

Thermal Stability of Electron Beam-Irradiated Polytetrafluoroethylene

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ABSTRACT: Polytetrafluoroethylene (PTFE) was subjected to 1 MeV electron beam irradiation in air. The thermal stability and the degradation fragments of the irradiated polymer were studied in dependence on the radiation dose up to 4 MGy by thermogravimetric analysis coupled with mass spectrometry. The TGA results confirm the known decrease in the thermal stability of irradiated PTFE with increasing radiation dose. At the thermal degradation, CO₂, HF, and fluorocarbon fragments are evolved from the irradiated samples. CO₂ and HF are formed by decomposition of peroxy radicals up to 250°C. In addition, low molecular weight fluorocarbons are desorbed from the irradiated PTFE. At temperatures above 300°C, CO₂ is formed by the decarboxylation of radiation-induced COOH groups inside the PTFE. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2287–2291, 1997

INTRODUCTION

Polytetrafluoroethylene (PTFE) has a unique position in the plastics industry due to its exceptional properties like chemical inertness and heat resistance. In addition, the low coefficient of friction is an advantage in many applications. Because of the frictional characteristics of PTFE, it is a potential lubricant additive for various materials, but the usual high molecular weight PTFE is unsuitable for this application. It is not possible to incorporate high molecular weight PTFE homogeneously into other polymers by blending. Low molecular weight tetrafluoroethylene polymers, called PTFE micropowders, are very much more suitable for these uses. PTFE micropowders are increasingly being compounded into inks, plastics, coatings, lubricants, and elastomers.¹ They are produced by thermal or radiation-induced degradation of high molecular weight PTFE.² It is already known that a small radiation dose leads

to a strong decrease in the molecular weight of PTFE. When the irradiation takes place in air, radiation-induced radicals react partially with oxygen. Acid fluoride groups (—COF) are formed inside the polymer in this way. These groups react with water vapor to form carboxylic acid groups (—COOH).^{3,4} In this manner, it is additionally possible to produce PTFE micropowders containing near-surface COOH groups. The concentration of COOH groups increases with increasing radiation dose.⁵ These COOH groups cause an increase in the surface free energy of the PTFE powder. It was shown that the homogeneous incorporation of this radiation-modified PTFE into other polymers is possible.^{6,7} We assume that the COOH groups contribute to this considerably.

But it is known that PTFE irradiated in air is much less thermally stable than is high molecular weight PTFE.⁸ The aim of the present study was to investigate the cause of the thermal instability of the radiation-modified PTFE. PTFE powder was irradiated in air with a dose up to 4 MGy using an electron beam accelerator. A copolymer of tetrafluoroethylene with hexafluoropropylene (FEP) was used for the purpose of comparison. During radiation-induced degradation of FEP, ox-

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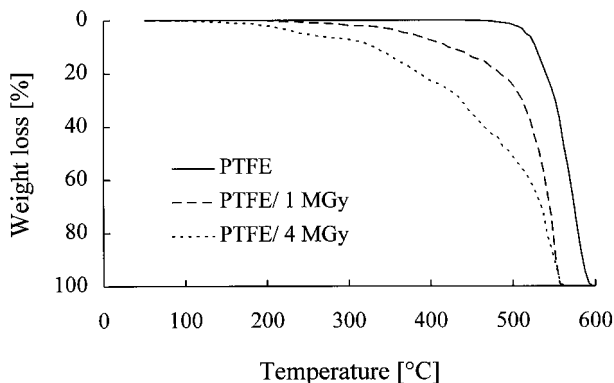


Figure 1 TGA curves of original PTFE and PTFE irradiated with a dose of 1 and 4 MGy (N_2 , 10 K/min).

xygen-containing groups are formed to a large extent inside the polymer because of the lower crystallinity compared with PTFE.⁹ The degradation products evolved during thermogravimetric analysis were detected by mass spectrometry. This offers the possibility to understand the mechanism of irradiated PTFE degradation.

EXPERIMENTAL

Materials

Two commercially available fluoropolymers, a tetrafluoroethylene homopolymer (PTFE, Hostafion TF-1760, Hoechst AG) and its copolymer with hexafluoropropylene (FEP, Teflon FEP 532-8000, DuPont), were used. The average particle size of the polymer powders were 23 μm (PTFE) and 15 μm (FEP). The FEP powder contains a small number of carboxylic acid end groups (identified by FTIR spectrometry), probably as a consequence of its polymerization process.

Electron Beam Irradiation

Experiments were carried out with a 1 MeV universal electron beam accelerator ELT 1.5 (made at the Institute of Nuclear Physics, Novosibirsk) combined with a sample transport system. The fluoropolymers were irradiated in air on a step-by-step basis using a radiation dose of 100 kGy each time.

FTIR Spectrometry

The infrared measurements were carried out with an IFS-66 (Bruker) spectrometer in the transmission mode. The samples were prepared by pressing the polymer powder into polymer films at room temperature.

Thermogravimetric Analysis (TGA)

TGA studies were carried out in a temperature range of 40–740°C, using a Perkin-Elmer TGS 2. All the heating runs were made at a constant rate of 10 K/min in a nitrogen atmosphere.

Mass Spectrometry

The nature of the gaseous degradation products was determined in dependence on temperature using a simultaneous thermal analyzer STA 429

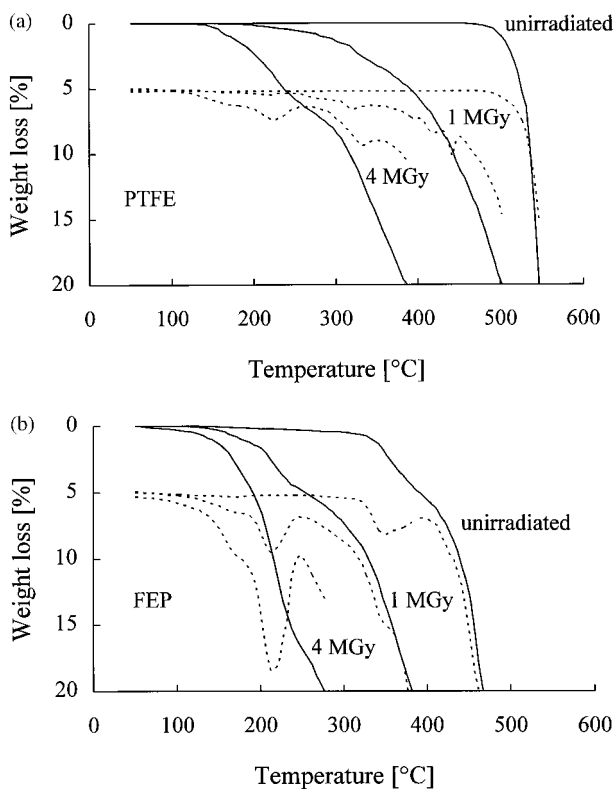


Figure 2 (a) TGA curves (—) up to 20% weight loss and derivative curves of (·····) original PTFE and PTFE irradiated with a dose of 1 and 4 MGy (N_2 , 10 K/min). (b) TGA curves (—) up to 20% weight loss and derivative curves (·····) of original FEP and FEP irradiated with a dose of 1 and 4 MGy (N_2 , 10 K/min).

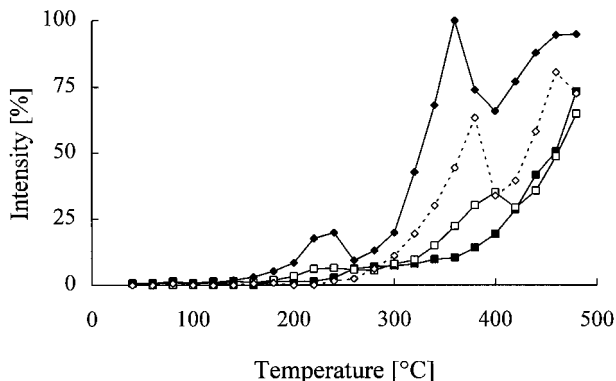


Figure 3 CO_2^+ evolution pattern of (■) original PTFE and PTFE irradiated with a dose of (□) 1 MGy and (◆) 4 MGy and (◇) original FEP.

(Netzsch) coupled with a quadrupole mass spectrometer QMS 403 (temperature range: 10–480°C, heating rate: 10 K/min, atmosphere: He). The intensity of the species evolved is related to the CO_2^+ peak intensity at 360°C of the sample “PTFE/dose 4 MGy.” This maximum observed value is taken as 100%.

RESULTS AND DISCUSSION

TGA curves of the original PTFE and the irradiated PTFE are presented in Figure 1. The original PTFE is stable up to approximately 450°C. Then, the degradation takes place in one step. In comparison with this, irradiated PTFE is degraded in a multistep process. The higher the radiation dose, the lower the temperature starting the degradation and the higher the weight loss of the

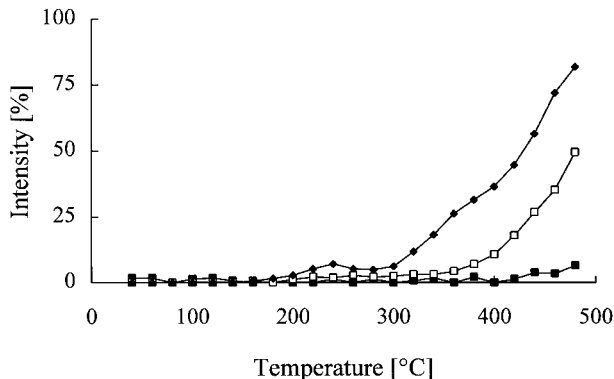


Figure 4 HF^+ evolution pattern of (■) original PTFE and PTFE irradiated with a dose of (□) 1 MGy and (◆) 4 MGy.

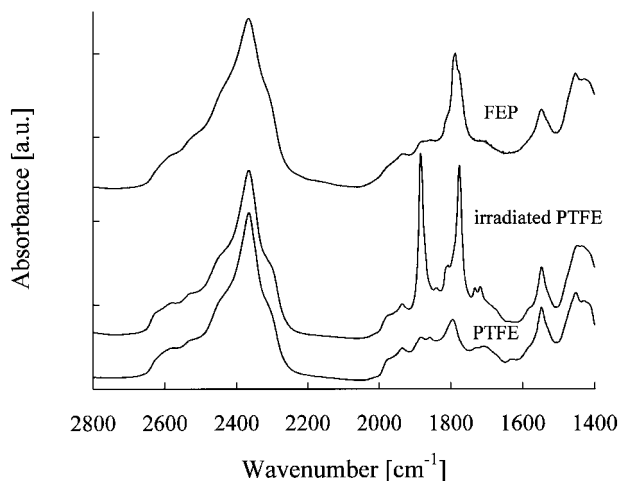


Figure 5 FTIR spectra of original PTFE, irradiated PTFE (dose 4 MGy), and original FEP.

sample at the same temperature. Figure 2(a) shows the beginning of the weight loss of the PTFE samples on an enlarged scale again. For the purpose of comparison, the weight loss of the original FEP and the irradiated FEP is shown in Figure 2(b). It can be seen that the first degradation step occurs at about 225°C in the case of both irradiated PTFE and irradiated FEP. Consequently, a characteristic degradation process of fluoropolymers irradiated in air takes place at about 225°C. This process is stronger in irradiated FEP than in irradiated PTFE.

Mass spectrometry was used to investigate the thermal degradation in detail, especially the first degradation step. The CO_2^+ evolution pattern of the PTFE samples is shown in Figure 3. Unfortunately, there are some problems with CO_2 adsorbed in the equipment. It causes a gradual increase of the CO_2^+ intensity with increasing temperature. In the case of the original PTFE, the CO_2^+ pattern can be attributed completely to this CO_2 desorption. The irradiated PTFE samples additionally show a two-step CO_2^+ evolution pattern, in which the intensity of CO_2^+ increases with increasing radiation dose. The first step of CO_2^+ evolution is in the temperature range of 200–250°C, and the second step, at temperatures above 300°C.

Which processes cause the CO_2 to be released? That is the point. Oxygen-containing groups in the irradiated PTFE have to be the cause of the CO_2 . It is known that radiation-induced peroxy radicals in PTFE are extremely stable for a long period of time at room temperature. Kagiya et al.¹⁰ reported that the peroxy radicals disappear

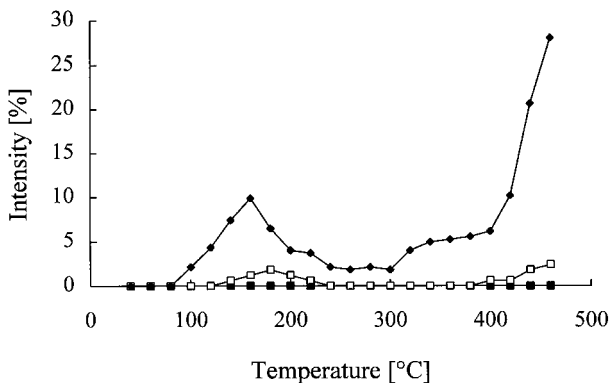


Figure 6 CF_3^+ evolution pattern of (■) original PTFE and PTFE irradiated with a dose of (□) 1 MGy and (◆) 4 MGy.

by heating up to 250°C. COF_2 is formed during heating primarily, but it is converted into CO_2 and HF in the presence of water traces.¹¹ It can be seen in Figure 4 that HF is also evolved from irradiated PTFE during heating. The greatest HF volume is produced in the case of PTFE irradiated with a dose of 4 MGy. Here, HF is evolved already in the temperature range of the first CO_2 peak, i.e., at 200–250°C. The source of the HF evolved in this temperature range is probably the decomposition of the peroxy radicals. However, there are also other processes especially evolving HF at high temperatures. According to the hypothesis of Hagiwara et al.,¹¹ we assume that the first CO_2 peak at about 225°C is attributed to the decomposition of peroxy radicals.

The next question is, Which processes are the source of the second CO_2^+ evolution at temperatures above 300°C? It is known that COF groups are created inside the PTFE by electron beam irradiation in air. These COF groups partly hydrolyze to COOH groups. FTIR spectrometry is able to detect both groups. FTIR spectra of the original and irradiated PTFE are shown in Figure 5. New strong bands appear at 1884 cm^{-1} (— COF [ref. 12]) and 1776 cm^{-1} (— COOH [ref. 13]) in the spectrum of irradiated PTFE. Furthermore, FTIR measurements showed that COOH groups exist already inside the original FEP. This original FEP releases also CO_2 , but only at temperatures above 300°C (Fig. 3). Consequently, the decarboxylation of COOH groups takes place at temperatures above 300°C. The decarboxylation process is connected, of course, to a weight loss, as shown in Figure 2(b). This comparison leads to the assumption that the decarboxylation of the

radiation-induced COOH groups inside the PTFE takes place also at temperatures above 300°C.

Various fluorocarbon fragments evolved during heating were also detected by mass spectrometry. It is interesting that the fragment CF_3^+ ($m/e = 69$) is observed already at relatively low temperatures in the case of irradiated samples (Fig. 6). According to Wheller and Pepper,¹⁴ this fragment is characteristic of saturated fluorocarbons. We assume that low molecular weight fluorocarbons desorbed from the irradiated PTFE powder are the source of the CF_3^+ fragment. The observed strong second step of CF_3^+ evolution at temperatures above 400°C is not well understood at present.

Figure 7 shows the evolution patterns of three fragments characteristic of unsaturated fluorocarbons.¹⁴ In the case of original PTFE, the fragments CF^+ ($m/e = 31$), CF_2^+ ($m/e = 50$), and C_2F_3^+ ($m/e = 81$) can be detected at temperatures

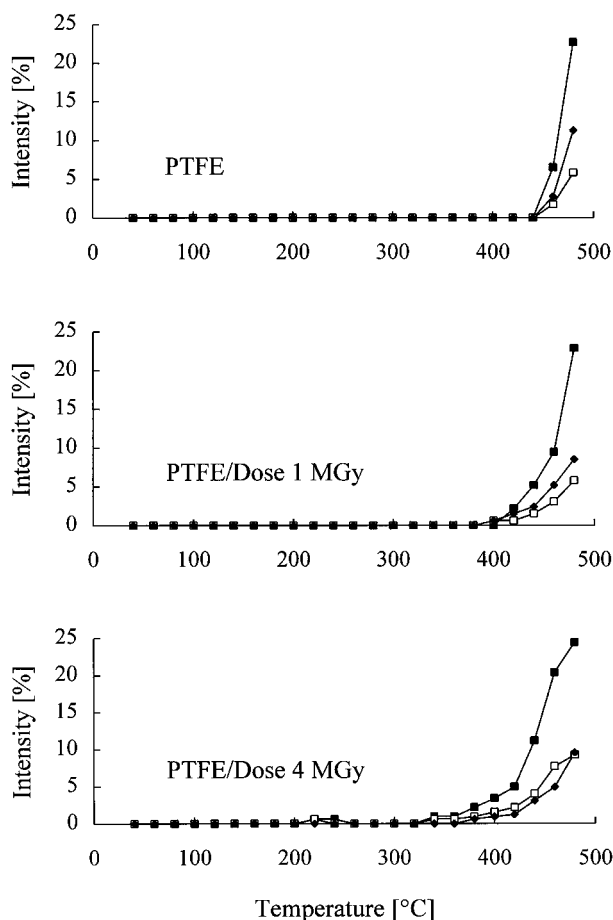


Figure 7 (■) CF^+ , (□) CF_2^+ , and (◆) C_2F_3^+ evolution pattern of original PTFE and PTFE irradiated with a dose of 1 and 4 MGy.

above 440°C. It is known that PTFE degrades to unsaturated low molecular weight products at this temperature.¹⁵ With increasing radiation dose, the starting temperature of this degradation process decreases up to about 320°C for PTFE irradiated with a dose of 4 MGy.

CONCLUSIONS

The thermal degradation of electron beam-irradiated PTFE was studied by thermogravimetric analysis. Furthermore, evolved gases were analyzed by mass spectrometry. The TGA results confirm the known decrease in the thermal stability of PTFE irradiated in air with increasing radiation dose. The results of mass spectrometry show that CO₂, HF, and fluorocarbon fragments are evolved from the irradiated PTFE. Saturated low molecular weight fluorocarbons desorb from the irradiated samples especially at temperatures below 250°C. In addition, CO₂ and HF are formed by decomposition of peroxy radicals in this temperature range. Both the decarboxylation of the radiation-induced COOH groups and the depolymerization process forming unsaturated fluorocarbons take place exclusively at temperatures above 300°C. Therefore, it should be possible to improve the thermal stability of PTFE irradiated in air by annealing at approximately 250°C because low molecular weight irradiation products become volatile and peroxy radicals are decomposed. At this annealing temperature, the decarboxylation of the COOH groups does not take place. We are going to investigate the annealing effect including ESR measurements soon. This study will be presented in a subsequent article.

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