

Radiation Initiated Grafting of Acrylic Acid onto Tetrafluoroethylene–Ethylene Copolymers

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SYNOPSIS

Hydrophilic carboxyl containing fluoropolymers was obtained by radiation grafting of acrylic acid onto tetrafluoroethylene–ethylene copolymers with different compositions. By using simultaneous (^{60}Co) and preirradiation (electron beam) techniques, the effect of the grafting conditions (monomer concentration, dose rate, dose, film thickness, etc.) on the degree of grafting was studied. A considerable effect of the polymer compositions, especially the C–F bonds content, and the batch irradiation on the degree of grafting was found. It was observed by scanning electron microscopy that the grafting took place mainly on the polymeric film surface and developed inward with increasing diffusion of the acrylic acid through the grafted layers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Many papers have recently been devoted to studies on radiation initiated grafting of hydrophilic monomers onto fluoropolymers to obtain cation exchange membranes (CEM) with various applications. Fluoropolymers are preferred for their excellent thermal and chemical stability and good mechanical properties. By using several grafting techniques^{1–10} mainly grafting of acrylic acid (AAc) onto poly(tetrafluoroethylene) (PTFE) was investigated. There were published results until now on grafting of AAc onto tetrafluoroethylene–ethylene (TFE–E) copolymers but there were a few about grafting of *N*-vinylpyrrolidone, 1-vinylimidazole, and dimethylaminoethylmethacrylate onto them.^{11,12} These copolymers have been found to be better processed compared to PTFE,^{13–15} considerably more radiation resistant, and can be irradiated without extensive degradation.^{15,16} Studies on the influence of the TFE–E polymer composition on the degree of grafting have not been reported.

In the present work, by using simultaneous and preirradiation grafting methods, the effect of AAc grafting conditions (monomer concentration, dose

rate, dose, film thickness, etc.) on the degree of grafting of TFE–E copolymers was studied.

EXPERIMENTAL

Materials

Laboratory synthesized TFE–E copolymers with different compositions (52.8; 49.3, and 46.5 mol % TFE content in TFE–E-I, TFE–E-II, and TFE–E-III copolymers, respectively^{17,18}), as well as commercial products were used: Hostaflon ET-VP 6235 (Hoechst, Germany) and tetrafluoroethylene–hexafluoropropene (TFE–HFP) copolymer Teflon FEP-100 (Du Pont) as a perfluorinated copolymer for comparative investigation. The 30–150 μm -thick films of the copolymers previously mentioned were washed in acetone and dried under vacuum to a constant mass prior to irradiation. AAc, stabilized with 0.05% *n*-methoxyphenol (Reachim, USSR), was purified by vacuum distillation. The Mohr's salt (98.5% purity) was also a commercial product (Reachim, USSR).

Graft Polymerization

Both the simultaneous and the preirradiation grafting techniques were employed. The irradiation was carried out on a ^{60}Co γ -ray facility at dose rate rang-

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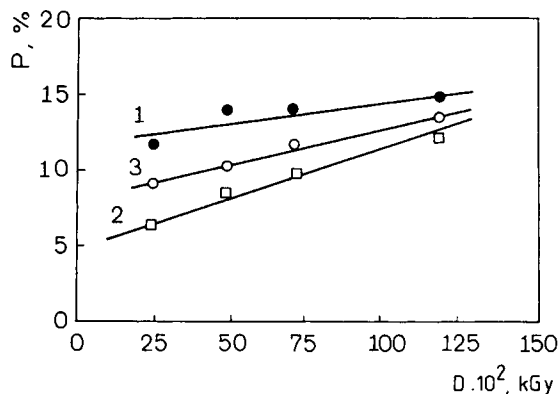


Figure 1 Dependence of the degree of AAc grafting onto TFE-E-I (curve 1), TFE-E-II (curve 2), and TFE-E-III (curve 3) copolymers on the dose. Grafting conditions: dose rate, 3.6 Gy/h; [AAc], 40 mass %; [Mohr's salt], 1.5 mass %; temperature, 298 K and film thickness, 75 μm .

ing within 3.6–800 Gy/h and hopolymerization inhibitor (Mohr's salt) for the simultaneous grafting method. A "Cockroft-Walton" electron beam accelerator at a dose rate of 6480 kGy/h was employed for the preirradiation grafting. When the simultaneous grafting method was used the copolymer films and the aqueous AAc, deaerated by bubbling argon, were introduced into glass ampoules. The ampoules were then irradiated on a ^{60}Co facility under certain conditions. After the irradiation, the grafted films were removed and washed thoroughly with hot distilled water, soaked for 24 h in the same medium to extract the residual AAc and poly(acrylic acid), PAAc. The films were subsequently dried under vacuum to a constant mass.

When the preirradiation grafting technique was used the films were irradiated in air at the conditions selected. The graft polymerization was then conducted in an inert atmosphere under heating.

Graft-Distribution

The distribution of the grafted PAAc into the depth of TFE-E copolymeric films was investigated by scanning electron microscopy (SEM). The films were put into epoxy resin and then, graphite from graphite electrodes was superimposed onto their cross sections under vacuum. Subsequently, a scanning electron microscope PSEM-500 (Philips, The Netherlands) was used for evaluation of the graft distribution.

RESULTS AND DISCUSSION

By the simultaneous grafting technique using ^{60}Co facility the dependence of the degree of AAc grafting (P) onto laboratory synthesized TFE-E copolymers with different compositions on the irradiation dose (D) was studied (Fig. 1). The higher content of TFE monomer units in the copolymer (52.8 mol % for TFE-E-I vs. 46.5 mol % for TFE-E-III) results in higher grafting degree. This is due to the lower radiation resistance and, consequently, to the higher radiation-chemical yield of radicals derived from C—F bonds than from C—H bonds.^{15,19} The higher concentration of radicals in the TFE-E-I copolymer and their long lifetime determine also a higher value of P onto TFE-E-I copolymer than onto TFE-E-III copolymer depending on the postpolymerization time (τ) (Fig. 2). On the other hand, the structures of the copolymers studied were known to possess

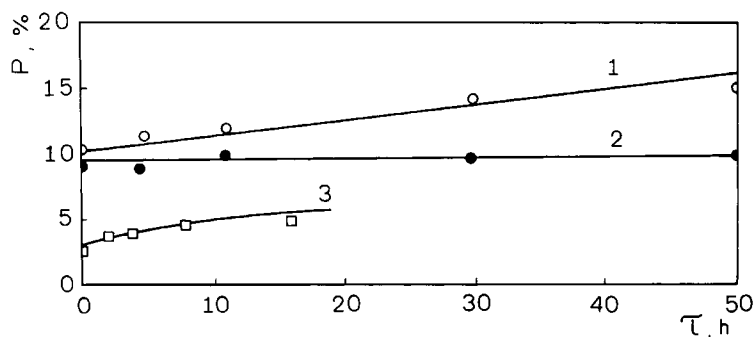


Figure 2 Dependence of the degree of AAc grafting onto TFE-E-I (curves 1, 3) and TFE-E-III (curve 2) copolymers on the post-polymerization time. Grafting conditions: dose rate, 3.6 Gy/h (curves 1, 2) and 500 Gy/h (curve 3); film thickness 75 and 95 μm and dose 0.70 and 20 kGy, respectively; [AAc], [Mohr's salt] and temperature are the same as in Figure 1.

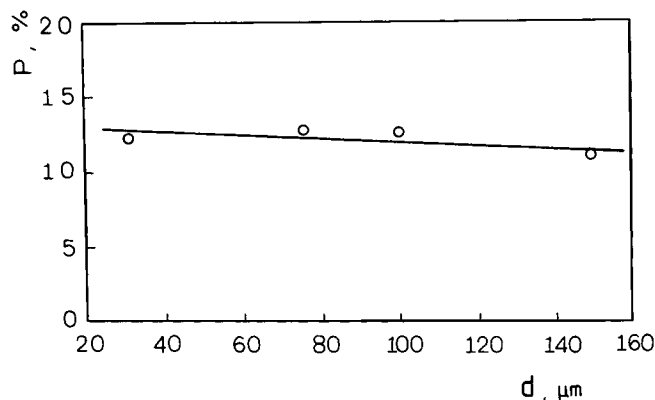


Figure 3 Dependence of the degree of AAc grafting onto TFE-E-I copolymer on the film thickness. Grafting conditions are the same as in Figure 1.

different distribution of monomer units. TFE-E-II was supposed to contain alternating monomer units, while TFE-E-I and TFE-E-III were block structure. The IR data confirmed that, in TFE-E-III copolymer, the proportion of $(-\text{CH}_2-)_4$ and $(-\text{CH}_2-)_{n>4}$ sequences (30 and 27%, respectively) was higher than in TFE-E-I copolymer (28 and 11%, respectively), while for the sequence $(-\text{CH}_2-)_2$ it was smaller (43 vs. 61%). These results indicated the more inhomogeneous character of TFE-E-III copolymer compared to TFE-E-I. The nature of the monomer units distribution and the higher TFE content in the copolymer composition determined the higher efficiency of grafting onto TFE-E-I copolymer and its good processability. That is why the next part of the basic studies was carried out mainly with this copolymer.

Despite the continuous irradiation, the effect of the film thickness (d) on the grafting at comparatively low dose rate was very weak (Fig. 3). The graft polymerization was diffusion controlled by the diffusion rate of AAc into the film, i.e., the grafting took place in the film depth. A weak tendency of reverse proportionality of P , and hence, of the grafting rate, related to the film thickness was observed.

The effect of AAc monomer concentration on the grafting is shown in Figure 4. The degree of grafting depends slightly on AAc concentration within the range of 20–60 mass % that shows that P is determined primarily by the quantity of the long-lived radicals obtained in the polymer support. At concentrations of AAc above 70 mass %, P and consequently the graft-polymerization rate rapidly increases. It is probably connected with the suppression of the growing chains termination reactions due to the insolubility of PAAc in its own monomer.

The rate of attaching monomer molecules of AAc to the growing polymer radicals does not change significantly which results in a rapid increase of the general grafting rate (gel-effect). At higher concentrations of AAc a portion of the Mohr's salt precipitates in the reaction medium and increases the viscosity thus additionally suppressing the reaction of chain termination. A similar effect of AAc concentration on the grafting for PTFE and TFE-HFP copolymers was observed by other authors.^{9,20}

The presence of Mohr's salt in the polymerization medium exerts a small influence on the grafting of AAc onto polymer support but suppresses considerably its homopolymerization.^{21,22} In Figure 5 is shown the dependence of P on Mohr's salt concen-

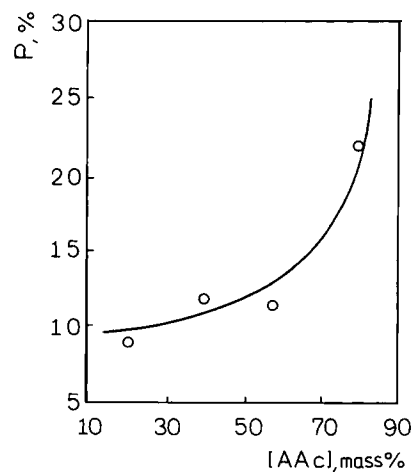


Figure 4 Dependence of the degree of AAc grafting onto TFE-E-I copolymer on the AAc concentration. Grafting conditions are the same as in Figure 1 but the dose is 0.60 kGy.

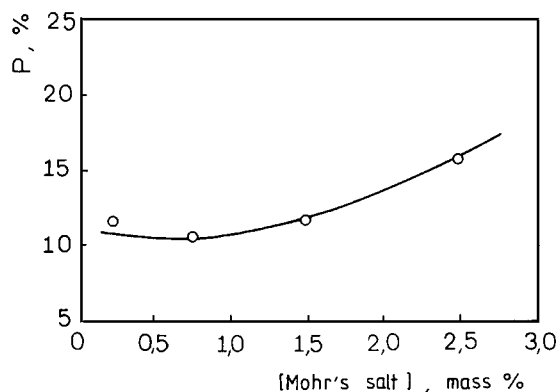


Figure 5 Dependence of the degree of AAc grafting onto TFE-E-I copolymer on the Mohr's salt concentration. Grafting conditions are the same as in Figure 1 but the film thickness is 40 μm .

tration. Obviously, at concentrations from 0.25–1.50 mass % it affects P slightly with a tendency to increase being further observed. Higher Mohr's salt concentrations are not acceptable because of its limited solubility, especially when AAc concentrations of over 40 mass % are used.

A parallel investigation was carried out by using continuous and batch (with posteffect) irradiation of different types of fluorocontaining copolymers in order to estimate the influence of the posteffects on P. The results are shown in Figure 6. At the batch irradiation [curves 1 (a,b,c)] the daily exposition was 5.30 h and the post-polymerization time was 18.30

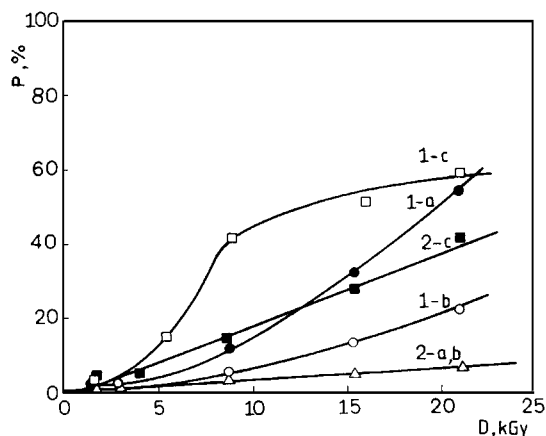


Figure 6 Dependence of the degree of AAc grafting onto (a) TFE-E-I, (b) Hostafion ET-VP 6235, and (c) TFE-HFP copolymers on the dose under batch (curve 1) and continual (curve 2) irradiation. Grafting conditions are the same as in Figure 1 but the dose rate is 0.5 kGy/h and the film thickness is 95 μm .

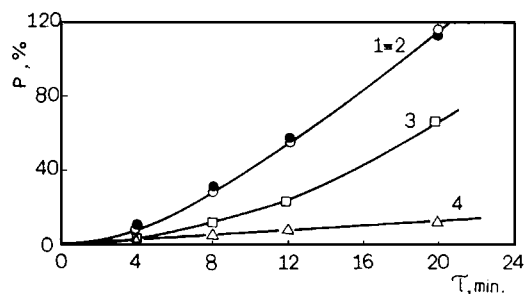


Figure 7 Dependence of the degree of electron beam AAc grafting on the grafting time for different fluoropolymers. Grafting conditions: dose rate, 1.8 kGy/s; dose, 18 kGy; irradiation temperature, 298 K; [AAc], 20 mass %; grafting temperature, 338 K, and film thickness, 55 μm . 1—TFE-E-I; 2—Hostafion ET-VP 6235; 3—Teflon FEP-100; 4—TFE-E-III.

h. Figure 6 shows that under continuous irradiation this type of TFE-E copolymer has almost no effect on P [curves 2 (a,b)], while under batch irradiation, when postpolymerization takes place, the grafting was considerably higher [curves 1 (a,b)]. The latter is related to the higher possibility for gradual monomer penetration into the polymer support depth, despite the fact that the fluoropolymer films scarcely swell in the monomer. Besides, the copolymer type is of importance too. For perfluorinated copolymer Teflon FEP-100 [curves 1,2(c)] the observed tendency is much more pronounced. This is due to the different content of C—F bonds in all the three copolymers, and hence, the quantity of the radicals obtained.

The preirradiation grafting technique in air by using an electron beam accelerator for grafting AAc onto the fluoropolymers studied was also used. Figure 7 shows the dependence of P on the grafting time (τ) for TFE-E-I and TFE-E-III copolymers and Hostafion ET-VP 6235. These curves are compared to the perfluorinated copolymer Teflon FEP-100. Probably the different nature of the polymer radicals obtained and the different monomer diffusion rate into the polymer support depth by electron beam and γ -ray grafting determine the different AAc grafting degree onto perfluorinated and partially fluorinated copolymers.

The distribution of the grafted PAAc in the polymer film depth was studied by SEM of the grafted film (Figs. 8 and 9). It was found that the grafting reaction took place mainly on the film surface at low P and progressed inwards with the increasing diffusion of the monomer through the grafted layer of PAAc. SEM images of grafted PAAc onto TFE-

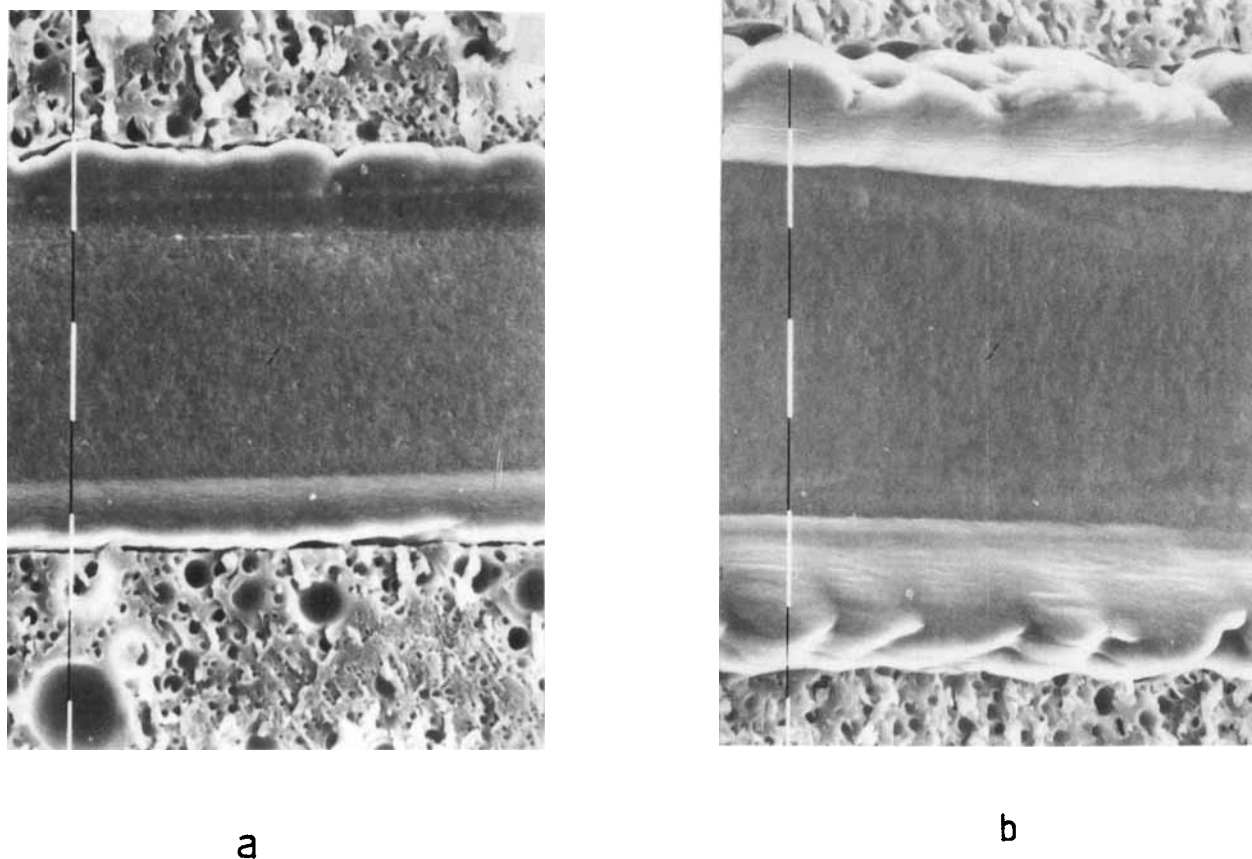


Figure 8 SEM images ($\times 1250$) of TFE-E-III copolymer films grafted by electron beam accelerator for grafting degrees (a) 18.4 and (b) 38.2%. Grafting conditions: (a) dose 18 and (b) 54 kGy; grafting time, 20 min and film thickness, 50 μm ; dose rate, irradiation, and grafting temperature are the same as in Figure 7.

E-III (Fig. 8) prepared by electron beam accelerator indicate that the increase of P from (a) 18.4 to (b) 38.2% leads to an increased grafted layer thickness

from 42 to 52%. When grafting of AAc onto TFE-E-I copolymer at the polymerization conditions described the thickness of the (d) nongrafted polymeric layer decreases to 48–55 μm , e.g., by half.

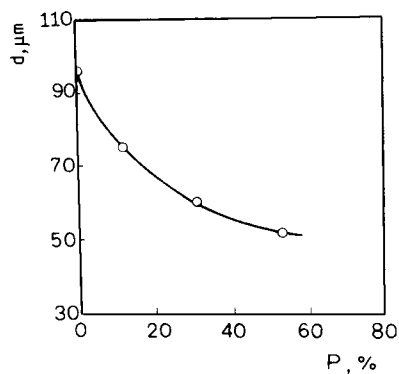


Figure 9 Nongrafted layer thickness of ^{60}Co γ -ray grafted films against the percent of grafting for TFE-E-I copolymer. Grafting conditions are the same as in Figure 6, curve 1.

CONCLUSION

1. By using ^{60}Co source simultaneous and electron beam preirradiation techniques the grafting of acrylic acid onto tetrafluoroethylene-ethylene copolymers with different polymer compositions was studied in order to estimate the effect of the grafting conditions. A considerable effect of the polymer composition and, above all, of the C—F bonds content on the degree of grafting was found.
2. The graft polymerization is diffusion controllable, takes place predominantly on the

polymer film surface, and progresses inward with the increase of the monomer penetration depth through the grafted layer. The post-polymerization effect significantly increases the degree of grafting.

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