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Correlating Crystallinity and Electrical Conductivity in Gamma-Irradiated PTFE

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Abstract— Exposing polytetrafluoroethylene (PTFE) to irradiation brings about significant alterations in both its crystallinity and conductivity. The primary objective of this study is to investigate the connection, if any, between crystallinity, a structural feature, and electrical conductivity, which represents a macroscopic property. This was accomplished by subjecting PTFE to varying doses of γ -rays, reaching up to 200 kGy. Various physicochemical characterizations were conducted to elucidate the impact of irradiation on dielectric properties. We show that irradiation produces chain scission and oxidized groups at chain ends. The material becomes more crystallizable after irradiation whereas the increase in conductivity would result from transport due to oxidized groups and short chain formation.

Keywords— *Gamma irradiation, Polytetrafluoroethylene, Crystallinity, Conductivity*

I. INTRODUCTION

Polytetrafluoroethylene (PTFE) is used as electrical and thermal insulating material in various wires and cables employed in applications where extreme gamma radiation conditions are present, such as in satellite industries and nuclear power plants [1][2]. Fluorocarbon polymers are recognized as relatively weakly resistant to radiation in contrast to their outstanding chemical and thermal stability [3]. Therefore, it is crucial to investigate the effects of gamma radiation on electrical properties.

The exposure to ionizing radiations significantly modifies the electrical characteristics of polymers, potentially impacting the reliability of insulation in radiative environments [4][5]. According to earlier studies on PTFE materials, radiation can lead to easier formation of space charges within the polymer when subjected to DC stress [6]. Notably, heterocharge formation was reported. Additionally, exposure to high doses of gamma radiation may result in polymer degradation through processes such as chain scission, as documented in this study [1][7]. The alterations in the electrical behavior of PTFE are linked to structural modifications induced by radiation, as discussed in our previous research [4][6]. The present study aims at investigating the connections between the process of crystallization and electrical conductivity, essentially endeavoring to establish a correlation between macroscopic characteristics and a microscopic property. For this purpose, PTFE thin films with a thickness of 200 μm were subjected to irradiation using a ⁶⁰Co gamma radiation source at various doses: 30 to 200 kGy. The irradiation was conducted at a consistent dose rate and a temperature of 20 °C. The objective

was to examine the influence of irradiation on the electrical behavior of the thin films.

II. EXPERIMENTAL CONDITIONS

We will first describe the principles underlying each characterization method, as well as the experimental measurement bench that was used.

A. Samples preparation

The material used in this study is a 200 μm thick PTFE film supplied by Goodfellow.

B. Gamma Irradiation

The polytetrafluoroethylene (PTFE) samples underwent irradiation with gamma rays produced by a cobalt-60 source at the Nuclear Research Center of Algiers. Throughout the irradiation process, the samples were maintained in ambient air at room temperature and positioned at a specified location in relation to the source. The dose rate from the source was 22 Gray per minute. Doses up to 200 kGy were applied.

C. Differential scanning calorimetry Analyses

The DSC was utilized to characterize the crystallinity of both virgin and irradiated PTFE. A TA Instruments Q2000 DSC (See Fig. 1), calibrated with indium, conducted the measurements. The aluminum-encased samples, typically 10 mg in weight, underwent two consecutive cooling and heating thermal cycles (with a rate of 10 °C/min).

D. FTIR Spectroscopy

FTIR spectroscopy was employed to study the effect of gamma irradiation on the molar ratios of such end groups as COF and COOH to CF₂ units as a fingerprint of chain scission and oxidation processes.



Fig. 1. The TA Instruments Q2000 DSC device was employed for conducting differential enthalpy analysis [8].

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FTIR spectra were taken in nitrogen atmosphere using a VERTEX 70 fully digital infrared (IR) spectrometer designed for mid-infrared region data acquisition ($400\text{--}4000\text{ cm}^{-1}$) in transmission mode with 32 scans and a resolution of 2 cm^{-1} .

E. Current measurements

Current measurements were conducted under a DC voltage of 40 kV/mm in the same irradiation conditions set at $20\text{ }^\circ\text{C}$ and normal air pressure.

The samples were coated with gold electrodes of 16 mm in diameter and 30 nm in thickness on both faces using a sputtering technique. These specimens were placed between brass electrodes while undergoing the measurement procedure (Fig. 2).

The current measurement protocol involves a 3-hour polarization phase followed by a 3-hour depolarization phase. Voltage was applied through a low ripple DC source model HCL35-35000 from Fug Gbmh, with $35\text{ kV}/0.1\text{ mA}$ specifications. Current values were recorded at 2-second intervals during both the polarization and depolarization phases using the Keithley 6512 electrometer.

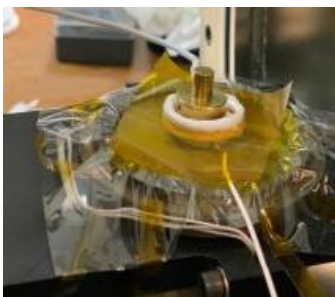


Fig. 2. Current measurement setup depicting a sample positioned between two electrodes [9].

III. RESULTS AND DISCUSSION

A. Effect of the absorbed dose on the structural properties of PTFE

We would like to emphasize that, as reported in our previous studies, PTFE undergoes structural changes, namely crystallinity increase, as a result from chemical degradation in the form of chain scission and oxidation produced during gamma irradiation [1]. These changes were manifested by an increase of the dielectric permittivity with the irradiation dose. It is noticeable that the crystallinity increase does not occur in an obvious way during the irradiation, but rather after melting and recrystallization. In other words, the ability to crystallize of the material changes and this can be the result notably of chain scission. Therefore, it is relevant to correlate dielectric properties to crystallinity degree on the one hand as a reflect of chain scission, and to the signature of end groups formation.

DSC data were used to determine the crystallinity values based on the melting enthalpy according to Suwa's method [10]. Table I presents the values for the enthalpy of melting and crystallization.

From Table I, it is clear that the effect of gamma rays on PTFE films leads to a significant increase in crystallinity. Based on this result, we can conclude that chain scission is the main effect.

TABLE I MELTING ENTHALPY AND CRYSTALLINITY RESULTS OF IRRADIATED PTFE.

Dose (kGy)	Melting enthalpy (J/g)	Crystallinity %
0 (virgin)	33	40
30	69	84
60	71	86
100	75	92
200	81	98

B. Charging Current of virgin and Gamma-Irradiated PTFE

The electrical conduction properties of both untreated (Reference) and gamma-irradiated PTFE films were investigated under an applied DC field of 40 kV/mm . Charging currents were measured for approximately 3 hours at $20\text{ }^\circ\text{C}$. Figure 3 illustrates the evolution of charge currents for both gamma-irradiated and virgin PTFE films. Note that data beyond 1000 s for 30 kGy are not represented due to noisy signal.

In reference PTFE, there is an observed decrease in charge currents by approximately two decades from the beginning to the end of the measurement period. Furthermore, a steady state has not been reached even after 3 h charging time. The difference in currents between virgin and irradiated PTFE is tremendous, even at a moderate gamma irradiation dose of 30 kGy . However, for doses of 30 kGy and above, the current gaps between the irradiated samples are not so strong, similar to the situation between doses of 100 kGy and 200 kGy .

C. Effect of the absorbed dose on the current behavior of PTFE.

In Figure 4, the current evolution at the end of the charging process is depicted as a function of the gamma dose for various electric fields in the range $10\text{--}40\text{ kV/mm}$. An increase in current is observed for the irradiated sample ($30\text{ to }200\text{ kGy}$) compared with the virgin sample. The general trend is that reported above: there is a great increase in current for 30 kGy and then the increase with the dose is smoother with a kind of plateau reached between 100 and 200 kGy . Regarding the effect of field, there is no specific difference noticeable at low dose: the current increases by about 2 decades in all cases between virgin and 30 kGy irradiated sample. However, at high dose the current becomes independent of the field.

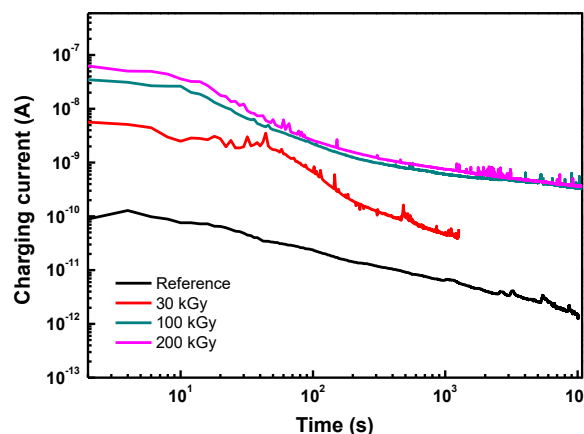


Fig. 3. Charging current measurements at $20\text{ }^\circ\text{C}$ for various γ doses (0 , 30 , 100 and 200 kGy) on a $200\text{ }\mu\text{m}$ -thick PTFE samples under a field of 40 kV/mm .

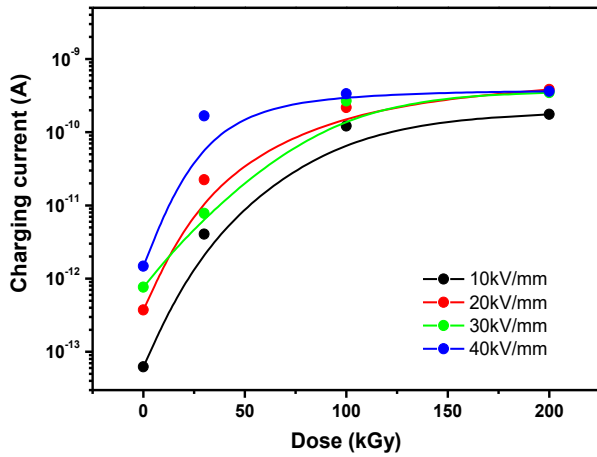


Fig. 4. Evolution of the charging current after 3 h as a function of dose for various applied field strengths. Solid lines are guides to the eyes.

It seems as if a kind of current saturation is being reached, and this could be the result of space charge build-up that modulates the field and the injecting electrode, supposing that the current is limited by the electrodes.

The increase in conductivity of PTFE films after the irradiation process can be attributed to the structural change that resulted in a significant increase in crystallinity. It will therefore be important to understand the relationship between crystallization and conductivity.

D. Correlation between crystallinity and electrical conductivity

Crystallinity and conductivity were normalized to the values obtained for the virgin sample. The obtained variations are presented in Fig. 5 as a function of the γ dose. The variation of the normalized conductivity with the dose was well fitted to the following empirical growing function:

$$\bar{\sigma}(D) \cong 1 + p \times \left(1 - \exp\left(-\frac{D}{D_0}\right) \right) \quad (1)$$

with $p = 265$ and $D_0 = 60$ kGy

With the proposed representation, a correlation between crystallinity and conductivity could be deduced. However, on the one hand there no specific reason that crystallinity increase leads to an increase in electrical conductivity (the reverse would be expected), and second the crystallinity shown here is that measured after melting and crystallization and is therefore not representative of the material on which the conductivity was measured. In other words, the correlation could be between the conductivity and the potential 'crystallization ability'. The reasons for the correlation have to be found in modifications imparted by the radiation that can be chain scission and, possibly, oxidation as a consequence of chain scission.

It is reasonable to attribute the increase in conductivity to the formation of polar groups induced by radiation. Previous studies have indicated an inverse relationship between molecular weight and crystallinity [1], [4]. Therefore, the average molecular weight M_n of irradiated PTFE can be estimated based on the quantitative analysis of the end group density [11]. Our suggestion is that the rise in conductivity is associated with the increase in carbonyl end group formation, as reported for polyethylene [12].

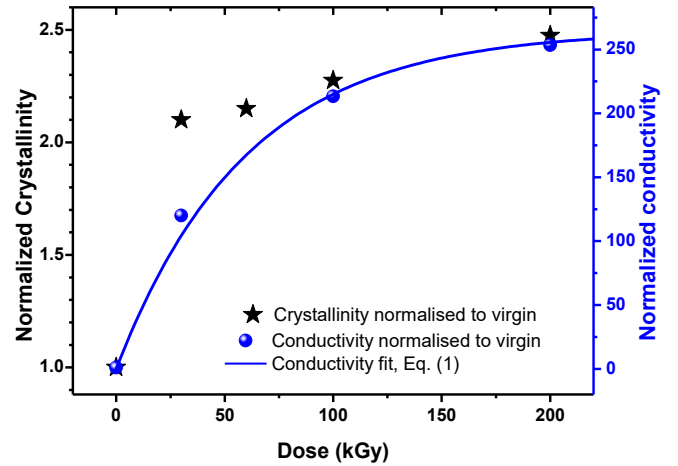


Fig. 5. Crystallinity and conductivity at 40 kV/mm, normalized to the value at dose $D = 0$, of γ -irradiated PTFE versus dose. The blue line is the fit to (1).

It is well known that gamma irradiation, in the presence of oxygen, changes the chemical structure of PTFE, resulting in chain scissions and the creation of carboxylic acid fluoride (-COF) and carboxylic acid (-COOH) end groups. The method detailed by Lappan et al [11, 13] has been adopted to determine the molar ratios of carbonyl end groups to CF_2 units using the FTIR spectrum. For each of the end group i , the ratio is given by:

$$\Gamma_i = \frac{[EG]_i}{[CF_2]} = A_i \times \frac{[IR]_i}{[d]} \quad (2)$$

where [EG] represents the density of a particular end group, A is a calibration factor, IR is the measured IR absorbance, and d is the thickness of the PTFE film. Calibration factors gathered by Lapplan et al [11] were applied to our FTIR data.

The total molar ratio of carbonyl end groups, being COF, and COOH group in either the free or H-bonded form, to CF_2 units is plotted in Fig. 6 as a function of the irradiation dose. The FTIR signatures of the group are at 1883, 1810 and 1777 cm^{-1} , respectively.

Figure 6 indicates an increase in the content of carbonyl end groups with higher doses of gamma irradiation. This suggests that the emergence of carbonyl end groups during irradiation, possibly due to oxidation or an imbalance of fluorine atoms along the polymer chain, is likely responsible for the observed increase in conductivity [1], [12].

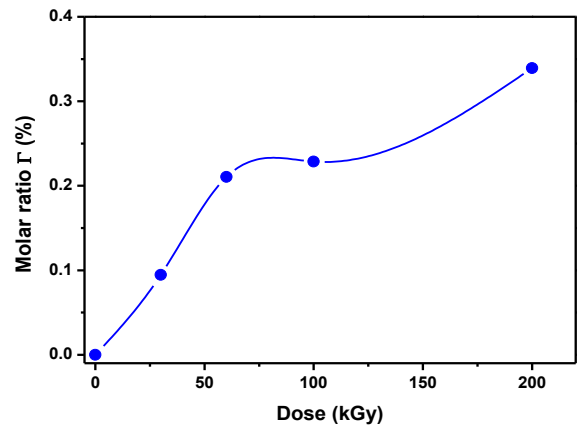


Fig. 6. Molar ratio of carbonyl end groups to CF_2 units in irradiated PTFE samples. The blue line is a guide to the eyes.

It can be reasonably anticipated that the increase in electrical conductivity is a result of charge movement in low molecular weight PTFE chains produced by chain scission. This process is also believed to be the cause of the emergence of heterocharges in irradiated PTFE.

IV. CONCLUSIONS

The following conclusions can be drawn on the scenario for gamma radiation effects on the electrical properties of PTFE:

i/ Irradiation produces chain scission and oxidation following the formation of radicals at the chain ends as irradiation is achieved in air. End groups as carboxylic acid fluoride (-COF) and carboxylic acid (-COOH) are formed;

ii/ Due to the reduction in molar mass, the material crystallizes much more easily once irradiated;

iii/ Due to the presence of oxidized groups, the conductivity of PTFE is substantially enhanced after irradiation;

iv/ Traps are presumably formed near the material surface with a greater density or with different depths than in volume, which would reduce the mobility of the charges. As a result, a region of heterocharges would be formed;

v/ The very significant variation in conductivity observed after irradiation can only be imagined with the formation of transport sites. Chain ends formation may not be sufficient to explain the behavior of the conductivity. Charges presumably move in low molecular weight PTFE chains produced by chain scission in the amorphous phase. A current saturation phenomenon seems to appear at high doses;

vi/ The conductivity-crystallinity correlation is very indirect. Both phenomena remain a consequence of chain scission and the structural modifications that follow.

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