

Radiation Effects in the PVDF/Graphene Oxide Nanocomposites

Juliana V. Pereira, Adriana S. M. Batista, Jefferson P. Nascimento, Clascídia A. Furtado, Luiz O. Faria

Abstract—Exposure to ionizing radiation has been found to induce changes in poly(vinylidene fluoride) (PVDF) homopolymers. The high dose gamma irradiation process induces the formation of C=C and C=O bonds in its $[\text{CH}_2\text{-CF}_2]_n$ main chain. The irradiation also provokes crosslinking and chain scission. All these radio-induced defects lead to changes in the PVDF crystalline structure. As a consequence, it is common to observe a decrease in the melting temperature (T_m) and melting latent heat (L_m) and some changes in its ferroelectric features. We have investigated the possibility of preparing nanocomposites of PVDF with graphene oxide (GO) through the radio-induction of molecular bonds. In this work, we discuss how the gamma radiation interacts with the nanocomposite crystalline structure.

Keywords—Gamma irradiation, grapheme oxide, nanocomposites, PVDF.

I. INTRODUCTION

THE modification of polymers with ionizing radiation is a field that has developed considerably, leading to numerous technological applications. PVDF, for example, has been the focus of several studies due to its applications as a biocompatible material and ferroelectric properties, with important applications in the pharmaceutical, aerospace, electronics, and food industries. One of the four possible crystalline phases of PVDF, namely phase II or β -phase, shows ferroelectricity, making this homopolymer very attractive for technological applications [1].

The search for polymer nanocomposites with GO loading aims to obtain materials with new properties. In the case of materials subjected to gamma irradiation, it is expected to be able to produce materials that support exposure to high doses, with lower radio-degradation. Industries such as aerospace and aeronautics are examples where there is demand for radio-resistant materials to electromagnetic radiation [2]. Biomaterials are also exposed to gamma radiation for pre-use sterilization in in vivo contact. In addition, there are situations of use that simultaneously lead to the exposure to radiation and high temperatures, which justifies the understanding of the thermal degradation processes of these materials.

Nanoparticles with nanometer size, high surface area, and associated performance of interfaces can be used as structure and morphology directors of the nanocomposites. However, another nanoscaled material, the graphene sheets, has generated enormous interest for its possible implementation in many devices. Graphene is considered a two-dimensional carbon nanofiller, with a one-atom-thick planar sheet of carbon atoms that are densely packed in a honeycomb crystal lattice. To have remarkable properties [3], filling polymeric materials with graphene is an attempt to transfer their properties to the resulting nanocomposites [4].

In this study, PVDF pure samples and PVDF/GO nanocomposite are compared with respect to their resistance to gamma irradiation process. Thermal analysis allowed us to check an increase in thermal stability of nanocomposites relative to pure samples of PVDF.

II. EXPERIMENTAL

Samples of pure grain PVDF were made into thin films with a plate press heated to 200 °C at a pressure of 300 bar for 10 seconds, with subsequent air-cooling to room temperature. Nanocomposites were produced by mixing solved PVDF in DMAc with 1.88% GO dispersed in an aqueous solution by sonication. The PVDF pure samples produced by melt at 200 °C under 300 bar are shown in Fig. 1.



Fig. 1 PVDF pure sample prepared by melt at 200 °C under 300 bar

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Fig. 2 shows scheme of the syntheses of the samples PVDF/GO. PVDF pure samples and the nanocomposites were irradiated in Gamma Irradiation Laboratory (LIG) of CDTN using a Co-60 source at constant dose rate (12.0 kGy/h), for doses ranging from 100.0 to 1000.0 kGy in a scheme like the one shown in Fig. 3.

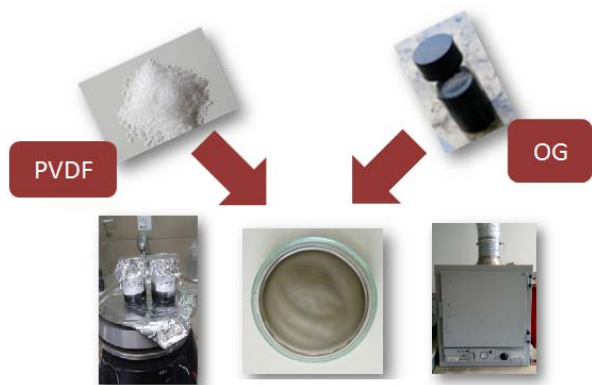


Fig. 2 Scheme of the syntheses of the sample of PVDF/OG obtained by the conventional casting technique (slow evaporation at 60 °C)

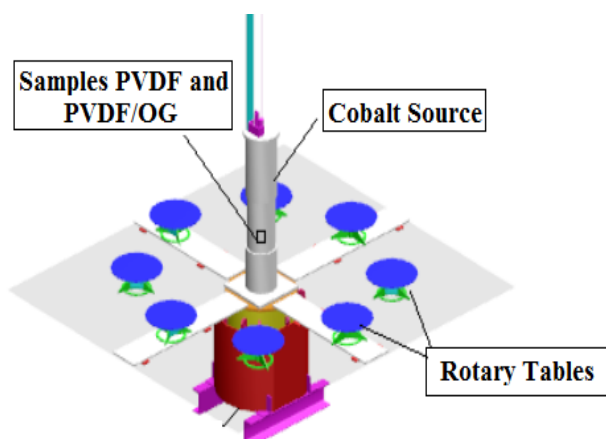


Fig. 3 Schematic of the LIG irradiation chamber, showing the position of the samples when irradiated

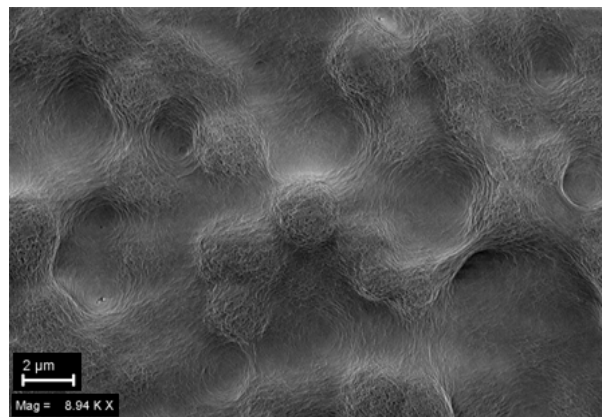
DSC TA Q10 was used for thermal behavior studies. TG and DTA curves were obtained using a Netzsch model STA 429. Samples were degraded in a dynamic nitrogen atmosphere at a heating rate of 10 °C/min. The FTIR spectra, collected with 32 scans each, were measured at a BOMEM 100 spectrometer for wavenumbers ranging from 300 to 4000 cm^{-1} . FE-SEM microscopy was performed at a SIGMA VP field emission scanning electron microscope ZEISS.

III. RESULTS AND DISCUSSION

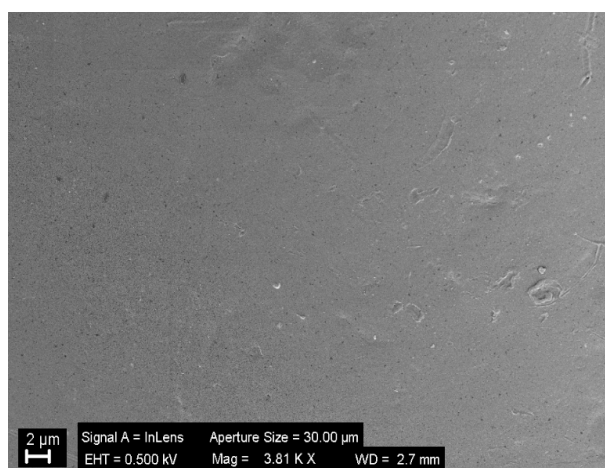
SEM images of pristine samples of PVDF and PVDF/GO nanocomposite are seen in Figs. 4 (a) and (b).

For PVDF pure samples, spherical aggregates of lamellar crystallites, called “spherulites”, can be observed in SEM images, as shown in Fig. 4 (a). However, this kind of crystallites is not observed in the samples of the PVDF/GO nanocomposites as it is seen in Fig. 4 (b). We remark that spherulite is a big crystalline structure compared to a crystalline lamella. In fact, spherulites are made of fibers that grow radially outward from the crystalline nuclei in the melt upon cooling. These fibers are in reality stacks of very thin platelet-like crystals called lamellae, which are ~10 nm thick

and several micrometers in lateral extension. Thus, we see here that the presence of GO sheets during the PVDF crystallization process strongly affects the crystallization phenomenon, modifying to a certain extent the mechanism of the crystalline component and the spherulite kinetics of crystallization. In the other words, the addition of GO sheets in PVDF has the same microscopic effect as adding, for instances, CHF-CF₂ monomers in the polymerization process, which in turn inhibits the spherulite formation.



(a)



(b)

Fig. 4 (a) SEM images of pristine PVDF and b) PVDF/OG nanocomposite

In Fig. 5, we show a magnified SEM image, displaying details of a GO sheet cluster. It is also seen that there are no spherulites at this image.

The thermal stability of PVDF and PVDF/GO nanocomposites behavior under gamma irradiation has been investigated by TG, DTA, and DSC techniques, and the results are summarized in Tables I and II. There is a significant number of works dealing with the thermal stability of polymers composites [4], but it is important to observe, by comparing Tables I and II, the absence of residues in the TG

analysis of PVDF/GO samples, as well as greater values of melting latent heat. The last property indicates that the addition of GO increase the resistance of the PVDF/GO crystalline structure against the radiation damages when compared to the PVDF ones.



Fig. 5 Magnified SEM images of pristine PVDF/GO, displaying details of the GO sheets

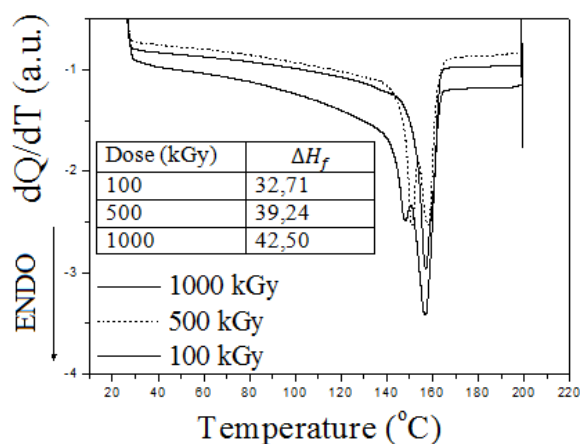
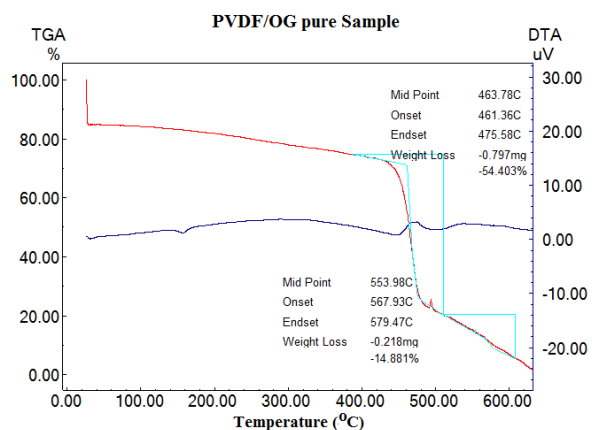
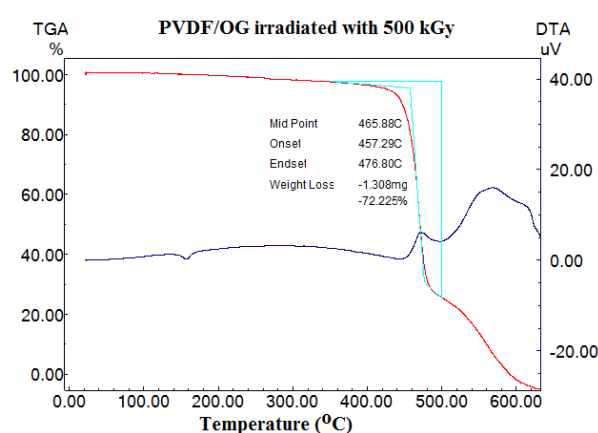


Fig. 6 2nd heating cycle thermograms for PVDF/GO samples exposed of gamma radiation

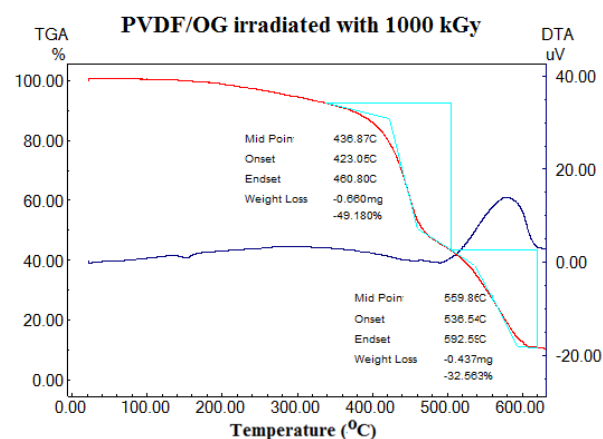
The loss of PVDF crystalline fraction after irradiation associated to the decrease of L_M has been characterized by DSC technique and is shown in Table I. However, we note, in Fig. 6 which shows the DSC thermograms for the PVDF/GO nanocomposites, the appearing of multiple peaks after irradiation with doses of 500 kGy and 1000 kGy. Although this phenomenon also occurs in pure PVDF samples, we observe that the decrease of T_M after irradiation with 1000 kGy is 16 °C for PVDF and 8 °C for the nanocomposite. This indicates that the PVDF/GO crystalline order degree is less affected than the PVDF ones.



(a)



(b)



(c)

Fig. 7 TG and DTA curves of (a) PVDF/OG pristine sample, (b) PVDF/OG irradiated with 500 kGy and (c) PVDF/OG irradiated with 1000 kGy

In Figs. 7 (a)-(c), we show the TG and DTA curves of PVDF/OG pristine sample and PVDF/OG irradiated with 500 kGy and 1000 kGy. After irradiation, a decrease of the degradation temperature is observed. However, it is lower than

that for PVDF sample, as shown in Table I. The high dose gamma irradiation process is well known to induce the formation of C=C and C=O bonds in pure PVDF chains. In the FTIR spectrum, these bonds are normally associated to vibrations bands at 1715 cm^{-1} and 1730 cm^{-1} , respectively, provoking chain scission and crosslinking [5].

TABLE I
RELATION BETWEEN RADIATION DOSES AND THERMAL PARAMETERS
OBTAINED WITH TG, DTA AND DSC OF PVDF SAMPLE

Radiation Dose (kGy)	RESIDUE (%)	Decomposition Temperature ($^{\circ}\text{C}$)	Heat of Fusion ($^{\circ}\text{C}$)	Melt Temperature ($^{\circ}\text{C}$)
0	2.01	410	44	160
100	26.12	410	42	155
750	35.46	348	28	149
1000	37.46	346	26	144

TABLE II
RELATION BETWEEN RADIATION DOSES AND THERMAL PARAMETERS
OBTAINED WITH TG, DTA AND DSC OF PVDF/OG SAMPLES

Radiation Dose (kGy)	RESIDUE (%)	Decomposition Temperature ($^{\circ}\text{C}$)	Heat of Fusion ($^{\circ}\text{C}$)	Melt Temperature ($^{\circ}\text{C}$)
0	-	567	51	152
100	-	440	32,71	150
500	-	440	39,24	163
1000	-	423	42,5	144

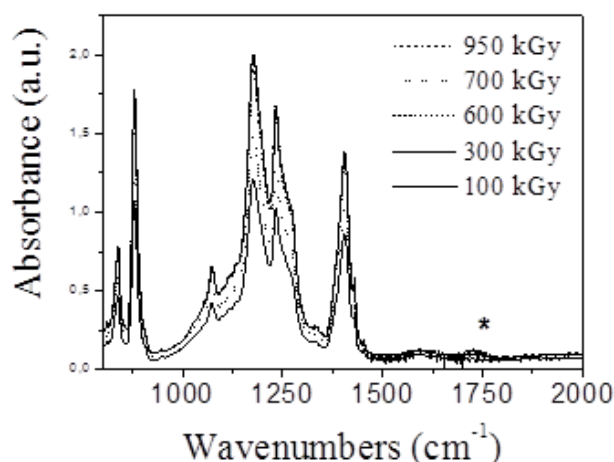


Fig. 8 FTIR spectra for PVDF /OG samples irradiated with doses between 100-950 kGy

In Fig. 8, we show the FTIR spectra of PVDF/GO nanocomposites taken just after irradiation. It is possible to see any significant new peaks appearing between 1500 and 2000 cm^{-1} . Thus, the addition of GO sheets to the PVDF matrix prevents against the chain scission and crosslinking events, which in turn helps to decrease the amount of crystalline destruction. This result is in agreement with the DSC and TG data.

IV. CONCLUSIONS

The introduction of 1.88 wt.% of GO material has provoked an increase of the maximum decomposition temperature in PVDF after gamma irradiation. This proportion of the GO in the PVDF matrix could result in a further improvement of the PVDF thermal stability. DSC, TG, and FTIR data analysis revealed that the addition of GO to PVDF polymer matrix prevents against spherulite formation but increases the crystalline fraction resistance to the radiation damages.

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REFERENCES

- [1] G. Botelho, S. Lanceros-Mendez, A.M. Gonçalves, V. Sencadas, J.G. Rocha, "Relationship between processing conditions, defects and thermal degradation of poly(vinylidene fluoride) in the β -phase" in *Journal of Non-Crystalline Solids*, vol. 354, 2008, pp.72-78.
- [2] M. Celina, T.R. Dargaville, R. A. Assink, J. W. Martin, "Selection and optimization of piezoelectric polyvinylidene fluoride polymers for adaptive optics in space environments" in *High Performance Polymers*, vol. 17, 2005, pp. 575-593.
- [3] R. D. Dreyer, S. Park, C. W. Bielawski, R. S. Ruoff, "The chemistry of graphene oxide" in *Chemical Society Reviews*, vol. 39, 2010, pp. 228-240.
- [4] C. Yu, D. Li, W. Wu, C. Luo, Y. Zhang, C. Pan, "Mechanical property enhancement of PVDF/graphene composite based on a high-quality graphene" in *Journal Materials Science*, vol. 49, 2014, pp. 8311-8316.
- [5] I. Boullier, S. Esnouf, A. L. Moël, "Radiooxidation of fluoropolymers: identification of oxidation products" in *Journal of Polymer Science Part B Polymer Physics*, vol. 41, 2003, pp. 1509 – 1517.