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DSC studies on gamma irradiated poly(vinylidene fluoride) applied to high gamma dose dosimetry

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ABSTRACT

Poly(vinylidene fluoride) homopolymer (PVDF) was investigated for use on high gamma dose dosimetry. Samples were irradiated with gamma doses ranging from 100 kGy to 3000 kGy. Differential scanning calorimetry (DSC) was used to construct an unambiguous relationship between the melting transition latent heat (L_M) and the absorbed dose (D). DSC thermograms were taken immediately, 1, 2 and 8 months after the irradiation process revealing that the L_M *x D* relationship presented no change for doses ranging from 100 to 2750 kGy. FTIR and UV–Vis spectroscopy data revealed the radio-induction of C=O and C=C bonds. These radio-induced bonds were responsible by the chain stiffening and chain oxidation, respectively. SEM microscopy demonstrates that the spherulitic large crystalline structures present in pristine PVDF are destroyed with doses as low as 100 kGy. The DRX analysis revealed that the main effect of high gamma doses in the crystalline structure of PVDF is to provoke a change from the pristine PVDF α-phase to the γ-phase. Both the ability to detect gamma doses in a large dose range and the low fading features make PVDF homopolymers good candidates to be investigated as high gamma dose dosimeters.

1. Introduction

International standards are routinely used to determine the dose distribution patterns and the delivered absorbed dose over a wide range of, industrial products and processes that make use of ionizing radiation. Examples can be found in food irradiation, surgery devices sterilization and gemstone treatment. In order to achieve the dose patterns, reliable high dose dosimetry systems are generally required all over the world. Calorimeters, Alanine and also Ceric-cerous sulphate, ethanol chlorobenzene (ECB) dosimeters, Ferrous Sulphate and dichromate solutions are some examples of standard reference dosimetry systems commercially available elsewhere (IAEA, 2002). Thermoluminescence (TL) and Optically Stimulated Luminescence (OSL) dosimetry and also polymer based dosimeters have been alternatively used for high gamma dose dosimetry (Ranjbar et al., 1996; Miller, 1996; Milman et al., 1993; Chadwick, 1973). Recent advances in high dose dosimetric systems include dose-mapping media with radiochromic films, optical waveguide systems for food irradiation and the solid-state devices for real-time and passive dosimetry. However, most of the existing dosimetric systems have performance limitations concerning measuring dose range, fading and resolution, making the search for novel high dose dosimeters an interesting research field.

PVDF homopolymer is, nowadays, the best polymer for application in electromechanical transducing devices (Lovinger, 1983). The irradiation of PVDF copolymers with high doses of very energetic radiations has provided interesting technological applications. For instances, the irradiation of its poly(vinylidene-trifluorethylene) (P(VDF-TrFE) copolymer with 3.0 MeV electrons, high gamma or UV doses provokes the appearing of C=C and C=O chemical bonds in the main chain, which in turn decreases its crystallinity degree, inducing ferroelectric relaxor features with exceptionally high electrostrictive response (approximately 4%) (Zhang et al., 1998; Welter et al., 2003; Faria et al., 2006). Another interesting application is concerned to high dose dosimetry. The P(VDF-TrFE), together with another fluorinated PVDF copolymer, poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), have been suggested to be investigated as high dose dosimeters in gamma fields. In these copolymers, the amount of radio-induced C=C conjugated bonds and C=O bonds, estimated by Ultraviolet–visible (UV–Vis) and Fourier transform infrared (FTIR) spectrometry, respectively, shows a linear relationship with the absorbed dose in the 0.1–1.0 MGy range (Medeiros and Faria, 2008; Liz et al., 2011). Thus, encouraged by the above mentioned applications in the field of high dose dosimetry, we decided to investigate about the features of irradiated PVDF homopolymer, exploring the radio-induced damages on its crystalline structure.

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In this work we have studied the decrease in the PVDF crystallinity when exposed to increasing gamma doses. The decrease of crystallinity in gamma irradiated PVDF and its copolymers can be estimated by X-ray diffraction using the Scherrer equation by measuring the decrease of the crystallite dimensions for increasing delivered doses (Scherrer, 1918). An alternative method consists in the evaluation of the melting latent heat (L_M) of the polymer crystalline fraction, using Differential Scanning Calorimetry (DSC). It should be noted that in crystalline polymers, such as PVDF, melting happens when the polymer chains fall out of their crystal structures, becoming a disordered liquid (Frith and Tuckett, 1944). The latent heat used to undergo the melting transition is associated with the crystalline volume. Thus, if there is a decrease in the polymer crystallinity, there will also be a decrease in $L_{M,}$ once it measures the amount of heat necessary to undertake the melting phase transition.

Calorimetry itself has being employed in high gamma dose dosimetry for more than 60 years due to several advantages such as no LET dependence, its relative stability against radiation damage at high doses and the large range of materials that can be used as the sensitive volume (Attix, 1986). In this dosimetric system, the absorbed dose is determined by the amount of energy transferred from the radiation beam to the sensitive volume. This amount of energy is evaluated by measuring the heat induced in the sensitive volume. In this work, however, we report the use of calorimetry data for dosimetry purposes by measuring the heat flow variation during a thermodynamic phase transition. In this context, we have investigated the changes in the melting latent heat of gamma irradiated PVDF samples, for increasing doses, aiming to find an unambiguous relationship between L_M and the absorbed dose.

2. Experimental

PVDF homopolymers were supplied by ATOCHEM (France). The film samples were produced by melting at 200 °C under 300 bar, with subsequent air-cooling to room temperature. This process produced uniform and transparent films with thickness 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 two constant dose rates (2.592 kGy/h and 12.0 kGy/h), with doses ranging from 100 to 3000 kGy. The sample irradiations were performed at 30 cm from the source, with a dose rate of 2.592 kGy/h and close from the source (0.01 cm), with a dose rate of 12.0 kGy/h. The FTIR spectra, collected with 32 scans each, were measured at a BOMEM 100 spectrometer for wavenumbers ranging from 300 to 4000 cm^{-1}. Optical transmission measurements were taken in a Shimadzu UV-2401 PC spectrometer, for wavelengths ranging from 190 to 900 nm. 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 weighting around 10 mg, using an aluminum crucible. DSC thermograms were taken immediately, 2 and 8 months after the irradiation process. Structural characterization was made using X – ray diffractometry Shimadzu XRD – 7000 Maxima –X. FE-SEM microscopy were performed at a SIGMA VP field emission scanning electron microscope ZEISS.

3. Results and discussion

The FTIR spectra for wavenumbers ranging from 350 to 4000 cm^{-1} for unirradiated and irradiated PVDF samples, for gamma doses ranging from 100 kGy to 2750 kGy, taken just after the irradiation process are shown in Fig. 1. The main changes observed in these spectra are localized in the infrared regions between 1450 and 1900 cm^{-1} and 2300 and 3700 cm^{-1}, as seen in Fig. 1(a) and (b), respectively. In the region between 1600 and 1900 cm^{-1} it is observed a well pronounced increase of an absorption band centered at 1731 cm^{-1}, for increasing gamma doses. It is also seen two absorption bands with lower intensities appearing at 1620 and 1850 cm^{-1}. In a first approach, this band may be closely correlated to the chain oxidation (C=O) during irradiation, once the irradiation was performed in the air. We remark that most of the infrared absorption bands observed between 1660 cm^{-1} and 1870 cm^{-1} are normally attributed to C=O stretching modes. However, as the PVDF chain is composed by the repetition of CH_2-CF_2 monomers, probably there may exist another absorption bands involved, such as C=C. This chemical bond can be induced by the CH and CF bonds scission during the irradiation. According to Boullier et al. (2003), the absorption bands seen between 1660 cm^{-1} and 1870 cm^{-1} can be described as the stretch of C=O bonds at 1730, 1760, 1790 and 1853 cm^{-1}, and as C=C stretching at 1715 and 1754 cm^{-1}. On the other hand, in Fig. 1(b) we observe two narrow bands, centered at 2983 and 3024 cm^{-1} respectively, normally attributed to the symmetric and anti-symmetric stretching modes of CH_2 bonds in linear polymers. These absorption bands attain their maximum intensities in the pristine PVDF spectrum. In the irradiated samples spectra, these intensities are slightly smaller, even for doses as higher as 2750 kGy. For wavenumbers below and above the at 1716 and 1755 cm^{-1} bands, there is a continuous increase in the absorption intensities, i.e. between 2000 and 2983 cm^{-1} and 3024 and 3750 cm^{-1}, which apparently may be attributed to the overlapping of several unknown chemical bonds, except for the three adjacent absorption bands at 3518, 3585 and 3673 cm^{-1}. These bands have very low intensities and may be associated with NH stretch of NH_2 bonds (3518 cm^{-1}) and to the OH stretch of COOH bonds (3585 and 3673 cm^{-1}). We attribute these new bonds to the interaction of nitrogen and oxygen atoms, present in the air, with the PVDF chains in the film surface, during the irradiation process.

In order to discuss the data presented in Fig. 1(a) in more detail, we have peak fitted the absorption bands between 1675 and 1775 cm^{-1}, using the results reported by Boullier et al. (2003) as a starting base. In this fit we have found a set of absorption peaks that could be applied to all doses, varying only the individual peak intensities. The results are shown in Fig. 2(a). For clarity purposes we show the peak fitting only for the spectrum taken for the sample irradiated with 1000 kGy. The individual peaks centered at 1716, 1731 and 1755 cm^{-1} are the ones that have considerable intensity increase for increasing doses. It is interesting to note that the peak fitting results give wavenumbers very close to the reported values by Boullier et al. (2003), i.e. 1730 cm^{-1}, which were attributed to the stretch of C=O bonds, and 1715 and 1754 cm^{-1}, which were attributed to the C=C stretching (Boullier et al., 2003).

Thus, based on the FTIR data analysis, we conclude that, for gamma doses ranging from 100 at 2750 kGy, the creation of C=O and C=C bonds are the predominant processes that occur during the irradiation.

In Fig. 2(b) it is also shown UV–Vis spectra collected just after the irradiation process, for 100, 500 and 1000 kGy of gamma doses. In these spectra it is observed the increase in the intensities of the absorption bands around 220 and 270 nm for increasing irradiation doses. In the inset of Fig. 2(b) it is shown the peak fitting of the spectrum for the sample irradiated with 100 kGy, using Lorentzian lines. This peak fitting reveals 3 individual absorption bands that we assigned to the formation of singlets (194 nm), doublets (223 nm) and triplets (274 nm) of conjugated C=C bonds, based on the similar results reported earlier related to P(VDF-TrFE) copolymers (Medeiros and Faria, 2008). Thus, the UV–Vis data confirms the radio-induction of C=C bonds observed by FTIR spectroscopy. We think that the radio-induction of C=C could be related to main chain stiffening and the radio-induction of C=O could be related to chain crosslinking.

In order to complement the sample characterization Fig. 3 displays the SEM images of pristine PVDF and samples irradiated with 100kGy, 750 kGy and 2250 kGy. The spherical structures observed in the image

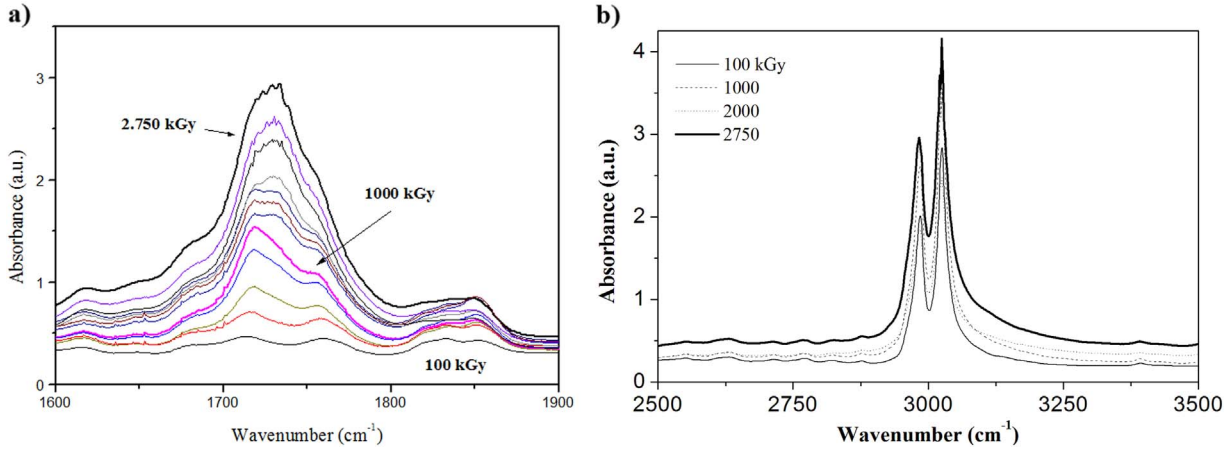

Fig. 1. FTIR spectra for samples irradiated with 100 at 2750 kGy, for wavelengths ranging from **(a)** 1600–1900 cm^{-1} and **(b)** 2500–3500 cm^{-1}.

of pristine PVDF in Fig. 3(a) are called "spherulites" which are spherical aggregates of lamellar crystallites.

The spherulitic structures are always present in PVDF samples but they are not observed in their copolymers. Spherulites can have dimensions of until 1 mm. These structures are not seen in Fig. 3(b), (c) and (d), which are images for PVDF samples irradiated with 100 kGy, 750 kGy and 2250 kGy, respectively. Thus, we infer that the gamma radiation destroys these large crystalline structures, probably by the radio-induction of chain scission, crosslink, chain oxidation and chain stiffening originated by the formation of C=C bonds, as revealed by FTIR and UV–Vis analysis.

Once the SEM images revealed damages to spherulitic structures, we may now investigate the effect of high gamma dose on the crystalline structure of PVDF. The DSC scans (a) and the XRD diffractograms (b) for pristine and irradiated samples are shown in Fig. 4. The thermogram taken for the sample irradiated with 100 kGy shows only one endothermic diffused peak. It corresponds to the melting of the crystalline portion of PVDF homopolymer. On the other hand, the thermograms for the irradiated samples with 500 at 3000 kGy show two diffused peaks. This evidences that the increasing gamma doses are provoking the appearing of a second distinct crystalline region, with a different melting temperature. It's well known that ionizing radiation provokes the radio-induction of new chemical bonds, chain scission and crosslinking in both the amorphous and the crystalline portion of polymers. PVDF homopolymer is basically constructed by 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 in the appearing of a second crystalline region full of defects, between the original one and the amorphous phase. This phenomenon can be attributed to the crystallization of the anchored amorphous phase (Moreira et al., 1989). Thus, we believe that the two DSC peaks observed in the irradiated samples thermograms are correlated to these two distinct crystalline phases. One with high crystalline order and another, the anchored amorphous phase, with high amount of radio-induced defects, i.e. C=O and C=C bonds, chain scissions and crosslinkings.

Another characteristic revealed by the DSC thermograms is the gradual decrease of the melting temperatures for increasing doses. We attribute this decrease of T_M to the loose of crystalline order. It is interesting to observe that, for gamma doses higher than 100 kGy, both the lower and the higher temperatures peaks decrease equally, maintaining the difference between them around 20 °C. However, the relative intensities are not kept constant. The X-ray diffraction of irradiated pristine and also for samples irradiated with 1000 and 2000 kGy are shown in in Fig. 4(b). The diffractogram of the pristine PVDF is characteristic of the α-phase. Comparing the diffractograms of pristine PVDF samples with the irradiated samples, we see that the peak (110) at 21.32° of the pristine PVDF is shifted to 20.14° for the irradiated samples, which is characteristic of the PVDF β-phase. The peak (021) at 26.75°, which is also characteristic of the β-phase, is only seen for the irradiated samples. The PVDF γ-phase is well known to shown some diffractions peaks of both α and β phases. Thus, the main effect of high gamma doses in the crystalline structure of PVDF is to provoke a change from the pristine PVDF α-phase to the γ-phase.

Now we may discuss about the melting latent heat involved in the

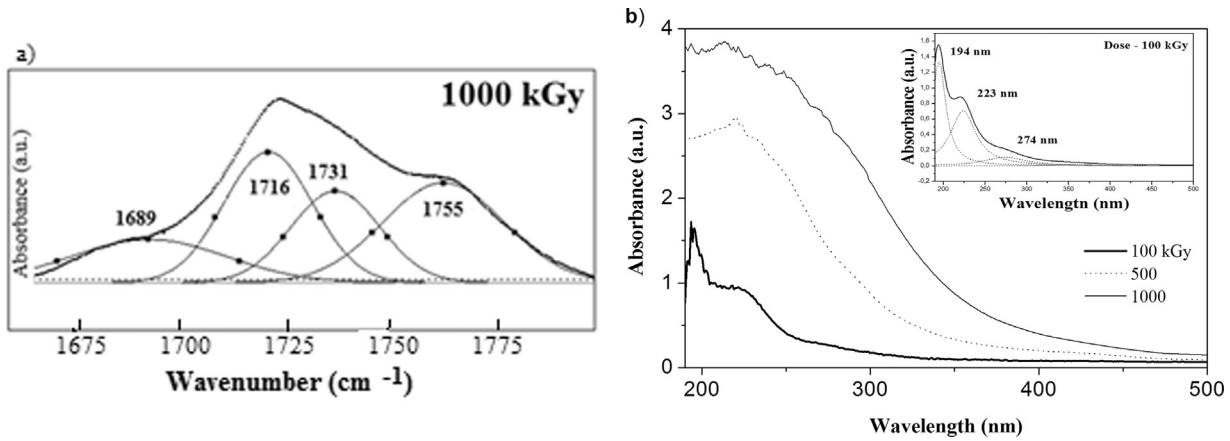

Fig. 2. Peak fitting for the FTIR data presented at Fig. 1(a), using the reported data by Boullier et al. as the starting base. The experimental spectrum presented here was taken for the sample irradiated with 1000 kGy **(a)** UV–Vis spectra the samples irradiated with 100, 500 and 1000 kGy and insert peak fitting for the sample irradiated with 100 kGy **(b)**.

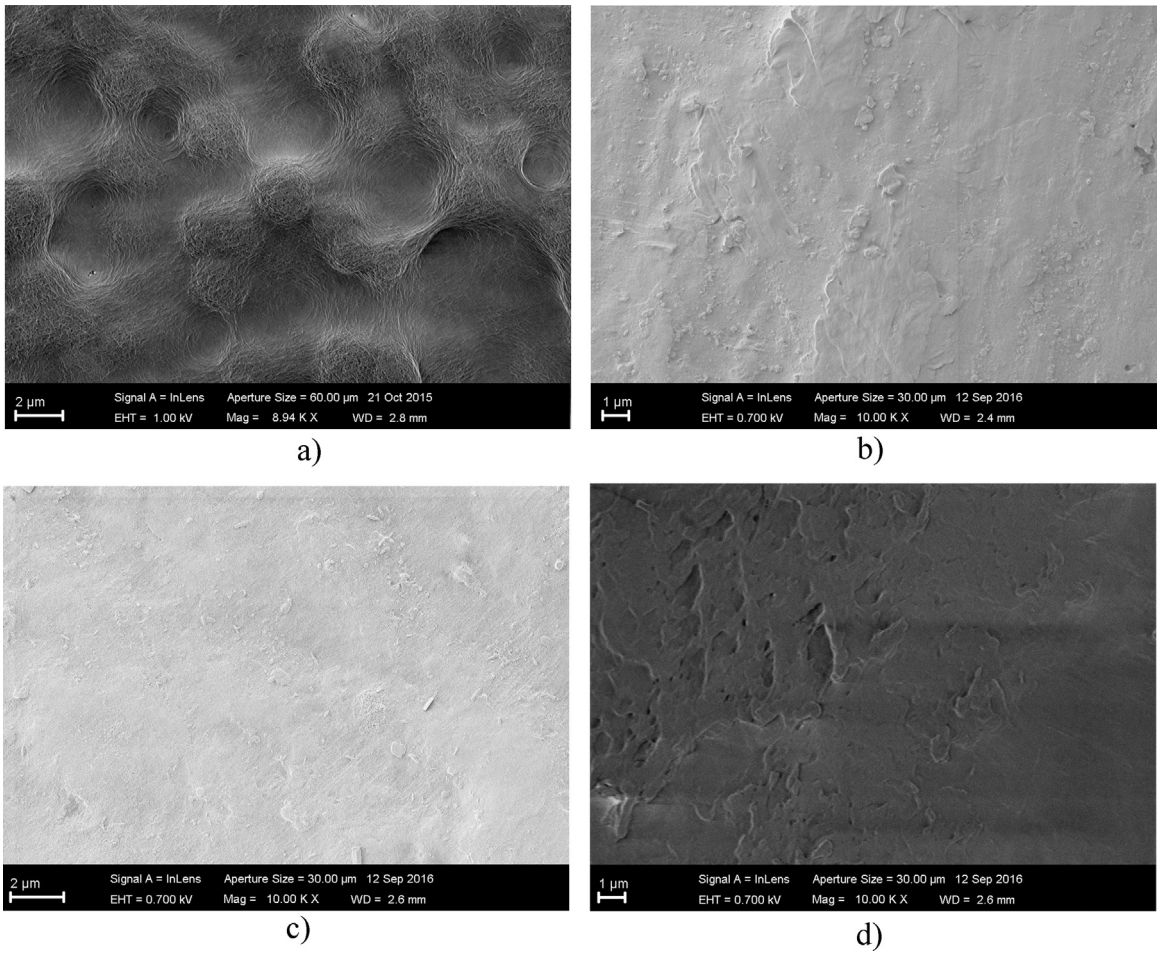

Fig. 3. SEM images of pristine PVDF **(a)** and samples irradiated with 100 **(b)**, 750 **(c)** and 2250 kGy **(d)**.

fusion process and its application for dosimetric purposes. The area under the melting peak in Fig. 4(a) is proportional to the latent heat (L_M) necessary to undergo the melting of the crystallites, i.e. the heat necessary to make the polymer chains fall out of their crystal structures, becoming a disordered liquid. For consistence purposes, in the case of the irradiated samples, we will denote L_M as being the sum of the latent heat of the two crystalline regions. One can see that for increasing doses, apparently, the melting latent heat (L_M) decreases. In fact, as we show in Fig. 5(a), there is an unambiguous relationship between L_M and the delivered dose that could be fitted quite well by some polynomial or exponential functions. The data displayed in Fig. 5(a) were collected 2 hs after irradiation. In order to perform fading evaluation, the samples were scanned again after 30, 60 and 240 days after the first DSC scanning. The scans reveal that there was practically no fading in the period investigated. On the other hand, in Fig. 5(a) it is also shown the higher dimension of the crystallites for samples irradiated with 500, 1000 and 2000 kGy. These values were obtained from the X-ray diffraction spectra by using the Scherrer Equation (Scherrer, 1918). As expected, the observed decrease in the crystallite dimensions for increased doses is consistent with the

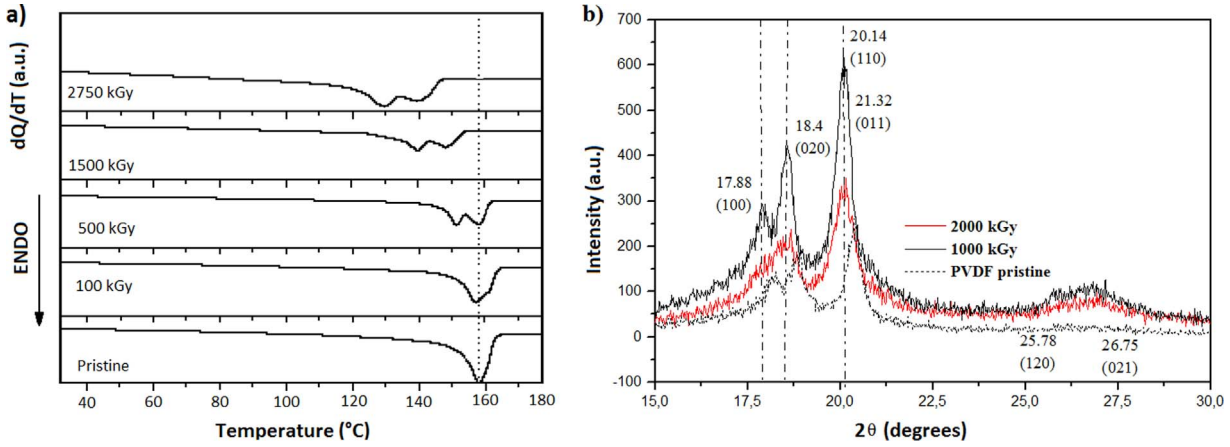

Fig. 4. Structural characterization of pristine PVDF and PVDF samples irradiated with gamma doses. DSC thermograms for doses ranging from 100 kGy to 2750 kGy **(a)** and X-ray diffractograms for doses ranging from 1000 and 2000 kGy **(b)**.

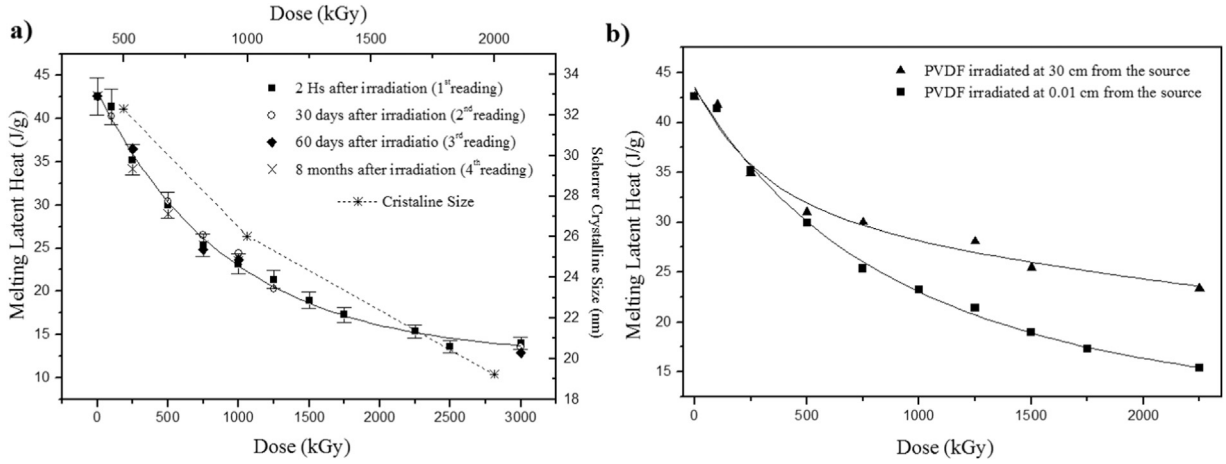

Fig. 5. (a) Plot of the *Dose x Melting Latent Heat* experimental data (left axis) obtained from Fig. 4(a) and crystalline size values (right axis) for the samples irradiated with 500, 1000 and 2000 kGy. The solid and dotted lines are just a guide to the eyes. **(b)** Plot of the exponential fitting (solid lines) for data obtained from samples irradiated at 30 cm and 0.01 cm from the gamma source.

Table 1
Fitting parameters obtained for the mathematical adjust for the L_M x Dose relationship for PVDF samples irradiated at 0.01 cm and 30.0 cm from de gamma source. In this Table, *d* is the distance between the gamma source and the samples.

	a_1	t_1	L_O	Correlation coefficient
d = 0.01 cm	29.7704	873.718	13.4363	0.99521
d = 30.00 cm	18.9151	589.388	24.0437	0.96725

decreasing values of L_M results, which in turn means that the crystalline volume of PVDF is decreasing for increased doses.

Once it is possible to associate a mathematical function between the delivered dose and melting latent heat, we will now discuss about the possibility of using L_M as a new tool to be used in high dose dosimetry. First of all, it is necessary to convert the measured calibration data into some form of smooth function that will enable us to evaluate the gamma dose from a measured signal. This could be as simple as a hand drawn graph, but in practice a mathematical fitting procedure of some form is generally used to obtain the relationship between the dosimeter signal and the absorbed dose (Sharpe and Miller, 1999). The regression analyses will be used to determine the relationship between absorbed doses and signal (Montgomery et al., 2002). The fitting is made based on least squares method in order to determine the calibration curve. The estimation of the regression coefficients is quite complicated and laborious, so it requires the use of specialized computer programs. We have used a statistical tool from ORIGIN® 8.0 software to determine the coefficients of an exponential fitting. Fig. 4(b) displays the fitted curve for samples irradiated at 30.0 cm and 0.01 cm from the gamma source. The first order exponential fittings can be expressed as

$$L_M = L_0 a_1. \quad e^{-(\frac{D}{t_1})} \tag{1}$$

where L_M is the melting latent heat in Joules/gram, D is the delivered gamma dose in kGy, and a_1, t_1

and L_O are the adjusting parameters. The main data obtained for both fittings are shown in Table 1.

We note that, in spite of the expected radiation field anisotropy at points very close to the gamma source (0.01 cm), both calibration curves demonstrate that the melting latent heat can be successfully used to evaluate high gamma doses in the range studied, i.e. for doses ranging from 100 kGy to 2750 kGy. The correlation coefficients (CC) where 0.99521 and 0.96725, for samples very close to the source and distant 30 cm, respectively.

Finally, taking into account that most of the existing dosimetric systems devoted to work at high dose dosimetry have performance limitations concerning to the measuring dose range and fading, the results obtained in this work indicate that the PVDF films are good candidates to be explored as a high dose dosimeter for doses ranging from 100 to 500 kGy, where there is practically no dose rate dependence. This is due to its very low fading measured until 8 months after irradiation and also to its large measuring interval ranging from 100 kGy to 2750 kGy. For comparison purposes, we remind that among all polymer-based high dose dosimeters available, the poly(methyl methacrylate) has the lager dose range, i.e. 1–100 kGy.

4. Conclusions

Poly(vinylidene fluoride) homopolymers [PVDF] were irradiated with gamma doses ranging from 100 to 3000 kGy. FTIR spectrometry and UV–Vis data analysis revealed that the creation of C=O and C=C bonds are the predominant processes during the irradiation. These processes were responsible for the chain oxidation and chain stiffening, respectively. X-ray diffraction analysis revealed a decrease in crystallite size, which was consistent with the results obtained by DSC analysis, and also that the main effect of high gamma doses in the crystalline structure of PVDF is to provoke a change from the pristine PVDF α-phase to the γ-phase. SEM microscopy demonstrated that the spherulitic large crystalline structures present in pristine PVDF are destroyed with doses as low as 100 kGy. The melting latent heat (L_M) of the crystalline phase of PVDF was measured using differential scanning calorimetry. We have found an unambiguous relationship between the delivered gamma doses and melting latent heat (L_M). The exponential relationship between L_M and the delivered dose (D) can be successfully used to evaluate high gamma doses from 100 kGy to 2250 kGy. DSC thermograms collected 2 hs after irradiation and also 30, 60 and 240 days after the first DSC scanning revealed that the L_M *x Dose* relationship has practically no fading range studied, i.e. for doses ranging from 100 kGy to 2750 kGy.

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