Studies on γ-Radiation Treatment of Poly(tetrafluoroethylene) Powder

K. LUNKWITZ, W. BÜRGER, U. GEIßLER, A. PETR, and D. JEHNICHEN

Institute of Polymer Research Dresden e. V., PO Box 120411, Hohe Str. 6, 01069 Dresden, Germany

SYNOPSIS

γ-Irradiation of poly(tetrafluoroethylene) (PTFE) in the presence of air results in degradation of polymer chains by insertion of oxygen. At first, in the low-dose range below 400 kGy, a rise in crystallinity can be observed due to main chain scission in the amorphous part of the macromolecules. Dose increase up to approximately 1000 kGy causes progressive degradation of molecular weight as well as a growing degree of carboxylation of PTFE and increased concentration of trifluoromethyl groups in near-surface regions. At constant irradiation temperature, the properties of irradiated PTFE hardly depend on dose rate and starting material. The degree of carboxylation of the irradiated unsintered PTFE is appreciably lower in comparison with electron-irradiated PTFE under comparable conditions. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The technical polymer PTFE can be applied and used variably in a wide temperature range due to its chemical consistency and broad applicability. Unfortunately, PTFE is very sensitive to irradiation; high-energy radiation causes degradation of PTFE and embrittlement by losing mechanical properties such as tensile strength and elongation at the break.[1] This fact restricts the application of the polymer if it is directly exposed to high-energy radiation sources (e.g., nuclear power stations, electron beam sources, etc.). Alternative sterilization techniques, even for one-cycle sterilization, have to be used for PTFE-based medical products.

Electron irradiation at room temperature causes chain degradation in PTFE and, in the presence of O_2, carboxylation of the macromolecules.[2] In a vacuum[3] [e.g., during electron spectroscopy for chemical analysis (ESCA) or scanning electron microscopy[4]], electrons are able to initiate defluorination reactions at the PTFE surface. The formation of a surface layer similar to graphite can be observed. Recently, it has been reported that PTFE tends to cross-link above its melting point under the influence of electron irradiation.[5] This fact is disputed[6] and needs further investigation.

Today, γ-radiation is used preferably to recycle PTFE materials.[7] Investigations concerning the influence of temperature and irradiation dose on PTFE have been performed. Zhong et al.[8,9] investigated the influence of γ-rays on sintered PTFE films in the temperature range of 75–220°C and the dose range of 20–260 kGy. They found a maximum for the first heat of fusion. With these findings, they discussed possible cross-linking of the molecules at a higher irradiation dose in addition to degradation of the macromolecules. Chipara[10] did not find a distinct dependence of the properties on irradiated, sintered and irradiated, or filled and sintered PTFE materials on dose rate in the dose range of 10–100 kGy. However, an increased degradation of molar mass to form peroxy radicals can be found in presence of O_2. Investigations concerning crystallinity and dependence of the thermal expansion coefficients on irradiation dose at constant dose rate have been performed by Subrahmanyan.[11] Rabolt[12] investigated the influence of γ-irradiation to unsintered Teflon 7A; he found a decrease of crystallinity with rising irradiation dose in the dose range of 500–10,000 kGy. This effect is connected with a strong low-temperature shift of the phase transition at

Table I   Radical Concentration as a Function of Irradiation Dose (8 kGy/h) and Annealing Temperature

PTFE Grade (Dose in kGy)	Total Spin No. per g PTFE	Total Spin No. per g PTFE after Heat	Total Spin No. per g PTFE[13]
TF 1750-1000	2.6×10^{18}	2.2×10^{17}	2.6×10^{18}
TF 1750-600	2.2×10^{18}	2.3×10^{17}	1.8×10^{18}
TF 1750-200	6.4×10^{17}	1.4×10^{16}	7.7×10^{17}
TF 1750-100	3.7×10^{17}	1.2×10^{16}	5.1×10^{17}
TF 1750-0	$<10^{13}$	$<10^{13}$	$<10^{13}$
TF 2025-1000	2.5×10^{18}	3.7×10^{17}	1.9×10^{18}
TF 2025-600	2.3×10^{18}	4.2×10^{17}	2.2×10^{18}
TF 2025-200	1.1×10^{18}	5.0×10^{16}	9.9×10^{17}
TF 2025-100	6.1×10^{17}	1.0×10^{17}	4.0×10^{17}
TF 2025-0	$<10^{13}$	$<10^{13}$	$<10^{13}$

19°C and therefore can be observed using Raman spectroscopy.

Pure PTFE is offered commercially as suspension and emulsion polymerizate, sintered PTFE semifinished product, and stretched membrane material. Thus, various materials due to thermal pretreatment must be considered.

We investigated the influence of γ-irradiation dose and dose rate at room temperature to virgin emulsion and suspension polymerizate and polymer properties in a wide range. We compared the results to electron-irradiated PTFE in the same dose range.[13] Therefore, it could be excluded that a thermal pretreatment of PTFE, usually applied when films or sheets are produced, influences the effects of irradiation and causes changes in crystallinity of the starting material.

EXPERIMENTAL

The fluoropolymers were irradiated in the dose range from 0–1000 kGy in one procedure. γ-Irradiation
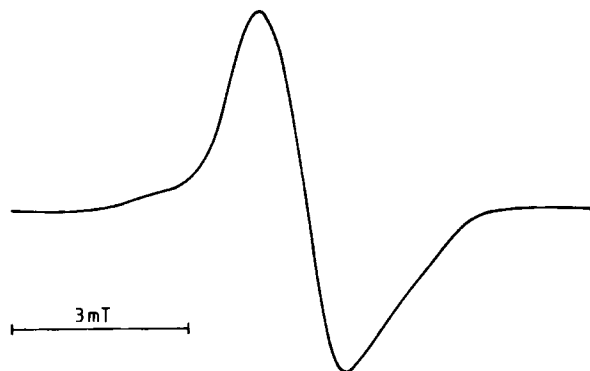

Figure 1   ESR spectrum of annealed end-chain peroxy radicals.

was carried out at room temperature in the presence of air by means of a ^{60}Co source with an activity of $2.4 \cdot 10^5$ Ci. The dose rate was 0.25 and 8.0 kGy h^{-1}.

After irradiation, the polymers were wetted with acetone/water and dried and heated (200°C, 60 min) for Fourier transform–infrared (FT-IR), differential scanning calorimetry (DSC), wettability, and crystallinity measurements. FT-IR measurements were obtained from cold-pressed samples on an IFS 66 (Bruker).

The DSC method was used to investigate changes in melting behavior in dependence on the irradiation conditions. Our measurements were carried out using a Mettler DSC 20, which was calibrated with In and Pb standards (temperature range of measurements, 200–400°C; cycle 1, heat to cool; cycle 2, heat; scanning rate, 10 K/min; sphere, pure nitrogen; sample weight, about 10.0 mg for irradiated micropowders). For the qualitative estimation of the change in molecular weight M_W of irradiated PTFE, we used the correlation between heat of recrystal-
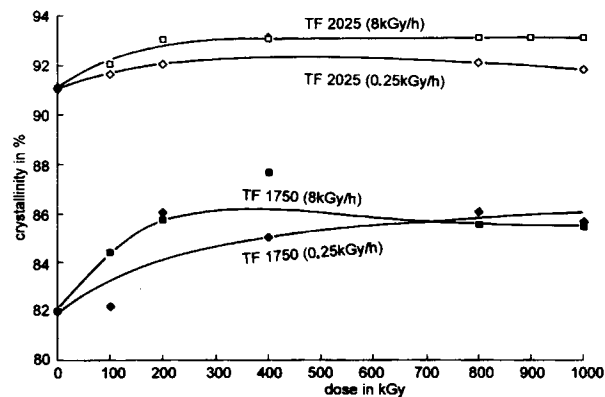

Figure 2   Crystallinity of PTFE γ-irradiated in air obtained from X-ray diffraction analysis as a function of radiation dose and dose rate.
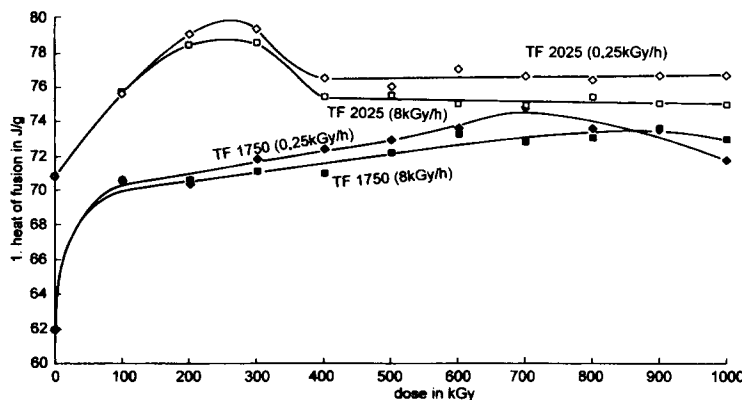
Figure 3   First heat of fusion of PTFE γ-irradiated in air as a function of radiation dose and dose rate.

lization $|H_c|$ and M_W. Suwa[14] found that the heat of recrystallization increases with decreasing M_W in a limited range. We determined the value of $|H_c|$ 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 first heating scan. Electron spin resonance (ESR) spectra of PTFE were obtained from irradiated samples with an X-band spectrometer ESP 300 E (Bruker) with an $H_{102\text{-cavity}}$. All measurements were carried out at room temperature with 100 kHz modulation and a microwave power of 2 mW.

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 below the transition temperature of 19°C at 15°C. All data were obtained from samples treated for 60 s.

X-ray diffraction patterns of irradiated samples were measured at room temperature on a wide-angle diffractometer HZG 4-A/2 (Seifert-FPM GmbH, Freiberg/Sa.) using the Cu Kα radiation in transmission technique.

The virgin PTFE resins used in all experiments reported here were virgin TF 2025 (emulsion polymerizate) and TF 1750 (suspension polymerizate), kindly supplied by HOECHST AG-HOSTAFLON. A 15 t 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

It has been shown that during irradiation, PTFE radicals reacted rapidly with oxygen to give the corresponding peroxy radicals.

An important insight into the formation of PTFE peroxy radicals is given by ESR spectroscopy.
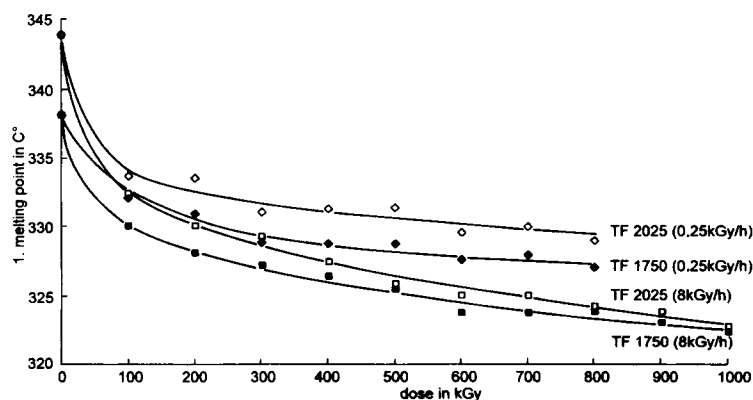

Figure 4   Temperature of melting point (determined in first heating) of PTFE γ-irradiated in air as a function of radiation dose and dose rate.
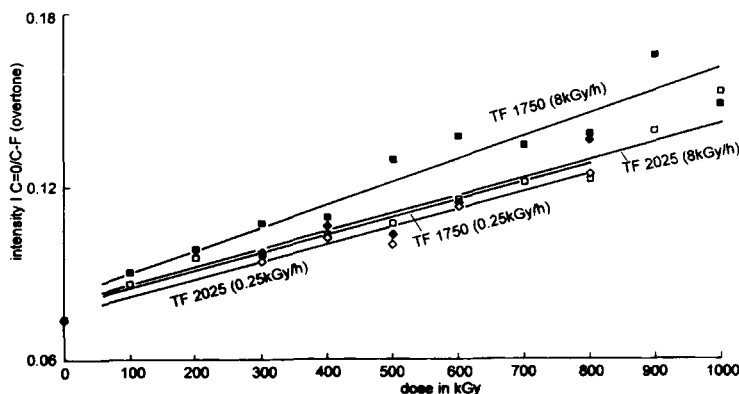
Figure 5   Intensity of FT-IR bands of the carboxyl group of PTFE γ-irradiated in air as a function of the radiation dose (limits: C — F overtone 2690–2200 cm^{-1}; C＝O 1900–1750 cm^{-1}).

The shape of the ESR spectra of the irradiated samples is due to a superposition of a single line and a powder pattern for a radical with axially symmetric g-tensor with the strongest peak at the lower field side. According to data from Moriuchi et al.,[15] we assigned the single nearly symmetric line to the end-chain peroxy radicals —CFOO· and the other to a midchain peroxy radical —CF$_2$—CF(OO·) —CF$_2$—.

Heating the samples at 200°C for 30 min decreases the total amount of the radicals (Table I) and changes the shape of the ESR spectra.

An ESR spectrum of the γ-irradiated PTFE sample is shown in Figure 1. The spectrum consists of a nearly symmetric line with g = 2.066. This is a result of the higher mobility of the end-chain radicals, by which rotational movement averages the anisotropic g-tensor components given in reference 15.

Schlick[16] reported the effects of temperature on the ESR spectrum of PTFE. He found that above 493 K, the signals from the peroxy midchain radicals decreased irreversibly.

Comparing radical concentration of irradiated PTFE samples (Table I) before and after heating, the following behavior was indicated:

• measurable radical concentration grew with rising irradiation dose;

• no significant difference was observed in the radical concentration between emulsion and suspension polymerizate;

• a thermal posttreatment at 200°C was not sufficient to remove especially end-chain peroxy radicals. The concentration of these radicals decreased to $\frac{1}{10}$ of the original value;

• subsequent reaction of the peroxy radical can be expected; and

• β- and γ-irradiation of PTFE at comparable dose values in the range of 100–1000 kGy results in similar concentrations of the peroxy radicals.[13]

After having demonstrated that the formation of peroxy radicals does not depend on starting material
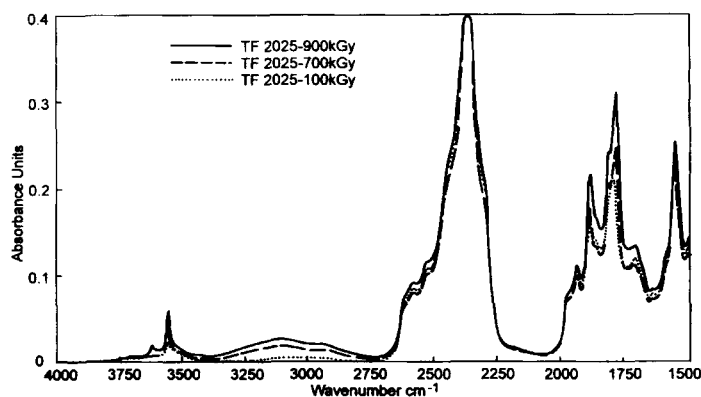

Figure 6   FT-IR spectra of TF 2025 and carboxylated TF 2025; dose rate is 8 kGy/h.
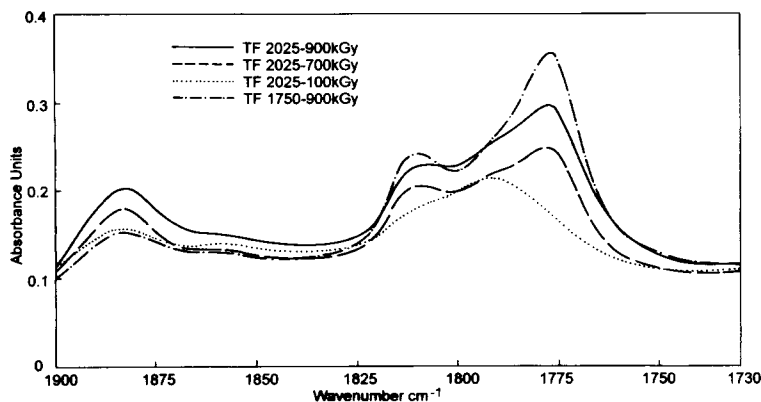
Figure 7 FT-IR spectra of carboxylated PTFE in the range of C=O stretching vibrations.

and on the kind of applied energy-rich radiation, we subsequently investigated the properties of irradiated PTFE powder for dependence on dose and dose rate. We paid attention to changing properties due to formation of radicals. Changes in crystallinity of partially crystalline polymers can be realized sufficiently by X-ray diffraction and DSC.

PTFE gives only one well-defined crystalline peak at a scattering angle of $2\theta = 17.85°$ (Bragg value d = 0.497 nm). We used the ratio of the area of this peak to the total scattering area, including the broad amorphous background as an index of crystallinity. The increase in crystallinity for emulsion and suspension-grade PTFE in the range of 100–1000 kGy is the result of chain scission in the amorphous regions and chain scission and recombination reactions in the crystalline regions.

Initially, the suspension polymerizate showed a stronger increase in crystallinity (Fig. 2) due to a lower extent of starting crystallinity as compared to emulsion polymerizate. The preferred chain scission in the amorphous range causes additional crystalline

contributions. We did not find any indication that dose rate changes significantly in crystallinity.

Heating of PTFE above the melting point resulted in a decreasing spin number. Thus, there was a probability of radical reaction. Processes such as recombination reactions and chain branching may occur. Considering these facts, we also investigated changes in crystallinity using DSC methods. We concentrated exclusively on the first heat of fusion in dependence on irradiation dose and dose rate.

Our results of X-ray diffraction experiments were confirmed. We found a significant increase in the first heat of fusion up to about 100 kGy, indicating a rise in crystallinity (Fig. 3). Considering the change in the first heat of fusion of emulsion polymerizate in dependence on dose, we found a maximum at 200–300 kGy. The maximum of the first heat of fusion of suspension polymerizate lies in the range of 600–800 kGy. We found a distinct dependence of the change in melting heat on dose rate. γ-Irradiation at a higher dose rate in the presence of air causes a lower increase of melting heat at con-
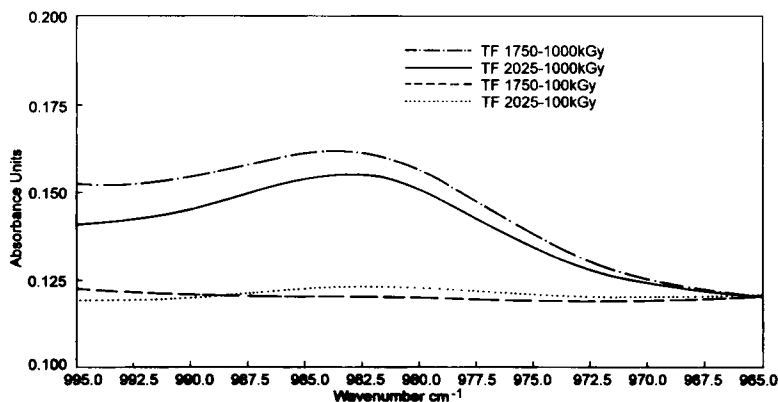

Figure 8 FT-IR spectra of trifluoromethyl-branched PTFE in the range of 965–995 cm^{-1}; dose rate is 8 kGy/h.
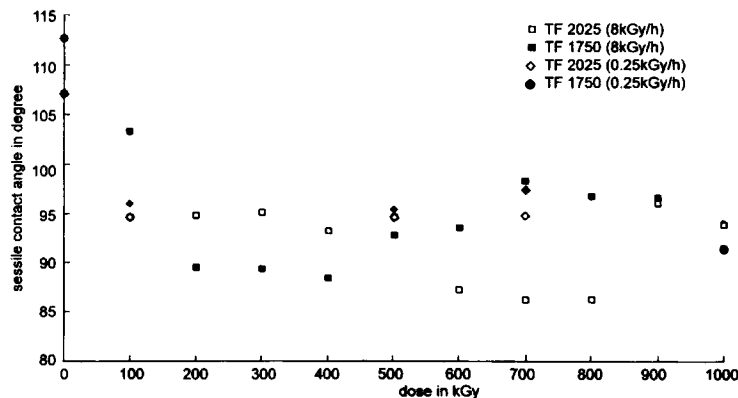
Figure 9 Sessile contact angle of cold-pressed PTFE samples γ-irradiated in air as a function of radiation dose.

stant total dose. This effect could be due to an increased formation of radicals at the higher dose rate applied. Sufficient supply of oxygen enables the formation of peroxy radicals; thus, irradiated PTFE should possess a lower molar mass and a higher degree of carboxylation at comparable total dose. Lower dose rates should favor recombination reactions. The radiation-initiated degradation of PTFE is delayed.

By investigating the dependence of the melting point on irradiation dose and dose rate, we actually found that the melting point of emulsion and suspension polymerizate was reduced with increasing dose; but at a dose rate of 0.25 kGy/h, the melting

Table II Properties of γ-Irradiated Micropowders

PTFE Grade (Dose in kGy)	Particle Size d_{50} [0.25 kGy/h (μm)][a]	Particle Size d_{50} [8 kGy/h (μm)][a]	Melt Flow Rate (0.25 kGy/h, 645 K, 2.16 kp; g/10 min)	Melt Flow Rate (8 kGy/h, 645 K, 2.16 kp; g/10 min)
TF 1750-0	23	23	—	—
TF 1750-100	25	22	—	—
TF 1750-200	25	24	—	0.02
TF 1750-300	25	21	0.004	0.1
TF 1750-400	25	22	0.04	0.4
TF 1750-500	25	20	0.01	2.5
TF 1750-600	25	19	0.1	4.3
TF 1750-700	25	20	0.1	4.6
TF 1750-800	23	21	0.7	3.3
TF 1750-900	25	17		28.2
TF 1750-1000	25	17		49.5
TF 2025-0	500[b]	500[b]	—	—
TF 2025-100	23	11	—	—
TF 2025-200	24	9	—	0.01
TF 2025-300	10	7	0.004	0.1
TF 2025-400	13	8	0.04	0.8
TF 2025-500	15	9	0.01	0.8
TF 2025-600	14	14	0.1	5.8
TF 2025-700	21	13	0.1	8.9
TF 2025-800	27	13	0.3	11.5
TF 2025-900	19	13		—
TF 2025-1000	24	14		69.3

[a] Rhodos unit; pressure, 0.5 bar.
[b] Size of agglomerates.

point was affected less drastically than at a dose rate of 8 kGy/h (Fig. 4). This behavior can be due to reduced degradation of the polymer. A comparison of the degree of carboxylation using FT-IR measurements also confirmed the theoretical expectation that PTFE will be carboxylated more strongly at higher dose rates (Fig. 5).

Figure 6 shows a FT-IR survey spectrum of cold-pressed irradiated TF 2025 powder (8 kGy/h). The carboxylation of PTFE at the increasing irradiation dose is clearly visible. OH-stretching vibrations of the acid group above 3000 cm^{-1}, a band of the terminal carboxylic acid fluoride group at 1885 cm^{-1} increasing with rising dose, as well as the carbonyl vibrations of associated (1770–1780 cm^{-1}) and isolated (1810 cm^{-1}) carboxyl groups, can be observed (Fig. 7). Comparable to β-irradiation, an insertion of oxygen into PTFE appears during the irradiation process, if oxygen is present. Associated phases of carboxyl groups, preferably in near-surface regions, and isolated carboxyl groups inside the powder particles are observed. Using FT-IR measurements to compare the degree of carboxylation of PTFE under the influence of both radiation types, a far stronger and measurable concentration of acidic terminal groups can be found with β-irradiation at identical irradiation doses. However, an increased degree of trifluoromethyl groups (Fig. 8; 985 cm^{-1}) at doses above 700 kGy is apparent in γ-irradiated PTFE. DSC and crystallinity measurements did not indicate cross-linking. We suspect that trifluoromethyl groups are concentrated at the surface due to radical reactions. Subsequent wetting experiments showed that our expectation was correct.

The change in surface energy with irradiation treatment was assessed by measurement of the sessile contact angles below the phase transition temperature of PTFE at 19°C with cold-pressed samples. It was evident that an increasing irradiation dose did not result in an appreciable change of wettability (Fig. 9). An irradiation dose of 100 kGy causes a decrease in the contact angle versus water of approximately 10 degrees in PTFE. Afterwards, the contact angle rose again at increasing dose.

Spin number determination indicated nearly the same number of radicals at β- and γ-irradiation. It seems probable that side reaction occurs at γ-irradiation, opposite to an increase of surface energy of PTFE. Comparing FT-IR spectra of electron-irradiated PTFE polymerizates,[13] it is apparent that a reduced carboxylation of PTFE occurs at identical experimental conditions and identical irradiation dose at γ-irradiation. However, a new vibrational band appears at higher dose values. The vibrational

band at 985 cm^{-1} can be assigned to trifluoromethyl groups.[17] The intensity of this band increases with rising irradiation dose. As the portion of trifluoromethyl branches grows, the wettability will be reduced. It is imaginable that trifluoromethyl radicals emerge during irradiation. Owing to their size relative to oxygen, they must be able to diffuse to newly formed radical centers and to initiate a radical reaction to form trifluoromethyl branches.

Thus, it can be supposed that a certain number of carboxyl groups and, at rising irradiation dose, an increased number of trifluoromethyl groups is localized at the particle surface. γ-Irradiated suspension and emulsion polymerizates do not show significant differences in the wettability versus water in the investigated dose range.

The particle properties summarized in Table II indicate the property changes of irradiated PTFE powders that we have described already at β-irradiation of PTFE. The melting flux index (MFI) rises with increasing irradiation dose. The MFI correlates with molecular weight and increases to a lower extent when the powder is irradiated at 0.25 kGy/h. Thus, the DSC investigations and the findings concerning molecular weight[18] have been confirmed. We found a reduced degradation of molar mass to occur at a lower dose rate when comparing with high dose rates. The higher MFI values at β-irradiation also indicate an enhanced chain degradation of PTFE under the influence of this ionizing radiation when compared to γ-irradiation.

The particle size of suspension polymerizate reduces very slightly with rising irradiation dose, especially under the influence of higher dose rate. In the case of emulsion polymerizate, we found agglomerates in the range of 5–30 μm after irradiation. Probably, this effect is also due to the insertion of carboxyl groups in the near-surface regions of the primary particles. Comparing irradiation dose, dose rate, kind of irradiation (β or γ), degree of carboxylation, and wettability behavior, it can be said that small particle sizes (TF 1750) and a decreased size of agglomerates (TF 2025) will be reached at a high dose rate.

CONCLUSIONS

Virgin PTFE appears to be somewhat more sensitive to irradiation than other polymers. In the presence of oxygen, chain degradation predominates at γ-irradiation. The degree of carboxylation of PTFE rises with increasing irradiation dose. Emulsion and suspension polymerizates show similar property

changes, especially at a higher irradiation dose (>500 kGy), depending on the dose. The irradiation of the macromolecules in the dose range of 100–400 kGy mainly influences the crystallinity. Crystallinity reaches a maximum, depending on starting crystallinity and irradiation dose.

At rising dose and at low dose rates, γ-irradiation of PTFE especially results in trifluoromethyl branching. High dose rates mainly cause carboxylation in PTFE. We assume that the carboxylic acid groups are associated at the surface and isolated inside the polymer. The wettability of the irradiated PTFE powder depends on the degree of carboxylation and the number of trifluoromethyl branches.

A very low dose rate reduces the rate of chain degradation. Recombination reactions become more probable, and property changes due to the influence of the ionizing radiation will be attenuated.

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