

RADIOLYSIS OF POLYTETRAFLUOROETHYLENE

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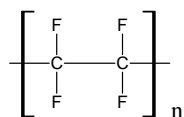
ABSTRACT

Polytetrafluoroethylene is a linear polymer with structure: $-\text{[CF}_2\text{-CF}_2\text{]}_n\text{-}$. Due to its singular properties, it is ideal for use at high temperatures and in chemically aggressive environments. It is extremely sensitive to ionizing radiation and is quickly degraded. PTFE radiolysis has been extensively studied. However, despite the many published papers, its degradation mechanism remains much uncertain. The degradation of polytetrafluoroethylene by γ irradiation yields perfluorinated carboxylic acids, olefin mixtures, and paraffins with different molecular weights. This process is a new alternative for the synthesis of aliphatic perfluorinated compounds used as intermediates for obtaining special products such as fluorosurfactants, electrical materials, special products for the textile industry, etc. PTFE scraps were irradiated with a uniform source of ^{60}Co gamma rays in oxygen atmosphere with a dose of 3 MGy. The radiolysis of PTFE yielded a water soluble material (probably fluorinated hydrocarbons with low molecular weight and main chains with 10-20 carbon atoms) and a water insoluble brittle polymeric material. Spectroscopy analysis in the infrared region of irradiated and non-irradiated PTFE were carried out. X-ray diffractometry pointed to changes in the crystalline structure of PTFE; scanning electron microscopy indicated alterations in samples irradiated under different conditions. Mass spectrometry was also used to identify the compounds formed after sample irradiation. Comparison of irradiated and non-irradiated FTIR spectra showed the formation of bands at 3450 cm^{-1} , associated with the O-H stretching, and at 1631 cm^{-1} , associated with the C=O stretching. The bands are characteristic of carboxylic acid, which indicates its formation in irradiated PTFE.

1. INTRODUCTION

Fluoropolymers, polymers formed by monomers with one or more fluorine atoms or copolymers of these monomers with other monomers, are characterized by their resistance to attacks by chemical products and high thermal stability. They are relatively stable in chemically hostile environments when compared to their protonated analogues, and thus have a broad range of applications in modern technology ranging from O-rings to computer chips to communication satellite reflective coatings [1].

Polytetrafluoroethylene – PTFE is a highly ordered linear chain crystalline polymer with structure:



Although it is highly stable and hardly degradable, when exposed to ionizing radiation such as γ radiation, PTFE undergoes physical and chemical property changes. The processes involved are break of polymeric chain and crosslinking.

PTFE irradiation with relatively low doses and in the presence of oxygen yields a product containing carboxylic groups. PTFE hydrophobicity and organophobicity are sensibly reduced by these functional groups, allowing the homogenization of this material by other means such as aqueous and organic dispersion with polymers, paints, lubricating resins. The functionalized products have been used to incorporate other materials in the production of composites that combine the properties of PTFE with those of conventional materials [1-3]. In this work, the effects of γ radiation on PTFE scraps and the products obtained were analyzed.

1.2 Radiolysis of PTFE

There is no consensus on the exact mechanism of the degradation of PTFE [4]. The irradiation atmosphere, dose, and temperature are some of the factors that affect the product obtained.

The predominant effect of ionizing radiation on PTFE is the degradation caused by the break of polymeric chains, generating low molecular weight products. This process is initiated by the rupture of the C-C and C-F bonds, forming primary and secondary radicals [1].

When irradiated in anhydrous O₂, wet O₂, or in air, PTFE forms perfluoroalkoxy radicals that may later lead to the formation of acid fluoride groups -COF. The -COF groups are hydrolyzed in the presence of water and form carboxylic acids [2].

In the presence of either air or oxygen, the irradiation product of PTFE is a powder with molecular weight significantly lower than that of non-irradiated PTFE. This partial degradation of PTFE is related to the formation of acid fluoride and carboxylic acids [3].

The predominant degradation processes of PTFE in oxygen atmosphere are -COF, -COOH, and -CF₃ groups. The amounts of each of these groups depend on the dose and the irradiation conditions [5].

PTFE irradiation may provoke either an increase or a decrease in crystallinity. The rupture of the polymeric chain forms more mobile low molecular weight molecules that may assume a low free energy conformation such as the regularly packed crystalline phase conformation. It also provokes a reduction in the tension between molecules, which allows the crystallization and results in the formation of functional groups in the amorphous region, leading to an increase in the crystalline phase [2].

2 EXPERIMENTAL

PTFE billet machining scraps were used in the experiments. The material was cleaned with a detergent and then soaked in 6*N* hydrochloric acid for a period of several days and rinsed with demineralized water. Approximately 10 g of polytetrafluoroethylene scraps were placed in borosilicate glass flasks, Fig. 1, in an inflatable polystyrene chamber with oxygen atmosphere at room temperature and pressure. To one of the flasks, it was added 1 mL of demineralized water.



Figure 1. Flask with PTFE scraps before irradiation.

Next, the samples were irradiated at the γ Irradiation Laboratory of CDTN at room temperature with a ^{60}Co – Panoramic Irradiator *GD 127* from MDS Nordion, Canada at a dose rate of approximately $20000 \text{ Gy}\cdot\text{h}^{-1}$. The dosimetry inside the irradiation chamber is based on the dose rate mapping generated during irradiator installation and is constantly updated due to radioactive decay.

The scraps were brittle after exposure to γ radiation (accumulated dose of 3 MGy). It was also noted the deposition of a viscous product on the flask walls, Fig. 2. All the material was washed with demineralized water and filtered. A white powder was obtained after the evaporation of the filtered at $40 \text{ }^\circ\text{C}$.

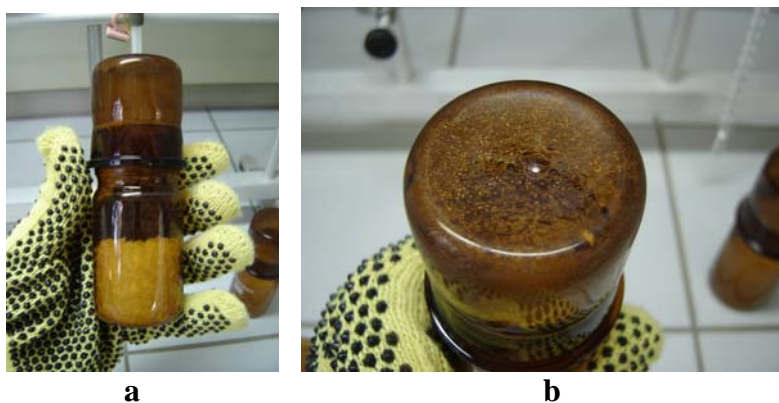


Figure 2. Typical flask with PTFE scraps after irradiation (a) with details of the product on the flask walls (b).

2.1. Analysis and Characterization of Irradiated PTFE

The diffractograms were obtained in a Rigaku model Geigerflex diffractometer. Spectroscopy in the infrared region (ABB Bomem, model MB 102) was used to identify changes in molecular structures. Electron scanning microscopy (JEOL model JSM-840 A) was used to obtain images of γ -ray irradiated and non-irradiated samples. A mass spectrometer MALDI-TOF, model Bruker *Daltonics flex Analysis* was used in the reflective mode to obtain mass spectra.

2.1.1 Electron scanning microscopy

The images of the non-irradiated PTFE sample show a homogeneous surface. The surface changes of non-irradiated PTFE (a), irradiated in dry O_2 atmosphere (g) (b), and irradiated in wet O_2 (g) atmosphere (c) with images enlarged 1000 times may be observed in Fig. 3.

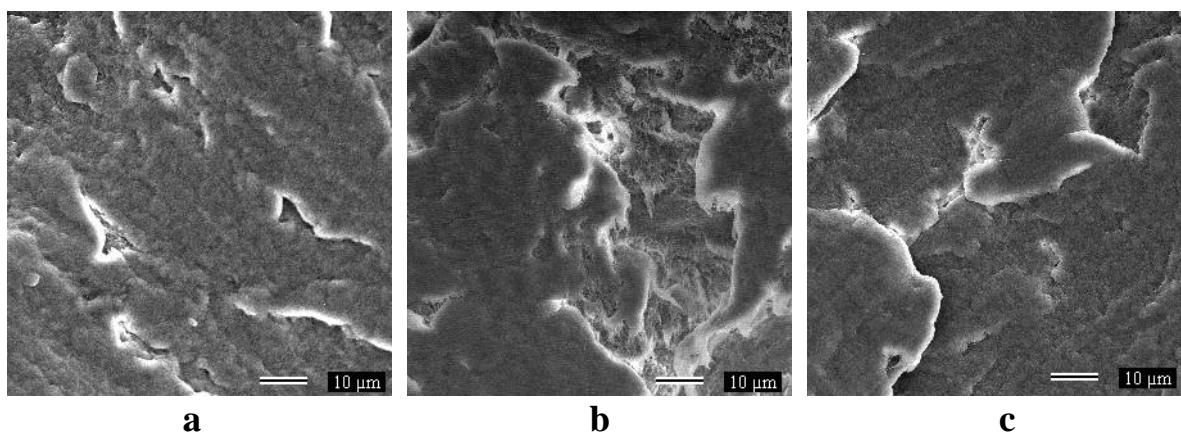


Figure 3. Non-irradiated PTFE surface (a), irradiated in dry O_2 (g) atmosphere (g) (b) and irradiated in wet O_2 (g) atmosphere (c), enlargement:1000 X.

2.1.2 X-ray diffractometry

The X-ray diffractograms show an increase in the crystallinity of PTFE provoked by the action of γ radiation [2], as may be observed in Fig. 4. Spectra a, b, and c refer to PTFE non-irradiated, and irradiated in dry and wet oxygen, respectively.

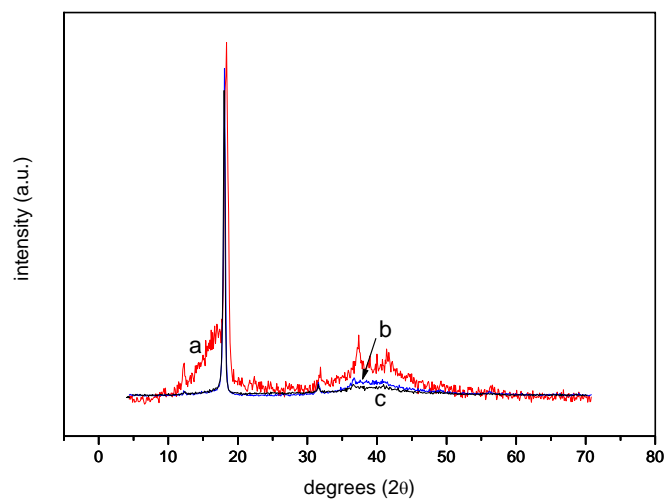


Figure 4. X-ray diffractograms of irradiated (a) and non-irradiated (b,c) PTFE.

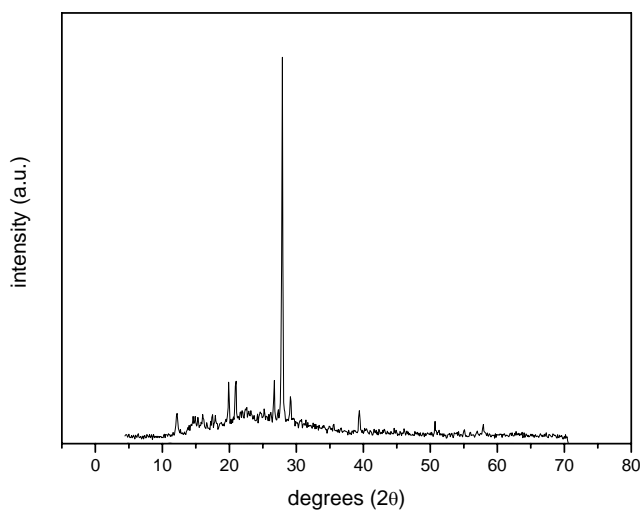


Figure 5. X-ray diffractogram of the water soluble substance extracted from irradiated samples.

2.1.3 Infrared spectroscopy

Infrared spectroscopy was used to identify changes in the molecular structure of PTFE after exposure to γ radiation. The analysis of the radiolysis product spectra (Fig. 6 and 7) reveals a reduction in the intensity of the characteristic absorption bands of $-\text{CF}_2$ groups, evidencing the break of the polymeric chain [6].

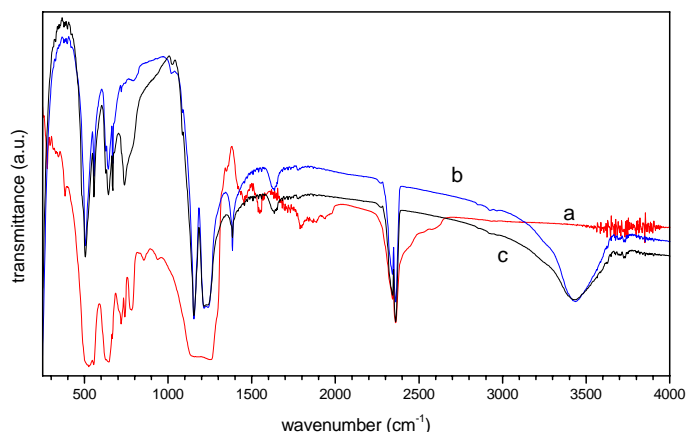


Figure 6. Infrared spectra of non-irradiated PTFE (a), irradiated in dry O₂ atmosphere (b), and irradiated in wet O₂ atmosphere (c).

Spectra **b** and **c** in figure 6 show the formation of carboxylic acid, evidenced by the bands at 3730 cm⁻¹ and 3440 cm⁻¹, characteristic of O-H stretching, and 1780 cm⁻¹, characteristic of C=O stretching [2, 6]. The absence of the band at 1880 cm⁻¹ is observed for the two products, indicating the hydrolysis of -COF [2].

The bands at 781 cm⁻¹, 743 cm⁻¹, 382 cm⁻¹, and 275 cm⁻¹ are caused by conformations of the amorphous phase and do not occur in the irradiated PTFE. The formation of functional groups -COF and -COOH occurs in the amorphous region, which explains the reduction of the absorption bands characteristic of this phase [2].

The spectra of the water soluble products are given in figure 7. It can be observed characteristic carboxyl functional group bands at 3395 cm⁻¹, 3230 cm⁻¹, and 1770 cm⁻¹ in both spectra. Acid fluoride groups -COF identified by the band at 1800 cm⁻¹ occur only for PTFE irradiated in dry O₂ [2, 6].

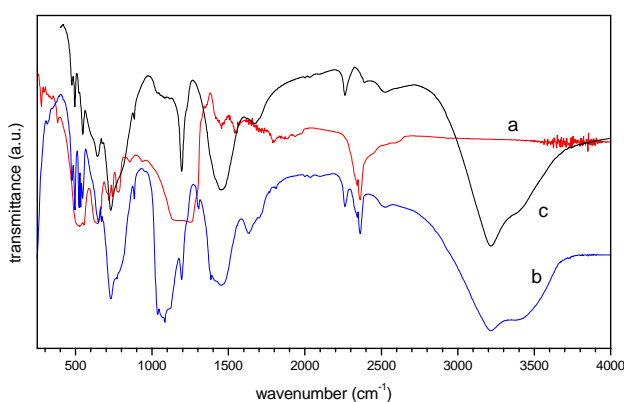


Figure 7. Infrared spectra of non-irradiated PTFE (a), of the water soluble substance extracted from irradiated samples (b,c).

The comparison of spectra **b** and **c** (Fig. 7) shows that the intensity of the carboxyl acid bands is nearly the same for the two products, indicating that there is no quantitative difference for the -COOH groups formed. It was expected a larger concentration of these groups in the product obtained in wet O₂ atmosphere; however, the manipulation of the product in dry O₂ atmosphere after irradiation occurred in the presence of water, allowing the hydrolysis of the -COF groups formed.

2.1.4 Mass spectrometry

Mass spectra obtained for water soluble radiolysis PTFE products revealed a series of molecular ion signals for molar masses between 700 gmol⁻¹ and 1500 gmol⁻¹. According to these data, it is observed the presence of modified polymers at the ends and the main chain varies between 10 and 20 carbon atoms.

The most intense signals obtained for PTFE irradiated in anhydrous O₂ atmosphere were molecular ions with molar mass 1066 gmol⁻¹, 860 gmol⁻¹, and 838 gmol⁻¹. The main polymer chain is formed by -CF₂-CF₂- monomers. Considering the data obtained in infrared spectroscopy, carboxyl acid chains with 19 carbon atoms were attributed to the molecular ion with molar mass of 1066 gmol⁻¹. This signal may also be attributable to chains with acyl fluoride functional groups. The signal at 860 gmol⁻¹ is attributed to a chain with 18 carbon atoms and the signal at 838 gmol⁻¹, to a chain with 14 carbon atoms.

The mass spectra of PTFE irradiated in wet O₂ atmosphere presented the following signals, 1014, 876, 845, and 840. Molecular ions with molar mass 1014 gmol⁻¹, 876 gmol⁻¹, and 840 gmol⁻¹ are attributed to carboxyl acid chains with 18, 17, and 15 carbon atoms, respectively. Chains with 15 carbon atoms are attributed to the molecular ion with mass 845 gmol⁻¹.

3 CONCLUSIONS

PTFE scraps were irradiated with γ -ray from a ⁶⁰Co source with activity of approximately 55000 Ci at room temperature under dry and wet oxygen atmosphere. Radiolysis of PTFE gave the following products: a water soluble material (probably fluoridated hydrocarbons with low molecular weight and main chains with from 10 to 20 carbon atoms) and a water insoluble brittle polymeric material. Infrared spectra indicated the formation of carboxyl acid and acyl fluorides. X-ray diffractometry study showed that the radiolysis product is more crystalline than the non-irradiated product. The molecular chains in the crystalline region pack more tightly in the irradiated PTFE. It could be observed changes on the polymer surface by electron scanning microscopy with a more homogeneous surface for the non-irradiated product and a roughened surface for the irradiated product due to the increase in sample density after irradiation.

Further investigation of the degradation of PTFE billet machining scraps used in the experiments (¹⁹F, ¹H, and ¹³C nuclear magnetic resonance and high-performance liquid chromatography/mass spectrometry) is underway.

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