Electron Beam Irradiation of Polytetrafluoroethylene in Vacuum at Elevated Temperature: An Infrared Spectroscopic Study

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ABSTRACT: Electron beam irradiation of polytetrafluoroethylene (PTFE) has been performed in vacuum both at elevated temperature above the melting point of PTFE and at room temperature for comparison. The changes in the chemical structure were studied by Fourier-transform infrared (FTIR) spectroscopy. The formation of double bonds in PTFE was confirmed as a result of irradiation in vacuum. Moreover, trifluoromethyl (CF_3) branches were detected. The concentration of CF_3 branches was found to be much higher in irradiation at elevated temperature than in room temperature irradiation. The CF_3 branches are assumed to cause the reduced crystallinity indicated by the transparency of PTFE specimens irradiated in the molten state. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 1571–1576, 1999

Key words: polytetrafluoroethylene; modification; electron beam irradiation; FTIR spectroscopy

INTRODUCTION

Polytetrafluoroethylene (PTFE) has a unique position in the plastics industry due to its exceptional properties, including chemical inertness and heat resistance. It is widely used in many industrial fields under severe conditions. However, PTFE is extremely sensitive to ionizing radiation; it is classified as a typical polymer that undergoes main chain scission by irradiation.[1] Even a small dose of irradiation causes PTFE's mechanical properties to decay in air or even in an inert gas atmosphere. This radiation sensitivity has been exploited by the conversion of PTFE into low-molecular-weight micropowders through ionizing radiation. A significant recycling of scrap PTFE uses the irradiation process to reduce the molecular weight to a range in which it can be comminuted to a micropowder.[2] PTFE micropowders are compounded into inks, plastics, coatings, lubricants and elastomers.[3]

Recently, it was found that PTFE is crosslinked by ionizing radiation under specific conditions: irradiation in an oxygen-free atmosphere at approximately 340°C; that is, a temperature just above the melting point of PTFE.[4–10] This crosslinking was assumed because the yield strength and modulus increase,[5] the heat of crystallization decreases with increasing radiation dose,[5] unirradiated white-colored PTFE sheets become transparent due to reduced crystallinity,[7] the mode of molecular motions changes,[6,8] and the radiation resistance is much improved.[6,7]

We investigated the irradiation of PTFE under the aforementioned conditions using the electron beam facility in our institute. Here, the PTFE specimens were set in a vacuum vessel with a heating device and irradiated up to a dose of 3 MGy. In this article we report on the characterization of the PTFE specimens by FTIR spectros-

copy. This is the first published work describing FTIR spectroscopic investigations of PTFE irradiated under such drastic conditions.

EXPERIMENTAL

Materials

PTFE peel film (PTFE Nünchritz GmbH, Glaubitz, Germany) with a thickness of 500 μm was used for the experiments. The copolymer poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP 6107; Dyneon GmbH, Burgkirchen, Germany), characterized by FTIR spectroscopy for the purpose of comparison, was a 100 μm-thick sheet.

Irradiation

The PTFE films were irradiated with 1,5 MeV electrons using an ELV-2 electron beam accelerator (Budker Institute of Nuclear Physics, Novosibirsk, Russia) installed at our institute. The complete irradiation facility is described in detail in an earlier article.[11] For irradiation, the specimens were set in a vacuum vessel (10^{-4} mbar) with a window for electron beam penetration (thin metal foil) and an electric heating device. The vacuum vessel was mounted on the conveyor system of the irradiation facility and passed under the electron beam at a rate such that the specimens received a dose calculated at approximately 25 kGy per pass. The high-temperature irradiation experiments were carried out at 365°C, measured with a resistance thermocouple in the sample holder. The temperature was controlled within ±2°K. After irradiation, the controlled heating was continued for 20 min. Other PTFE specimens were irradiated at room temperature, under the other experimental conditions just described.

Measurement

The FTIR transmission spectra of the films were recorded using a Bio-Rad FTS-155 spectrometer. Postannealing of some specimens in air was performed using a Carbolite 12/38/400 tubular furnace.

RESULTS AND DISCUSSION

According to Oshima's observation,[7] PTFE sheets irradiated in vacuum in the molten state become
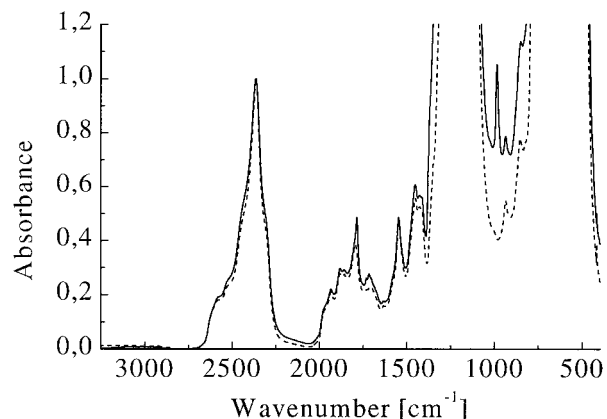

Figure 1   FTIR spectra of PTFE irradiated in vacuum at 365°C with a dose of 1 MGy (solid line) and unirradiated PTFE (dashed line).

transparent, compared to unirradiated white-colored PTFE. This change indicates that the crystallinity of the irradiated PTFE is reduced. We investigated whether radiation-induced changes in the chemical structure causing the reduced crystallinity are detectable by FTIR spectroscopy.

Figure 1 shows FTIR spectra of PTFE irradiated with a dose of 1 MGy in vacuum in the molten state and of unirradiated PTFE. The specimens used are nontransparent for the IR radiation in the region of the very strong CF_2 bands. However, their 500-μm thickness is favorable for the detection of slight changes in other regions of the spectra. For calibration of the spectra in Figure 1 and the following spectra, the band at 2365 cm^{-1}, assigned to a combination band of two modes associated with the CF_2 backbone,[12] was used as an internal standard. The absorbance at 2365 cm^{-1} was set to 1. The calibration is necessary despite the use of sheets, because the thickness of the specimens was significantly reduced by high doses. A control specimen was also subjected to thermal treatment at the same temperature and for the same time as the sample irradiated with 1 MGy. The spectrum of this specimen (not shown in Fig. 1) is not changed compared to that of unirradiated PTFE, although some new bands appear in the spectrum of PTFE irradiated in the molten state.

The interesting regions of the spectra are shown in Figures 2 (1950–1450 cm^{-1}) and 3 (1075–825 cm^{-1}) on an enlarged scale. In these figures, the spectra of other PTFE specimens irradiated with different doses are added. For the purpose of comparison, Figure 2(b) and Figure
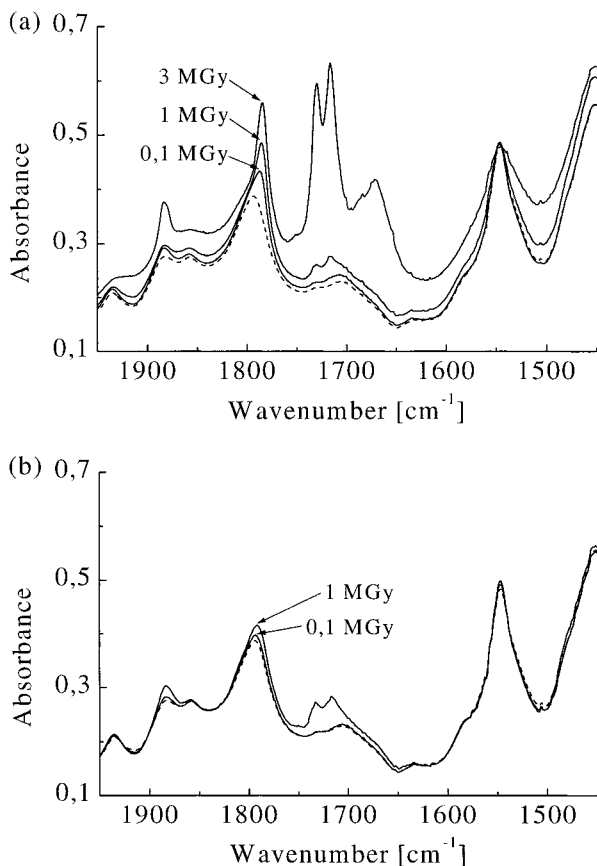
Figure 2 FTIR spectra of PTFE irradiated in vacuum at (a) 365°C and (b) room temperature, with different doses in the region of 1950–1450 cm^{-1} (unirradiated PTFE: dashed line).

3(b) show the partial spectra of PTFE irradiated in vacuum at room temperature. Note that the spectra in both parts of Figures 2 and 3 are plotted in the same scale. Figure 2(a) shows that after irradiation of molten PTFE in vacuum with a dose of 3 MGy, the intensity of the weak band at 1884 cm^{-1} increases and new bands appear at 1785, 1730, 1717, and 1671 cm^{-1}. As expected, the lower the dose, the lower the intensities of the new bands. In the spectrum of PTFE irradiated with a dose of 0,1 MGy, only the band at 1785 cm^{-1} can be clearly observed. The band at 1884 cm^{-1} was identified with the acid fluoride (COF) group.[13] Furthermore, we assume that the band at 1785 cm^{-1} is caused by terminal double bonds (—CF=CF$_2$), because bands at 1785 cm^{-1},[14] 1790 cm^{-1},[15] and 1795 cm^{-1},[16] are assigned to this end group in the literature. The other three bands, at 1730, 1717, and 1671 cm^{-1}, are assumed to be characteristic of olefin formation in the polymer chain because of results obtained in earlier stud-

ies of PTFE degradation in nitrogen atmosphere at very high doses.[17–19] By this procedure, mixtures of perfluoroparaffins and perfluoroolefins with terminal and internal double bonds were obtained. The IR spectra of these mixtures show a band at 1740 cm^{-1} (—CF=CF—) in addition to the band at 1795 cm^{-1} (—CF=CF$_2$).[17] Radiation-induced reaction routes forming the olefinic structures are discussed in an earlier work.[20] In some cases, both a splitting into two bands at 1743 cm^{-1}/1730 cm^{-1},[18] and 1736 cm^{-1}/1722 cm^{-1},[19] and the appearance of a third band at 1690–1680 cm^{-1} (—CF=CF<; i.e., branching at α position) was observed.[18,19] In contrast to these observations, Fisher and Corelli[15] postulated that absorption bands, which were found at 1735 and 1715 cm^{-1}, are caused by branched or crosslinked structures.

The appearance of COF end groups indicates that oxidation reactions occurred. Note that the corresponding absorption band at 1884 cm^{-1} is
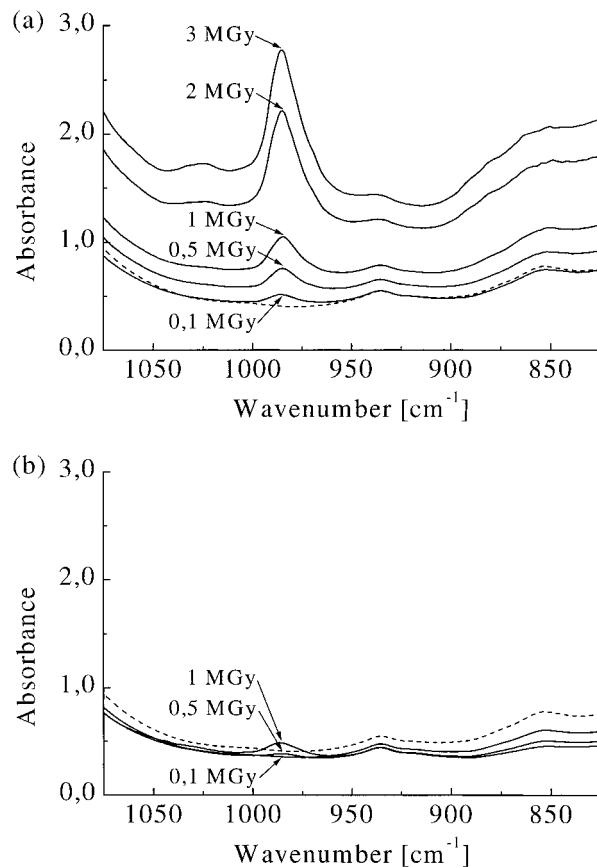

Figure 3 FTIR spectra of PTFE irradiated in vacuum at (a) 365°C and (b) room temperature with different doses in the region of 1075–825 cm^{-1} (unirradiated PTFE: dashed line).
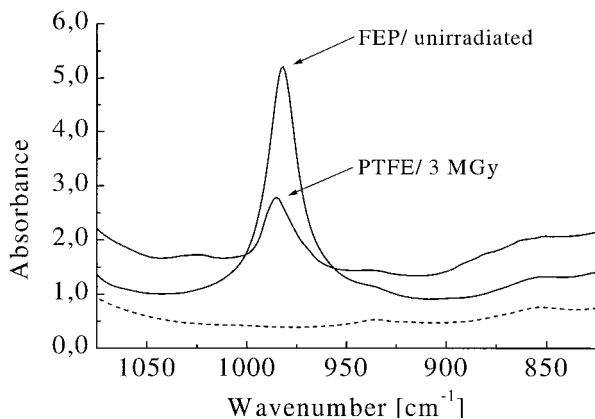
Figure 4   FTIR spectra of PTFE irradiated in vacuum at 365°C with a dose of 3 MGy and unirradiated FEP (unirradiated PTFE: dashed line).

weak, except in the case of the specimen irradiated with 3 MGy. The formation of COF groups may be due to the reaction of radicals with oxygen traces in the vacuum vessel and/or oxygen dissolved in the polymer film. Furthermore, oxygen traces could attack the irradiated PTFE as nitrogen was allowed to flow into the vacuum vessel after irradiation. Because this step was performed at elevated temperature, oxidation of double bonds could occur (as discussed later).

The spectra in Figure 2(b) show that after irradiation at room temperature, bands at 1884, 1785, 1730, and 1717 cm^{-1} also appear. Unfortunately, specimens irradiated with higher doses are extremely brittle, and IR spectra of the films could not be recorded. The intensity of the band at 1785 cm^{-1} is significantly lower in the spectra of both irradiated specimens compared to that irradiated at elevated temperature with the same dose.

The greatest difference in the spectra of specimens irradiated at room temperature and at 365°C can be observed in the region 1075–825 cm^{-1} shown in Figure 3. After irradiation at elevated temperature, a new band appears at 985 cm^{-1} of a relatively high intensity compared to the other radiation-induced bands discussed before (see also Fig. 1 for a direct comparison). The intensity of the band at 985 cm^{-1} increases with increasing dose. This band can also be observed if the irradiation is performed at room temperature; however, it is of much lower intensity [see Fig. 3(b)].

Figure 4 shows that the radiation-induced band at 985 cm^{-1} can be attributed to a chemical structure that also exists in the copolymer FEP.

Therefore, this band is assumed to arise from trifluoromethyl (CF_3) branches. In contrast, Fisher and Corelli[15] discussed the formation of CF_3 end groups indicated by the appearance of a band at 985–980 cm^{-1}. However, we assume that the band at 985 cm^{-1} arises exclusively from CF_3 branches,[21] in agreement with Golden,[22] who attributed this band to a —C—CF(C)—C— skeletal vibration (i.e., branches). We assume that the CF_3 branches are formed by the following reaction:

$$\sim CF_2-\overset{\bullet}{C}F-CF_2\sim \; + \; \overset{\bullet}{C}F_3 \rightarrow \sim CF_2-\underset{\underset{CF_3}{|}}{CF}-CF_2\sim$$
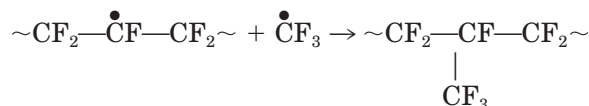
The branching at the mid-chain radical is hindered at room temperature, because diffusion is a primary condition for this reaction. At a temperature above the melting point of PTFE, the branching increases because of higher radical mobility. Nevertheless, the concentration of CF_3 branches in PTFE irradiated with the highest dose (3 MGy) is significantly lower than that in FEP.

To induce oxidation reactions and obtain more information about chemical species formed during irradiation in this way, we annealed some specimens in air. Figure 5 shows spectra of PTFE irradiated in the molten state with a dose of 1 MGy and postannealed in air at different temperatures for 1 h. Figure 6 shows the difference spectra calculated by subtracting the spectrum of the original PTFE from the spectra of the annealed specimens. The intensity of the band at 1785
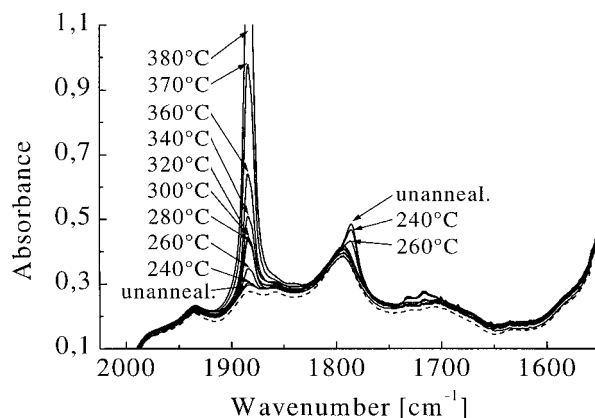

Figure 5   FTIR spectra of irradiated PTFE (1 MGy in vacuum at 365°C) before and after annealing at different temperatures.

cm^{-1} ($-CF=CF_2$) decreases with rising temperature. Simultaneously, the intensity of the band at 1884 cm^{-1} ($-COF$) increases. After annealing at 280°C, the band at 1785 cm^{-1} disappears. Moreover, the intensity of the band at 1884 cm^{-1} remains nearly constant at 300 and 320°C. The changes in the spectra up to 320°C can be interpreted by the oxidation of terminal double bonds to COF end groups, as described in the literature:[2,23]

$$\sim CF_2-CF=CF_2 + O_2 \rightarrow \sim CF_2-COF + COF_2$$
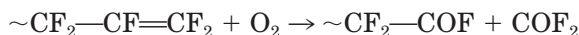
Above 320°C, the intensity of the COF band increases rapidly with rising temperature up to 380°C, followed by decomposition of the specimen with the release of gaseous products. The intensity of the band at 985 cm^{-1} (CF_3 branches) remains constant up to 380°C. Similar results, apart from a slight shift of the processes to lower temperatures, were obtained by annealing the specimen irradiated with 2 MGy (Fig. 7). For this specimen, the behavior of the radiation-induced bands at 1730, 1717, and 1671 cm^{-1} could be studied because of their high intensities in the spectrum. After annealing at 320°C, these bands also disappeared. This indicates that assigning these three bands to olefinic structures, as mentioned before, is plausible.

CONCLUSIONS

FTIR spectroscopy was used to study the changes in the chemical structure of PTFE induced by
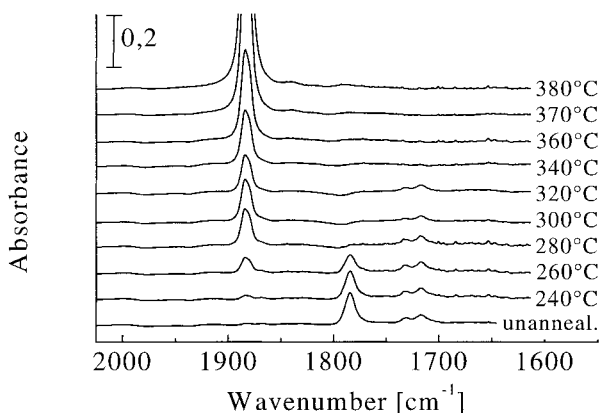

Figure 6 Difference spectra of irradiated PTFE (1 MGy in vacuum at 365°C) annealed at different temperatures and unirradiated PTFE.
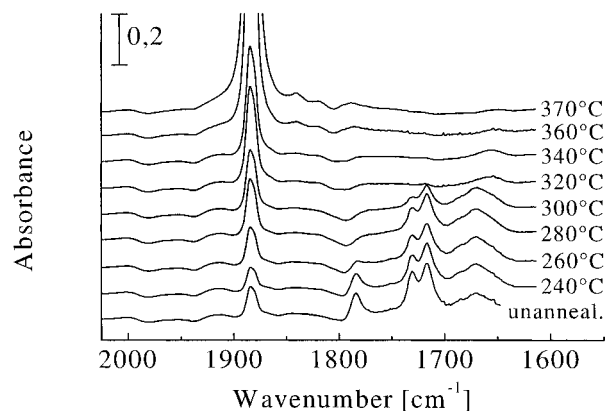

Figure 7 Difference spectra of irradiated PTFE (2 MGy in vacuum at 365°C) annealed at different temperatures and unirradiated PTFE.

electron beam irradiation in vacuum. The spectra discussed in this article confirm the formation of double bonds as a result of irradiation under oxygen-free conditions. Both terminal and internal double bonds originate in the radiation-induced process. Annealing experiments have established that assigning several IR bands to olefinic structures is correct.

In addition, CF_3 branches were detected in the irradiated PTFE. It was found that the concentration of these branches is much higher after irradiation at elevated temperature (molten PTFE) than after irradiation at room temperature (solid PTFE). This indicates that the diffusion of CF_3 radicals is influenced considerably by the state of the polymer. It is reasonable to assume that the transparency of PTFE films irradiated at elevated temperature is caused by CF_3 branches, because FEP films are also transparent.

We note that results published recently by Oshima et al.[5,7–10] and Tabata et al.[6] indicate branching and crosslinking of PTFE by irradiation under similar conditions. Of course, the possibility that branches with side chains longer than the CF_3 group or crosslinked structures are formed by irradiation of molten PTFE cannot be ruled out. IR bands of these structures may appear in the regions of the strong CF_2 bands. However, in this case of superimposition, the bands cannot be observed in the spectra.

Dedicated to Hans-Jörg Jacobasch in memoriam.

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