

Influence of Absorbing Materials on the Functionalization of Poly(tetrafluoroethylene) During γ -Irradiation

Thorsten Hoffmann, Marcel Heller, Dieter Jehnichen, Thomas Engelhardt, Dieter Lehmann

Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069, Dresden, Germany

Correspondence to: T. Hoffmann (E-mail: hoffmann-thorsten@ipfdd.de)

ABSTRACT: This contribution describes the effect of absorbing materials on the functionalization and the concentration of radicals of poly(tetrafluoroethylene) (PTFE) during the γ -irradiation compared to the results without absorbing materials. Different absorbing calcium-based materials were used to study their efficiency to avoid the release of fluorinated gases that occur within the irradiation procedure in the environment. It was found, that the type of the absorbing material had a significant effect on the formation and concentration of functional groups (carbonyl fluoride, carboxylic acid) and persistent radicals within the radiation-treated PTFE samples. In addition, by means of wide angle X-ray scattering (WAXS) the quantitative determination of fluorine (F^-) concentration after irradiation in the absorbing materials could be followed. It may be used for scientific investigations of radiation induced PTFE chain scission mechanisms as well as for the monitoring of industrial γ -irradiation processes. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1787–1793, 2013

KEYWORDS: functionalization of polymers; irradiation; degradation

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INTRODUCTION

Ionising radiation treatment on poly(tetrafluoroethylene) (PTFE) is a well-established technology to prepare micropowders used as ingredients for inks, coatings and lubricants. Exposure of PTFE to irradiation of electron-beams, γ -rays or X-rays causes a dramatic degradation and structural changes in the polymer.

The irradiation in air leads to degradation by chain scission, which is associated with the formation of perfluoroalkyl(peroxy) radicals and end groups such as $-CF_3$, $-COF$, and $-COOH$ groups, in the presence of moisture.^{1–3} Either mid-chain or end-chain species are formed at first. It was reported, that mid-chain perfluoroalkyl(peroxy) radicals are more temperature stable than the end-chain perfluoroalkyl(peroxy) radicals due to their low mobility in crystalline structures.³ Different positions of perfluoroalkyl(peroxy) radicals in the PTFE chain are causing different reaction pathways. This results in the formation of functional groups ($-COF/-COOH$) for mid-chain perfluoroalkyl(peroxy) radicals (a) or in the formation of carbonyl difluoride (COF_2) for end-chain perfluoroalkyl(peroxy) radicals (b). In the presence of water COF_2 will react further to CO_2 and 2 HF.³

The irradiation of PTFE in the presence of air (oxygen) causes chain scission and subsequent radical reactions within the

polymer. Figure 1 shows a simplified radical-induced degradation scheme of PTFE by irradiation in air.³

The radical concentration of irradiated PTFE micropowders decline only slightly and can be detected by electron spin resonance (ESR) spectroscopy even after years. The perfluoroalkyl (peroxy) radicals can be utilized for coupling reactions with olefinic compounds to enhance their tribological characteristics.^{4–6}

During the complex radical reactions between high-energy rays and PTFE polymer chains, also volatile and gaseous fluoride-containing species are generated. Besides HF, which is formed from $-COF$ end groups or COF_2 in the presence of water, the formation of tetrafluoromethane (CF_4) and hexafluoroethane (C_2F_6) was reported.^{7–9} F_2 might also be an intermediate reaction product. During the thermal decomposition of PTFE the species hexafluoropropene (C_3HF_6) and trifluoroacetate ($CF_3-C(O)OH$) were also identified.¹⁰

Because such compounds have serious harmful and corrosive potential, the release into the environment must be avoided. The addition of fluorine absorbers is a common method to avoid such outgassing. Calcium easily forms very stable CaF_2 (fluorspar) with various fluoride-containing gases. Therefore, calcium minerals such as $CaCO_3$, CaO , or $Ca(OH)_2$ are suitable absorbing materials. Ca minerals are low-cost products, used as

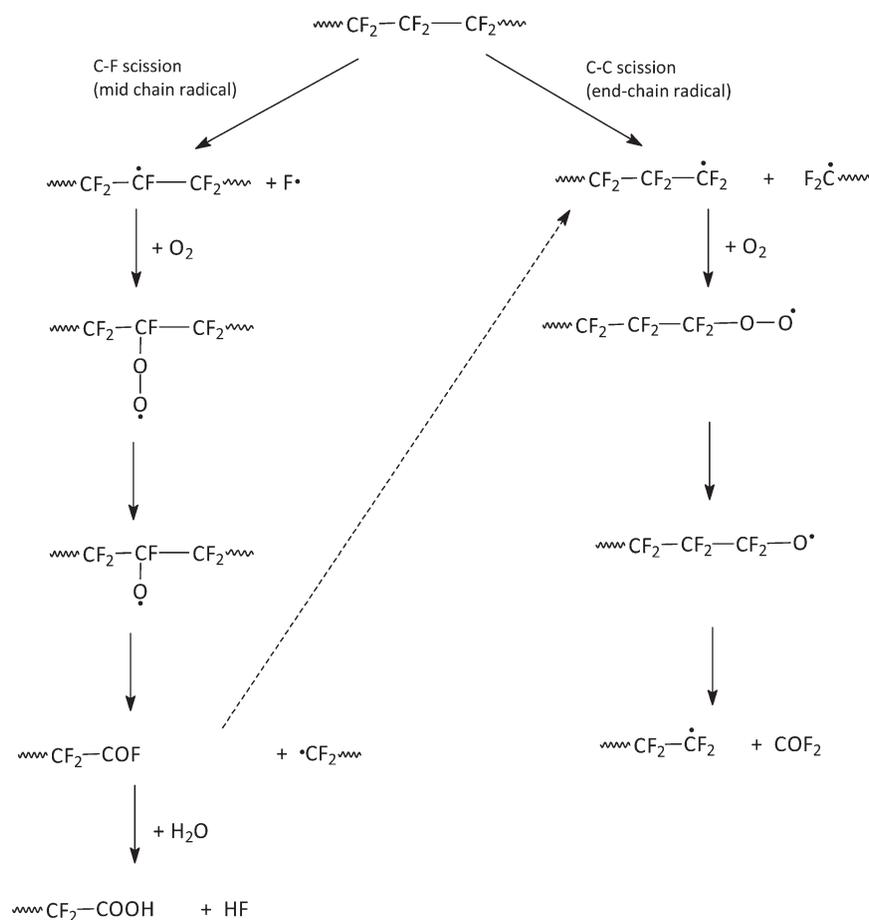


Figure 1. Radical-reaction scheme of irradiated PTFE in air.³

hydrated and unhydrated lime or chalk in agricultural and building industries. Sodium-based (e.g. NaCO_3 , NaOH) absorbing materials or silicon-containing materials (e.g. SiO_2) should not be used. NaF is known to be water soluble and toxic and silicon reacts with fluoride to form SiF_4 , a toxic and corrosive gas. During our studies on the γ -radiation treatment of PTFE we found that all tested Ca-based absorbing materials are suitable to prevent fluoride-containing gases from the release into the environment. No pungent odor or even a formation of smoke could be observed like it happened after irradiating PTFE without any absorbing material. Nevertheless, we discovered that the type of absorbing material used had a significant effect on the formation and concentration of functional groups and perfluoroalkyl(peroxy) radicals within the irradiated PTFE samples.

Within this contribution it was investigated, how much fluoride (F^-) is released during the irradiation of PTFE and whether the extent of such gases depends from the irradiation dose and other process parameters. In general, quantitative fluoride analysis is not trivial. In principle, one can analyze a defined volume of air within the reaction vessel by gas chromatography or by potentiometric measurement of an aqueous absorbing solution with a fluoride sensitive electrode. But every contact with glass surfaces will distort the result. This is one of the reasons why

serious conclusions are quite complicated to achieve. We found, that wide angle X-ray scattering (WAXS) of the absorbing materials after irradiation is an appropriate method for the quantitative determination of fluoride concentration. This method was shown to be easy to handle, reproducible, nondestructive and to deliver adequate F^- -sensitivity.

We found, that the different absorbing materials (CaCO_3 , CaO , and Ca(OH)_2) have a different influence on the PTFE radical concentration and the amount of functional groups. CaCO_3 , CaO seem to increase the portion of $-\text{COF}$ groups. On the other hand, Ca(OH)_2 ($\text{CaO} + \text{H}_2\text{O}$) reduces the $-\text{COF}$ concentration clearly. The implementation of the γ -irradiation process, without absorbing materials, results in less functional groups and more radicals. To determine the generation of the fluoride-containing gases quantitatively, it is possible to detect the concentration of the formed CaF_2 using wide-angle X-ray scattering (WAXS). It was shown, that up to ten times more fluoride is found within the absorbing materials bound as CaF_2 , compared to the quantity of fluorine calculated from FTIR spectroscopic data (HF generated from the reaction of $-\text{COF}$ groups with water). This confirms the mechanism of chain scission during γ -irradiation which shows that each scission step generates one fluoride atom, which — besides recombination with chain atoms—can form F_2 , gaseous fluorocarbons and COF_2 .

EXPERIMENTAL

In this contribution, two different poly(tetrafluoroethylene) qualities have been used. Emulsion-polymer based PTFE (PTFE-P) was used as received (TF 2025, Dyneon GmbH/3M, Germany). Sintered suspension-polymer based PTFE (PTFE regenerate) was purchased as industrial scrap chips (PTFE Nünchritz GmbH, Germany) and ground to free-flowing bulk material (3 mm) before the γ -irradiation treatment was started. Four different absorbing materials were used for comparative investigations: CaCO₃ as industrial grade chalk (>90 %, “Reasorb”, Kreidewerke Dammann KG, Germany); CaO purum, from marble (>97%, irregular pieces, Fluka, Germany); Ca(OH)₂ purum p.a. (>96%, Sigma-Aldrich, Germany) and CaO as industrial grade white lime (77%, white lime, Kreidewerke Dammann KG, Germany). The γ -irradiation treatment was carried out by Beta-Gamma-Service GmbH KG in Wiehl, Germany with a 5 MCi ⁶⁰Co source under normal pressure, at room temperature and in the presence of air. The average dose rate was about 5 kGy h⁻¹. The total dose was varied between 200 and 700 kGy (for PTFE-P). Modified PTFE regenerate (PTFE-S) was prepared by 500 kGy only. Five barrels, filled with PTFE-S regenerate (18 kg, bulk density 0.6 g cm⁻³) were irradiated in a γ -source with a total dose of 500 kGy. As reference, one barrel was irradiated without any absorbing material. Into each of the other four barrels, a different calcium-containing absorbing material (200 g each) was put: (a) grainy CaCO₃ (chalk from industrial mining with 10% other mineral components), which is commonly used as flue gas washing material; (b) CaO, where by the absorbance of fluorine, other by-products are formed; (c) Ca(OH)₂, which in contrast to CaO is not hygroscopic; (d) white lime, which is a burnt industrial mining product containing 77% of CaO and other mineral components. After irradiation, the modified PTFE-S regenerate was milled to receive a homogeneous fine powder.

By DSC studies (DSC Q-1000, TA Instruments, US) the molecular weights of the crystallization were determined according to Weigel.¹¹

The IR spectra were recorded using the Fourier transform infrared (FTIR) spectrometer Tensor 27 (Bruker, Germany) in transmission mode (32 scans, 2 cm⁻¹ resolution, 4000–400 cm⁻¹). Powders were pressed into films at room temperature with the thickness (*d*). Molar ratios of —COF and —COOH were calculated according to eq. (1) using a calibration factor (*CF* in mm) as described in Ref. [12]. The IR absorbance (*A*) was measured at 1883 cm⁻¹ (—COF), 1815/1809 cm⁻¹ (—COOH_{free}) and 1777 cm⁻¹ (—COOH_{associated}), respectively.

$$\frac{[\text{end group}]}{[\text{CF}_2]} = \frac{A \cdot CF}{d \cdot 10^6} \quad (1)$$

The electron spin resonance (ESR) spectra were recorded with an ESR spectrometer MiniScope, MS 200 (MagnetTech GmbH, Germany) at room temperature. The modulation amplitude was 0.1 mT and the microwave power 1.0 mW.

Wide angle X-ray scattering (WAXS) in reflection mode under grazing incidence (with two-circle diffractometer XRD 3003 T/T (GE Sensing & Inspection Technologies GmbH,

Vertriebszentrum Seifert-FPM Freiberg, Germany) and Cu K α radiation was used for study the scattering curves of the components of the chalk inside the calcium-containing absorbing materials after the irradiation procedure to characterize the uptake of fluorine (grazing incidence $\omega = 1.44^\circ$, prim. slit width 0.5 mm, sec. divergence 0.7° , measuring parameters: 25° – 60° (2θ), $\Delta 2\theta = 0.02^\circ$, $\Delta t = 4$ s).

RESULTS AND DISCUSSION

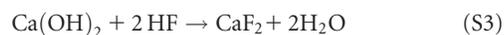
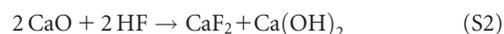
Influence of Absorbing Material on the PTFE Functionalization

As discussed within the introduction and shown in Figure 1, the irradiation of PTFE leads to functionalization with —COF and —COOH groups (in the presence of water). Both, —COF and —COOH can be detected and quantified by FTIR spectroscopic analysis of the specific bands.^{7,12–15} The content of perfluoroalkyl(peroxy) radicals of PTFE after irradiation can easily be measured by ESR spectroscopy.^{7,14,15} We found, that irradiated PTFE samples, processed with or without absorbing materials, showed significant differences of the carboxylic concentrations. Further investigations on different absorbing materials have been carried out to understand the root causes of this effect.

The concentrations of —COF and —COOH groups (by FTIR spectroscopy) as well as of radicals (by ESR spectroscopy) found after the irradiation experiments of PTFE-P and PTFE-S at 500 kGy are shown in Table I. In Figure 2 the ESR signal intensities are plotted. Because only an internal comparison of the samples was intended, the estimation of the total spin number using a reference crystal was renounced.

The differences in the quantities of carboxyl groups and radicals, shown in Figure 2, depend on the type of absorbing materials used. Compared to the reference without any absorber, the COF-concentration is reduced considerably if Ca(OH)₂ is used as absorbing material, whereas CaO seems to increase the amount of COF. If PTFE was moisturized with water before irradiation, surprisingly almost no radicals or carboxylic PTFE species could be detected. This suggests that water acts as an inhibitor for the radical reactions or at least prevents the formation of persistent perfluoroalkyl(peroxy) radicals and carboxyl functionalization. Mechanisms leading to this phenomenon are not yet understood.

Looking on the supposed reaction schemes of the different absorbing materials with fluorine containing gases (e.g., HF), different by-products like CO₂ or H₂O are formed. These may interact in different ways with intermediate PTFE reaction species or act as radical quencher. The corresponding reaction pathways are shown in the schemes (S1–S3) at the example of HF as reaction partner for: CaCO₃ (1), CaO (2), and Ca(OH)₂ (3).



Ca(OH)₂ generates water, whereas CaO will always absorb existent water, which may promote PTFE functionalization, looking

Table I. Amount of —COF and —COOH Groups and Radicals Found After γ -Irradiation in Dependence of the Presence of Absorbing Materials by FTIR Spectroscopy and ESR Analysis (Integrated Signal Intensity = Radicals mg^{-1} PTFE)

PTFE grade	Exp. No.	Dose (kGy)	Absorbing material	FTIR evaluation after adjustment with correction factor (CF) related to non-irradiated PTFE-P				ESR [radicals] (mg)
				[COF] (10^6 —CF ₂ ⁻)	[COOH] _{free} (10^6 —CF ₂ ⁻)	[COOH] _{assoc.} (10^6 —CF ₂ ⁻)	total (10^6 —CF ₂ ⁻)	
PTFE-P	1/02	200	CaCO ₃	109	74	76	259	521
	1/08	500		179	74	72	324	1043
	1/10	700		418	100	179	697	982
	3/39	200	CaO	232	83	71	387	289
	3/40	400		296	53	57	406	629
	2/20	500		313	68	23	403	912
PTFE-S	1/70	500	CaCO ₃	226	51	39	316	956
	3/46	500	CaO	321	25	1	346	745
	3/47	500	Ca(OH) ₂	78	11	0	89	344
	3/48	500	Fertiliser	224	11	0	235	851
	3/49	500		184	17	0	201	875

at the negative influence of water on the amount of functional groups. However, a conclusive explanation of the phenomenon of the absorbing materials as a function of the degree of PTFE functionalization cannot yet be made.

For the practical use of absorbing materials this means, that by the choice of the type of the absorbing material the degree of the PTFE functionalization can be controlled, dependent on the designated application.

Quantitative Determination of Fluoride Ions Formed Upon Irradiation of PTFE

HF and other fluoride-containing gases may irritate mucous membranes and are highly corrosive. This makes the quantitative determination of fluorine containing gases formed during the irradiation of PTFE to become not only of general interest, but may also help to estimate necessary safety measures for handling and processing of PTFE during irradiation.

Figure 1 shows, that HF is generated through the hydrolysis of PTFE—COF groups in the presence of water (in air). IR spectroscopy can be used for the quantitative determination of HF formed by this reaction. First, the molar ratio of —COOH is calculated by eq. (1). Equation (2) then delivers the corresponding amount of emitted HF. The maximal HF concentration is given by the quantity of water in the reaction atmosphere (with N_{COOH} = amount of —COOH groups, M_{HF} , M_{CF_2} = molecular weights).

$$\frac{\text{HF (g)}}{\text{PTFE (kg)}} = \frac{N_{\text{COOH}}}{10^6 \text{CF}_2} \cdot \frac{M_{\text{HF}}}{M_{\text{CF}_2}} = N_{\text{COOH}} \cdot 4 \cdot 10^{-4} \quad (2)$$

According to eq. (2) the mass of HF that was generated per mass of PTFE (g kg^{-1}) was calculated for different radiation doses, with the assumption that HF is only formed (according to Figure 1). The results are summarized in Table II.

The maximum amount of HF, released from one kg of PTFE is, in fact, very small and reaches a maximum of 0.1 g kg^{-1} PTFE.

This contradicts to the practical observation of strong smelling “smoky clouds” escaping from a 35-L barrel of PTFE after first opening of the cover plate after the radiation procedure. As Figure 1 suggests, there are more F-species to be generated during PTFE irradiation. To find out the overall emission of fluoride, WAXS technology was used to determine the CaF₂ content in given samples of the absorbing materials CaCO₃ and CaO, formed according to the reaction schemes (1) or (2), respectively.

To achieve a calibration curve for subsequent determination of the concentration of CaF₂ of the samples, different amounts of pure CaF₂ was added to each of the non-irradiated absorbing powders. Because of the crystalline structures both, CaF₂ and the components of the chalk (CaCO₃, SiO₂) show distinct diffraction reflections in the wide angle X-ray scattering (WAXS). The reflection signals are assigned to the three main substances. To analyze the concentration effect, the range between the reflection positions of 52.5° to 60° was examined, since there the mathematical separation (peak fitting using pseudo-Voigt

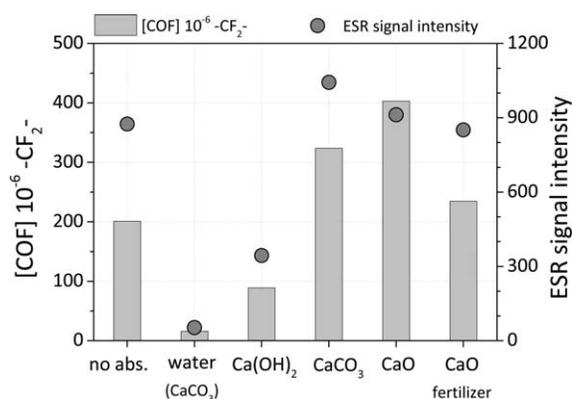


Figure 2. Influence of different absorbing materials on C=O (F, OH) concentration and ESR signal intensity (radical content) for PTFE-S at 500 kGy.

Table II. Calculated Mass of HF (g) Generated per mass of PTFE (kg) After γ -Irradiation at 500 kGy

PTFE grade	Exp. No.	Dose (kGy)	Absorbing material	N [COOH] _{free+assoc.} (10 ⁶ -CF ₂ ⁻)	HF/PTFE (g kg ⁻¹)
PTFE-P	1/02	200	CaCO ₃	150	0.06
	1/08	500		149	0.06
	1/10	700		279	0.01
	3/39	200	CaO	154	0.06
	3/40	400		110	0.04
	2/20	500		91	0.03
PTFE-S	1/70	500	CaCO ₃	90	0.03
	3/46	500	CaO	26	0.01
	3/49	500		17	< 0.01

functions) is optimal. Table III shows the reflection areas of CaF₂ and CaCO₃ after adding of various amounts of CaF₂ to the nonirradiated CaCO₃ absorbing material. As shown in Table III, for the evaluation the ratio of the reflection areas (net integral of the related fit function) from CaF₂ and CaCO₃ are necessary. The ratio of CaF₂ and CaCO₃ signal depends from the amount of CaF₂ in the CaCO₃ sample.

Therefore a WAXS calibration curve of the CaF₂ signals had to be prepared at first by mixing of CaF₂ puriss. (>99%, Fluka, Germany) with the non-irradiated absorbing materials in different weight percentages of CaF₂, before the characterization of the used absorbing materials could be carried out. The related scattering area is shown in Figure 3, in which the increased CaF₂ proportion in the nonirradiated absorbing materials is clearly visible.

Calibration curves have been calculated from the integrals of the CaF₂ reflection areas for different CaF₂ concentrations in CaCO₃ or in CaO, respectively. The relationships are illustrated in Figure 4.

WAXS measurements allow the recording of the concentration of CaF₂ formed, to estimate the quantitative HF formation.

Using the respective calibration curve the determination of CaF₂ content (wt %) in the CaCO₃- and CaO-consisting absorbing material after different irradiation experiments with PTFE could be carried out successfully. These results are summarized in Table IV for CaCO₃ (a) and for CaO (b), respectively. The weight percentages of F⁻/PTFE are calculated based on 200 g absorbing material used for 18 kg PTFE in each barrel that means 11g kg⁻¹ PTFE.

The reaction of HF with calcium to nonpoisonous CaF₂ was used to assess the quantity of required absorbing material, according to scheme (4).



As a result from the Table IV, considerably more fluoride-containing gases were found than the HF quantity calculated from FTIR spectroscopic data. This leads to the conclusion that significant amount of fluoride comes from other fluorinated gases (e.g., COF₂ and intermediately formed F⁻ radicals).¹

Table III. Areas of Related Reflections (hkl) of CaF₂ (A_[CaF₂]) and CaCO₃ (A_[CaCO₃]) or CaO (A_[CaO]) into Dependence of the Concentration of CaF₂ (ratio(CaCO₃) = $\frac{A_{[\text{CaF}_2]}}{A_{[\text{CaF}_2]} + A_{[\text{CaCO}_3]}}$, ratio(CaO) = $\frac{A_{[\text{CaF}_2]}}{A_{[\text{CaF}_2]} + A_{[\text{CaO}]}}$)

CaF ₂ (wt %)	F (wt %)	Reflection areas (A) ^a						Reflection ratio of CaCO ₃	Reflection ratio of CaO
		CaF ₂ (311) 5.76°	CaCO ₃ (211) 56.56°	CaCO ₃ (122) 57.40°	CaCO ₃ (1.0.10) 58.08°	CaF ₂ (311) 55.76°	CaO (220) 53.86°		
1	0.24	311.8	1979.7	5148.3	656.0	-	-	0.04	-
2	0.48	475.7	1821.0	5839.9	666.8	-	-	0.07	-
4.8	1.17	1175.4	1674.2	4420.7	514.3	431.7	11323.5	0.12	0.04
9.2	2.24	2677.0	1496.4	3852.0	637.2	617.8	12289.6	0.24	0.05
20.2	4.92	4461.2	1641.0	4188.1	711.3	1316.8	12225.5	0.45	0.10
30	7.31	-	-	-	-	-	-	-	0.16
35	8.52	-	-	-	-	2272.3	11667.8	-	0.28
40	9.74	8597.1	1001.7	2734.1	420.8	3578.4	10473.2	0.67	0.25
50	12.18	10832.5	780.7	2044.5	377.6	4657.1	4899.6	0.77	0.49

^aNet integrals of selected reflections named by compound, Miller's indices (hkl), and scattering angle (2 θ).

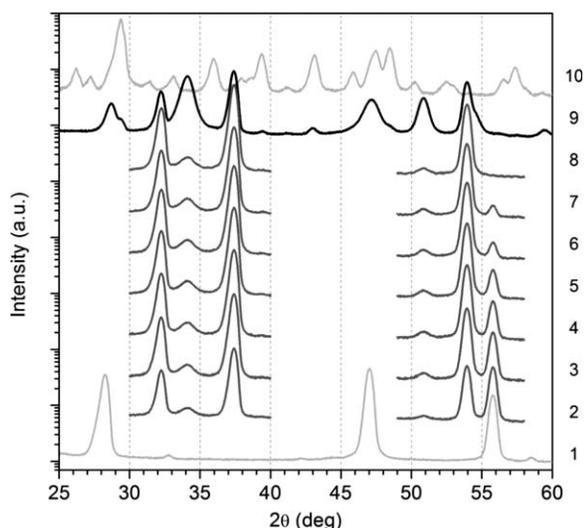


Figure 3. Comparison of WAXS curves of calibration samples and further samples for phase identification; No. 1: CaF_2 , Nos. 2–8: calibration samples (with 50..40..30..20..10..5..0 wt % CaF_2), No. 9: $\text{CaO}/\text{Ca}(\text{OH})_2$ (mix), No. 10: CaCO_3 .

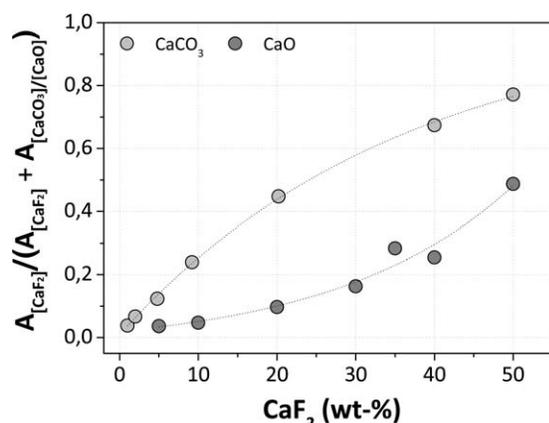


Figure 4. Calibration curve of the CaF_2 concentration in the absorbing material using WAXS for CaCO_3 (○) and CaO (●).

Figure 5 represents the graphical evaluation of the findings in Table IV by plotting the F^-/PTFE against the irradiation dose for both PTFE-P and PTFE-S in presence of CaCO_3 or CaO .

As can be seen in the Figure 5, the fluoride concentration in PTFE-P using CaCO_3 as absorbing material (●) rises linearly within a series of increasing irradiation dose (200 → 500 → 700 kGy). For CaO absorbing material (⌘), the trend seems to be the same, looking at the samples with 200 and 400 kGy. For an irradiation dose of 700 kGy originate ~1.5 g fluoride is generated per kg PTFE. This means up to 27 g HF equivalents are generated per 35-L barrel. Nevertheless, 200 g of absorbing material per barrel (11 g kg^{-1} PTFE) are sufficient to bind all HF completely and securely. This demonstrates, that for safety reasons the addition of absorbing materials during PTFE irradiation are highly recommended.

Looking at the results of our FTIR data analysis, HF gas is only a minor contributor to the overall amount of fluoride found in the absorbing materials. Comparably large amounts of other fluoride species must be generated. As shown in Figure 1 COF_2 and intermediately formed F radicals are the main by-products during chain degradation through PTFE irradiation. In the presence of oxygen, highly reactive COF_2 is formed during end-chain scission. Fluoride radicals are always formed if a mid-chain scission takes place. Those radicals can — besides the recombination with chain ends—react to F_2 or gaseous fluorocarbons. These gasses can then react immediately with the absorbing material to CaF_2 and CO_2 .

Provided that each chain scission generates one fluoride species, these findings might help to estimate the amount of chain scissions forced by the irradiation, taking into account recombination mechanisms and -statistics.

CONCLUSIONS

Fluoride-containing gases are generated by radical chain scission reactions during the irradiation of PTFE.

Because such gases like HF are very corrosive and become toxic in contact with water, a safe processing is necessary to protect

Table IV. Comparison with the Irradiation Experiments of PTFE-P and PTFE-S at Varying Dose in Presence of CaCO_3 and CaO as Absorbing Materials

PTFE grade	Exp. No.	Dose (kGy)	Reflection ratio ^a	CaF_2 (calc.), WAXS (wt %)	CaF_2 (g)	$\text{HF}_{(\text{absorbed})}$ (g)	F^-/PTFE (g kg^{-1})
(a) = CaCO_3							
PTFE-P	1/02	200	0.283	11.8	22	11.3	0.67
PTFE-P	1/08	500	0.431	18.4	37	19.0	1.12
PTFE-P	1/10	700	0.524	22.6	46	23.8	1.40
PTFE-S	1/07	500	0.614	26.6	52	26.7	1.41
(b) = CaO							
PTFE-P	3/39	200	0.045	9.0	18	9.2	0.51
PTFE-P	3/40	400	0.088	15.0	30	15.4	0.86
PTFE-P	2/20	500	-	-	-	-	-
PTFE-S	3/46	500	0.043	9.0	18	9.2	0.51

^a Definition of the reflection ratios see Table III.

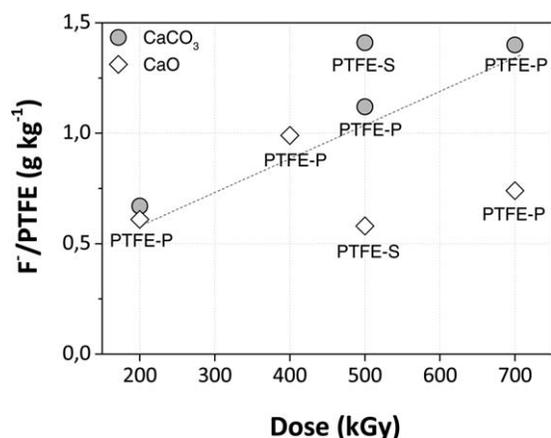


Figure 5. Fluoride formations during the irradiation treatment of PTFE-P and PTFE-S depending on the absorbing materials used.

health and production facilities. By the use of absorbing materials (e.g. chalk, CaO etc.) fluoride gases are bonded during the irradiation treatment.

We found, that different absorbing materials (CaCO₃, CaO, and Ca(OH)₂) have a different influence on the PTFE radical concentration and the amount of functional groups. CaCO₃, CaO seem to increase the portion of —COF groups. On the other hand, Ca(OH)₂ (CaO + H₂O) reduces the —COF concentration clearly. The intermediately formed water can affect the radical concentration negatively. CaCO₃ and CaO as absorbing materials formed more functional groups and radicals in PTFE-P. Ca(OH)₂ shows a negative influence on the amount of functional groups and radicals. The implementation of the γ -irradiation process, without absorbing materials, results in less functional groups and more radicals.

To determine the generation of the fluoride-containing gases quantitatively, it is possible to detect the concentration of the formed CaF₂ using wide-angle X-ray scattering (WAXS). It was shown, that up to 10 times more fluoride is found within the absorbing materials bound as CaF₂, compared to the quantity of fluorine calculated from FTIR spectroscopic data (HF generated from the reaction of —COF groups with water, Figure 1). This confirms the mechanism of chain scission during γ -irradiation which shows that each scission step generates one fluoride atom, which — besides recombination with chain atoms—can form F₂, gaseous fluorocarbons and COF₂.

In summary, WAXS is a suitable method for quantitative fluoride analysis in absorbing materials used for PTFE irradiation. It may be used for both, scientific investigations of radiation

induced PTFE chain scission mechanisms as well as for the monitoring of industrial γ -irradiation processes.

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