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# GAMMA IRRADIATION EFFECTS ON POLY(VINYLIDENE FLUORIDE) FILMS

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## ABSTRACT

In this work, the properties of Poly(vinylidene fluoride) PVDF films after exposing to gamma radiation at different doses (5, 10 and 15 kGy) were investigated. PVDF is a semicrystalline polymer that shows good properties in terms of chemical, thermal and electrical stabilities. The gamma radiation is a convenient and effective way of modification perfluorinated and partially fluorinated polymers such as PVDF. The properties of the pristine and irradiated PVDF films were studied by infrared spectroscopy, thermal analysis (TGA and DSC) and mechanical measurements at room temperature and at melting temperature of the PVDF. The infrared spectra of the irradiated PVDF samples do not present significant alterations in the absorption bands at all irradiated doses. The results obtained by thermal analysis indicate that the radiation does not alter significantly the decomposition temperature of the pristine PVDF film. Tensile strength measurements at room temperature before and after exposition to gamma radiation showed decrease of elongation at rupture in relation of pristine PVDF, suggesting that the radiation caused the crosslinking or chain scission of the PVDF film.

## 1. INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is a semicrystalline polymer that shows excellent mechanical and chemical properties and thermal and electrical stabilities. PVDF has been widely studied due to its piezoelectric properties and the abundance of its polymorphic forms [1]. This polymer can crystallize at least five crystal forms, $\alpha$, $\beta$, $\delta$, $\varepsilon$ and $\gamma$ depending upon crystallization conditions and can be converted from one to the other by various processes such as mechanical deformation, poling under large electric fields, annealing or crystallization at high temperatures. However, the most known are $\alpha$ and $\beta$ forms. In the crystal form $\beta$ the chains are packed in the unit cell in such a way that the dipoles associated with individual molecules are parallel, leading to a non-zero dipole moment of the crystal. Then, the crystal presents a large spontaneous polarization in its unit cell and when oriented and then poled under an electric field exhibits the high piezoelectric properties. In the other hand, crystal form $\alpha$ the chains are packed in the unit cell in such a way that the molecular dipoles are anti-parallel and there is no net (crystal) dipole [1-3].

Radiation is a convenient and effective way of modifying existing polymers. Such changes may be in the form of crosslinking or main chain scission depending on the chemical and physical properties of the polymer and irradiation dose [4].

The radiation chemistry of the fluorinated ethylenes are characterized by extensive crosslinking and elimination of HF generating unsaturation. In the case of PVDF the crosslinking occurs readily when exposed to ionizing radiation. The mechanical properties of irradiated PVDF are described for high doses. It was observed that the tensile strength of irradiated PVDF increased by about 40% from its original value after a dose of about 1000 kGy. Upon further irradiation the tensile strength dropped to about 80% of the original value, due to limited movement of the chain segments in the crosslinked network [5].

While many investigations have been carried out to characterize the deformation of PVDF films and are well established, up to now few systematic evaluations of the effect of low gamma radiation dose on the tensile strength were described. In this work, the properties of PVDF films after exposing to gamma radiation at different doses (5, 10 and 15 kGy) were investigated. Thermal analysis and stress-strain tests were conducted before and after interaction with gamma radiation to understand better the effects of this radiation on the thermal and mechanical properties of the PVDF film.

## 2. EXPERIMENTAL

### 2.1. Film preparation

PVDF films with 125µm thickness purchased from Goodfellow Ltda were used in this study. The films were put into nylon bags under air atmosphere and submitted to gamma radiation doses, 5, 10 and 15kGy, at 10.7 kGy $h^{-1}$.

### 2.2. Characterization

The thermogravimetric (TG) was recorded with a Mettler-Toledo TGA / SDTA 851 thermobalance in nitrogen atmosphere, from 25 up to 750 °C at a heating rate of 10 °C $min^{-1}$. The differential scanning calorimetry (DSC) curves for the pristine and irradiated PVDF films were obtained in a DSC Mettler Toledo apparatus. The samples (10-15 mg) were heated from room temperature to 350 °C under nitrogen atmosphere at heating rate of 10 °C $min^{-1}$. DSC apparatus was calibrated with Indium (m.p 156.61 °C; $\Delta H$ = 28.54 kJ $kg^{-1}$). Crystallinity was calculated according to Eq. 1:

$$X_c(\%)=(\Delta H_f \times 100) / \Delta H_0 \quad (1)$$

$\Delta H_f$ = melting enthalpy of the sample, $\Delta H_0$ = melting enthalpy of the 100% crystalline PVDF which is assumed to be 104.7 (J $g^{-1}$) [6].

Infrared spectroscopy was performed at Nicolet 6700 FT-IR spectrometer equipped with ATR. The spectra were measured in transmittance mode in a wave number range of 4000-400

$cm^{-1}$. Tensile tests were carried out at room temperature at EMIC DL 300 universal tensile/compression testing machine equipped with a data acquisition system. The speed velocity of testing was 500 mm/min and at least six specimens were tested from each sample. Tensile strength was also measured using mechanical tester Instron equipped with a heating chamber at 165 °C. The speed velocity of testing was 50 mm/min and at least four specimens were tested from each sample.

## 3. RESULTS AND DISCUSSION

The infrared spectrum of pristine PVDF film, Fig. 1., is characterized by the presence of vibrational bands at 615, 763 and 795 $cm^{-1}$ that are characteristics of $CF_2$ bending, skeletal bending and $CH_2$ rocking, respectively, of crystalline phase α. This spectrum also exhibits a weak band at 840 $cm^{-1}$ that according to literature [1] is uniquely characteristic of the crystalline phase β. As can be seen in the spectrum of the irradiated PVDF with 15 kGy, the films after irradiation process do not present significant alterations in the absorption bands, suggesting that the radiation has no effects on the crystalline phases.

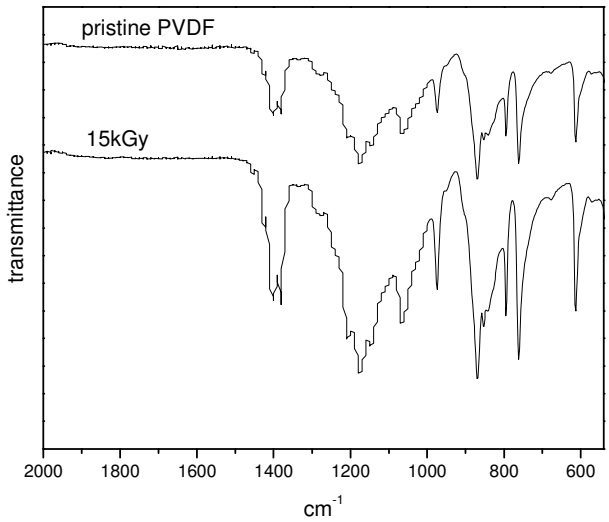


**Figure 1. Infrared spectra for pristine and irradiated PVDF films.**

The pristine and irradiated PVDF were characterized for their thermal properties by TGA and DSC, Figs. 2 and 3, respectively. The pristine PVDF film exhibits a single step degradation started at about 400 °C and finished at 510 °C. The irradiation does not alter significantly the decomposition temperature of the pristine PVDF film.

The DSC curve of pristine PVDF film shows a bimodal melting endothermic with melting temperatures, respectively, at 165.3 and 169.2 °C due to the different crystal structure present on this polymer [7]. The DSC curve for the irradiated films presents the same profile, except the film irradiated with 10kGy that shows three different peaks. The crystallinity obtained

was quite similar for pristine (47.7%) and irradiated films with 5 (48.6%) and 10kGy (47.1%). However, for 15 kGy was observed a slight increase (49.7%), but these differences may be ascribed to the uncertainty of the measurement.

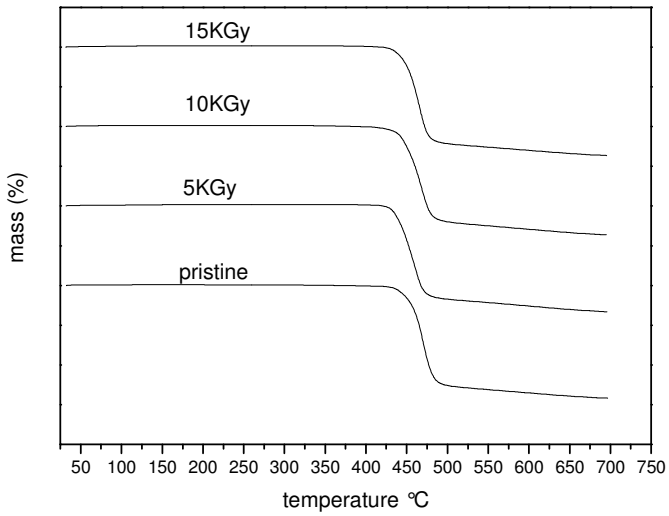


**Figure 2. TGA curves for pristine and irradiated PVDF films.**

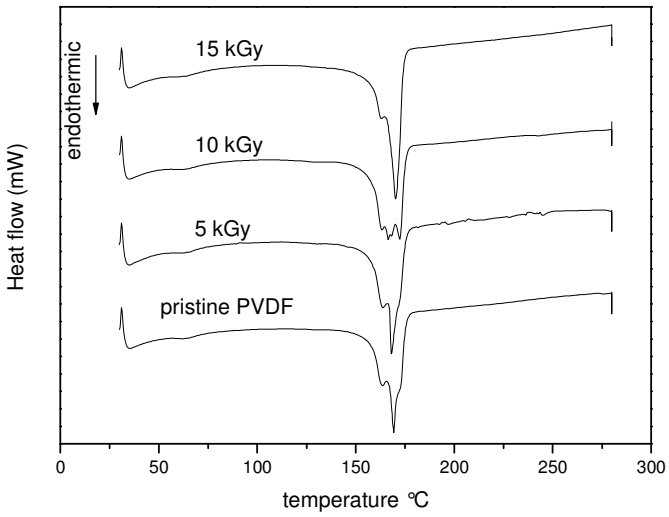


**Figure 3. DSC curves for pristine and irradiated PVDF films.**

The tensile behaviour of the pristine and irradiated PVDF films was investigated at room temperature, Fig. 4 and at 165 °C, Fig. 5. This work focused on mechanical parameters such as yield strength and rupture strength.

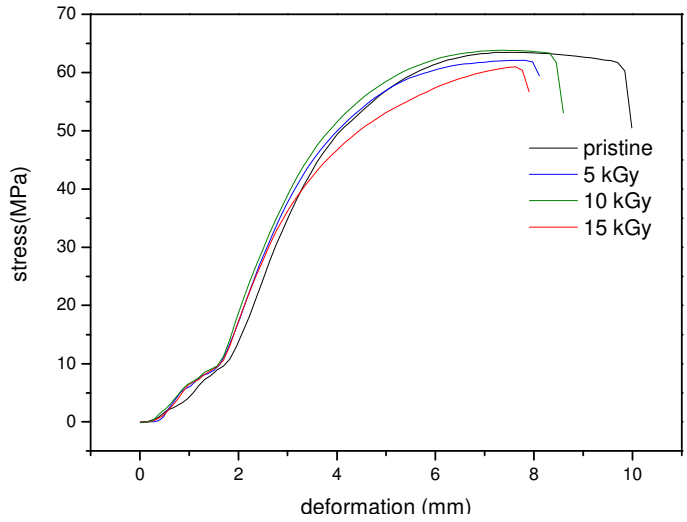


**Figure 4. Stress–strain curves for pristine and irradiated PVDF films obtained at room temperature.**

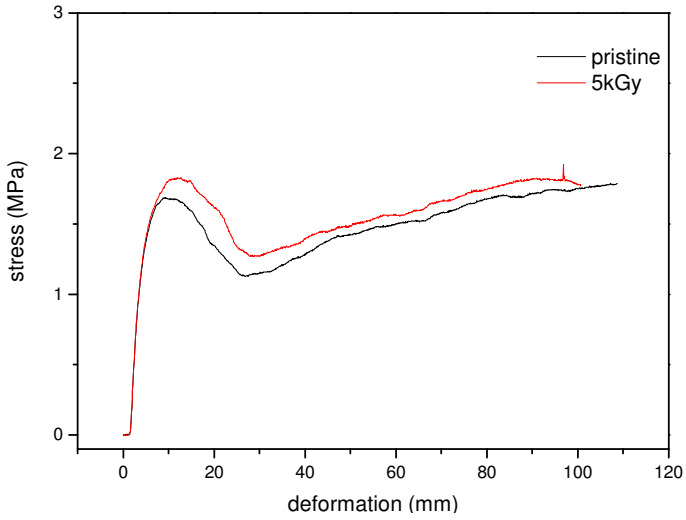


**Figure 5. Stress–strain curves for pristine and irradiated PVDF films obtained at 165°C.**

The stress–strain curves obtained at room temperature for pristine and irradiated PVDF films show basically two regions. The first one at lower strain is characterized by two stages. This mechanical response in the initial strain region probably is due to different crystalline structures present in the PVDF film. The second region is typical of strain hardening consequently as the deformation occurs as more stress is needed to continue the deformation process. All samples irradiated showed decrease of elongation at rupture and a slight decrease of tensile strength after irradiation, mainly for 15 kGy, in relation of pristine PVDF. These results can be explained by the fact that mechanical properties of irradiated films reflect the structural changes taking place during the irradiation. As mentioned above, the radiation can causes the polymer modification in the form of main chain scission or crosslinking. The chain

scission results in a decrease of the molecular weight, while the crosslinking decreases the mobility of polymer chain segments, and both these factors can contribute to the decrease in elongation at break with increasing radiation dose as observed in the stress-strain curves.

The stress–strain curves obtained at 165 °C before and after the irradiation process with 5 kGy exhibit a maximum in the stress and then decrease at higher strains. The irradiated film showed similar stress at yield when compared to the pristine film. At this temperature can be inferred that occurs the melting of the crystalline region and the effects observed on tensile strength are due to amorphous phase.

## 3. CONCLUSIONS

The properties of PVDF films after exposing to gamma radiation at low doses were investigated. The irradiated samples do not show significant alterations in the profile of the pristine FT-IR, while the results of thermogravimetric analysis indicate that the radiation does not alter significantly the decomposition temperature. However, by DSC analysis the PVDF film irradiated with 15 kGy presented little increase on crystallinity in relation to the respective pristine PVDF, but this difference may be ascribed to the uncertainty of the measurement. Preliminary tensile strength measurements showed decrease of elongation at rupture for all irradiated samples in relation to pristine PVDF at room temperature, suggesting that the radiation caused the crosslinking or chain scission of the PVDF films. The main conclusion is that these low doses do not affect significantly the analysed properties.

## ACKNOWLEDGMENTS

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