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## Structural changes of polytetrafluoroethylene during irradiation in oxygen



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## HIGHLIGHTS

- The structural change of PTFE irradiated in O<sub>2</sub> is different from that in vacuum.
- The double bond is not found in PTFE after irradiation in oxygen.
- The new groups like COF, COOH and CF<sub>3</sub> are formed in PTFE after irradiation.
- The expansion of crystallite size is observed in the irradiated PTFE.

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## ABSTRACT

To study the effect of irradiation on PTFE structure and prepare modified PTFE micropowder, PTFE was irradiated with dose up to 4 MGy in oxygen at room temperature. The structures of both irradiated and unirradiated PTFE samples were comparatively characterized by IR, XPS, Raman spectra and XRD measurement. The results showed that new groups of acyl fluoride (COF), carboxylic acid (COOH) and trifluoromethyl (CF<sub>3</sub>) were formed under heavy radiation exposure in oxygen. In addition, the expansion of crystallite size or crystal lattice was first reported for the irradiated PTFE. The formation of new chemical groups and the expansion of crystallite size were elucidated by structural changes occurring in irradiation.

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## 1. Introduction

Polytetrafluoroethylene (PTFE) is an outstanding polymer with excellent properties like chemical inertness, self-lubrication, thermal stability and dielectric properties (Mark, 1999). Therefore, it is widely used in many industrial fields under harsh conditions. On the other hand, PTFE is known to be extremely sensitive to high energy radiation. It undergoes both cross-linking and/or chain scission by irradiation depending on the radiation conditions (Lappan et al., 2002, 2001, 2007; Pugmire et al., 2009; Sun et al., 1994; Tabata et al., 2001, 2013). In general, the chain scission of PTFE often occurs when irradiated at room temperature in air or vacuum, even exposed to very low irradiation dose. On the other hand, PTFE was reported to undergo cross-linking and branching when irradiated in melt state (about 330–340 °C) under vacuum or inert gas (Forsythe and Hill, 2000; Lappan et al., 2007; Lunkwitz et al., 2004). The chain scission reaction under irradiation, most

researchers focused on, has been found a practical application in preparing low molecular weight PTFE micropowder (Khan et al., 2008, 2009; Lappan and Geißler, 2008). PTFE micropowder has been compounded into inks, plastics, coatings and lubricants for the property enhancement of the products (Frick et al., 2013; Hoffmann and Lehmann, 2013). For some applications, the polar groups on the surface of the irradiated PTFE micropowder are desired in order to ensure the properties of ultimate purpose (Klöpffel and Lehmann, 2006).

It is reported that PTFE undergoes defluorination firstly with the formation of macromolecular free radicals (Oshima et al., 1999). The free radicals are inactivated by several reactions to form trifluoromethyl and double bond during irradiation. When irradiated in air, the carbonyl groups are also originated (Ignatieva et al., 2007; Lappan and Geißler, 2008; Lunkwitz et al., 1996), which could improve the dispersibility of the PTFE micropowder. While the effects of irradiation on chain structures are fully investigated, the effects of irradiation on the aggregation structure of the irradiated PTFE is seldom reported.

In this paper, we report the irradiation of PTFE under oxygen atmosphere at relatively high irradiation dose. The structures of

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irradiated and unirradiated PTFE are comparatively characterized. We observed that the new groups of COF, COOH and CF<sub>3</sub> are formed when PTFE irradiated in oxygen. Furthermore, the expansions of crystallite size of the irradiated PTFE are reported. To our knowledge, this is the first time that the expansions of crystallite size of the irradiated PTFE have been investigated. These provide a creationary thought for recognizing the irradiation effect on polymers.

## 2. Experimental

### 2.1. Materials

PTFE with average particle size of about 14 μm was a commercial product (Code FR 002A) of Shanghai 3F New Materials Co. Ltd. (China) and used as received.

### 2.2. Irradiation of PTFE

The irradiation of PTFE was conducted on an electron beam accelerator (GJ-2, Sichuan Institute of Atomic Energy, China) operated at 1.8 MeV and 10 kW in oxygen atmosphere at room temperature under normal pressure. Prior to irradiation, the PTFE sample in polyethylene bag was degassed and filled with oxygen, and then sealed. The irradiation dose was accumulated to 1, 2, 3 and 4 MGy with the same rate, respectively.

### 2.3. Characterization

FT-IR spectra were recorded on a Nicolet 6700 (Thermo Electron Co., USA) spectrometer over the range of 400–4000 cm<sup>-1</sup>. The powdery samples were cold-pressed into films under 10 MPa pressure at room temperature for the measurement.

X-ray photoelectron spectra (XPS) were carried out on an AXIS Ultra<sup>DL</sup>X-ray photoelectron spectroscopy (Kratos Co., UK).

Raman spectra were given by a LabRAM HR Raman Spectrometer (Horiba Jobin Yvon Co., Japan) with a laser at λ of 632 nm using powdery samples.

Wide-angle X-ray diffraction (XRD) measurements were performed on a DX-2700 X-ray diffractometer (Dandong Haoyuan Instrument Co., China) using Cu Kα radiation (λ = 1.54 Å). The data were collected from 5° to 50°.

## 3. Results and discussion

### 3.1. Chemical structure changes

FTIR spectra of unirradiated and irradiated PTFE are illustrated in Fig. 1. For calibration of the spectra in Fig. 1a, the band at 2365 cm<sup>-1</sup>, assigned to a combination band of two modes associated with the CF<sub>2</sub> backbone, was used as an internal standard. It is noted that the broad band at 1760–1830 cm<sup>-1</sup> for the unirradiated PTFE splits into two absorptions centered at 1811 and 1773 cm<sup>-1</sup> in the irradiated PTFE samples. These two absorptions are reasonably designated to the vibration of isolated and associated COOH groups (Fisher and Corelli, 1981; Pianca et al., 1999). Compared with the spectrum of unirradiated PTFE, the spectra of the irradiated PTFE samples also exhibit other two new bands at 1884 cm<sup>-1</sup> and 985 cm<sup>-1</sup>, respectively. They are designated to the vibration of COF and CF<sub>3</sub> (Ignatieva et al., 2007). With the increase of irradiation dose, these absorption peaks become more apparent and sharper.

The formation of these groups has been explained on the basis of ESR spectroscopic analysis. It is deduced that two radicals, ~CF<sub>2</sub>-CF-CF<sub>2</sub>~ (located at mid-chain) and ~CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub> (at end-chain), are formed during the radiation of PTFE (Oshima et al., 1999). The radicals then may undergo the following reaction to inactivate their activity: eliminating fluorine to form double bonds; reacting with oxygen to generate peroxy radical and then to form new end groups like COF; recombining with F to yield CF<sub>3</sub>; and undergoing main chain scission to produce low molecular weight PTFE.

Different from the previous experiments conducted in vacuum and nitrogen atmosphere (Lappan et al., 1999, 2000), the irradiated PTFE samples in oxygen do not show the absorption of double bonds in this work (Fig. 1a). According to the reaction mechanism of PTFE under the irradiation (Lunkwitz et al., 2004), the double bonds should be generated under the irradiation conditions. Its disappearance could be elucidated by their oxidation conversion in oxygen atmosphere, that is, the generated double bonds would immediately react with oxygen to form such oxygen containing groups as COF. Furthermore, the COF groups in the irradiated PTFE samples in Fig. 1a might also be generated via the peroxy radicals intermediates (Ignatieva et al., 2007; Lunkwitz et al., 1996; Schierholz et al., 1999). The appearance of carboxylic acid groups is thus postulated as the hydrolysis of acyl fluoride when exposed to moisture. The result further indicates that the polar groups such as COF and COOH are formed when PTFE is irradiated in oxygen. It is

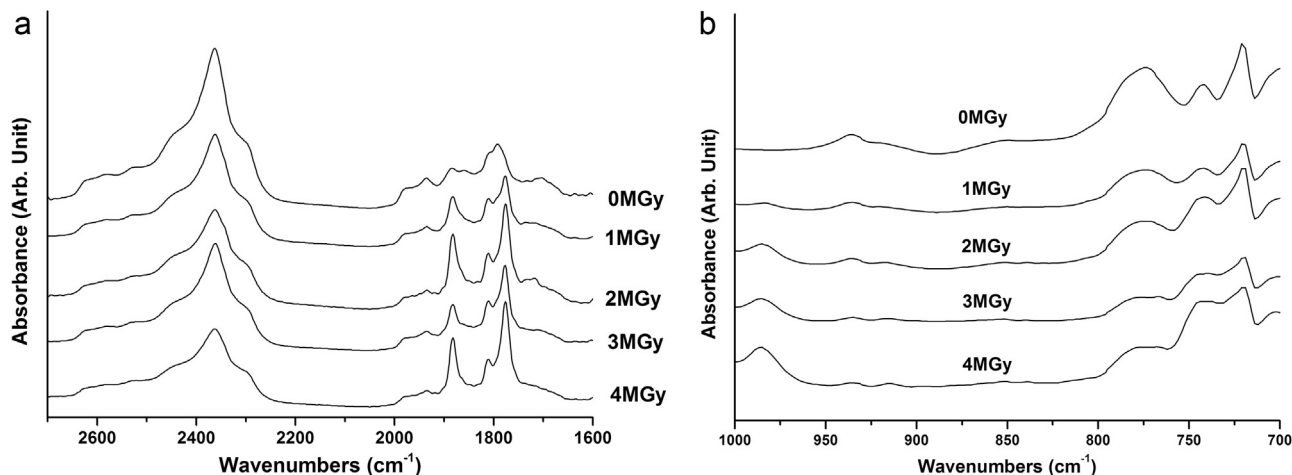


Fig. 1. IR spectra of PTFE samples. (a) 1600–2700 cm<sup>-1</sup> and (b) 700–1000 cm<sup>-1</sup>.

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