

Characterization of Gamma Irradiated PVDF and PVDF/Graphene Oxide Composites by Spectroscopic Techniques

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

Abstract—The combination of the properties of graphene oxide (OG) and PVDF homopolymer makes their combined composite materials as multifunctional systems with great potential. Knowledge of the molecular structure is essential for better use. In this work, the degradation of PVDF polymer exposed to gamma irradiation in oxygen atmosphere in high dose rate has been studied and compared to degradation of PVDF/OG composites. The samples were irradiated with a Co-60 source at constant dose rate, with doses ranging from 100 kGy to 1,000 kGy. In FTIR data shown that the formation of oxidation products was at the both samples with formation of carbonyl and hydroxyl groups amongst the most prevalent products in the pure PVDF samples. In the other hand, the composites samples exhibit less presence of degradation products with predominant formation of carbonyl groups, these results also seen in the UV-Vis analysis. The results show that the samples of composites may have greater resistance to the irradiation process, since they have less degradation products than pure PVDF samples seen by spectroscopic techniques.

Keywords—Gamma irradiation, PVDF, PVDF/OG composites, spectroscopic techniques.

I. INTRODUCTION

GRAPHENE based on a single layer of carbon in two-dimensional lattice has been attracted much attention due to its fascinating physical properties [1]. Poly(vinylidene fluoride) (PVDF) $-(CF_2-CH_2)_n-$ is a very attractive ferroelectric semi-crystalline polymer, exhibiting high permittivity, extraordinary piezo-, and pyroelectric properties and other excellent physical properties [2]. PVDF exist in at least four different crystalline phases: phase I (β form), phase II (α form), phase III (γ form) and phase IV (δ form). Two of these stable crystalline forms have been well characterized. Phase I has a planar zigzag chain conformation, producing a polar crystal, and is the most important of the PVDF polymorphs. Phase II is the most common polymorph of PVDF, with TGTG' chain conformation, producing a nonpolar crystal [3].

In recent years, many researches carried out many relative

Juliana V. Pereira, and Adriana Souza M. Batista are with the Universidade Federal de Minas, Belo Horizonte, MG 31270-970Brasil (phone: 55-31-3409-6666, 31-55-3409-9770; fax: 55-31-3409-6660,31-55-3409-9770; e-mail: julianaviegas1@yahoo.com.br, adriananuclear@yahoo.com.br).

Jefferson P. Nascimento, Clascidia A. Furtado, and Luiz O. Faria are with Serviço de Nanotecnologia e Materiais Nucleares, Belo Horizonte, MG 31270-901 Brasil, on leave from the Centro de Desenvolvimento da Tecnologia Nuclear, Minas Gerais, Brasil (e-mail: nascimentopatricio@yahoo.com.br, clas@cdtn.br, farialo@cdtn.br).

studies in fabrication and application of graphene/polymer composites [4]-[6]. The superior properties of graphene compared to polymers are also reflected in polymer/graphene nanocomposites. Polymer/graphene nanocomposites show superior mechanical, thermal, gas barrier, electrical and flame retardant properties compared to the neat polymer [5].

γ -rays are electromagnetic radiation of high frequency usually naturally produced on Earth by decay of high energy states in atomic nuclei. As a well-established non-contact process, the γ -ray irradiation technique has already been used widely and safely in sterilization and material processing based on well-rounded radiation protection [6]. Modification in polymeric structure of plastic material can be brought either by conventional chemical means or by exposure to ionization radiation from other radioactive sources or highly accelerated electrons. The prominent drawbacks of chemical cross-linking typically involve the generation of noxious fumes and by products of peroxide degradation.

PVDF/graphene oxide (PVDF/OG) composites were prepared using a solution method with dimethylacetamide (DMAc) as the solvent. FTIR and UV-Vis showed radiation degradation induced by process in the PVDF pure samples and in the nanocomposites.

II. 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 transparent films of about 160 μ m.

Graphene Oxides (GO) nanosheets were synthesized by the Hummers method, using graphite supplied by Aldrich as the starting material. Nanocomposites were produced by mixing solved PVDF in DMAc with GO dispersed in an aqueous solution by sonication. In Fig. 1, we present PVDF/OG sample produced with good dispersion of the OG in the PVDF matrix.

Samples were irradiated in Gamma Irradiation Laboratory (LIG) of CDTN using a Co-60 source at constant dose rate (3.5 kGy/h), for doses ranging from 100 to 1000 kGy. Optical transmission measurements were taken in a Shimadzu UV-2401 PC spectrometer, for wavelengths ranging from 190 to 900 nm. The FTIR spectra, each collected with 32 scans each, were measured at a BOMEM 100 spectrometer for wavenumbers ranging from 300 to 4000 cm^{-1} .



Fig. 1 Sample of PVDF/OG obtained by the conventional casting technique (slow evaporation at 60°C)

III. RESULTS AND DISCUSSION

All samples were irradiated with gamma doses between 100 kGy and 1,000 kGy. The UV-Vis and Infrared (FTIR) spectrophotometry have been used to monitor the appearing of C=C conjugated bonds and radio-oxidation of carbon (C=O), and also the appearance of new chemical bonds linking PVDF chains to OG nanosheets in the nanocomposites. Fig. 2 shows the PVDF pristine samples and irradiated with 100 kGy, 500 kGy and 1000 kGy. Fig. 3 shows the PVDF/OG pristine and irradiated with 100 kGy, 900 kGy and 1000 kGy.

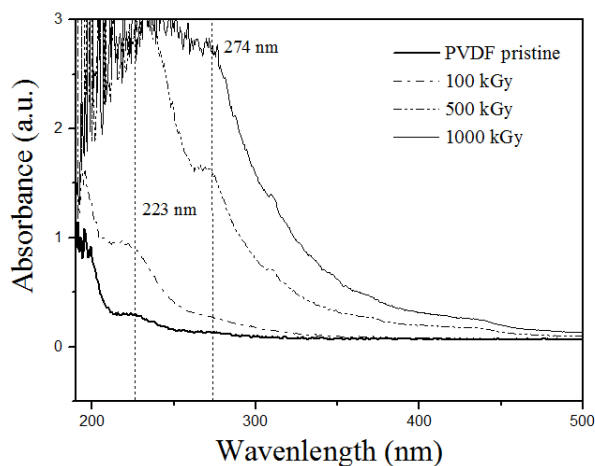


Fig. 2 (a) UV-Vis spectra for unirradiated PVDF and irradiated with 100, 500 and 1000 kGy

It can be seen in Figs. 2 and 3 that the absorption peaks of conjugated C=C bonds appear at 195 nm, 223 nm and 274 nm. These peaks correspond to the radio-induction of singlet, duplet and triplet of C=C bonds, respectively [7]. The reported absorption peak for unirradiated graphene oxide is centered at 230 nm, and they are not observed in Fig. 3 [8].

Fig. 4 shows the FTIR spectra by PVDF pure samples pristine and irradiated with gamma doses between 100 and 1000 kGy. In the region between 1500 and 1900 cm^{-1} it is observed a well pronounced increase of an absorption band centered at 1730 cm^{-1} , for increasing gamma doses. It seems that this band is closely correlated to the chain oxidation (C=O) during irradiation indicating previous occurrence of the chains scission. According to [9], these bands can be described

as the stretch of C=O bonds at 1730, 1760, 1790 and 1853 cm^{-1} , respectively, and as C=C stretching at 1715 and 1754 cm^{-1} . The PVDF is characterized by the presence of symmetric and asymmetric stretching vibrations of CH_2 groups at 2981 and 3023 cm^{-1} [10]. On the other hand, sample of the PVDF/OG irradiated present minor absorbance in region between 1700 cm^{-1} and 1790 cm^{-1} . In Fig. 5, one can see absorbance centered at 1585 cm^{-1} , which we attributing to in plane vibration modes of COOH bonds. To compare the irradiated PVDF pure samples and PVDF/OG composites in Fig. 6 show in detail the region of absorption between 1500 cm^{-1} to 1950 cm^{-1} . In this figure we see more clearly the different bands appearing in pure PVDF and the samples of the composites after the process irradiation.

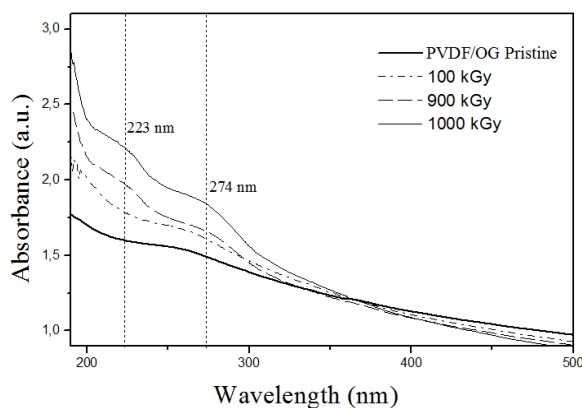


Fig. 3 UV-Vis spectra for unirradiated PVDF/OG and the PVDF/OG samples irradiated with 100, 900 and 1000 kGy

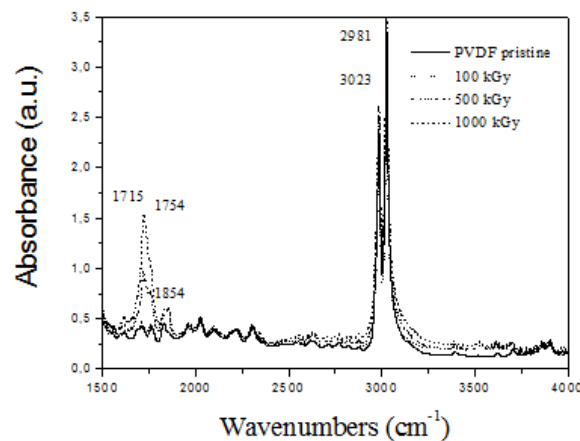


Fig. 4 FTIR spectra for pristine sample of PDVDF pure and samples irradiated with 100, 500 and 1000 kGy for wavenumbers ranging from 1500 to 4000 cm^{-1}

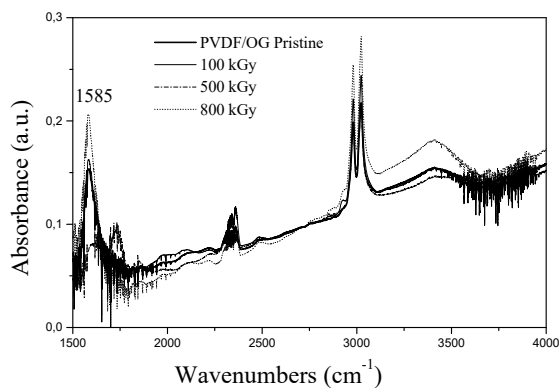


Fig. 5 FTIR spectra for pristine sample of PVDF/OG and samples irradiated with 100, 500 and 800 kGy for wavenumbers ranging from 1500 to 4000 cm^{-1}

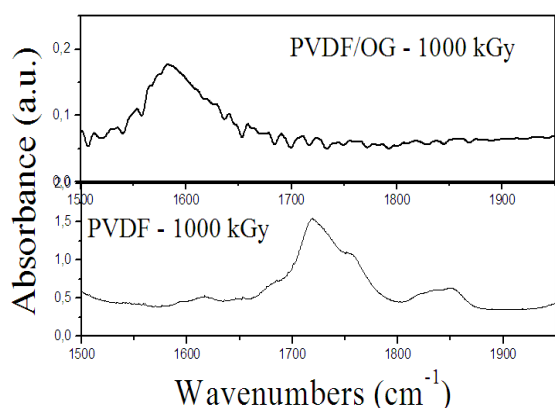


Fig. 6 FTIR spectra for PVDF/OG irradiated with 1000 kGy and PVDF pure sample irradiated with 1000 kGy for wavenumbers ranging from 1500 to 1950 cm^{-1}

PVDF exhibits polymorphism of several crystalline phases and shows at least five possible types of crystal phase, the so-called nonpolar α -phase, polar β -phase, and γ , δ , and ϵ -phase. The most common polymorph of PVDF is the α -phase, having a monoclinic unit cell with TG^+TG^- chain conformation. The β -phase is the more attractive and desirable among the PVDF phases, with conformational sequences of TTT (all trans) [1]. In this conformation, PVDF is ferroelectric, i.e. it presents piezo and piroelectricity, which renders to this polymer application as sensors and actuators.

In Table I show the infrared absorption bands characteristic of the various phases of the PVDF, which allows us to identify, by means of this method, the crystalline phase of the polymer and of the composite after irradiation.

In Fig. 7, we can see the pure sample of the PVDF after irradiated shows transmittance characteristic bands of α phase, β and γ phase. We must remember that the γ phase is a combination of the presence of α and β phase, which leads us to consider that the sample is in the γ phase.

Samples of PVDF /OG show less intense absorption peaks in the region between 500 and 840 cm^{-1} , characteristic of β phase of PVDF (Fig. 8).

Absorption Bands α Phase (cm^{-1})	Absorption Bands γ Phase (cm^{-1})	Absorption Bands β Phase (cm^{-1})
3026	3023	3020
2986	2981	2978
1425	1431	1430
1404	1406	1400
1385		
1294		
1213	1234	
1185	1176	1180
1150	1140	
976		
874	880	880
855	838	840
	813	
796	792	
765	776	
	723	
	688	
615	656	
	552	
532	511	
490	482	508
410		490
	430	470
	400	445
355	348	
287	300	

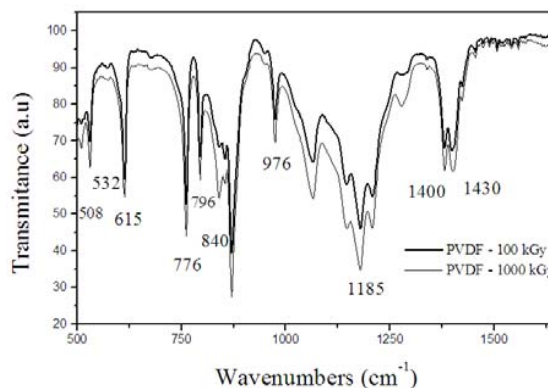


Fig. 7 FTIR spectra for PVDF irradiated with 100 and 1000 kGy for wavenumbers ranging from 500 to 1650 cm^{-1}

The spectroscopic results demonstrate since they have less degradation products in PVDF/OG samples. The results show that the samples of composites may have greater resistance to the irradiation process. In the fact, other authors have related about PVDF/OG composites, advantages on mechanical properties involving higher ductility, rigidity and storage modulus [2].

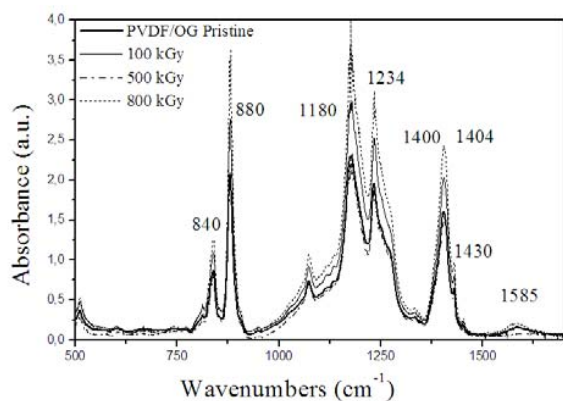


Fig. 8 FTIR spectra for PVDF/OG irradiated with 100, 500 and 800 kGy for wavenumbers ranging from 500 to 1650 cm^{-1}

[10] Z. Zhudi, Y. Wenxue, C. Xinfang, "Study on increase in crystallinity in γ - irradiated poly(vinylidene fluoride)" in *Radiation Physics and Chemistry*, vol. 65, 2002, pp. 173 – 176.

IV. CONCLUSIONS

PVDF pure samples and PVDF/OG nanocomposites were irradiated with gamma radiation with doses between 100 kGy and 1000 kGy. The spectroscopic techniques indicated degradation products formation with higher intensities in the PVDF pure samples. The presence of the graphene oxide can contribute with higher resistance of composites.

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REFERENCES

- [1] J. Yu, P. Jiang, C. Wu, L. Wang, X. Wu, "Graphene nanocomposites based on poly(vinylidene fluoride): structure and properties" in *Polymer Composites*, 2011, pp. 1484 – 1490.
- [2] 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.
- [3] M.M. Nasef, H. Saidi, K.Z.M. Dahlan, "Investigation of electron irradiation induced-changes in poly(vinylidene fluoride) films" in *Polymer Degradation and Stability*, vol. 75, 2002, pp. 85-92.
- [4] C. Yu, D. Li, W. Wu, C. Luo, Y. Zhang, C. Pan, "Mechanical property enhancement of PVDF/grapheme composite based on a high-quality grapheme" in *Journal Materials Science*, vol. 49, 2014, pp. 8311-8316.
- [5] T. Kuilla, S. Bhadra, D. Yao, N. H. Kim, S. Bose, J. H. Lee, "Recent advances in grapheme based polymer composites" in *Progress in Polymer Science*, vol. 35, 2010, pp. 1350 – 1375.
- [6] B. Zhang, L. Li, Z. Wang, S. Xie, Y. Zhang, Y. Shen, M. Yu, B. Deng, Q. Huang, C. Fan, J. Li, "Radiation induced reduction: an effective and clean route to synthesize functionalized grapheme" in *Journal of Materials Chemistry*, vol. 22, 2012, pp. 775 – 7781.
- [7] A. S. Medeiros, L. O. Faria, "High gamma dose response of poly(vinylidene fluoride) copolymers", in *Nuclear Instruments and Methods in Physics Research, Section B, Beam Interactions with Materials and Atoms (Print)*, v. 268, 2010, pp. 2740 – 2743.
- [8] F. T. Thema, I. M. J. Moloto, I. E. D. Dikio, I. N. N. Nyangiwi, L. Kotsedi, M. Maaza, M. Khenfouch, "Synthesis and Characterization of Graphene Thin Films by Chemical Reduction of Exfoliated and Intercalated Graphite Oxide", in *Journal of Chemistry*, 2013, pp. 1-6.
- [9] S. Boullier, A. Esnouf, Le Moël, "Radiooxidation of fluoropolymers: identification of oxidation products", in *Journal of Polymer Science Part B Polymer Physics*, vol. 41, 2003, pp. 1509–1517.