ABSORBED DOSE/MELTING HEAT DEPENDENCE STUDIES FOR THE PVDF HOMOPOLYMER

Adriana S. M. Batista[1], Maritza R. Gual[1,3], Claubia Pereira[1] and Luiz O. Faria[2]

[1] Departamento de Engenharia Nuclear
Universidade Federal de Minas Gerais
Av. Antônio Carlos 6627, 31270-970 Belo Horizonte, MG
adriananuclear@yahoo.com.br
maritzargual@gmail.com
claubia@nuclear.ufmg.br

[2] Centro de Desenvolvimento da Tecnologia Nuclear
Av. Antônio Carlos 6627, C.P. 941, 31270-901,
Belo Horizonte, MG
farialo@cdtn.br

[3] Instituto Superior de Tecnologías y Ciencias Aplicadas (InsTEC),
Departamento de Ingeniería Nuclear,
Av. Salvador Allende y Luaces, CP 10300, La Habana, Cuba

ABSTRACT

Differential Scanning Calorimetry (DSC) of gamma irradiated Poly(vinylidene Fluoride) [PVDF] homopolymer has been studied in connection with the use of material in industrial high gamma dose measurement. Interaction between gamma radiation and PVDF leads to the radio-induction of C=O and conjugated C=C bonds, as it can be inferred from previous infrared (FTIR) and ultraviolet-visible (UV-Vis) spectrometric data. These induced defects result in a decrease of the polymer crystallinity that can be followed with DSC scans, by measuring the latent heat during the melting transition (Hmelt). After a systematic investigation, we have found that Hmelt is unambiguously related to the delivered doses ranging from 100 to 2,000 kGy of gamma radiation. One the other hand, further fading investigation analysis has proved that the Hmelt x Dose relationship can be fitted by an exponential function that remains constant for several months. Both the very large range of dose measurement and also the possibility of evaluating high gamma doses until five months after irradiation make PVDF homopolymers very good candidates to be investigated as commercial high gamma dose dosimeters. The high gamma dose irradiation facilities in Brazil used to develop high dose dosimeters are all devoted to industrial and medical purposes. Therefore, in view of the uncertainties involved in the dose measurements related to the electronic equilibrium correction factors and backscattering in the isodose curves used at the irradiation setup, a validation process is required to correctly evaluate the delivered absorbed doses. The sample irradiations were performed with a Co-60 source, at 12kGy/h and 2,592 kGy/h, in the high gamma dose facilities at Centro de Desenvolvimento da Tecnologia Nuclear CDTN/CNEN, Belo Horizonte, Brazil. The comparison of the curve of the Hmelt vs Dose is presented in this paper.

1. INTRODUCTION

Dosimeters can be classified based on the nature of changes induced by radiation: physical and chemical dosimeters. Several organic polymers, semi-crystalline or amorphous materials, are used as chemical dosimeters. They are based on the generation of free radicals produced by the deposition of energy radiation in these materials [1]. Example of solid phase chemical dosimeters are polymers as Poly(methyl methacrylate) (PMMA), Poly(vinyl butyral) (PVB) and Poly(vinyl chloride) (PVC) [2]. The use of dosimetric systems based on polymers has several advantages such as atomic composition, which can be closer to the material of interest

for radiation processing industry, among others. One of the main disadvantages is related to signal loss over time (Fading) [3]. This limitation is not unique to polymeric dosimeters and it is present in all chemical dosimeters. In this paper we shall describe the results of our investigation of a new proposed polymeric dosimeter for high gamma dose dosimetry. Poly(vinylidene Fluoride) (PVDF) is a semicrystalline linear homopolymer known worldwide by its good chemical, mechanical and electromechanical properties. Its polymeric chain is composed by the repetition of CH_2-CF_2 monomers [4]. In this work, we will report the results of further investigation related to the long term effect of gamma radiation in the crystalline phase of PVDF homopolymer, for gamma doses extended up to 3,000 kGy. In this study we have used Differential Scanning Calorimetry (DSC) to associate absorbed doses to the crystallites melting latent heat, for doses ranging from 100 kGy to 2,000 MGy.

2. EXPERIMENTAL, RESULTS AND DISCUSSION

2.1. Experimental

PVDF homopolymer resins were supplied by ATOCHEM (France). The film samples were produced by melting at $200^{o}C$ under 300 bar, and subsequent air-cooling to room temperature. This process produced transparent films of about 170 μm. The samples were irradiated with a Co-60 source at constant dose rate (12 kGy/h and 2,592 kGy/h), with doses ranging from 100 kGy to 3,000 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°C to 180°C. The equipment was calibrated using an Indium sample ($T_{melting}$ = 156.6 ºC) and the measurements were taken with samples weighting around 10 mg, using an Aluminium crucible. All after-irradiation DSC data were collected until two hours after the end of exposition.

2.2. Results and Discussion

2.2.1. Results to First Irradiation

The Fig. 1 shows DSC curves for the pristine sample and for the samples irradiated with 250, 1,000, 1,500 and 3,000 kGy. In the curve for the pristine sample it is possible to see one endothermic peak related to the melting phase transition. The area under the melting peak is proportional to the latent heat necessary to undergo the melting of the crystallites. One can see that for increasing doses, apparently, the melting latent heat (L_{Melt}) decreases. In fact, as it is shown in the Fig. 2, there is an unambiguous relation between L_{Melt} and the delivered dose, which can be described by an exponential fitting. In this figure it also plots the values from the measurements, taken 30 and 240 days after the irradiation process, at the same sample stored in the aluminum crucible. It can note that the L_{Melt} barely changes in the rereading process. It should be remarked that, in the DSC measurement process used here, the data are collected only in the second run. In each run the sample is heated until 180°C, i.e., above the melting point, and subsequently cooled to room temperature, when the sample is recrystallized.
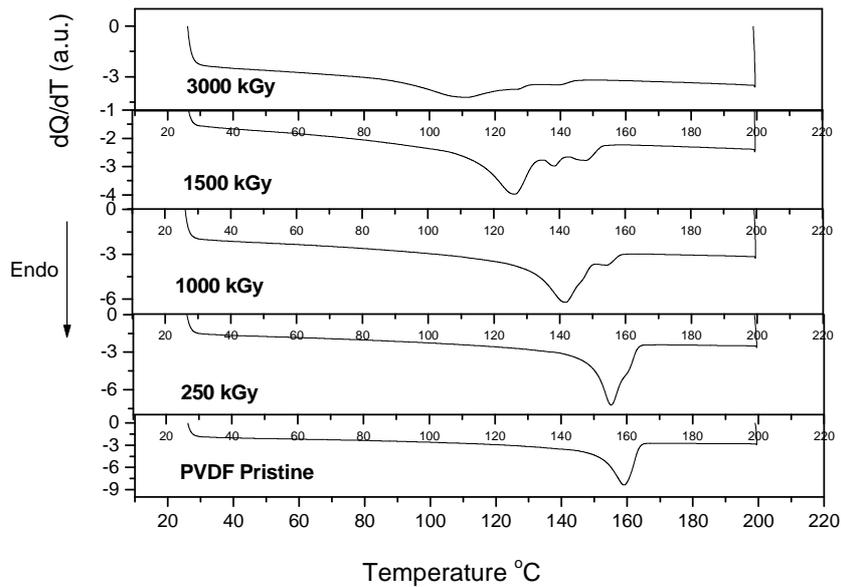
Figure 1: DSC curves for pristine PVDF and samples irradiated with gamma doses ranging from 1.0 kGy to 3.0 MGy.
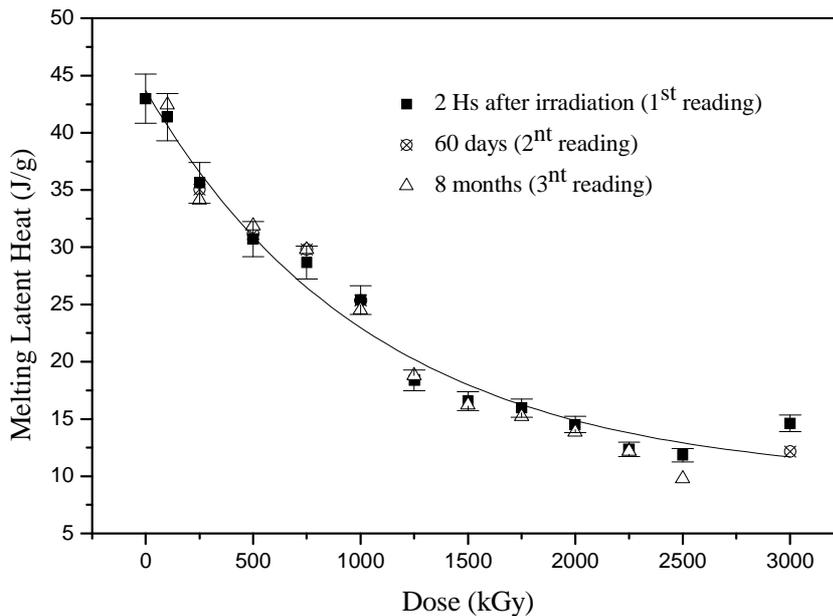

Figure 2: Plot of the Melting Latent Heat (obtained from the DSC curves) as a function of the delivered gamma dose, for the homopolymer PVDF. Samples were irradiated with gamma doses ranging from 100 kGy to 3,000 kGy. The symbols represent the 1st, 2nd and 3rd readings performed 2 hours, 60 days and 8 months after the irradiation process, respectively, at the same crucible.

Thus, once the sample is irradiated, in spite of the damages provoked in the homopolymer, such as chain scission and cross-linking, the radio-altered crystalline fraction is recovered even after melting and recrystallization. This finding is very interesting from the point of view of polymer stability. However, for dosimetric purposes, it only means that the irradiated sample can be used as a dosimetric record of the delivered dose, in the same way as the well known dosimetric photographic emulsions. But, irradiations were carried out in two steps with different dose rates. The necessity of using different distance from the source was determined by the results achieved by modulation source by Monte Carlo method. The results showed considerable uncertainties regarding the absorbed dose in samples close to the source due to the anisotropies and demonstrated that to be reliable results, samples should be irradiated at distances greater than or equal to 30 cm. Details of these results are presented in the previous papers devoted to detailing the study of the source characterizations [5]. Under these conditions (30 cm to the source) PVDF homopolymer shown that theoretically is suitable for dosimetric measurements.

2.2.2. Results to Second Irradiation

It is necessary to convert the measured calibration data into some form of smooth function that will enable dose to be obtained from a measured dosimeter 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 dosimeter signal and absorbed dose [6]. In general there not specific form to express the relationship between signal and dose and a mathematical expression has to be that will successfully approximate the observed relationship. In many cases a polynomial function will adequately describe the relationship, but other functions, such as exponentials can be used [6]. In this work, in first irradiation was used a exponential function at first order, but the results at second irradiation the best fit was exponential function at third order (Fig. 3). Difference too between the results was the range dose at calibration: 100 at 3,000 kGy for first irradiation and 100 at 2,000 kGy for second irradiation.

The Fig. 4 presents a comparison of the results to different radiation dose rates. It is clear from the DSC data that a destruction of the crystalline phases has occurred under gamma irradiation. But this destruction is more severe for high dose rate.
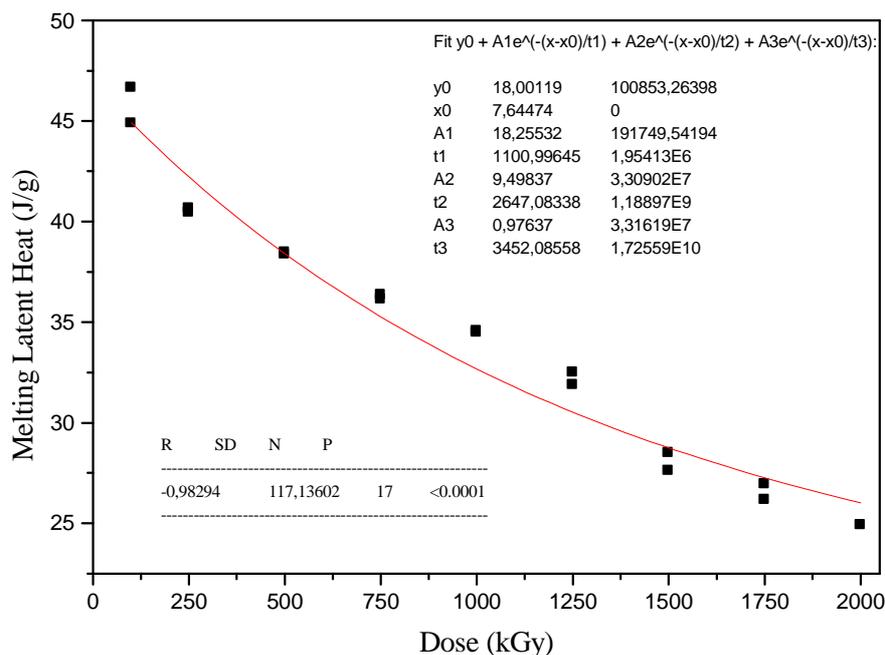
Fit y0 + A1e^(-(x-x0)/t1) + A2e^(-(x-x0)/t2) + A3e^(-(x-x0)/t3):

y0	18,00119	100853,26398
x0	7,64474	0
A1	18,25532	191749,54194
t1	1100,99645	1,95413E6
A2	9,49837	3,30902E7
t2	2647,08338	1,18897E9
A3	0,97637	3,31619E7
t3	3452,08558	1,72559E10

R	SD	N	P
-0,98294	117,13602	17	<0.0001

Figure 3: Plot of the Melting Latent Heat as a function of the delivered gamma dose, for the homopolymer PVDF irradiated at 30 cm from the source.

The Fig. 4 presents a comparison of the results to different radiation dose rates. It is clear from the DSC data that a destruction of the crystalline phases has occurred under gamma irradiation. But this destruction is more severe for high dose rate.
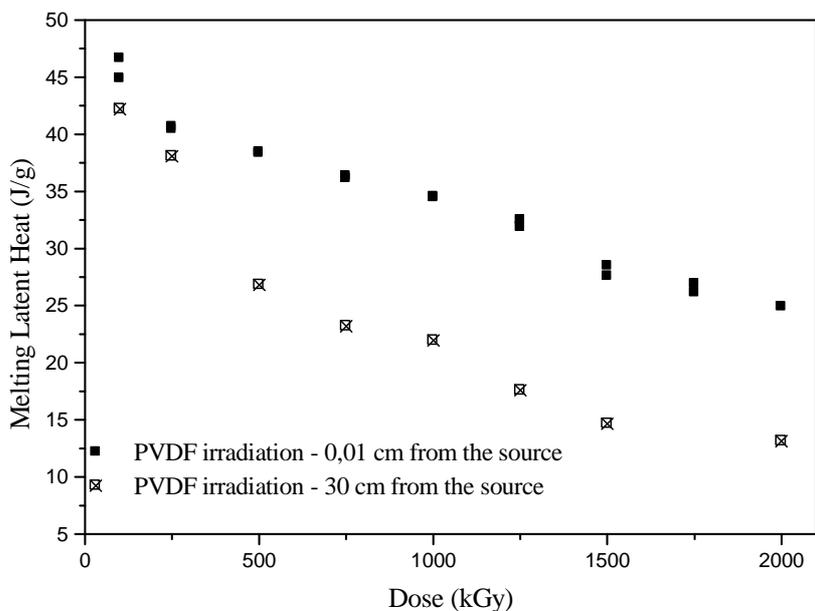

Figure 4: Plot of the Melting Latent Heat as a function of the delivered gamma dose, for the homopolymer PVDF irradiated at 0,01 cm and 30 cm from the source.

Irradiation of the polymer with the same doses, but at low dose rates allows better recovery of damages by the polymer chains which tends to drive out defects of crystalline region to region amorphous. Further experimental studies are been planning to validate the use of homopolymer PVDF as a dosimeter because of the low fading presented. It is the one fundamental advantages of this polymer.

3. CONCLUSIONS

Both the very large range of dose measurement and also the possibility of evaluating high gamma doses until months after irradiation make PVDF very good candidates to be investigated as commercial high gamma dose dosimeters. The advantages of PVDF as dosimeter are: being machinable and molded to variety of shapes and sizes, usable in wide range of doses (1 to 2,000 kGy), persisting of signal until large period of time after irradiations (low fading) which allows evaluating a gamma doses in convenient time, simplicity and good price compared with other polymers, the instrumentations for doses measurements are cheaper than TLDs.

ACKNOWLEDGMENTS

REFERENCES

1. J. W. Boag, G. W. Dolphin, J. Rotblat, *Radiat. Res*. Vol. 9, pp. 589-610 (1958)
2. Technical Report Series, *IAEA*, 409 (2002).
3. A. Miller, P. Sharpe, R. Chu, *ICRU News* (2000).
4. A. J. Lovinger, "Developments in Crystalline Polymers", in: I, D. C. Basset (Ed.) *Applied Science*, London, chapter 5(1982).
5. Maritza Rodríguez Gual, Adriana de Souza Medeiros Batista, Claubia Pereira, Felix Mas-Milian, Pablo Andrade Grossi, "Dose rate distribution of the GammaBeam - 127 Irradiator using MCNPX code", Send to publication.
6. P. Sharpe, A. Miller. "Guidelines for Calibration of Dosimeters for use in Radiation Processing". National Physical Laboratory (1999).