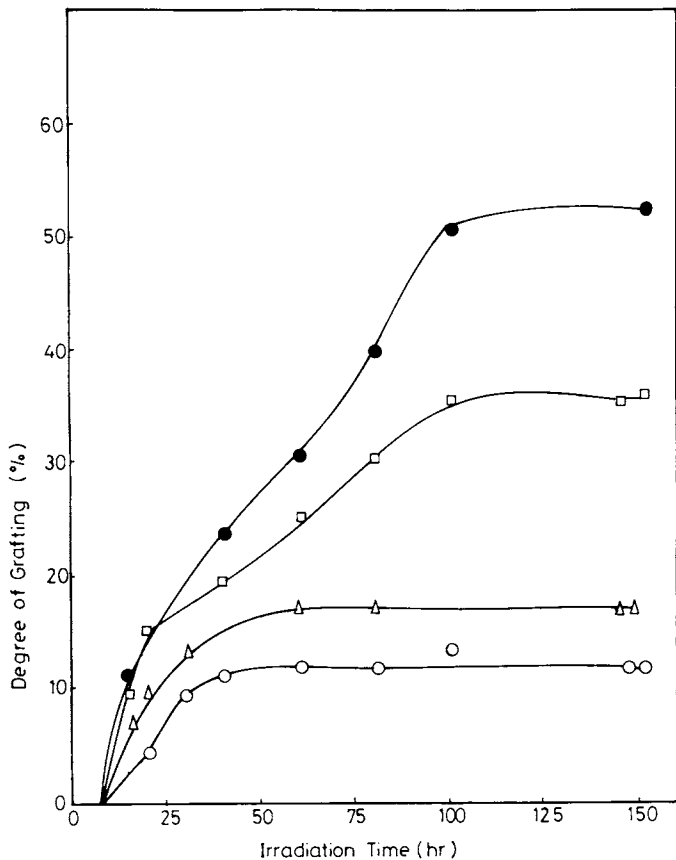Fig. 2.   Degree of grafting onto 75 μm-thick FEP films as a function of irradiation time at various MAA concentrations (wt %); (○) 20; (△) 40; (□) 60; (●) 75.
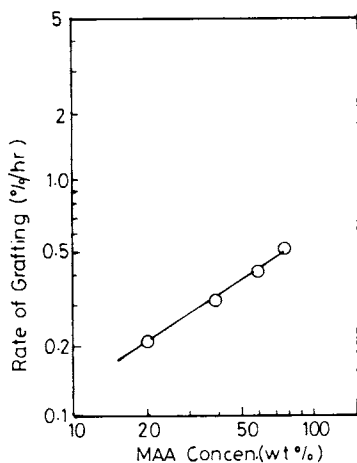

Fig. 3.   Logarithmic plots of grafting rate of MAA solution onto PFA films vs. MAA concentration.
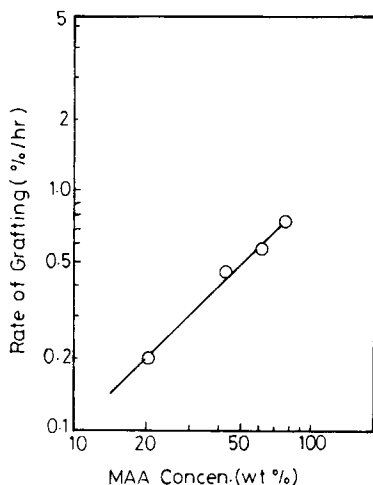
Fig. 4. Logarithmic plots of grafting rate of MAA solution onto FEP films vs. MAA concentration.

The degree of grafting was determined by the percentage increase in weight as follows

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

where W_o and W_g represent the weights of initial and grafted films, respectively.

Swelling Behavior of the Grafted Films

The clean dried grafted films with known weights were immersed in distilled water at 25°C until equilibrium had been reached (24 h in almost all cases). The films were then removed and the excess water on the surface quickly removed by a blotting paper and weighed. The water uptake percent was calculated as follows

$$\text{Water uptake } (\%) = \frac{W_s - W_g}{W_g} \times 100$$

where W_g and W_s represent the weights of dry and wet grafted membranes, respectively.

Electrical Conductivity Measurements

The carboxylic acid groups of the grafted copolymer were converted into their potassium salts by refluxing with 2.5 wt % KOH solution for 24 h at 100°C. The electrical conductivity measurements were carried out using a multi-Mega Ohm meter-MOM II (WTW Instruments, W. Germany).
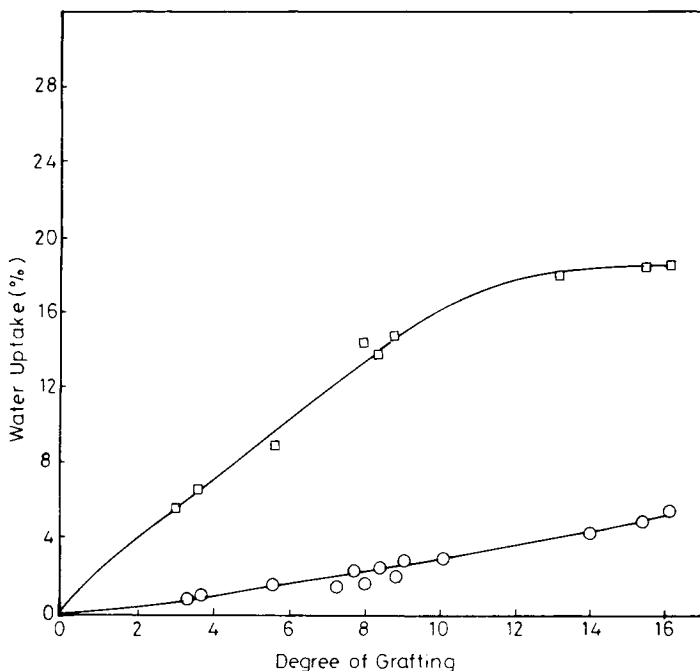
Fig. 5.   Water uptake percent against degree of grafting for (□) KOH-treated and (○) KOH-untreated PFA grafted films.

Mechanical Properties Measurements

Dumbbell-shaped samples 50 mm long with a neck of 28 mm and 4 mm wide were used. Tensile strength and elongation percent at break were measured using an Instron (Model-1195) at crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

Preparation of hydrophilic fluorinated membranes by means of radiation-induced graft polymerization of MAA solution onto both PFA and FEP films, was carried out. The effect of preparation conditions on the grafting process was investigated.

Monomer Concentration Effect

The effect of MAA concentration in methanol/water mixture on the degree of grafting onto PFA and FEP films at various irradiation times was investigated in the presence of 0.5 wt % $FeCl_3$ as shown in Figures 1 and 2, respectively. It can be seen that for the grafting of MAA onto FEP and PFA films, no significant grafting yield was observed at the early stage of irradiation time below 10 h also shown in Figures 1 and 2. This may be due to low grafting yields which are undetectable by the weight increase especially for low-MAA concentration. Such an induction period is also probably due to oxygen impurities consumption
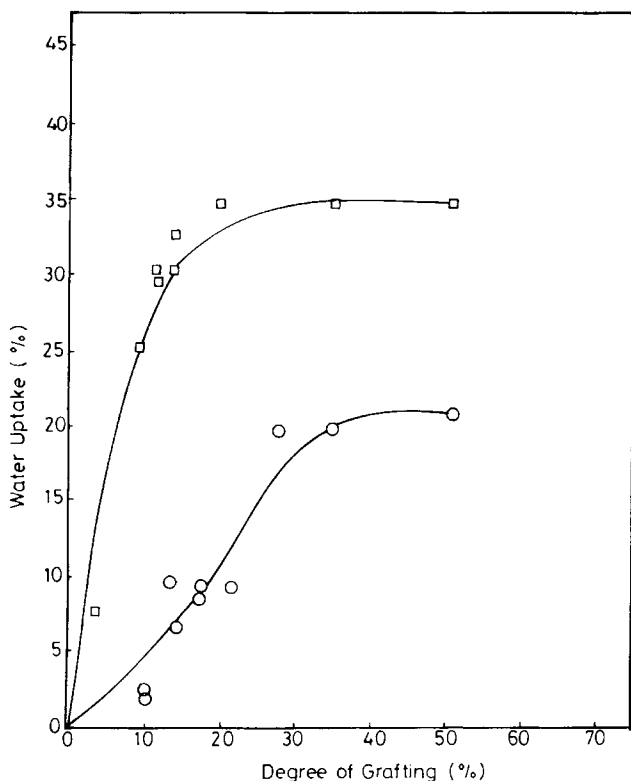
Fig. 6. Water uptake percent against degree of grafting for (□) KOH-treated and (○) KOH-untreated FEP-grafted films.

contained in the commercial nitrogen gas used. At higher irradiation time, the grafting begins and the degree of grafting increases with time and tends to level off above 50 h. Meanwhile, the higher the monomer concentration the higher the initial grafting rate and the degrees of grafting obtained. For the grafting of MAA solution, almost the same behavior was observed with PFA and FEP films. However, in the case of FEP, the grafting tends to level off above 100 h for higher MAA concentrations. For lower MAA concentration it levels off above 50 h as in the case with PFA films.

The initial rate of grafting was calculated from Figures 1 and 2 and plotted logarithmically as a function of MAA concentration as shown in Figures 3 and 4. The rate of grafting increases linearly with log MAA concentration and the dependence of the grafting rate on monomer concentration was calculated to be 0.63 and 0.94 order for PFA and FEP films, respectively.

In the previous study[6] it was found that the dependence of the grafting rate on MAA concentration in the presence of Mohr's salt is of the order 2.9. This very high dependence of grafting rate on MAA concentration was due to the highly viscous medium occurring because of the homopolymerization of MAA. Consequently, the diffusion of monomer was hindered in such a viscous medium.

In the present study, however, the order dependence on MAA concentration is somewhat low due to the fact that no restriction of the diffusion of monomer
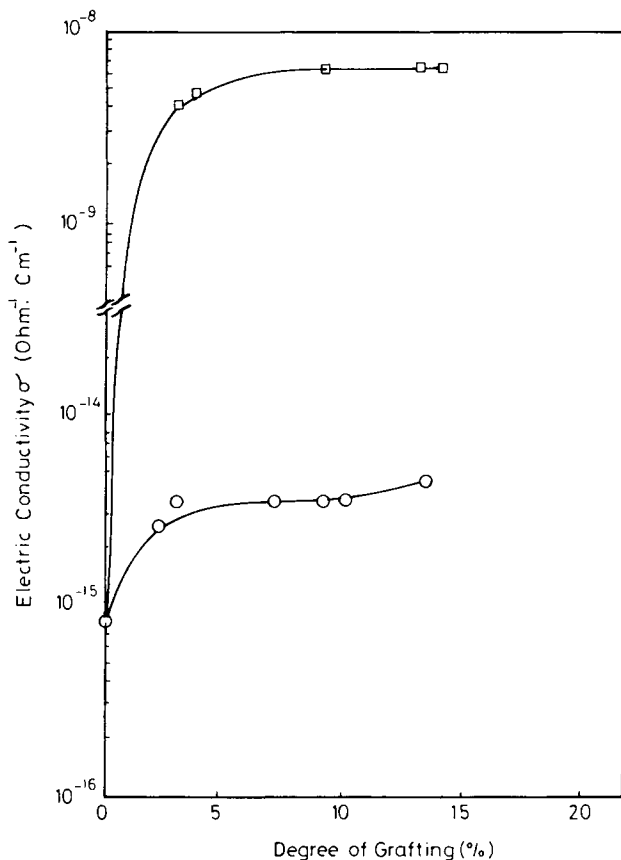
Fig. 7. Electrical conductivity for PFA grafted films as a function of degree of grafting. ($\square$) KOH-treated; ($\bigcirc$) KOH untreated grafted films.

in the presence of $FeCl_3$ acts as a good inhibitor for the homopolymerization process of MAA solution.

The grafting process of MAA solution onto FEP films proceeds more successfully and much higher degrees of grafting were obtained as compared with those of PFA films. This may be due to the difference in the structures of polymer substrates and also to the polymer morphology which plays a great role in the diffusivity of the monomer through the already grafted layer formed initially. The reactivity of the active sites formed upon irradiation is also affected by the polymer morphology. The vinyl ether groups contained in PFA structure may restrict the graft polymerization and cause the lower degrees of grafting as compared with FEP films.

These results suggest that this grafting system greatly depends on the diffusivity of monomer solution into the polymer matrix since the fluorine-containing polymers do not swell in any solvent or monomer solutions. It can be assumed that this grafting system proceeds by the front mechanism[6] in which the monomer diffuses through the grafted layer formed initially near the film surface.
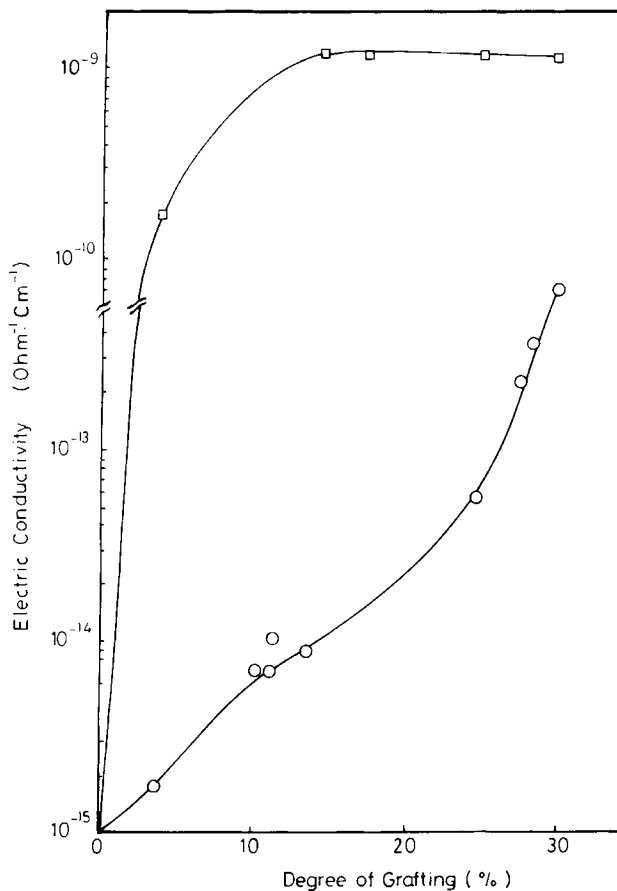
Fig. 8.　Electrical conductivity for FEP-grafted films as a function of degree of grafting. (□) KOH-treated; (○) KOH-untreated grafted films.

Some Properties of Graft Copolymer

The grafting of hydrophilic monomer such as MAA onto hydrophobic polymers results in graft copolymers exhibiting hydrophilic properties as well as good swelling behavior.[18,19] Moreover, in some cases, further modification of the graft copolymer is required to introduce easily ionizable groups[12,20] and, consequently, the swelling behavior and electrochemical properties will improve as well. The alkaline treatment of poly(methacrylic acid) graft copolymer was carried out for the preparation of cation-exchange membranes.

Swelling Behavior of the Grafted Films

Figures 5 and 6 show the water uptake percent for PFA and FEP grafted films as a function of degree of grafting, respectively. Alkaline treatment of the graft chains was carried out to confer a more ionic character in the graft copolymer which may result in improving the hydrophilic properties of the films. It is obvious that the water uptake percent increases with the degree of grafting
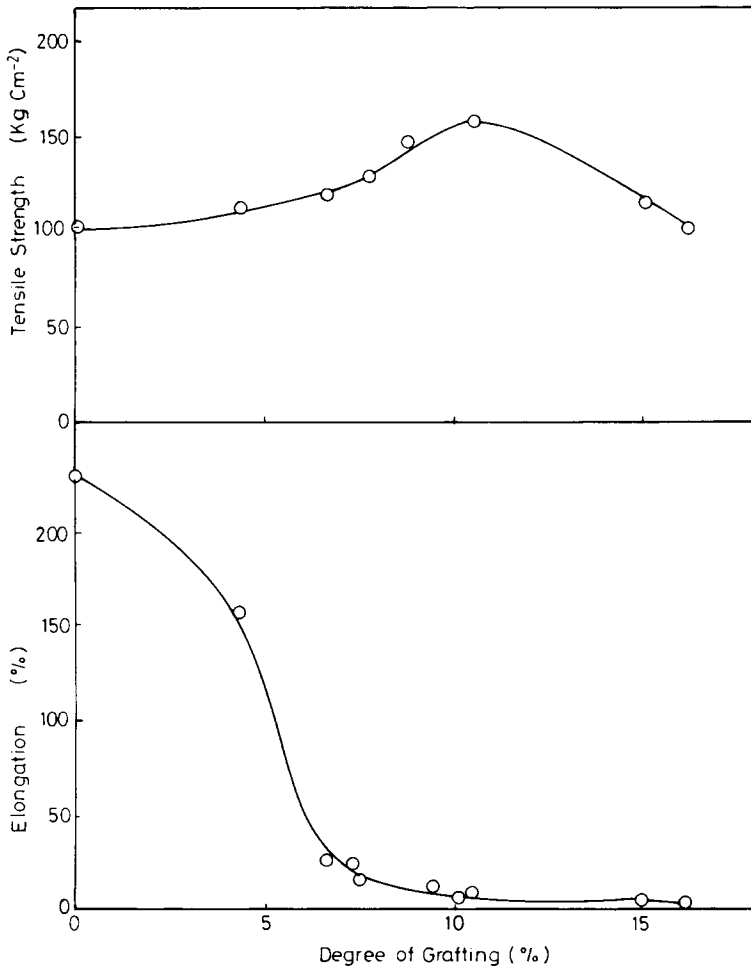
Fig. 9.   Change in tensile strength and elongation percent with degree of grafting for PFA-grafted films.

for the alkali-untreated and alkali-treated grafted films (Figs. 5 and 6). The alkali-treated films possess higher hydrophilic properties than alkali-untreated ones. It can be also noted that, the grafted FEP films (both alkali-untreated and treated) possess much higher water uptake than that of PFA grafted ones, at a given degree of grafting. Such difference may be due to the change in morphology of polymer substrate, which greatly affects the diffusion of solutions through the grafted chains and polymer matrices.

Electrical Properties

Figures 7 and 8 show the semilogarithmic relationship between the electric conductivity and the degree of grafting for the grafted PFA and FEP films, respectively. It is obvious that the electrical conductivity of the alkali-treated grafted films is much higher than that of the alkali-untreated ones. The easily
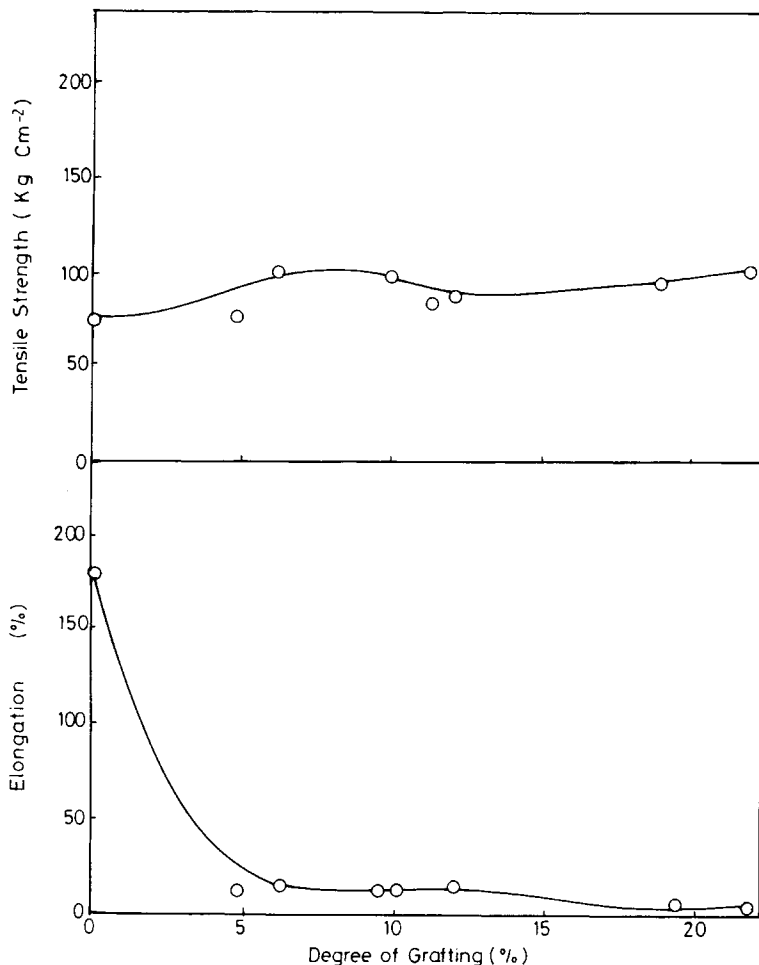
Fig. 10. Change in tensile strength and elongation percent with degree of grafting for FEP-grafted films.

ionizable groups introduced into the grafted films by the alkaline treatment improved the electrochemical properties of the graft copolymers. The FEP-grafted films showed electrical conductivity values somewhat lower than that of PFA-grafted ones, especially the alkali-treated films.

Mechanical Properties

Figures 9 and 10 show the changes in tensile strength (T_b) and percent elongation (E_b) at break point for the grafted PFA and FEP films as a function of grafting degree. It can be seen that, T_b slightly increases with degree of grafting for both FEP- and PFA-grafted films while the E_b sharply decreases as the degree of grafting increases.

Generally, increasing the degree of grafting results in increasing the rigidity of some graft copolymers, especially if the grafted chains possess higher T_g.[18]

Consequently, a decrease in the elongation percent and an increase in the tensile strength are expected for such grafted films.

It is important that the grafted films show good tensile properties acceptable for handling in practical applications. The grafted fluorinated polymers obtained by the radiation-grafting method show good tensile properties which may make them acceptable for practical uses. It must be taken in account that, in most practical uses, the grafted films will be used in the wet form. Therefore, more elasticity and improvement in E_b will be expected due to the hydrophilic properties of such grafted films which swell in water and create more space for chain movement.[18]

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