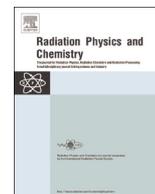




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# Thermal analysis for study of the gamma radiation effects in poly (vinylidene fluoride)



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## HIGHLIGHTS

- A systematic study of the effects of gamma irradiation on PVDF has been conducted.
- The samples were irradiated with a Co-60 source at constant dose rate (12.0 kGy/h).
- The doses ranged from 100 kGy to 3000 kGy.
- The DSC data reveals a decrease in the melting temperature and melting latent heat.

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## ABSTRACT

Poly(vinylidene fluoride) (PVDF) has attracted interest in the technology and industrial sectors, due to its mechanical and electrical properties, its resistance to weathering and its thermostability. It is well known that polymer properties change after irradiation. Thermal degradation studies after irradiation of the polymers play an important role in establishing the threshold temperature for breakdown and information about the molecular and crystalline structure. A systematic study of the effects of gamma irradiation on PVDF using DSC, TG, DTA, FTIR and XRD techniques has been conducted. The samples were irradiated with a Co-60 source at constant dose rate (12.0 kGy/h), with doses ranging from 100 kGy to 3000 kGy. The DSC data reveals a decrease in the melting temperature and melting latent heat for increasing doses. There is a remarkable decrease in the melting latent heat ranging from 46 J/kg (pristine sample) to 26 J/kg (3000 kGy). The data analysis suggests that the decrease observed in the onset decomposition temperature is due to the radio-induction of C=C bonds in the crosslinking process and that the increase of the residual amount is due to the radio-induction of C=O bonds, via chain scission.

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## 1. Introduction

Poly(vinylidene fluoride) [PVDF] is a linear semi-crystalline homopolymer and its polymeric chain is composed by the repetition of CH<sub>2</sub>-CF<sub>2</sub> monomers. There are four possible distinct crystalline phases, the β-ferroelectric phase that being with many technological applications, finding applications as sensors and transducers (Lovinger, 1983). When in the non-polar α-phase, it is considered as a high-performance polymer with high resistance to mechanical straining. It is also biocompatible, used in cardiac sutures and studied in orthopedic prosthesis (Laroche et al., 1995; Celina et al., 2005). PVDF is one of the most radiation-resistant polymers in the market, maintaining most of its mechanical

properties after irradiation in the MGy range. This feature is linked to its extensive use in the aerospace industry and the need for radiation sterilization for medical use (Celina et al., 2005; Seal et al., 2001). Gamma sterilization is becoming popular in the medical device and packaging industry because of convenience and low cost. The high-energy gamma rays, however, can also initiate ionization events in the material being sterilized. They can create peroxy and hydroperoxy free radicals in the presence of oxygen, and start the degradation cascade (Premnath et al., 1996). The integrity of the polymer depends on energy deposition and requires a detailed understanding of the material responses that are expected to deteriorate owing to gamma rays and high-temperature use. Initial radiation aging studies have shown complex material changes with lowered melting points, morphological transformations and significant crosslinking (Zhudi et al., 2002). Complex aging processes have also been observed in accelerated

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temperature environments (Seal et al., 2001). There are a large number of applications where high-dose irradiation is necessary. So, this work studied the effects of high gamma dose irradiation in PVDF using differential scanning calorimetry (DSC) and X-ray diffraction (XRD) techniques for evaluation of the effects in the crystalline structure and melting properties, and thermogravimetry (TG), differential thermal analysis (DTA) and Fourier Transform Infrared (FTIR) techniques to investigate the effects of the radio-induction of C=O and C=C chemical bonds on the thermal stability of irradiated PVDF samples.

## 2. Experimental description

ATOCEM (France) supplied PVDF homopolymers. The film samples were produced by melting at 200 °C under 300 bar, with subsequent air-cooling to room temperature. This process produced transparent films of about 160 μm. The samples were irradiated with a Co-60 source in the Gamma Beam-127 irradiator at Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) at constant dose rate (12.0 kGy/h), with doses ranging from 0.1 to 3000.0 kGy. Thermal behavior studies were made using a DSC TA Q10, with heating and cooling rates of 10 °C/min, in the second run, from 25 to 180 °C. The equipment was calibrated using an Indium sample ( $T_M=156.6$  °C) and the measurements were taken with samples weighing around 10 mg, using an aluminum crucible. TG and DTA curves were obtained using a Netzsch model STA 429. Samples of 10 mg were degraded in a dynamic nitrogen atmosphere at a heating rate of 10 °C/min. The FTIR spectra, collected with 32 scans each, were measured at a BOMEM 100 spectrometer for wavenumbers ranging from 300 to 4000  $\text{cm}^{-1}$ . Structural characterization was made using X-ray diffractometry Shimadzu XRD-7000 Maxima-X. All measurements were taken immediately after the irradiation process.

## 3. Results and discussion

The TG and DTA curves for the pristine samples are shown in Fig. 1a–d. For pristine PVDF sample, the degradation is seen to start at 410 °C. A first stage is observed after which a further stage begins at 460 °C (Fig. 1a). The first stage resulted in 72.69% weight

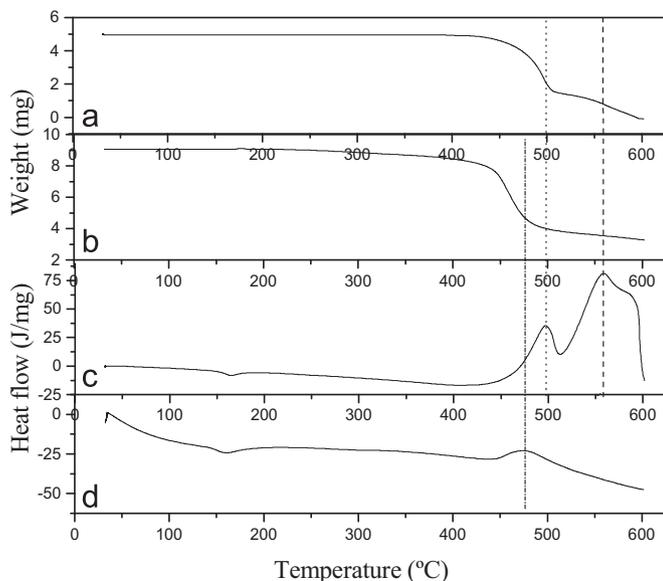
**Table 1**  
Relation between radiation doses and increasing residue and decreasing decomposition temperature.

Sample	Residue (%)	Decomposition temperature (°C)
Pristine	2.01	410
100 kGy	26.12	410
750	35.46	348
1000	37.46	346
1750	43.03	331
2500	38.39	311

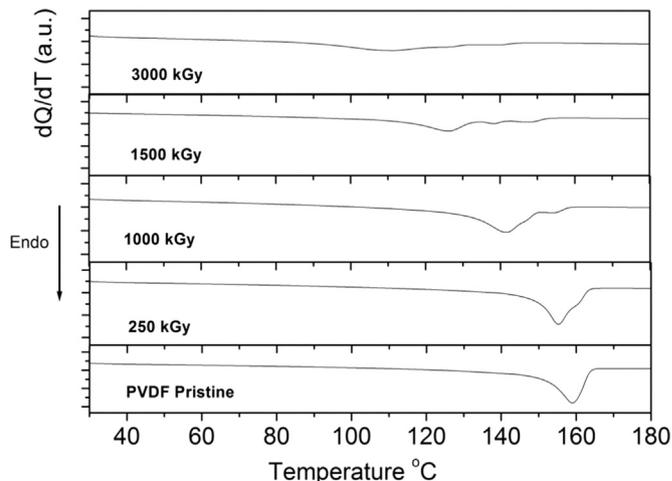
loss, and the second stage resulted in 25.30% weight loss with a residue of 2.01%.

Comparing the TG curves with DTA curves for pristine samples, we can see that the respective process is exothermic (Fig. 1c) and that the DTA curves present one endothermic peak at 150 °C which is associated with the melting temperature of the crystalline phase. Botelho et al. (2008) have proposed a mechanism for the thermal degradation of PVDF. They suggest that in a first degradation step, carbon–hydrogen scission occurs and that the presence of both hydrogen and fluorine leads to the formation of hydrogen fluoride (HF). In a second step, a complex degradation process takes place resulting in a poly(aromatization) reaction. The TG curve for the irradiated sample (Fig. 1b) shows a reduction in the onset temperature of thermal degradation, when compared with the pristine sample. In Fig. 1d it is possible to see, in the DTA curve, the absence of the exothermic peaks above 460 °C, which indicates that the material was already in the degradation process before the temperature increase. Thus, this degradation was probably caused by gamma radiation. Table 1 shows the relationship between the increasing radiation doses with the increasing residues and the corresponding decomposition temperature.

The DSC and X-ray diffraction techniques have been used in order to follow the radio-induced changes in the melting transition parameters and, particularly, the changes in the PVDF crystalline structure. Fig. 2 shows the DSC thermograms for pristine and irradiated PVDF samples. The diffuse endothermic peak observed at 160 °C for pristine PVDF is attributed to the melting of the crystalline volume. On the other hand, the thermograms for the irradiated samples reveal that the melting temperatures ( $T_C$ ) gradually decrease as the gamma dose increases, leading to a quasi-total amorphisation of the crystalline region for doses as high as 3000 kGy. Also, there is a remarkable decrease in the melting latent heat ranging from 46 J/kg (pristine sample) to 26 J/kg (3000 kGy),



**Fig. 1.** TG (a and b) and DTA (c and d) curves for PVDF sample pristine (a and c) and irradiated with 1000 kGy (b and d).



**Fig. 2.** 2nd Heating cycle thermograms for pristine PVDF and samples exposed of gamma radiation.

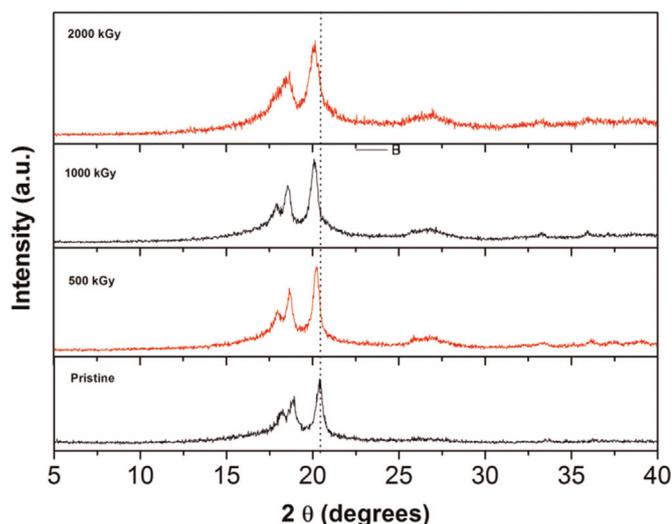


Fig. 3. X-rays diffractograms for the pristine and the irradiated samples of PVDF with 0.5, 1.0 and 2.0 MGy.

which is proportional to the area under the peak, confirming the decrease in the crystalline fraction. An interesting anomaly is observed in these curves, where the appearance of additional smaller endothermic peaks in the higher temperature side of the main melting peak can be seen. It remarks that PVDF homopolymer is constructed sandwiching several alternated lamellas of amorphous and crystalline regions. Particularly, when the radiation damages are located in the crystalline lamellae, they are considered as crystalline defects, which in turn are removed to the amorphous phase by the increase of the chain fold (Lovinger, 1983). This phenomenon results in a decrease of the original crystalline volume and the appearing of a second crystalline region full of defects, between the original one and the amorphous phase. It is believed that the additional peaks observed in Fig. 2 may be related to this phenomenon.

The X-ray diffractograms for pristine PVDF and also for samples exposed to 500, 1000 and 2000 kGy are shown in Fig. 3. In these XRD patterns, it observes a gradual shift of the (110) Bragg reflection at  $2\theta = 20.6^\circ$ , characteristic of  $\alpha$ -PVDF, to  $2\theta = 20.1^\circ$  in the sample irradiated with 2000 kGy. This shift corresponds to an increase of 2.46% in the distance ( $d$ ) between the crystallographic planes. Taking into account that it can estimate the parameters  $a$  and  $b$  of the elementary crystalline lattice as  $d \approx a/2 \approx b\sqrt{3}/2$ , it can conclude that the lattice swells in these directions ( $a$  and  $b$ ) in order to accommodate the radiation-induced defects within it. It is important to remark that this effect is not expected to occur simultaneously in all crystalline lamellas, leading to the appearance of a second crystalline region full of defects, together with the original pristine PVDF lattice. Thus, may be, these additional crystalline lattices full of defects are those that were commented in the above DSC data analysis, when explaining the additional melting peaks in the DSC thermograms for the irradiated samples (Fig. 2).

Finally, it discusses the chemical radio-induced defects that are behind the crystalline changes in the gamma irradiated PVDF samples. Fig. 1 and Table 1 show that a decrease in the onset decomposition temperature could be due to the scission of polymer-chains and, the increase of the residual amount could be associated with the formation of crosslinking between the polymeric chains (Gil et al., 1998). In fact, ionizing radiation-induced chain crosslinking has been reported to start to occur for doses as low as 50 kGy (Lim et al., 2006). In Fig. 4 we show the FTIR spectra for unirradiated and irradiated PVDF samples for gamma doses ranging from 0.1 MGy to 1.0 MGy, taken just after the irradiation

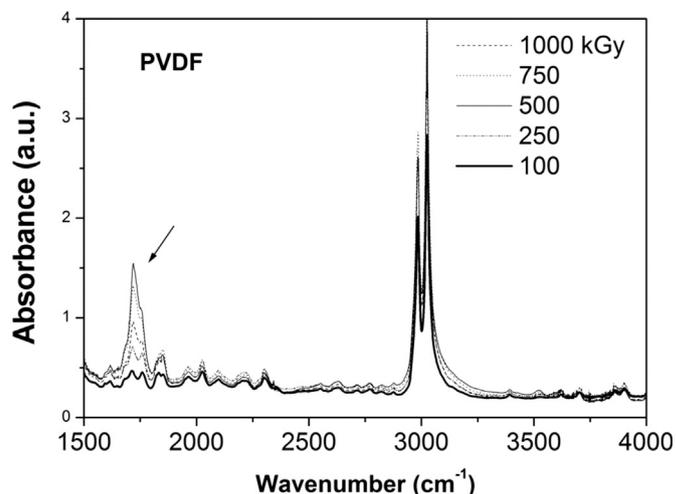


Fig. 4. FTIR spectra for pristine sample and samples irradiated with 0.1, 0.25, 0.5, 0.75 and 1.0 MGy, for wavelengths ranging from 1500 to 4000  $\text{cm}^{-1}$ .

process. The two prominent absorption peaks centered at 2984 and 3024  $\text{cm}^{-1}$  are attributed to the symmetric and antisymmetric stretching modes of  $\text{CH}_2$ . These two peaks are kept constant for all gamma doses. However, in the region between 1450 and 1900  $\text{cm}^{-1}$ , it can observe a well pronounced increase of a wide absorption band centered at 1720  $\text{cm}^{-1}$ , for increasing gamma doses. In a previous work, this band was attributed to the sum of the increasing individual bands at 1715, 1730 and 1754  $\text{cm}^{-1}$  (Liz et al., 2011). According to Boullier et al. (2003), these bands can be described as the stretch of C=C bonds (1715 and 1754  $\text{cm}^{-1}$ ) and C=O bonds (1730  $\text{cm}^{-1}$ ). The increase of the absorption peak at 1853  $\text{cm}^{-1}$  is also seen, which is also attributed to the stretch of C=O bonds. It is important to remark that the radio-induced creation of C=C bonds by the formation of  $-\text{CF}_2-\text{CH}=\text{CF}-\text{CH}_2$  and  $-\text{CH}=\text{CF}_2$  segments may generate chain crosslinking. On the other hand, the radio-induction of C=O bonds, by the formation of  $-\text{CF}_2-\text{CH}_2-\text{COOH}$  segments, may be linked to the chain scission process (Boullier and Esnouf, 2003). Thus, the thermal results of Fig. 1 and Table 1 may conclude that the decrease observed in the onset decomposition temperature is due to the radio-induction of C=O bonds and that the increase of the residual amount is due to the radio-induction of C=C bonds.

#### 4. Conclusions

It was observed that pristine PVDF samples are very stable until temperatures as high as 410  $^\circ\text{C}$ . After that, the degradation occurs in two weight loss steps. The residue was estimated to be 3%. On the other hand, for the PVDF samples irradiated with gamma doses ranging from 0.1 to 3000 kGy, it observed a decreasing onset decomposition temperature and the increase of the amount of residue, for increased doses. The FTIR analysis suggests that the decrease observed in the onset decomposition temperature is due to the radio-induction of C=C bonds in the crosslinking process and that the increase of the residual amount is due to the radio-induction of C=O bonds, via chain scission. The DSC data reveals a decrease in the melting temperature and melting latent heat for increasing doses. It also shows the appearance of small additional endothermic peaks near the melting peaks. The XRD data indicates that the high gamma dose irradiation provokes an expansion of the crystalline lattice. This expansion was explained in terms of the creation of lattice space in order to accommodate the radio-induced crystalline defects.

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