

Radiation Degradation of Fluoropolymers: Carboxylated Fluoropolymers from Radiation Degradation in Presence of Air

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SYNOPSIS

Irradiation of PTFE by accelerated electrons in the presence of air gives rise to a carboxylated structures at doses above 50 kGy. The surface of the irradiated suspension polymerizate TF 1750 is more carboxylated than is the bulk. The influence of oxygen content and radicals is much higher than it is with the emulsion polymerizate TF 2025. The melting point of irradiated PTFE increases at low doses. Electron-beam irradiation of the fluorinated copolymers perfluoroalkoxy (PFA) and tetrafluoroethylene-hexafluoropropylene (FEP) leads to loss of fluorine. In all cases, the oxygen uptake was higher near the surface than in the bulk. PFA was better carboxylated than was FEP. The fact that cross-linking was not found to a measurable extent up to 800 kGy suggested that double-bond formation was important. The main effects of electron-beam irradiation are chain scission, oxidation, and unsaturation depending on dose rate, oxygen content, and particle size. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The poor bondability of perfluorocarbons in their native state is well known. This absence of specific interactions between perfluorinated polymers (PTFE) and other materials makes it also a good model polymer for studying the properties of surfactants, additives, and fillers. On the other hand, the resistance of fluorocarbon polymers to oxidation and reduction makes such polymers attractive candidates for application of high-energy radiation. PTFE's well-known sensitivity to radiation limits its use in many cases. Modification of PTFE films by vacuum ultraviolet radiation induces reduction in the water contact angle, probably as a result of cross-linking and desaturation of the linear polymer.¹ Plasma treatment of PTFE with air, oxygen, and water vapor causes modified surfaces that are more polar and have a higher surface energy. XPS spectra for the C1s region of PTFE indicates that the formation of CF₃ groups may occur.² Oxygen-

derived plasma species do not efficiently react with the surface radicals.

Soft X-rays introduce compositional changes to PTFE. Perfluoroalkenes and trifluoromethyl branches are observed from XPS C1s spectra³ and infrared spectroscopic data.⁴ No trend is found in the energy-dependent damage over the range 1–2.5 keV. Defluorination of the surface is the rate-determining step in electron beam-induced adsorption of nitrogen-containing species (ND₃).⁵ Irradiation of PTFE with 3 keV electrons damaged PTFE more near the surface than in the bulk. Saturated and unsaturated fluorocarbons are evolved from the surface. The degree of damage and weight loss depends on the dose rate.⁶

It was found that PTFE when exposed to UV light in the presence of a reducing agent became more hydrophilic. The reducing agents are good nucleophiles and many of them react with the unsaturated part of PTFE.⁷ PTFE can be carboxylated by reduction with dipotassium benzoate dianion.⁸

The treatment of PTFE surfaces with Na/naphthalene and alkali metals in liquid ammonia in a reduction process leads to an unsaturated and partially oxidized surface.^{9,10} The reduced surface is hy-

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drophilic with much improved adhesion but is also sensitive to moisture and light.

When irradiated with high-energy radiation, such as gamma rays, PTFE undergoes scission of the polymer backbone.¹¹ The degree of crystallinity, determined from X-ray analysis, increases with the radiation dose at low and moderate dosages and decreases at a radiation dose above 3 MGy, this being associated with a disordering of the crystallites.¹²

The effect of gamma or electron-beam irradiation on tetrafluoroethylene-hexafluoropropylene copolymers (FEP) is degradative. In the absence of air, low-dose irradiation at temperatures above 150°C results in cross-linking.¹³ Perfluoroalkoxy resins (PFA) have the same rate of degradation as do PTFE resins (30–100 kGy) in air. High-energy irradiation effects take place at doses of about 500 kGy.¹⁴

In the following, we report a convenient two-step radiation procedure to introduce stable carboxylic acid groups to fluoropolymers: First, we obtained a small-sized micropowder from radiation-induced degradation of PTFE with stable end groups and different chemical and physical properties or carboxylated copolymers from degradation of perfluorinated copolymers and, second, use of higher-energy doses in the procedure led to ionomers. A thin layer of carboxylic acids near the surface was connected with a chemically inert, nonswellable polymer. Further reactions can be carried out to prepare esters, amides, and so on.

The work reported here involved an investigation of the influence of beta irradiation in presence of air on virgin emulsion and suspension grade of PTFE. The purpose of this study was to describe the response of a range of fluoropolymer structures to beta rays (50–1000 kGy), so as to understand better the role of chemical structure, particle size, and dose-dependence. A future paper will then attempt to investigate the influence of gamma rays and higher-energy doses on fluoropolymers.

EXPERIMENTAL

The experiments were performed with an electron-beam accelerator ELT 1.5 in the presence of air. We used a transport system. The samples were bombarded with electrons at 1.0 keV and 4.0 mA.

The fluoropolymers were irradiated in the dose range from 0.7 to 200 kGy in one step. Higher doses up to 1 MGy were applied on a step-by-step basis using 0.2 MGy each time.

Gamma irradiation with doses ranging from 100 to 400 kGy was carried out at room temperature in the presence of air in a ⁶⁰Co source. The dose rate was 0.25 kGy h⁻¹. FTIR measurements were made on a Nicolett 510 and a IFS 66 (Bruker). All spectra were obtained using cold-pressed samples of PTFE and hot-pressed sheets of copolymers.

DSC was used to investigate changes in melting and recrystallization behavior with irradiation. Measurements done on both a Perkin-Elmer DSC 2 off-line computer coupled for data analysis and a Perkin-Elmer DSC 4 with the thermal analysis data station, which were calibrated with In and Pb standards [temperature range of measurements: 200–360°C; cycle: (1) heat-cool, (2) heat; scanning rate: 10 K/min, sphere: pure nitrogen; sample weight: about 6.2 mg for beta-irradiated micropowders]. For the qualitative estimation of the change in molecular weight M_w of irradiated PTFE, we used the correlation between heat of recrystallization $|\Delta H_c|$ and M_w . Suwa et al.¹⁵ found that the heat of recrystallization increases with decreasing M_w in a limited range. We determined the value of $|\Delta H_c|$ from data of cooling thermograms in the temperature range between 247 and 322°C. To characterize the melting behavior of irradiated modified PTFE, we used the peak temperature T_{max} of the second heating scan.

Electron spin resonance spectra of electron-beam irradiated PTFE were obtained from both irradiated and irradiated annealed samples (350°C, 5 min). The wettability of PTFE films was assessed using a modified contact angle meter G1 (Krüss GmbH). Sessile contact angles were measured on cold-pressed material above the transition temperature of 19°C. All data were obtained from samples treated for 60 s. X-ray diffraction patterns of irradiated samples were determined by comparing the area under the principal crystalline diffraction peak to the area of the broad amorphous background on an HZG-4 (Präzisionsmechanik Freiberg GmbH).

Specimen's

The virgin PTFE used in all experiments reported here were Russian Ftoroplast 4 D; TF 2025, TF 2071 (emulsion polymerizate) or TF 1700, and TF 1750 (suspension polymerizate), were kindly supplied by HOECHST AG HOSTAFLO. In addition, work was done on fluorinated ethylene propylene (FEP 6107) and perfluoroalkoxy copolymers (PFA 6515). After irradiation, the polymers were wetted with acetone/water and dried and heated (200°C, 60 min). A press was used to obtain 0.120–0.200 mm-

thick cold-pressed sheets from unsintered PTFE for analytical purposes. Measurements were made at 21–25°C.

RESULTS AND DISCUSSION

Degradation of PTFE

The PTFE may be regarded as consisting of crystalline and amorphous regions. PTFE is degraded by doses higher than 100 Gy. The decrease of molecular weight can be accompanied by a decrease of melt viscosity and melting points as well as by an increase in the specific weight.

When C—C bonds in PTFE-polymer chains are broken by β -irradiation, pairs of chain ends generated in the crystalline fraction are hindered from moving away by neighboring molecules. Pairs of radicals very likely recombine. Radicals in the amorphous fraction recombine less often because of the relatively loose packing of molecules. Scission of main chains is to be expected in the amorphous fraction. Radiation of PTFE yields perfluoroalkyl radicals. In successive reactions, terminal as well as internal peroxy and oxy radicals can be formed if oxygen is present.

Golden,¹⁶ Hagiwara et al.,¹⁷ and Lunkwitz¹⁸ suggest the following mechanism (Fig. 1): At the particle surface, the terminal perfluoro radical is specifically and gradually degraded via an intermediate of the peroxy or oxy radical, respectively, to shorter chains and carbon difluoride. Both perfluorocarbonyl fluoride and a terminal perfluoroalkyl radical are formed from the internal radical by carbon-carbon scission. The scission of the internal peroxy radical and the formation of carboxylic fluoride end groups have been proved by Hagiwara et al.¹⁷ using mass spectroscopy and infrared spectroscopy. Electron spin resonance spectra of electron-beam-irradiated PTFE in vacuum show typical peaks of primary and secondary radicals.^{19,20}

Sufficiently high-energy flux-density accelerates the degradation of PTFE to such a degree that oxygen cannot be provided fast enough in the inner parts of the polymer. That means that carboxylation takes place mainly near surface regions. Furthermore, internal radicals in crystalline regions are able to recombine because of their hindered mobility. X-ray diffraction patterns combined with other methods have shown^{12,21–23} that at low irradiation doses. The crystallinity of PTFE increases due to main-chain scission in the amorphous region of the ma-

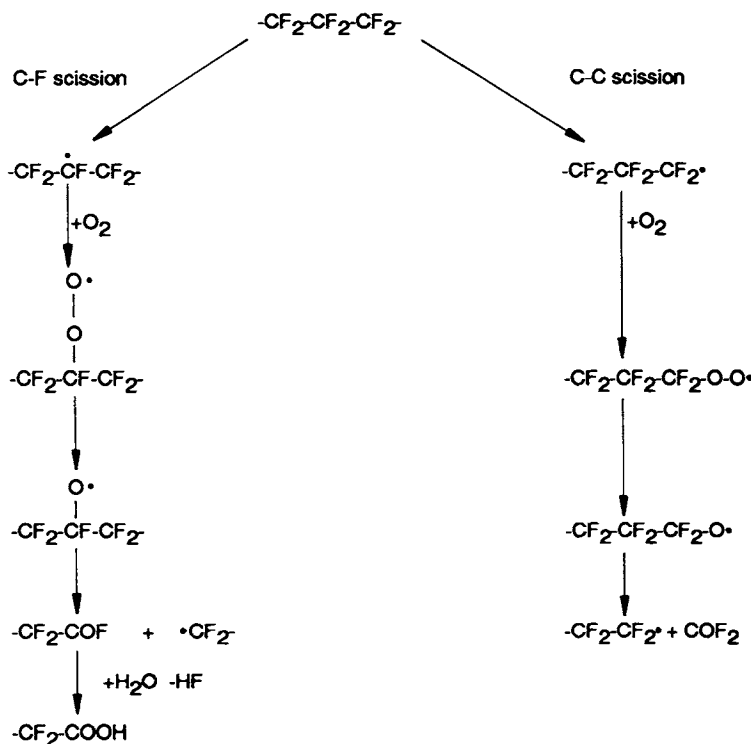


Figure 1 Degradation of PTFE by electron irradiation in air.

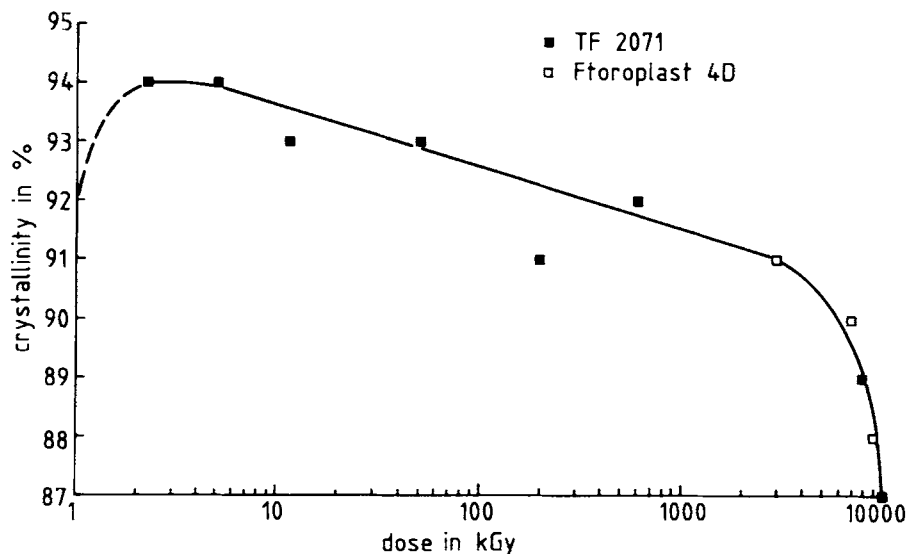


Figure 2 Crystallinity of PTFE (emulsion grade) electron irradiated in air obtained from X-ray diffraction analysis as a function of radiation dose.

terial. Our X-ray investigations showed an increase in crystallinity from 91% (nonirradiated PTFE) to 94% (at dose of 5–7 kGy) for the TF 2071 sample. Later, crystallinity gradually decreased at radiation doses up to 2 MGy connected with enhanced lattice defects in the crystallites. Above 2 MGy, crystallinity decreases more strongly with rising doses (Fig. 2).

The FTIR absorption band at 780 cm^{-1} characterizes the amorphous part of PTFE samples and has been widely adopted in analytical determination of the amorphous content of PTFE. Rabolt²⁴ found an increasing intensity of this band at doses > 900 kGy. The amorphous content of PTFE can be estimated using the relation

$$\text{amorphous content (in \%)} = 30.26a + 1.73a^2$$

(a = absorption at 780 cm^{-1} /absorption at 2370 cm^{-1} ; the band at 2370 cm^{-1} is a nonspecific band and was used for normalization). Table I lists the dose and amorphous content of TF 2025 samples used in this work.

Table I Amorphous Content in β -Irradiated TF 2025

	Dose (kGy)								
	1	5	11	50	100	300	600	800	900
Content (%)	2.7	2.6	2.7	2.6	2.9	2.3	2.4	2.6	2.7

Upon measuring the A_{780}/A_{2370} ratio for the irradiated samples, we did not obtain a qualitative correlation. The values of crystallinity estimated with the help of infrared measurements were higher than the values found in X-ray investigations. Although various emulsion polymerizates were used (TF2025 at FTIR, TF2071 at X-ray), the difference was presumably caused by the errors and particularities of methods. A broadening of the amorphous band at higher dose rates and rising carboxylation also complicated the determination of the peak absorbance ratio.

Investigations of recrystallization behavior of irradiated and molten PTFE give information on the change in the M_w distribution. Figures 3 and 4 show the heat of recrystallization $|\Delta H_c|$ dependence on dose for emulsion and suspension polymerizates, respectively. In these half-logarithmic diagrams, we observed a linear correlation between crystallinity and dose at doses less than 7–10 kGy. The increasing crystallinity corresponds to a decrease of M_w .¹⁵ The values of $|\Delta H_c|$ increase weakly for further rising doses and achieve a maximum at a dose in the range of 200–600 kGy. This result correlates with the change in the total spin concentration for emulsion polymerizates (see below).

The peak temperature T_{max} determined in the second heat scan shows a maximum of dependence on the dose for each polymerizate (see Fig. 5). For sample TF1750, this temperature achieves, at a dose of about 60 kGy, a maximum value of 329°C , which is 5 K higher than the T_{max} of nonirradiated molten

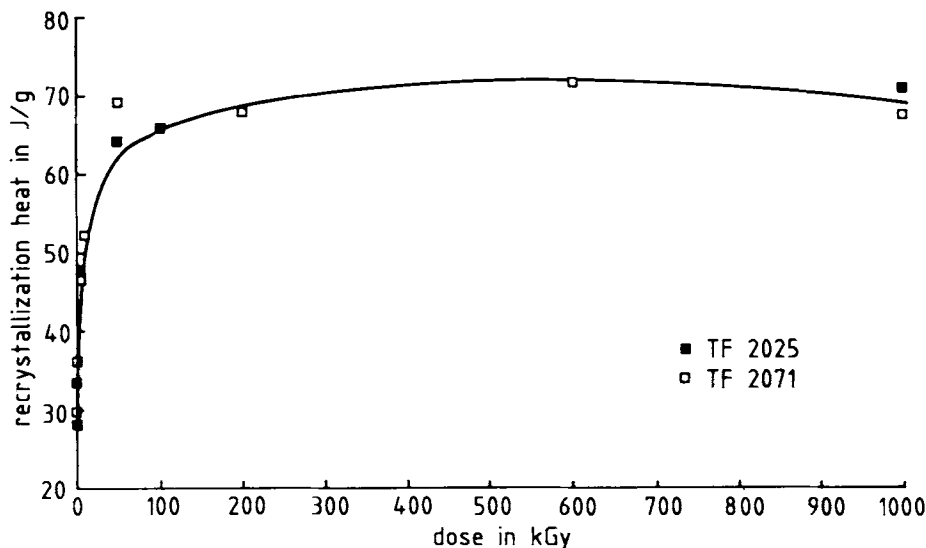


Figure 3 Heat of recrystallization $|\Delta H_c|$ of PTFE (emulsion grade) electron irradiated in air as a function of radiation dose.

PTFE. In the beginning, the increasing temperature T_{\max} correlates with increasing crystallinity. At higher doses, the crystallinity increases further, but T_{\max} and also the height of the melting peak decrease. We simultaneously observed a broadening of the low-temperature side of the melting peak as a result of a broadening of M_w distribution at high irradiation dose. This change in melting behavior increases strongly with further increasing doses.

It seemed possible for us to use ESR investigations of micropowders to follow the changes in rad-

ical concentration during radiation and the total radical concentration. To obtain the spin concentration, we used a single crystal of ruby as a secondary standard. We determined the total number of spins on samples directly after irradiation and also after annealing of the micropowders (5 min at 350°C). As expected, the spin concentrations rose in both TF2025 and TF1750 with increasing radiation dose (see Table II). Apparently, a maximum value in radical concentration exists at 600 kGy for emulsion polymerizate. Comparison of the carbox-

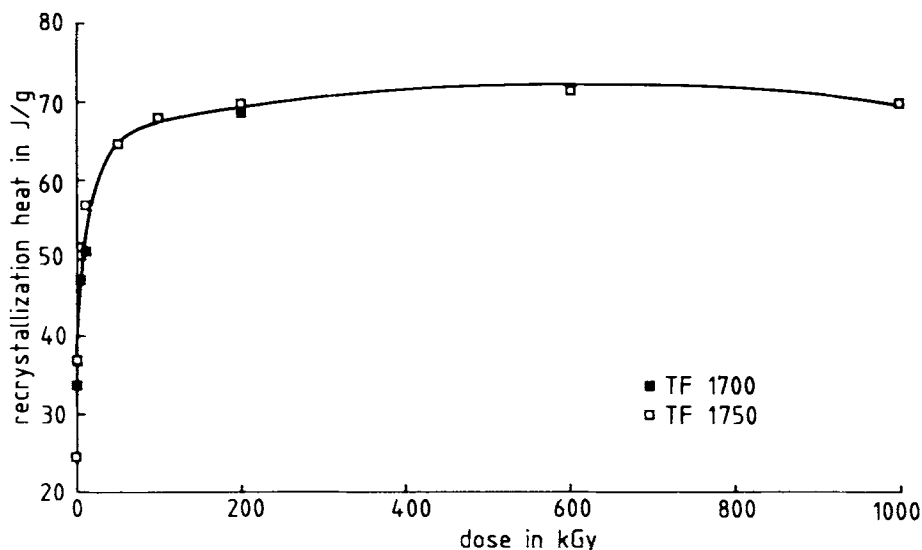


Figure 4 Heat of recrystallization $|\Delta H_c|$ of PTFE (suspension grade) electron irradiated in air as a function of radiation dose.

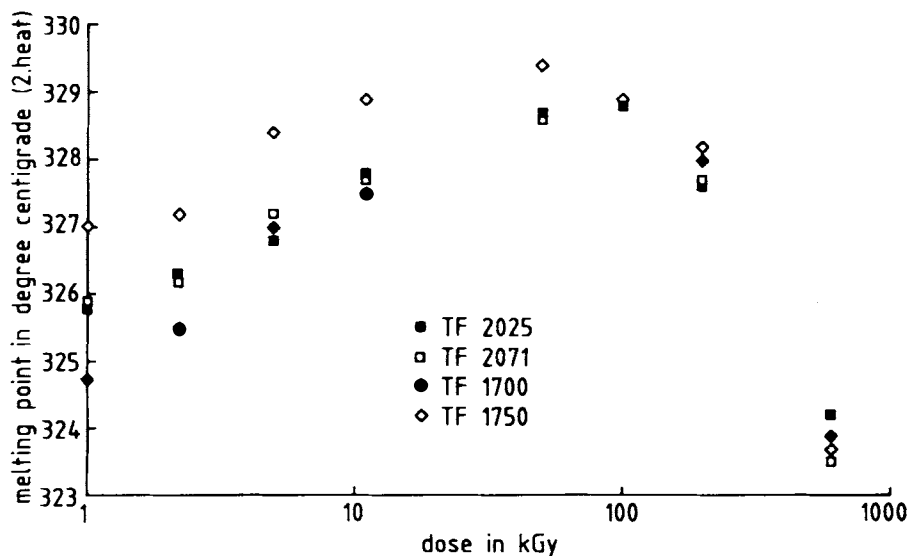


Figure 5 Temperature of melting point (determined in second heating) of PTFE electron irradiated in air as a function of radiation dose.

ylic acid content of the micropowders, which is a result of radical interaction, allows the finding of the following correlations:

- Rising radical concentration increases incorporation of COF end groups.
- TF 1750 shows at 1000 kGy a higher ion-exchange capacity than does TF 2025.
- Furthermore, an increasing spin number allows more internal COF groups to be incorporated in the molecule. These end groups are stable against hydrolysis (reaction with water and alkali); they are embedded in inaccessible regions of the polymer matrix.

- Surface reactions seem to be dominant with suspension micropowders since hydrolysis minimizes the COF content drastically and the total spin number decreases more rapidly by annealing.

In the previous work, we estimated the total radical concentration and observed a long lifetime of several years for the radicals. The recent results indicated that the total radical concentration drastically influences the interaction with other molecules (oxygen, gases, inhibitors) and changes in mechanical properties to a certain extent occur.²⁵ Fisher and Corelli²⁶ claim that the rise in melting viscosity at

Table II Radical Concentration as Function of Irradiation Dose and Annealing Temperature

PTFE (dose in kGy)	Total Spin No. per g PTFE	Total Spin No. after Heat	COF Content per 10 ⁶ C	Ion-exchange Capacity (IEC) ^a
TF1750-1000	2.6×10^{18}	2.6×10^{16}	40	0.008
-600	1.8×10^{18}	1.8×10^{16}	20	
-200	7.7×10^{17}	1.2×10^{17}	20	
-100	5.1×10^{17}	1.7×10^{16}	20	
-0	$< 10^{13}$			
TF2025-1000	1.9×10^{18}	4.8×10^{17}	540	0.005
-600	2.2×10^{18}	4.4×10^{15}	250	
-200	9.9×10^{17}	1.5×10^{17}	100	
-100	4.0×10^{17}	1.6×10^{17}	40	
-0	$< 10^{13}$			

^a Per gram polymer in mmol.

Table III FTIR Spectra of β -Irradiated PTFE

Frequency (cm^{-1})	Assignment	Calibration Factor ²⁷
3570	O—H, isolated	
3100	O—H, associated	
2370	C—F, overtone	
1885	C=O, COF	406
1810	C=O COOH, isolated	335
1790	C=C CF=CF ₂	635
1770-80	C=O COOH, associated	320

radiation doses between 25 and 50 kGy is connected with the formation of cross-links and branches. Tetrafluoroethylene is eliminated. This leads to branching with radicals. Our FTIR spectra indicate that carboxylation, beginning at radiation doses above 50 kGy, is a competitive reaction.

The spectrum of damaged samples (Table III) showed in addition to the bands of virgin PTFE the following vibrational components: In the IR spectrum, we see characteristic C=O carbon-oxygen stretching vibrations partially associated via hydrogen bridges. Rising energy dose causes rising concentration of carbonyl groups in TF 1750-600 kGy compared to nonirradiated TF 1750 (see Fig. 6). In the IR spectrum, the band intensities of both the associated and the isolated groups grow. At high dose values (more than 800 kGy), associated groups dominate.

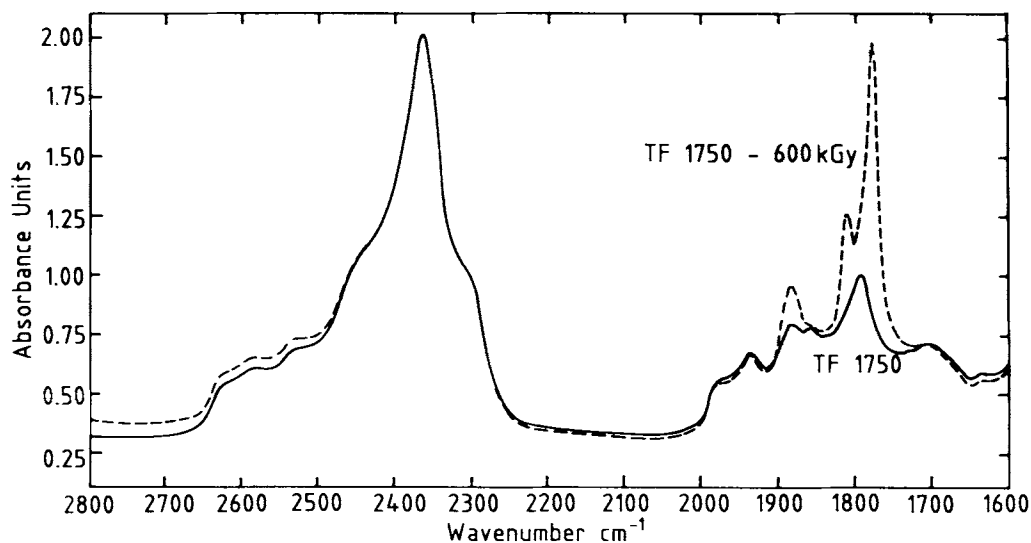
Furthermore, the association behavior suggests that there are definite phases of both carboxylated end groups and fluorocarbon structures in the polymer. When comparing FTIR spectra of the micropowders with increasing energy dose, the integral ratio (quotient of band absorption of the C=O stretching vibration and nonspecific C—F overtone) reflects the rise of carboxylation. S-TF1750 shows a higher degree of carboxylation than does E-TF2025 above 200 kGy (see also Fig. 7).

With rising energy dose, the concentration of carboxyl groups in the micropowder increases and causes rising of the free surface energy. But, mainly, the polar term of the free surface energy is changed, while the dispersion term remains nearly the same. That means that radiation-chemically carboxylated micropowders retain essential properties of PTFE. The degree of carboxylation affects interactions.

γ -Irradiation of PTFE with a comparable energy dose leads mainly to degradation of the polymer. The end groups in a fluorocarbon polymer are determined from the infrared spectrum of compression films.²⁷ We used this technique on cold-pressed films of PTFE. Using a calibration factor and the following mathematical equation, we obtained end group values in terms of ends per 10^6 carbon atoms:

$$\text{End groups} = \text{absorbance} \times \text{CF/film thickness} \\ (\text{film thickness in mm, end groups} \\ \text{per } 10^6 \text{ C atoms})$$

Some peaks interfere with others. Corrections have been developed²⁷ (— COOH associated and

**Figure 6** FTIR spectra of TF 1750 and carboxylated TF 1750 (600 kGy).

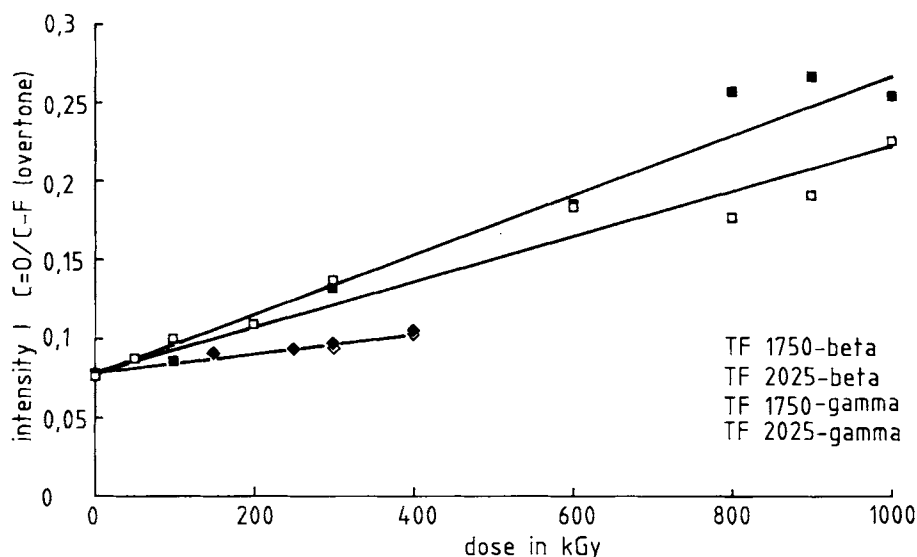


Figure 7 Intensity of FTIR bands of carboxyl group of PTFE irradiated in air as a function of the radiation dose (limits: C—F overtone 2690–2200 cm^{-1} ; C=O 1900–1750 cm^{-1}).

—CF=CF₂, but irradiated PTFE shows no terminal olefins up to radiation dose of 1 MGy). Our results given in the Table IV are in the same order of magnitude obtained by other techniques for doses of 600–1000 kGy.²⁸ We observed in this dose range a maximum of $|\Delta H_c|$ and of total spin number connected with a maximum of isolated carboxylic end groups. With rising dose rates, an association behavior is detected: The polymer changes its structure.

The change in surface energy with β -irradiation treatment was assessed by measurement of the sessile contact angle. Untreated PTFE showed a contact angle of 109° (± 3) to water. In all cases of increasing dose, the contact angle was reduced (Fig. 8). The treated PTFE surface showed different behavior. TF 1750 provided a substantial increase in the polar content of the surface energy (see also carboxylic acid content).

Motions of short-chain molecules took place in annealing of the PTFE sample occurring during irradiation and in a separate following annealing process. Local rearrangement of the short-chain molecules and diffusion to the surface in combination with increased carboxylic content results in less decreased contact angle than expected with increasing radiation dose. DSC measurements showed also a broadening of the melting range of PTFE at doses up to about 100 kGy. This behavior will be discussed in a following paper. Some special properties of β -irradiated micropowders are given in Table V. The melt flow index (MFI) of micropowders irradiated at 600 kGy became too high for measurements (see also dynamic measurements of melt viscosity^{29,30}). This high radiation dose value is interesting for carboxylation reactions to reduce the hydrophobicity and to change the electrophoretic mobility³¹ of the perfluorinated particles. The carboxylated surface

Table IV End-group Analysis of PTFE

PTFE	COF	COOH, Monomer	COOH, Dimer	Sum	M_n	M_n , Brady ²⁸
TF2025-50	56	44	57	157	320,000	
-100	74	61	86	221	230,000	
-300	174	170	324	668	75,000	
-600	247	299	714	1260	40,000	35,000
-800	372	358	916	1646	30,000	21,000
-1000	541	259	900	1700	14,000	

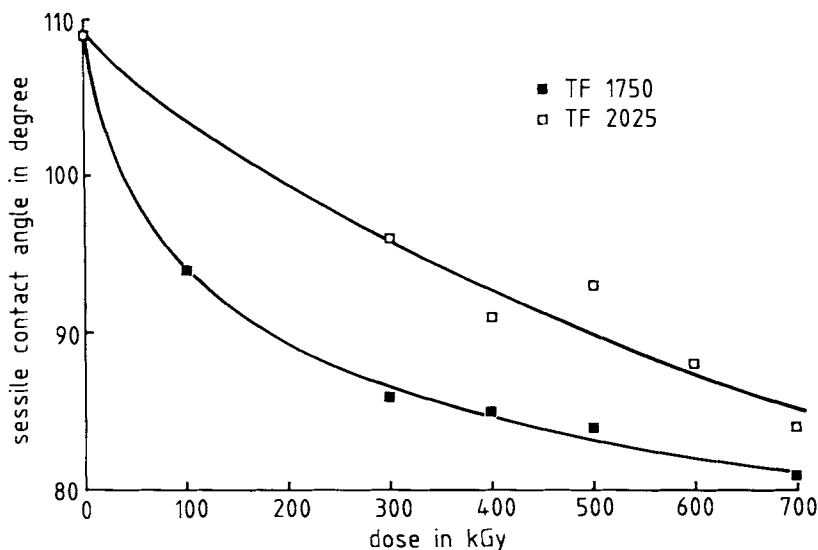


Figure 8 Sessile contact angle of cold-pressed PTFE samples electron irradiated in air as a function of radiation dose.

of the micropowders was acidic relative to unmodified PTFE. TF 2025 consists of smaller agglomerates of particles after irradiation than does virgin PTFE. A reduction of molecular weight is connected with a carboxylation process step by step with increasing dose. The specific surface area of unmilled polymer is not varied.

CONCLUSIONS

C—C bonds in PTFE are broken by β -irradiation. A cage effect caused by neighboring chains hinders radicals generated in the crystalline fraction to move away. Radicals are likely to recombine.³² Annealing of PTFE increases this behavior of radical reactions.

Table V Properties of β -Irradiated Micropowders

Micropowder-Dose (kGy)	Particle Size (μm)	Specific Surface Area (m^2/g)	Melt Flow Rate (g, 645 K, 2.16 kp, 10 min)
Radiation			
TF1750-100	24	2.7	—
-200	22	2.7	—
-300	19	2.1	1.6
-400	15	2.9	5.9
-500	13	2.4	30.7
-600	11	2.8	Too high
-700	10	1.9	
-900	9	2.3	
-1000	7	2.7	
TF2025-100	6	8.6	—
-200	8	8.9	—
-300	3	8.8	3.4
-400	4	9.7	3.1
-500	4	8.3	12.7
-600	4	5.6	28
-700	4	10.5	Too high
-900	4	8.5	
-1000	4	10.2	

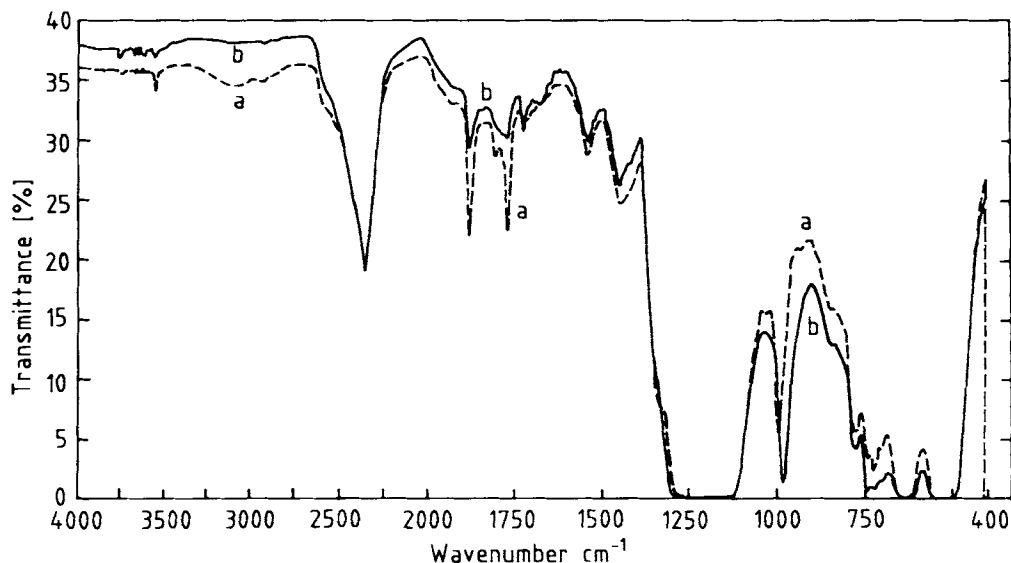


Figure 9 FTIR spectra of carboxylated copolymers: (a) FEP, 1000 kGy; (b) PFA, 1000 kGy.

Scission of main chains is observed in the amorphous fractions. The analysis of recrystallization behavior of PTFE, irradiated and molten, points out that the increase of $|\Delta H_c|$ and, thus, of the crystallinity is proportion to the logarithmic value of dose for all samples of β -irradiated PTFE powders. According to Suwa et al.¹⁵ an analogous relation is, consequently, valid for the decrease of M_w . The analytical data indicates the development of a carboxylated structure at about 50 kGy. The melting point of PTFE β -irradiated in air increases at low doses. The surface of irradiated suspension polymerizate TF 1750 is more carboxylated than in the bulk. The influence of oxygen content and radicals is much higher than by emulsion polymerizate TF 2025. The oxygen content in air near the TF 1750 surface (specific surface area 2 m²/g) is enough for sufficient carboxylation reactions during the radiation process. The high specific surface area and content of free radicals in TF 2025 after irradiation and annealing indicate an oxygen deficit during irradiation at dose of 200 kGy. The gas evolved during the process is considered to consist of COF₂ and oligomers with low molecular weight (1000 kGy: 2% weight loss). Furthermore, the association behavior of carboxylic end groups suggests that there are definite phases of both carboxylated end groups and fluorocarbon structures in the polymer matrix. The thermal instability of β -irradiated PTFE is evident. Radical reactions and decarboxylation at about 230°C evolve fragments from the surface.

Degradation of Perfluorinated Copolymers

The investigations reported here involve the modification of tetrafluoroethylene-hexafluoropropylene copolymers (FEP) and perfluoroalkoxy resins (PFA) in granular form by exposure to radiation degradation in air. Comparing FTIR spectra of hot-pressed sheets of copolymers in the dose range from 0.2 to 5 MGy, we observed that PFA can be better surface oxidized under the same irradiation conditions (Fig. 9). From the spectra we conclude that C=C bonds are formed by electron irradiation treatment of FEP. These tendencies to form oxygen-containing species on the surface or unsaturations are marked distinctly at about 0.2 MGy (Table VI).

The first step of degradation probably involves the breakage of C—F or C—C bonds (see Fig. 1) that occur by accelerated electrons, resulting in splitting off of fluorine atoms, trifluoromethyl rad-

Table VI FTIR Spectral Peaks Due to the Degradation of Perfluorinated Copolymers in Air

Assignment	PFA ν (cm ⁻¹)	FEP ν (cm ⁻¹)
OH isolated	3557	3556
OH associated	3096	3096
COF	1884	1884
COOH dimer	1775	1775
CF=CF	1718	1718

Table VII End-group Analysis from Spectral Peaks Observed

Polymer-Dose (kGy)	COF Per 10 ⁶ C Atoms	COOH-M Per 10 ⁶ C Atoms	COOH-D Per 10 ⁶ C Atoms	Sum
Radiation				
FEP-200	100	—	51	151
-400	154	—	63	217
-600	180	—	105	285
-1000	168	—	135	303
PFA-200	246	163	244	653
-400	207	184	250	641
-600	345	239	300	884
-1000	754	342	386	1482

icals, and formation of carbon-centered radicals. This process is followed by a reorganization step.

Two carbon radicals are bound mainly to each other (recombination). Another possibility is the disproportionation reaction that yields saturated and unsaturated species. Terminal olefins can change their position about a F⁻-supported migration into internal olefins. This reaction is known from many branched or unbranched fluoroolefins.³³ The defluorination step indicates various pathways:

1. — $\dot{C}F$ — radicals react with oxygen-containing species near the surface.
2. The recombination of carbon-centered radicals leads to C=C bonds if they are neighboring or form cross-linkings.

Our FTIR spectra showed that surface radicals are expected to react rapidly with oxygen and form COF groups. This process is dependent on the particle size, the oxygen content, and the radiation dose. We observed that in the bulk of the fluoropolymers recombination reactions and unsaturations dominate because of lower oxygen content.

FEP undergoes more unsaturation during irradiation. The trifluoromethyl group stabilizes the formation of internal or terminal olefins (see also dehalogenation reactions of partially fluorinated copolymers³⁴).

The spectra of the two homopolymers give information about their relative sensitivity to β -irradiation. On the other hand, we observed a high content of unsaturation at low doses from radical reactions

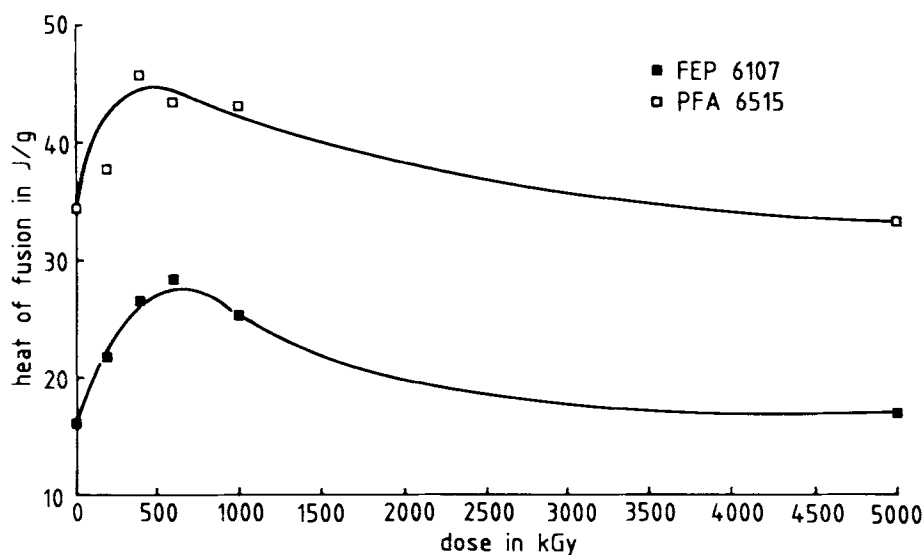


Figure 10 Heat of fusion $|\Delta H_f|$, determined in first heating of copolymers electron irradiated in air as a function of radiation dose (temperature limits of calculation of $|\Delta H_f|$: PFA: 210–320°C; FEP: 161–284°C).

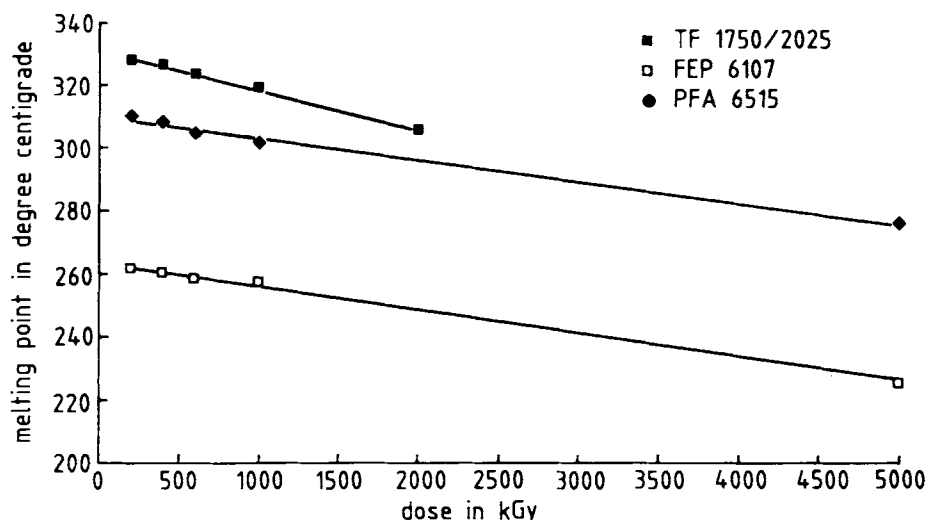


Figure 11 Temperature of melting point (determined in first heating) of polymers electron irradiated in air as a function of radiation dose.

in the inner part of the particle. This effect depends on the particle size and can also be observed if one uses PTFE scrape or a granular resin with a particle size at about 0.5 mm.

The most important reactions are the oxidation near surface regions and unsaturation in the bulk of the polymer. The different carboxylation ratio is shown in Table VII. End-group determination was carried out according Buckmaster and Alan²⁷ from the IR spectra. The concentration of carboxylic end groups in PFA increases with rising radiation dose. Partially degraded FEP copolymers showed a very low content of isolated carboxylic groups. Appearance of C=C groups correlates with the decrease of O₂ content in the bulk. Although corrections have

been developed, we could not estimate the C=C concentration because irradiated FEP showed too different olefinic structures.

It is easy to understand that the morphology of semicrystalline perfluorinated copolymers will be changed if irradiation takes place. Figure 10 shows fusion heat $|\Delta H_f|$ from copolymers (rate: 20 K/min) in dependence on the dose. We observed in the dose range from 0 to 600–800 kGy an increase in the fusion heat with rising dose. It seems that β -irradiation can increase the crystallinity of perfluorinated copolymers like PTFE. The recrystallization heat or fusion heat of all β -irradiated samples exhibit a maximum value. The value at which the maximum appears (FEP: 600 kGy; PFA: 800

Table VIII Properties of β -Irradiated Perfluorinated Copolymers

Polymer-Dose (kGy)	Melting Temperature (°C)	MFI in 10 min, 372°C, 5 kg	Weight Loss at 300°C (%)	Hydrolyzable F ⁻ Per g Polymer
Radiation				
FEP-200	261.9	62	—	0.0078
-400	260.6	166	0.31	0.0094
-600	258.9	Too high	0.20	0.0079
-1000	257.6		0.59	0.0130
-5000	225.4			0.0290
PFA-200	310.0	62	—	0.0069
-400	308.5	265	0.71	0.0079
-600	304.8	Too high	0.74	0.0130
-1000	301.8		1.17	0.0015
-5000	276.3			0.0230

kGy) is polymer-dependent. In comparison with PTFE, the copolymers showed lower values, indicating a lower crystallinity of the copolymers.

The melting point (T_{\max}) is also dose-dependent. We observed a continuous decrease of T_{\max} with rising dose up to 5000 kGy (Fig. 11). The decrease is a linear function and it seems possible to develop a mathematical correlation among molecular weight, end groups, and T_{\max} .

The present results indicate the same radiation degradation effects comparing β -irradiation of PTFE. Degree of degradation, crystallinity, spin concentration, and carboxylation reactions can be influenced by the dose. It can be concluded from the discussion that radiation degradation and carboxylation are the predominant reactions. Tetrafluoroethylene segments in the chain lead to $-\text{CF}-$ radicals during irradiation, which influence, in dependence on oxygen concentration, neighboring groups, temperature, radiation dose, and particle size, the radiation degradation process. The surface energy of fluoropolymers will be changed. It is evident that with increasing irradiation dose in air the melting point and the melt flow index (Table VIII) decrease rapidly, which means that cross-linking reactions can be ignored.

CONCLUSIONS

We concluded that it is feasible to surface modify perfluorinated copolymers in air with the help of an electron accelerator using a transport system at reasonable speeds. FTIR data indicated that the electron beam leads to loss of fluorine from all copolymers. In all cases, the amount of oxygen uptake near the surface was higher than in the bulk. PFA was better carboxylated than was FEP. The absence of a measurable content of cross-linking up to 800 kGy suggested that double-bond formation was important. The main effect of electron-beam irradiation is chain scission, oxidation, and unsaturation. It depends on dose rate, oxygen content, and particle size.

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