

Properties of Cation-Exchange Membranes Prepared by Radiation Grafting of Acrylic Acid onto Tetrafluoroethylene–Ethylene Copolymers

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SYNOPSIS

Some properties of the ion-exchange membranes prepared by simultaneous and preirradiation techniques of grafting of acrylic acid onto tetrafluoroethylene–ethylene copolymer films, including porous microfilters, have been studied. The water content, electric resistance, transport number, distribution of grafting, thermal and chemical stability, and mechanical characteristics of the membranes were determined as a function of the grafting degree. Graft polymerization proceeds from both surfaces of the polymer film into the polymeric matrix depth. Cation-exchange membranes prepared possess good electrochemical and mechanical properties, high thermal and chemical stability at grafting degrees from 30 to 50%, and can be successfully used in electro dialysis processes. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The interest toward synthetic membranes and membrane processes is growing rapidly nowadays. During the last 20 or 30 years, membranes have been increasingly employed in various fields as effective means for separation of molecular mixtures.

Fluoro-containing polymers have drawn the attention of the researchers for their excellent mechanical properties and thermal and chemical stabilities. By using simultaneous and preirradiation techniques, the grafting of acrylic acid (AAc) mainly onto polytetrafluoroethylene (PTFE) and tetrafluoroethylene–hexafluoropropene copolymers (TFE–HFP) was studied and cation-exchange membranes (CEM) were obtained.^{1–7} Although partly fluorinated polymers like tetrafluoroethylene–ethylene copolymers (TFE–E) exhibit good properties similar to those of PTFE and offer some advantages in their processing,^{8,9} grafting onto them to prepare ion-exchange membranes has not been studied thoroughly yet. Ellinghorst et al.^{10,11} used an

electron-beam accelerator and preirradiation grafting method in vacuum to obtain ion-exchange membranes by grafting various hydrophilic monomers onto a substrate of partly fluorinated polymers and copolymers, including TFE–E copolymers. Based on TFE–E copolymer fibers, by using an electron-beam accelerator and preirradiation grafting method, acrylamide was grafted to prepare ion-exchange material possessing selectivity toward some metal cations.¹²

In our previous work, the effect of AAc grafting conditions (monomer concentration, dose rate, film thickness, etc.) on the degree of grafting of TFE–E copolymers (TFE–E–gAAc) at TFE content 52.8 mol % was studied.¹³ Both the simultaneous and the preirradiation grafting techniques were employed. In this paper, the water content and the electrochemical, mechanical, and other properties of the grafted TFE–E films were studied to examine the possibilities for their practical application as ion-exchange membranes.

EXPERIMENTAL

The TFE–E–gAAc grafted films were prepared by a simultaneous method by using a ⁶⁰Co facility and

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repeated grafting (exposition 5 h and postpolymerization time 19 h each for 5 days). The preirradiation method in air, using a Cockroft-Walton electron-beam accelerator, was also employed. The degree of AAC grafting (%) was determined as the ratio between the weight of grafted AAC and the weight of the original (initial) polymer. The procedure and the determination of the grafting distribution by scanning electron microscope PSEM-500 (Philips, The Netherlands) as graphite superimposition were described in detail previously.¹³ The conversion of the carboxylic acid groups into the potassium form was carried out in 2.5% KOH solution for 24 h at 373 K. The water content was determined as the ratio between the weight of the water in the membrane (immersed in distilled water for 24 h at room temperature) and the weight of the dry one. The specific electric resistance of the membrane at 293 K and 1000 Hz was calculated using the equation $R = (R_{m+c} - R_c)S/d$, where R_{m+c} and R_c represent apparent values with and without the membrane, respectively, measured with platinum electrodes in laboratory electrolytic cell; S is the active area (0.785 cm²); and d is the thickness of the membrane swollen in the solution. The transport number was measured after the membrane in the potassium form was conditioned by being kept in a 0.5N KCl solution for 5 min at 373 K and overnight at 293 K and then placed in between two compartments of a laboratory cell. KCl solutions, 0.5 and 1.0N, were made to flow individually through the compartments until equilibrium had been reached. The potential was measured at 293 K. The transport number of the counterions in the membrane was calculated from the value of the measured potential (E_m) by using the equation $E = E_m/2E_0 + 0.5$, where E_0 is the theoretical value of the potential calculated by the Nernst equation. The mechanical properties were determined by TIRATEST-2150 (Germany) after the grafted film was soaked in distilled water for 24 h at room temperature. The methods mentioned above have been described previously.^{3,5,7}

The thermal and chemical resistances were determined by weight loss and the increase of the specific electric resistance, respectively, under various conditions by methods described in Refs. 14–19. CEM were prepared also by the simultaneous method of grafting onto porous films with pore size from 0.5 to 2.0 μm under the following conditions: AAC concn, 40 wt %; Mohr's salt, 1.5 wt %; temp, 298 K; dose, 9 kGy, obtained by repeated irradiation, 3 periods, 5 h each, at dose rate 0.6 kGy/h, for each day.

RESULTS AND DISCUSSION

Water Content

Water content (P) is very important for the practical application of a membrane, especially concerning the ion-exchange and reverse osmosis phenomena. The membrane should exhibit suitable hydrophilicity, as well as good electrochemical and mechanical properties. By grafting hydrophilic monomers such as AAC onto hydrophobic polymers, the graft copolymers exhibit hydrophilic properties and can swell in water. In this study, the water content of TFE-E-gAAC-grafted films in the H form obtained under different grafting conditions was investigated. Figures 1(a) and (b) show the water content of the grafted TFE-E film by simultaneous (a) and preirradiation (b) methods as a function of the degree of grafting (W) of AAC. Water content increases almost linearly with the increase of W . The conversion of the carboxylic acid groups into their potassium salt additionally increased the water content of the grafted film within the range from 20 to 85–95% depending on the degree of AAC grafting (from 15 to 65%, respectively).

The results suggest that the water content depends mainly on the degree of grafting, i.e., on the amount of hydrophilic groups in the films obtained.

Electric Resistance

It is well known that one of the fundamentals of the ion-exchange membranes is their low electric resistance. The hydrophilic groups content in grafted polymer films strongly affects their specific electric resistance (R). The dependence of R , associated with the H and K forms in 0.5N NaCl and 3N KCl,^{3,5} respectively, of membranes prepared by using a ⁶⁰Co facility, on the degree of grafting is shown on Figures 2(a) and (b), respectively. Obviously, the R values vary with both the ionic forms and decrease with the increase of the grafting degree. At high grafting degrees (over 40%), R decreases sharply to (2–10) $\times 10^3$ and 10–50 ohm-cm for H and K forms, respectively.

These results could be reasonably understood by assuming that the grafting proceeds from the surface of the film inward, with progressive diffusion of AAC. Under the experimental conditions mentioned above, the specific electric resistance depends mainly on the amount and the distribution of the hydrophilic groups within the grafted films. The grafting is not likely to proceed deep into the polymeric ma-

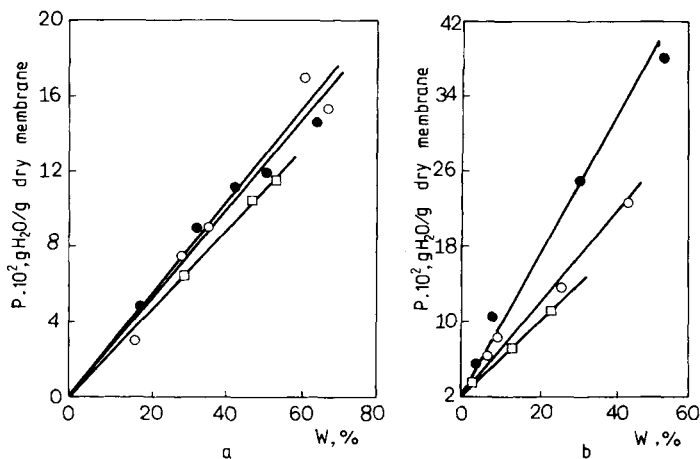


Figure 1 Dependence of the water content in CEM in the H form on the degree of AAc grafting onto different fluoropolymers by (a) the simultaneous and (b) the preirradiation methods. Grafting conditions: (a) Dose rate, 0.6 kGy/h; AAc concn, 40 wt %; grafting temp, 298 K; Mohr's salt, 1.5 wt %; film thickness, 75 μ m (110 μ m for Teflon FEP-100). (b) Dose rate, 1.8 kGy/s; dose, 18 kGy; irradiation temp, 298 K; AAc concn, 20 wt %; grafting temp, 343 K; film thickness, 75 μ m (110 μ m for Teflon FEP-100). (●) TFE-E; (○) Hostafon ET-VP 6235; (□) Teflon FEP-100.

trix and there is a region where the grafted film has higher specific electric resistance, i.e., the graft polymerization of the AAc onto the TFE-E matrix is heterogeneous.

Transport Number

The permselectivity is one of the most important properties of an ion-exchange membrane. The

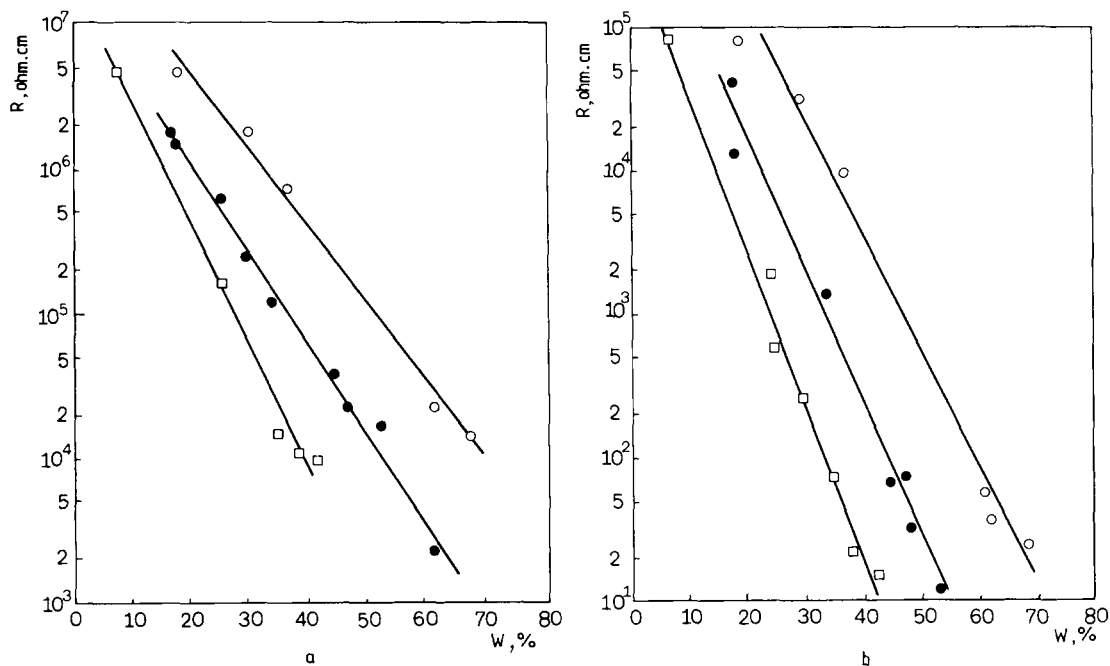


Figure 2 Dependence of the specific electric resistance of CEM on the degree of AAc grafting onto various fluoropolymers in semilogarithmic coordinates for the (a) H and (b) K forms. Grafting conditions and indications are the same as in Figure 1(a).

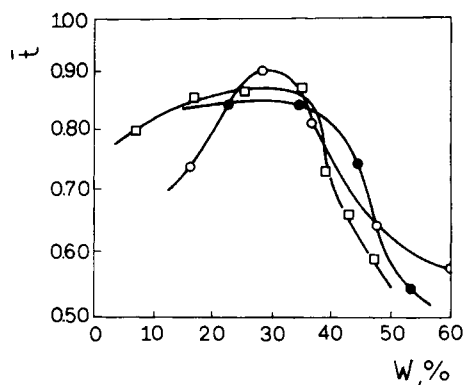


Figure 3 Dependence of the transport number of CEM in the K form on the degree of AAc grafting onto various fluoropolymers. Grafting conditions and indications are the same as in Figure 1(a).

transport number (\bar{t}) of the counterion in the grafted TFE-E films in the K-form⁵ was measured. Figure 3 shows the dependence of \bar{t} of the ion-exchange fluoropolymer membranes prepared by the simultaneous grafting technique on the grafting percent. It can be seen that \bar{t} passes through a maximum at a grafting degree within the range from 30 to 40%.

The dependence of R and \bar{t} of ion-exchange membranes obtained by the electron-beam preirradiation method in air on the grafting degree for several fluoropolymers is shown in Table I. The transport number of CEM in the K form increases from 0.60 to

0.67 at a grafting degree within 4–9% and from 0.77 to 0.83 at a grafting degree within 44–57%. Despite the high grafting degree of AAc onto the polymer matrix (44–57%), R values remain high and approximately the same. This is because the process of grafting by an electron beam takes place mainly on the surface because of the smaller penetration of the electrons into the polymer film as compared to the γ -rays.

Both R and \bar{t} values of ion-exchange membranes prepared by a simultaneous method of grafting onto porous films are shown in Table I. Because of the better diffusion of AAc into the polymer porous matrix, the specific electric resistance of the H and K forms was found to be from 7 to 20 times lower than the one observed for the nonporous substrate.

The data in Figures 2(a) and (b) and Table I show that R values depend not only on the quantity but also on the mode that PAAc is distributed within the polymer matrix.

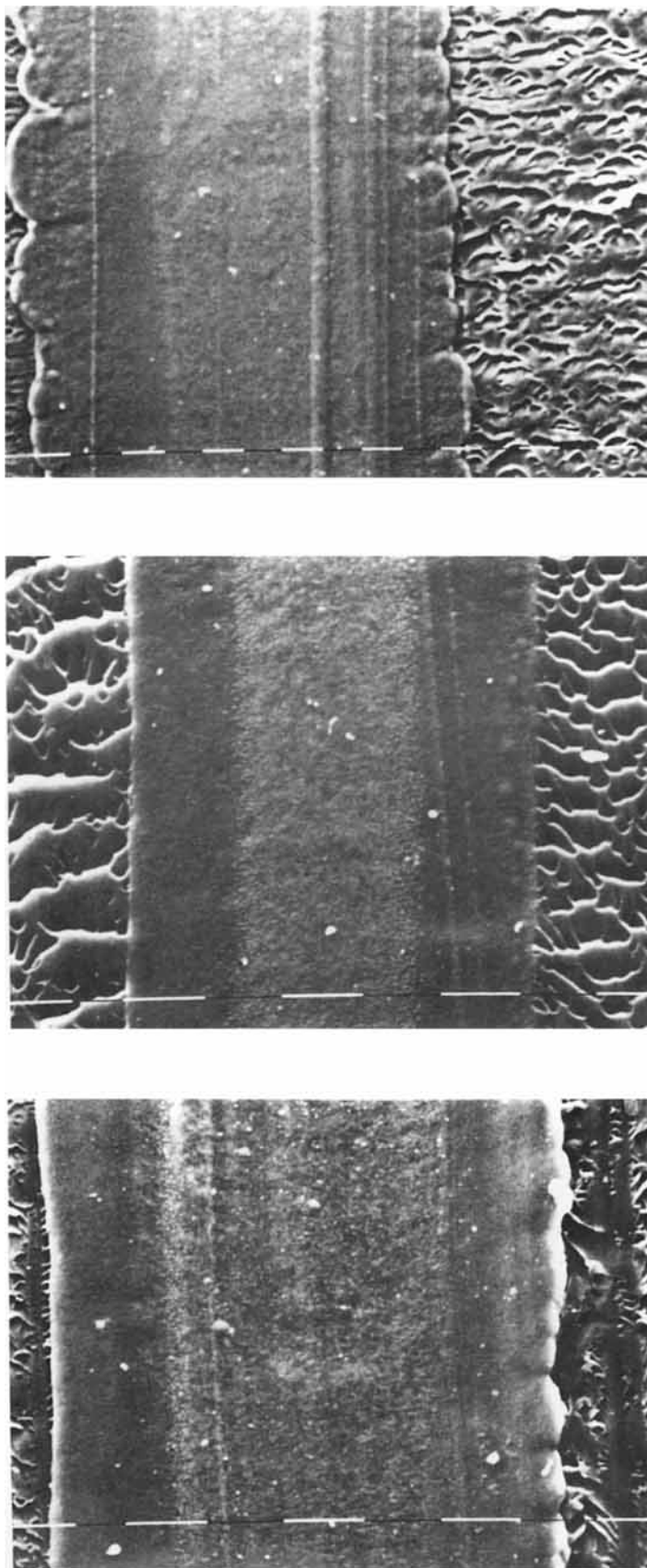
Distribution of Grafting

An important property for the preparation of membranes is the suitable distribution of grafted PAAc within the polymeric matrix. The distribution of grafted PAAc in the polymer film depth was studied by SEM [Figs. 4(a) and (b)]. Obviously, the grafting proceeds from both surfaces of the polymer film inward. By using the preirradiation method of

Table I Dependence of the Specific Electric Resistance and Transport Number of Ion-exchange Membranes on the Degree of Grafting of AAc^a

No.	Copolymer Type	Degree of Grafting (%)	Specific Electric Resistance (ohm-cm)		Transport No.
			H form	K form	
1	TFE-E	7.8	2.0×10^6	2.0×10^6	0.67
		30.6	2.0×10^6	—	—
		53.8	1.7×10^5	5.7×10^3	0.83
2	Hostafion ET-VP 6235	8.8	1.5×10^6	2.2×10^5	0.63
		27.4	2.3×10^6	—	—
		44.1	1.2×10^6	1.9×10^4	0.77
3	Teflon FEP-100	3.8	1.6×10^6	2.2×10^5	0.60
		13.0	1.4×10^6	—	—
		22.9	1.3×10^6	6.9×10^3	—
4	ET-VP 6235 Pores 0.9–2.0 μm Pores 0.5–1.3 μm	58.7	1.0×10^3	7	0.74
		48.6	2.2×10^3	7	0.77

^a Grafting conditions are the same as in Figure 1(b).



c

b

a

Figure 4 SEM images of grafted PAAc by the preirradiation (a,b; $\times 1250$ and 640 , respectively) and the simultaneous (c; $\times 1250$) method onto TFE-E films. Grafting conditions are the same as in Figures 1 (b) and (a), respectively.

Table II Chemical Resistance of Grafted Cation-exchange Membranes in Various Media^a

No.	Reagents and Conditions	Degree of Grafting (%)			Weight Loss (%)		
		TFE-E	Hostafion ET-VP 6235	Teflon FEP-100	TFE-E	Hostafion ET-VP 6235	Teflon FEP-100
1	5N NaOH (30 min, boiling)	10.7	15.8	27.6	0.0	0.0	0.0
		23.3	30.8	34.3	0.0	0.0	2.1
		57.6	63.1	42.3	0.0	0.0	2.2
2	5N H ₂ SO ₄ (30 min, boiling)	10.7	15.8	27.6	0.0	0.0	6.2
		23.3	30.8	34.3	0.0	0.0	7.8
		57.6	63.1	42.3	0.0	0.0	10.6
3	40% KOH (24 h, 370 K)	16.5	15.8	27.6	0.0	27.9	0.0
		49.1	60.7	42.3	28.9	27.9	0.0
4	3% H ₂ O ₂ (4 ppm/L Fe ^{II} , 16 h, 343 K)	10.7	15.8	27.6	0.0	0.0	20.9
		23.3	30.8	34.3	11.1	14.2	23.4
		57.6	63.1	42.3	28.9	29.9	31.3

^a Grafting conditions are the same as in Figure 1(a).

membrane preparation, under the selected conditions, the depth of the grafted layer of PAAc was found to increase from 21.4 to 36.4%, with the increase of the grafting degree from 23.8 to 31.8% [Fig. 4(a)]. The use of the simultaneous method showed that the corresponding grafted layer depth was 30.0% at a grafting degree of 10.7% [Fig. 4(b)]. These results suggest that the nongrafted layer remains in the middle part of the polymeric matrix,

especially at low grafting degrees or under the preirradiation treatment.

Thermal and Chemical Stability

The ion-exchange membranes synthesized possess good thermal and chemical stability.

The thermal stability of CEM in the K form was studied at 343 and 373 K for periods of 24 and 48

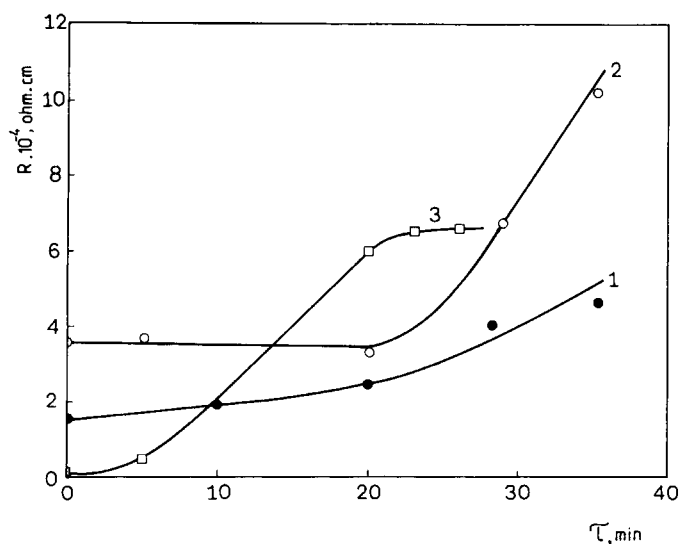


Figure 5 Dependence of the specific electric resistance of CEM (K form in 3N KCl) on the exposure to 10% H₂O₂-1.85 g ion/L Fe²⁺ system at 363 K: (1) TFE-E with 16.5% grafted PAAc; (2) Hostafion ET-VP 6235 with 16.5% grafted PAAc; (3) Teflon FEP-100 with 34.3% grafted PAAc. Grafting conditions are the same as in Figure 1(a).

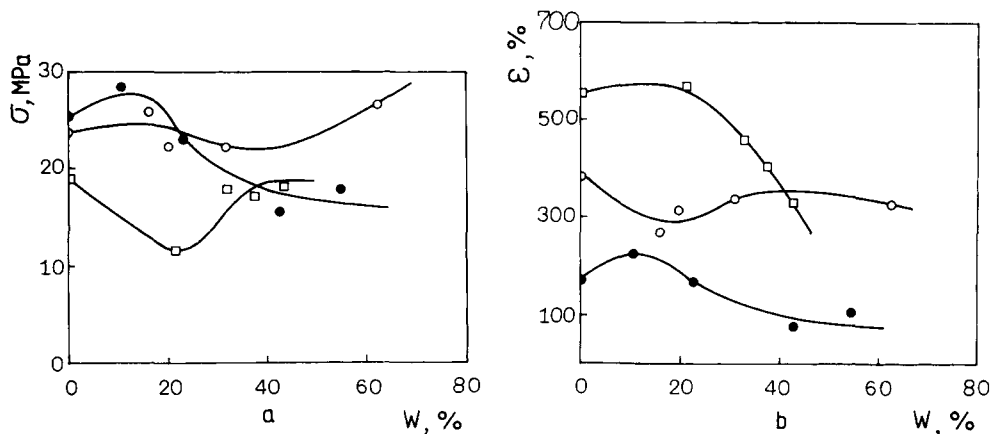


Figure 6 Dependence of (a) the tensile strength and (b) the elongation at break of CEM on the degree of AAc grafting. Grafting conditions and indications are the same as in Figure 5.

h. The chemical stability was examined in concentrated hydrochloric, sulfuric, nitric, and glacial acetic acids at 298–303 K for periods also of 24 and 48 h.¹⁴ In both cases, within grafting degrees from 10 to 60%, no weight loss was observed or it was lower than 0.004% for the higher grafting degrees.

The membranes' chemical stability (Table II) was studied under more severe conditions, including immersion in strongly oxidative systems at higher temperatures, typical for grafted membranes.^{15–19} The data in Table II show that the chemical stability of the ion-exchange membranes based on fluoropolymer-grafted PAAc depends mainly on the grafting degree and, to a much lower extent, on the polymeric matrix nature. Figure 5 shows that R in the K form increases significantly after the CEM have been preliminarily immersed into the oxidative system (τ period of treating) and depends strongly on the grafting degree of AAc.

Mechanical Properties

Figure 6 shows the dependence of both the tensile strength and elongation (σ and ϵ , respectively) of a wet CEM on the grafting degree of AAc. The mechanical properties depend on the grafting (associated, in turn, with the membrane hydrophilicity), which determines their swelling in water.

CONCLUSIONS

1. The KOH-treated grafted membranes exhibit a higher swelling in water than do the untreated ones (H form).

2. The specific electric resistance of the membranes is largely dependent on the degree of grafting and the grafting distribution of the PAAc in the polymer matrix. CEM prepared by a repeated simultaneous grafting technique with a ⁶⁰Co facility possess good electrochemical characteristics at grafting degrees from 30 to 50%. The membranes, prepared on the basis of TFE-E porous microfilters, possess significantly better characteristics.
3. The grafting distribution was observed by scanning electron microscopy. It was proved that the graft polymerization takes place predominantly on the polymer film surface and progresses inward through the grafted layer into the polymer matrix depth.
4. CEM based on grafted PAAc onto TFE-E copolymer films by using the repeated simultaneous method on a ⁶⁰Co facility possess good physicochemical properties and thermal and chemical stability, which, combined with their good electrochemical properties, stipulate the possibilities for their practical application.

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