

Cross-linking of Tetrafluoroethylene–Perfluoro(methylvinyl ether) Elastomers with Electron Beam Irradiation

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SYNOPSIS

Perfluoroelastomeric articles were cross-linked by electron beam irradiation. Irradiation experiments were carried out on the pure polymer free of fillers, processing aids, or curing chemicals. Doses of 10–15 Mrads are adequate to give gel content of >95%. The compression set, tensile strength, and chemical resistance of O-rings thus cross-linked are very good and comparable to those of chemically cross-linked ones. There is little difference in terms of efficiency of cross-linking and properties among perfluoroelastomers containing various functionalities, such as nitrile, iodine, bromine, hydrogen, and perfluorobenzene. In addition to cross-linking, irradiation causes structural changes, such as formation of acid fluorides on the polymeric chain ends as a result of main-chain scissions and generation of small amounts of volatile products (CF_4 , COF_2 , CO_2 , CF_3OCF_3) attributed to side-chain scissions. The cross-links appear to be thermally and chemically stable carbon–carbon bonds. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Perfluoroelastomers are copolymers of tetrafluoroethylene (TFE) and perfluoro(alkyl vinyl ethers) and contain only carbon, fluorine, and oxygen. Small amounts of a functional monomer (about 0.5 mol %) are incorporated to permit chemical cross-linking. The functionalities being used commercially are nitrile, perfluoroalkoxyalkylbenzenes, hydrogen, bromine, and iodine.^{1–8}

The sensitivity of fluoropolymers to ionizing irradiation is well known. Polytetrafluoroethylene (PTFE) and crystalline copolymers of TFE rapidly degrade when subjected to even mild doses of irradiation.^{9–14} Amorphous polymers like perfluoro (polyethers), irrespective of their backbone composition, undergo main-chain scission by an unzipping process.^{15–19} Lyons¹⁴ reviewed recently the irradiation chemistry of fluoropolymers, including fluoroelastomers such as copolymers of vi-

nylidine fluoride or TFE/propylene. Uschold²⁰ reported in 1984 that irradiation of perfluoroelastomers results in cross-linking but the properties of samples were poor because of the large amount of main-chain scission.

In this paper, we report the results of irradiation treatment of TFE/perfluoro(methylvinyl ether) (PMVE) perfluoroelastomers where the main-chain scission is minimal and cross-linked materials are obtained with physical properties comparable to those that are chemically cross-linked.²¹

EXPERIMENTAL

Polymers

The TFE/PMVE polymers tested were made in a continuous reactor with ammonium persulfate free radical initiation in an emulsion system.¹ The polymers containing various functionalities were made similarly.^{22–23} The polymers contain 32–33 mol % PMVE units.

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Sample Preparation for Irradiation Treatment

Dumbbells of about 2–3 mm thickness were made by pressing the polymer in a mold at about 100°C for 10 min. AS-214 O-rings (approximately 4 mm thick and 25 mm in diameter) were also pressed in a mold at about 100°C for 10 min. The samples were placed in polyethylene bags, swept with a stream of argon for a few minutes, sealed, and then exposed to an electron beam. No effort was made to rigorously exclude air from the samples. The samples were placed on trays, which were passed under the electron beam source at 0.1 Mrads per pass. The irradiations were carried out at Electron Technologies Inc., S. Windsor, Connecticut. After irradiation, the samples were placed in a vacuum oven and heated at 80°C for 24 h to remove any volatile products. The samples were then tested for physical properties, their infrared spectra were taken, and their gel content determined. In some experiments, where it was decided to rigorously exclude air, the samples were placed in Pyrex™ tubes. The tubes were evacuated for 2 h, sealed under vacuum, and then irradiated at room temperature. The tubes were cracked open in an evacuated chamber, and the gaseous products formed during irradiation were analyzed by gas chromatography and identified by mass and infrared spectroscopy. The cross-linked perfluoroelastomer was removed from the tubes and analyzed by infrared, and the gel content determined.

Chemical Cross-linking

For comparison purposes, we carried out chemical cross-linking experiments with polymers containing 1.8 wt % of nitrile and 0.12 wt % iodo groups. The chemicals were incorporated in the polymer on a two-roll high shear mill by first fluxing the polymer at 60–70°C to give a smooth band and then slowly adding tetraphenyltin maintaining a smooth band on the roll. Dumbbells and O-rings were made from these compounds. AS-214 O-rings were crosslinked by placing die cut “preforms” in the proper molds at 190°C for 30 min, followed by heating in an oven at 305°C for 42 h under an atmosphere of nitrogen. The same process was used to add triallyl isocyanurate (TAIC) to the polymer. O-rings and dumbbells were molded at 100°C for 10 mins and then irradiated.

Physical Properties

The tensile properties were measured according to ASTM methods D-412 (large dumbbells), D-1708 (small dumbbells), and D-1414 (compression set and tensile properties of O-rings). All measurements were done in triplicate, and the values averaged.

Chemical Resistance

Cross-linked O-rings were weighed, and their dimensions were measured and then exposed to the chemical under the conditions indicated. After exposure, the O-rings were allowed to come to room temperature, and, after blotting the surfaces with a paper towel, they were weighed, and the dimensions measured. From the initial and final measurements the percent weight gain and percent swell were calculated.

Infrared Spectra

Infrared spectroscopy was used to determine the perfluoro(methylvinyl ether) content in the polymer, as well as the nitrile functionality. The iodine and bromine content was determined by elemental analysis. The O-rings were microtomed to give disks about 50 μm thick. These were analyzed by Fourier transform infrared spectroscopy (FT IR) with a Nicolet 740 instrument and SX software. The infrared spectra showed that the irradiated O-rings had uniform composition throughout their thickness. The composition of the polymers before and after irradiation were compared by using the nitrile absorption intensities at 2270 cm^{-1} , carboxylic acid at 1773 cm^{-1} , carboxylate at 1690 and 1725 cm^{-1} , and the C—F overtone peak at 2363 cm^{-1} . Carboxylate peaks are present in the polymer and are formed as a result of the initiation system. Upon irradiation, a strong carboxylic acid absorption peak appears, which overlaps and covers the weaker carboxylate peak. The infrared spectra were run in air with no precautions taken to avoid exposure to moisture. Thus, any polymeric acid fluorides formed during irradiation would have been hydrolyzed to the corresponding carboxylic acids by the time the infrared spectra were taken.

Fluorination

Irradiated O-rings were placed in a “Hastelloy” shaker tube at room temperature; the tube was

closed and evacuated and pressured to 0.7 Mpa with a 1 : 3 mixture of fluorine and nitrogen. Experiments were run at room temperature, 40, 70, 100, and 150°C for 6 h. In all cases, the O-rings that were exposed to elemental fluorine retained their shape, remained colorless and clear, and their tensile and compression set properties were relatively unchanged. Infrared spectra of microtomed samples indicated that the fluorine treatment had invariably eliminated the 1773 cm^{-1} carboxylic acid peak, but the rest of the polymer composition remained the same. These are indications that the cross-links were not attacked by the fluorine. A control experiment in which chemically cured O-rings (nitrile-containing polymer cross-linked to triazines and bromo-containing polymer cross-linked by peroxides) were exposed to the fluorine/nitrogen (1 : 3) mixture as above, the O-rings were badly distorted and fused together. No physical properties could be measured because of the distortion. In addition, while the starting chemically cross-linked material was insoluble in Fluorinert FC-75 (from 3M Co.), the fluorinated O-rings displayed considerable solubility, indicating that the chemically formed cross-links had been destroyed by the fluorine attack.

Gel Determination

Pieces of approximately 0.5 g of irradiated O-rings were weighed and placed in individual vials with a 50-fold excess of FC-75. The vials were capped

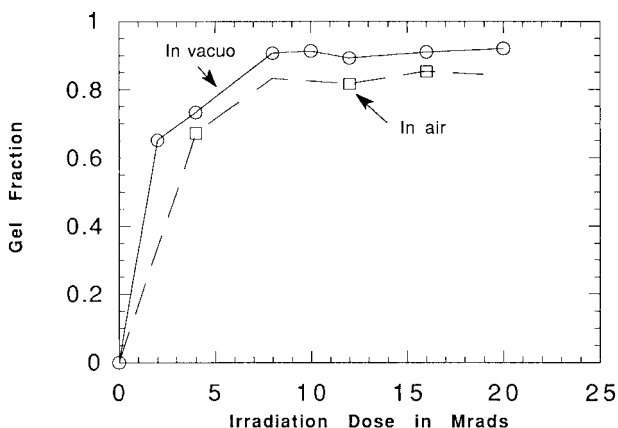


Figure 1 Gel fraction as a function of irradiation dose after room temperature electron beam exposure of TFE/PMVE copolymer in vacuo and in air. Fluorinert FC-75 was used as the solvent to determine gel content.

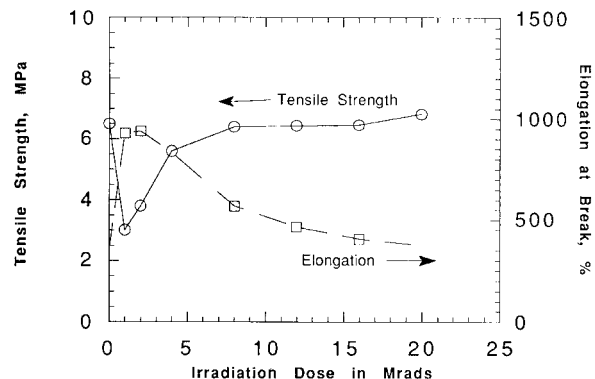


Figure 2 Tensile strength and elongation at break as a function of irradiation dose for room temperature electron beam cross-linked TFE/PMVE copolymer. The test specimens were AS-214 O-rings.

and rolled at room temperature for 72 h. The solvent was decanted, fresh solvent was added, and the process was repeated for another 72 h. The O-rings were removed, and the surface was wiped with a paper towel to remove any solvent on the surface. The swollen sample was weighed to determine the wt % solvent uptake. The O-ring was then dried under vacuum at 80°C for 24 h and weighed again. The amount of gel was determined from the original and final weights. Since the irradiated polymers were completely soluble in the FC-75 solvent, it is assumed that any uncrosslinked polymer in the irradiated O-ring would be extracted.

RESULTS

The following observations were made when a TFE/perflu(methylvinyl ether) copolymer, which contains no reactive functionalities, was exposed to electron beam irradiation.

- There is a loss of weight proportional to the irradiation dose ranging from 0.1 wt % loss at 4 Mrads, 0.5 wt % at 20 Mrads, 5 wt % at 350 Mrads, and 10 wt % at 700 Mrads. The weight loss is due to the formation of gaseous products identified by infrared spectroscopy and gas chromatography–mass spectroscopy (GC/MS) as CF_4 , COF_2 , CO_2 , and CF_3OCF_3 .
- The polymer after irradiation contained acid

Table I Changes in Polymer^a Composition Upon Irradiation

Irradiation (Mrads)	Weight Loss ^b (wt %)	PMVE ^c (wt %)	Nitrile ^d (wt %)	Iodine (wt %)
0	—	43.3	1.8	0.12
1	—	42.4	1.7	0.11
2	0.074	41.9	1.7	0.11
4	0.105	44.7	2.2	0.10
8	0.141	42.3	1.8	0.10
16	0.347	41.8	1.9	0.10
20	0.518	41.2	1.9	0.10

^a A TFE/PMVE copolymer that also contains a nitrile and an iodine functionality.

^b CF₄, COF₂, CF₃OCF₃, and CO₂ were identified as gaseous products.

^c PMVE = perfluoro(methylvinyl ether).

^d Nitrile-containing monomer.

fluoride groups, which hydrolyze during handling of the polymer films in moist air to carboxylic acid groups, as identified by the infrared absorption peak at 1773 cm⁻¹.

- The polymers that are originally soluble in the perfluorinated solvent become insoluble upon irradiation. Little difference was observed in the results when the irradiation

was carried out in the presence or absence of air (see Fig. 1).

- The tensile strength of irradiated O-rings or dumbbells decreases to a minimum value with 1–2 Mrads irradiation, then increases and eventually levels off as the irradiation dose is increased to 20 Mrads. The elongation at break does the opposite, increasing to a maximum value at 1–2 Mrads, followed by a decrease and finally flattening out (see Fig. 2).

A TFE/PMVE copolymer that also contained 1.8 wt % of nitrile and 0.12 wt % iodine functional groups was next irradiated under the same conditions. Similar weight loss, evolution of the same gaseous products, and gel formation were observed, together with appearance of the carboxylic acid groups. Interestingly, neither the nitrile nor the iodine groups were affected by the irradiation treatment. The polymer composition within the experimental error of the analysis showed no significant change after irradiation up to 20 Mrads (Table I). The infrared nitrile peak at 2270 cm⁻¹ (Fig. 3) is clearly unchanged, while the carboxylate peaks at 1690 and 1725 cm⁻¹ are hidden under the much stronger carboxylic acid peak at 1773

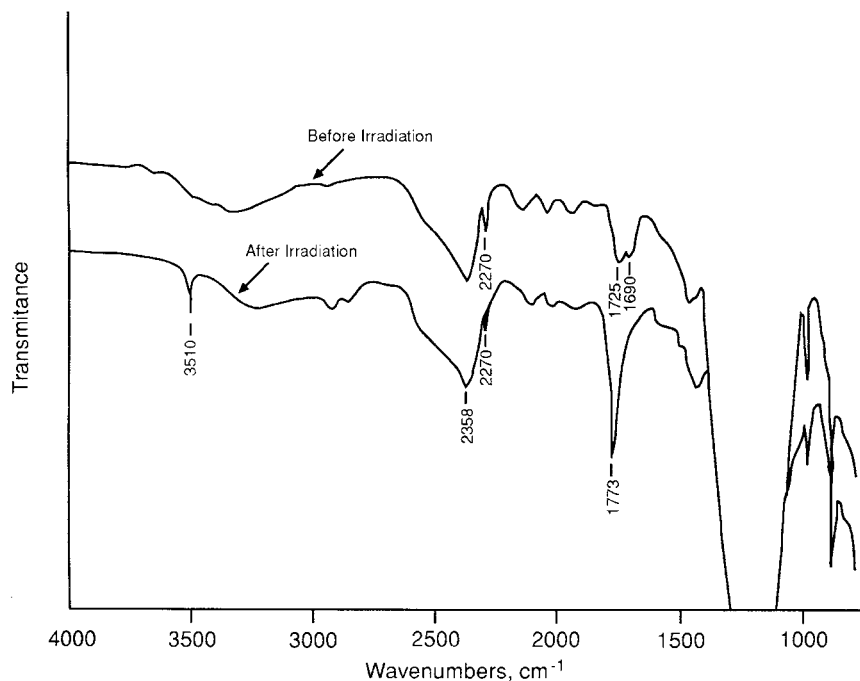


Figure 3 The infrared spectra of TFE/PMVE copolymer containing the nitrile functionality before and after electron beam irradiation (12 Mrad). Peaks at 2270 and 1773 cm⁻¹ indicate the presence of nitrile and carboxylic acid groups, respectively.

Table II Physical Properties of Irradiation-Cross-linked Perfluoroelastomer

Property	Cross-linking System	
	Irradiation ^{a,c} (12 Mrad)	Triazine ^{a-c}
Compression Set		
336 h at 23°C	35	23
70 h at 175°C	22	25
336 h at 175 °C	28	25
70 h at 204°C	72	30
Tensile Properties		
Stress at 100% elongation (MPa)	2.1	1.5
Tensile strength (MPa)	7.8	8.6
E _b (%)	285	240
Hardness, Shore A	70	68

^a The TFE/PMVE copolymer also contains a nitrile functionality.

^b Crosslinked by tetraphenyltin catalysis at 200°C for 30 m and heat-treated under nitrogen at 305°C for 42 h.

^c AS-214 O-rings were used as test samples.

cm⁻¹. This polymer with the nitrile functionality present was also cross-linked by chemical means, i.e., by conversion of the nitrile functionality to the corresponding triazine by treatment with tetraphenyltin.^{1,2} This was done to compare the physical properties of the same polymer cross-linked by irradiation versus chemical means. The tensile and compression set properties of irradiation cross-linked O-rings are comparable to those

obtained by chemical cross-linking (Table II) as was the chemical resistance (Table III). Similar properties were obtained when a Co-60 γ -ray source was used on the same polymer instead of an electron beam.²⁴

The cross-links formed upon irradiation are stable to elemental fluorine. O-rings cross-linked by irradiation were treated with a 1 : 3 mixture of fluorine and nitrogen at various temperatures

Table III Chemical Resistance of Irradiation-Cross-linked Perfluoroelastomer

Chemicals	Temperature (°C; for 70 h)	Cross-linking System	
		Irradiation ^{a,c} (12 Mrad; % swell)	Triazine ^{a-c} (% Swell)
Ethylene diamine	90	36	28
Nitric acid (70%)	85	2	2
Trifluoroacetic acid	50	28	26
Acetic acid	100	3	3
Hydrofluoric acid (5%)	100	35	31
Hydrofluoric acid (60%)	100	30	28
Hydrofluoric acid gas	100	25	23
Fluorocarbon 113	50	25	26

^a The TFE/PMVE copolymer also contains nitrile functionality.

^b Crosslinked by tetraphenyltin catalysis at 200°C for 30 m and heat-treated under nitrogen for 42 h at 305°C.

^c AS-214 O-rings were used as test samples.

Table IV Fluorination of Cross-linked Polymer Physical Properties

Properties ^a	Before Fluorination ^{b,d}	After Fluorination ^{c,e}
Stress at 100% elongation (MPa)	2.1	1.6
Tensile strength (MPa)	8.3	8.3
E_b (%)	243	283
Hardness, Shore A	73	69
Compression Set		
150°C for 70 h	27	14
204°C for 70 h	72	33

^a Properties measured on O-rings.

^b The O-rings had been irradiated with 12 Mrads.

^c The fluorination was carried out at 70°C/ 6 h under 200 psi pressure.

^d The starting O-ring contained a nitrile and carboxylic acid functionality.

^e After fluorination, both the nitrile and the carboxylic acid functionalities disappeared and could not be detected by infrared.

ranging from room temperature up to 150°C. No decrease in the cross-linking density was observed as judged by gel content, tensile properties, and compression set resistance. Table IV shows that exposure to elemental fluorine results in a small improvement in the stability of the cross-links after fluorination, as indicated by the lower compression set values. The values are similar enough to indicate that the cross-linked network remained intact. The only structural change observed was the elimination of the carboxylic acid peak in the infrared. Presumably, the fluorine attacked the carboxylic acid groups and converted them to CF₃ groups. Similar reactions have been observed with monomeric perfluorocarboxylic acids and carboxylate salts.²⁵ By comparison, when chemically cross-linked O-rings were exposed to similar conditions, their cross-links were degraded by fluorine attack.

Incorporation of TAIC in the polymer improves the physical properties of irradiated O-rings, particularly the tensile strength at 100% elongation, the tensile strength at break, and elongation at break (Table V). Surprisingly, the compression set values are about the same. When the tensile properties are examined as a function of the irradiation dose, the polymer that contains TAIC reaches the maximum tensile strength (Fig. 4) and the minimum elongation at break (Fig. 5) at lower doses than the control. The presence of the TAIC results in a faster cross-linking, i.e., it increases the cross-linking efficiency. TAIC is a well known “radical trap” and is used as a coagent in the peroxide-induced cross-linking of fluoro- and perfluoroelastomers containing bromine or iodine functionality. It reacts with the intermediate polymeric radicals and becomes part of the cross-linked network.^{1,26–28}

Table V Physical Properties of Cross-linked Perfluoroelastomer Containing Triallyl Isocyanurate (TAIC)

Properties	Control ^{a,b}	Polymer with TAIC ^{a-c}
Stress at 100% elongation (MPa)	1.6	7.3
Tensile strength (MPa)	5.1	10.0
E_b (%)	308	117
Compression Set (150°C for 70 h)	25	28

^a O-rings were irradiated for a total of 15 Mrads.

^b The polymer also contained 0.12 wt % of iodine and 1.8 wt % of a nitrile functionality.

^c Triallyl isocyanurate (2 wt %) was mixed with the polymer on a high shear mill.

DISCUSSION

It is reported²⁹ that exposure of hydrocarbon polymers to high-energy irradiation sources, such as electron beam or Co-60 γ -rays, results in the excitation of the macromolecules. The reactive intermediate radicals and ions produced by the ionization and excitation steps undergo chemical reactions that cause (a) formation of small molecules, (b) scission of the polymeric chains, and (c) cross-linking of the macromolecules.

Our data indicate that similar processes take place in the irradiation of perfluoroelastomers, i.e., (a) side-chain scission, (b) main-chain scission, and (c) cross-linking of the macromolecule. The side-chain scission is indicated by the evolution of the gaseous products CF_4 , COF_2 , CO_2 , and CF_3OCF_3 . Pacansky et al.³⁰ ran electron beam irradiation experiments on a TFE/PMVE copolymer under vacuum at low temperatures, and identified these same gases by infrared. They also measured their G values for CF_4 , COF_2 , CO_2 and CF_3OCF_3 as 0.93, 0.31, 0.055, and 0.14, respectively. The G value represents the number of molecules formed or destroyed per 100 ev of absorbed energy. The main-chain scission is demonstrated by the formation of perfluoroacyl fluorides (identified by the infrared absorption at 1885 cm^{-1}) in irradiation runs at room temperature.³⁰ Pacansky et al.³⁰ calculated side-chain and main-chain scission G values of 1.11 and 0.34, respectively, from weight loss and infrared data. The G value of the main-chain scission of polytetrafluoroethylene is

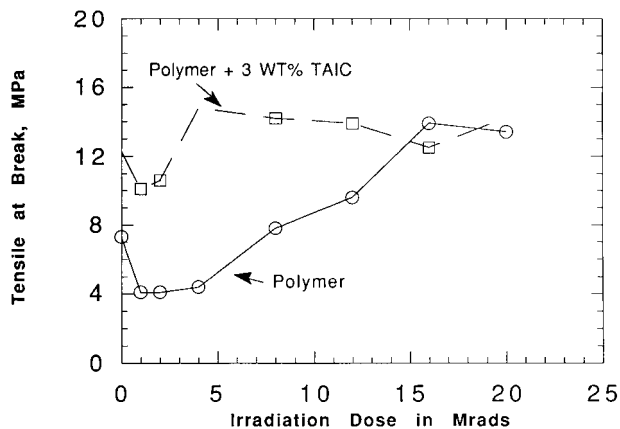


Figure 4 Tensile strength of dumbbell samples of TFE/PMVE copolymer that contains nitrile and iodine functionalities after electron beam irradiated in the presence and absence of triallyl isocyanurate (TAIC) as a function of the irradiation dose.

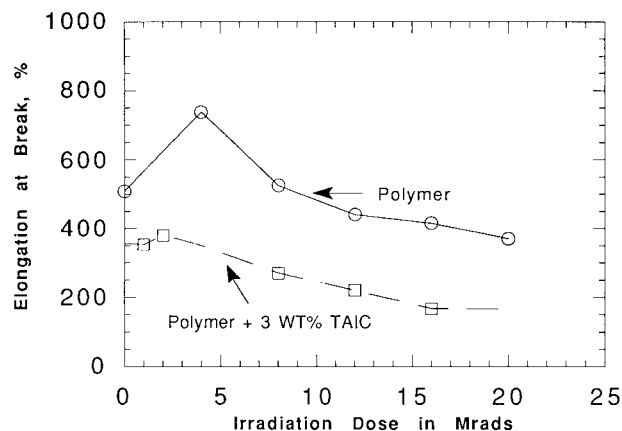


Figure 5 Elongation at break measured on dumbbell samples of TFE/PMVE copolymer that contains nitrile and iodine functionalities after electron beam irradiation, in the presence and absence of triallyl isocyanurate (TAIC), as a function of the irradiation dose.

estimated as 0.1–0.2,³¹ and that of vinylidene fluoride/hexafluoropropylene elastomer is estimated as 0.82,³² the perfluoroelastomers having G values of 0.34, i.e., falling somewhere in between.

Cross-linking of the irradiated samples is evidenced by formation of gel as well as by the change in physical properties. Compression set resistance measurements and tensile properties are particularly informative because they reflect the robustness of the cross-linked network. While the starting material has zero compression set resistance, the compression set resistance after irradiation becomes comparable to that of the chemically cross-linked materials (Table II). These results differ from those reported previously²⁰ for irradiated perfluoroelastomers of similar structure, which displayed very poor compression set resistance and mechanical properties. These differences are attributed to the extensive main-chain scission that took place during irradiation in the earlier study.²⁰ We observed that the tensile strength at low irradiation doses shows a minimum value; and as the dose increases, it reaches a plateau, while the opposite happens with elongation at break (Fig. 1). It appears that at low irradiation doses, main-chain scission dominates the process, resulting in a decrease in tensile strength. As the irradiation dose increases, however, cross-linking begins to dominate the process, and the tensile strength values begin to rise and eventually reach a plateau.

The data obtained so far indicate that radical

intermediates are involved both in the chain-scission and cross-linking processes. It has been reported that irradiation of fluoro- and perfluoropolymers generates free radicals, and Florin⁹ invoked such radicals in the degradation of PTFE and crystalline copolymers of TFE during irradiation. Carezza and coworkers³² detected free-radical intermediates by electron spin resonance (ESR) spectroscopy during the irradiation of vinylidene fluoride/hexafluoropropylene elastomers. Irradiation of perfluoroelastomers also generate free radicals. This assumption is also supported by our experiment in which triallyl isocyanurate was added to the sample to be irradiated. It was observed that the cross-linking process became faster (Figs. 4, 5) and that better properties were obtained (Table V). This behavior resembles the chemical cross-linking of bromine-containing perfluoroelastomers with peroxides in which radical intermediates are known to be involved.^{26,27} Addition of triallyl isocyanurate makes the process more efficient. It appears that the free radicals formed on the perfluoroelastomeric chains are relatively stable and do not react readily with each other. However, these radicals, being strongly electrophilic, are quite reactive towards electron-rich olefin like triallyl isocyanurate by adding across the double bonds. Thus, the TAIC becomes part of and is incorporated in the cross-linked network.

Irradiation of perfluoroelastomer in air and vacuum gave approximately the same results. Since the evidence shows that radical intermediates are formed, one would expect that atmospheric oxygen would have some serious effect on the course of the reaction.^{31,32} We attribute the lack of oxygen effect to the fact that the samples subjected to irradiation were relatively thick (2–5 mm) and irradiated at relatively high intensity. The reaction of the radical intermediates with oxygen in such thick parts is diffusion-controlled; thus, the effect of air present during irradiation is minimal. Carezza et al.³² observed similar behaviour during Co-60 γ -irradiation of vinylidene/hexafluoropropylene elastomers. He found that irradiation of powdered samples at low dose rates showed significant differences when irradiated in vacuo (less scission and more cross-linking) than in air (more scission and less cross-linking). These differences practically disappeared when the powder samples were replaced with thicker samples (2–10 mm thick), and the

irradiation was carried out at higher doses per unit time.

SUMMARY AND CONCLUSIONS

In electron and γ -irradiation, the energy is high enough to cause ionization of the substrate molecules through ejection of electrons. The excited macromolecules thus formed eventually generate free-radical intermediates and ions, which, in turn, undergo chemical reactions that result in (a) side-chain scission, (b) main chain scission, and (c) cross-linking. There is little selectivity during irradiation because of the high energies involved. Thus, the presence of functional groups such as iodine, nitrile, bromine, hydrogen, and perfluorobenzene seem to have little noticeable effect on the properties of the crosslinked polymer. These functional groups remain unchanged and are observed on the crosslinked polymer after irradiation. The only change detected on the polymer is the formation of carboxylic acid end groups. Their origin appears to be from the polymeric acid fluorides formed initially, which slowly hydrolyze to the carboxylic acid functionality on exposure to atmospheric conditions. The most likely processes are shown in Figure 6. The side-chain scission produces mainly the volatile small molecules. The main-chain scission produces oligomeric and polymeric carbonyl fluorides, along with some gaseous small molecules. The crosslinks appear to be carbon-carbon bonds, as indicated by their stability toward aggressive chemicals (Table III) and even to elemental fluorine. In control experiments with chemically crosslinked samples, the fluorine attacked and destroyed the crosslinks, which were either triazines or hydrocarbons. We assume, therefore, that the irradiation-induced crosslinks are different from those formed by chemical means and most likely are C—C bonds, which are known to be stable to elemental fluorine.

Crystalline perfluoropolymers, like PTFE or copolymers of TFE with perfluoroalkyl vinyl ethers (Teflon[®] PFA) and with hexafluoropropylene (Teflon[®] FEP), show predominantly degradation due to main-chain scission when subjected to high energy irradiation. We attribute the difference between PTFE and perfluoroelastomeric polymers to the fact that the latter materials are amorphous and have a low glass-transition temperature (T_g , -5°C). Since the irradiations are carried out at room temperature, which is above the glass

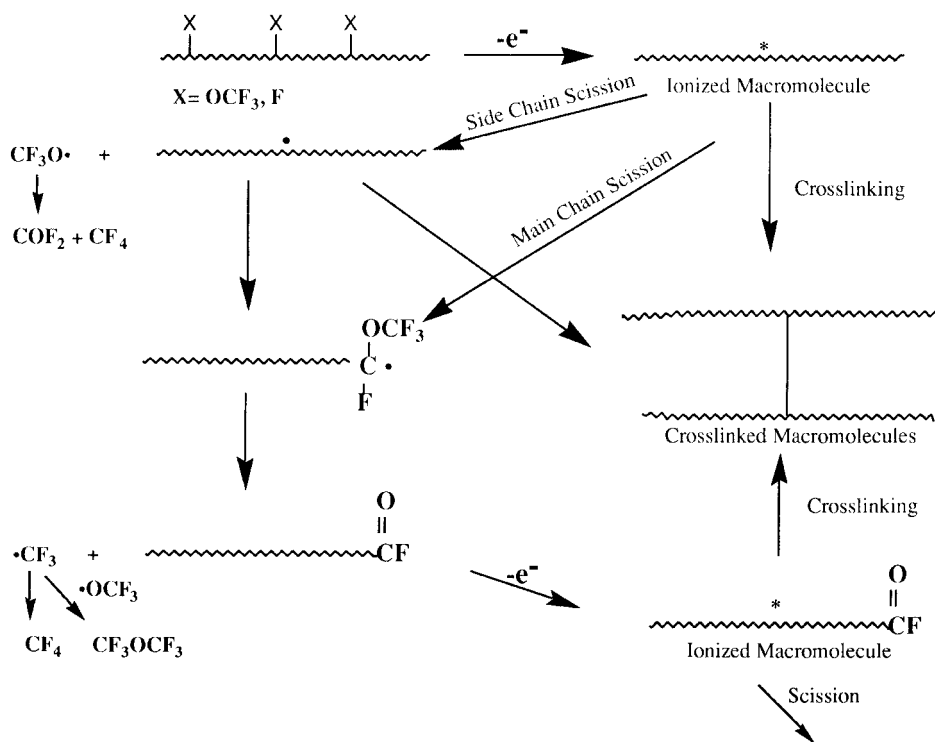


Figure 6 Proposed steps during the electron beam induced reactions leading to cross-linking and scission of TFE/PMVE copolymers.

transition temperature, the macromolecules are mobile and free to undergo molecular motions. Thus, the relatively stable free radicals generated on the backbone from the ionized macromolecules have a good chance to come to close proximity and couple with radicals from another macromolecule. The higher concentration of radicals present due to higher irradiation doses also maximizes cross-linking and minimizes scission.

The author wishes to thank Bruce Smart for numerous suggestions and discussions, John Legare for the chemical test evaluations, and Ta-Chen Mo for his valuable technical assistance. The author is very appreciative for the electron beam work carried out at the IBM laboratories by J. Pacansky and his coworkers and the Co-60 γ -irradiation work done by the group of the late Prof. J. H. O'Donnell at the University of Queensland, Brisbane, Australia, and for communicating to the author their preliminary results.

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Received May 30, 1996

Accepted June 25, 1996