Nuclear Instruments and Methods in Physics Research A 619 (2010) 177–180

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research A

journal homepage: www.elsevier.com/locate/nima

Study on application of PTFE, FEP and PFA fluoropolymers on radiation dosimetry

A.M.S. Galante [a,*], O.L. Galante [b], L.L. Campos [a]

[a] Radiation Metrology Centre, Institute of Energetic and Nuclear Research, IPEN–CNEN/SP, Av. Prof. Lineu Prestes, 2242, Cidade Universitária, 05508-000 São Paulo, Brazil
[b] Borrachas Vipal S/A–Divisão Plásticos, Av. Torres de Oliveira, 329, Bairro Jaguaré, 05347-020 São Paulo, Brazil

ARTICLE INFO

Available online 28 October 2009

Keywords:
Fluoropolymers
Radiation dosimetry
Gamma radiation
Optical analyses

ABSTRACT

Changes induced by radiation in the UV–vis and Infrared absorbance spectra of fluoropolymer films were investigated. Samples ($3 \times 1\,cm^2$) of commercially available fluoropolymers, tetrafluoropolymer homopolymer (PTFE–Tecnofluor/DuPont) and its copolymers with hexafluoropropylene (FEP 1000 C–DuPont) and perfluoroalkoxy (PFA 500 CLP–Dupont) were irradiated with ^{60}Co gamma radiation in free air at electronic equilibrium conditions with absorbed doses between 1 and 150 kGy. Studies of environmental condition effects, such as temperature and light, pre- and post-irradiation stability and dose range useful response were carried out. Fluoropolymers are very stable when exposed to different ambient conditions; the dosimetric wavelength is characteristic for each type of fluoropolymer and a linear correlation was found between gamma radiation dose and optical response.

1. Introduction

Ionizing radiation treatment on a variety of polymers is a well-established technology. Polymeric materials exposed to electron beams, γ-rays and X-rays undergo structural changes due to molecular cross-linking and chain scission (degradation) reactions and these properties are in strong contrast with the original polymer properties and can be used for dosimetric purposes [1–6].

The radiation treatment of polymeric materials changes chemical resistance, electrical properties, thermal stability, surface properties and other characteristics. The final result depends on the nature of the material, dose, dose rate and energy of the incident radiation.

Fluoropolymers represent a group of rather specialized polymeric materials. The term "fluoropolymers" is a broad grouping of polymers made from monomers containing one or more fluorine atoms, or copolymers of such monomers with other monomers. The backbone is formed of carbon–carbon bonds and carbon–fluorine bonds. Both are extremely strong bonds (C–C=607 kJ/mole and C–F=552 kJ/mole). The majority of the fluoropolymers are crystalline plastics (PTFE has a very high degree of crystallinity of up to 90% in the virgin state) but some are amorphous (Teflon® AF). This range of structures means that the optical clarity of fluoropolymers can range from opaque (PTFE) to excellent (Teflon® AF has a high luminous transmittance and excellent optical clarity). Fluoropolymers are among the most chemically inert of all polymers and remain stable in almost all chemical environments. It presents excellent thermal resistance and can be handled without special care in the environment under normal conditions of temperature and light. Fluoropolymers transmit more UV, visible and infrared radiation than ordinary window glass.

FEP (copolymer of hexafluoropropylene and tetrafluoroethylene-DuPont) and PFA (perfluoroalkoxy polymer resin-DuPont) are very similar in composition to the fluoropolymers PTFE (polytetrafluoroethylene Tecnofluor/DuPont). The radiation tolerance of FEP in the presence or absence of oxygen is higher than that of PTFE by a factor of 10:1. PFAs, like other perfluoropolymers, are not highly resistant to radiation.

The ionizing radiation induced changes on fluoropolymers have been extensively studied in order to know its radiation sensitivity. The degradation effect is more severe in the presence of oxygen (in air) than in vacuum, and is further intensified at elevated temperature, resulting in reduction of the molecular weight.

In this work it was evaluated the radiation induced changes in the UV–vis and Infrared optical absorbance of the fluoropolymers samples aiming to assess the absorbed dose. Further studies regarding environmental condition effects, such as temperature and light, pre- and post-irradiation stability and the dose range over which there is a useful response were also carried out.

2. Experimental

Commercially available fluoropolymers: tetrafluoropolymer homopolymer (PTFE–Tecnofluor/DuPont) and its copolymers with hexafluoropropylene (FEP 1000 C–DuPont) and perfluoroalkoxy (PFA 500 CLP–Dupont) in film form, cut in plates of $3 \times 1\,cm^2$ with

* Corresponding author. Tel.: +55 11 3133 9664.
E-mail address: sgalante@ipen.br (A.M.S. Galante).

0168-9002/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.nima.2009.10.103

thickness of 200, 250 and 125 μm, respectively,were irradiated free in air with absorbed doses between 1 and 150 kGy and dose rate of 2.14 kGy/h using a ^{60}Co gamma radiation source.

Optical absorption measurements of irradiated and non-irradiated samples were taken in a Shimadzu spectrophotometer UV-2101PC at wavelengths ranging between 190 and 900 nm.

The FTIR spectra of the same samples were obtained using an ABB FTLA 2000 spectrometer (Fourier transform infrared spectroscopy) from 500 to 4000 cm^{-1}.

The presented results are the average of 3 individual measurements and the error bars the standard deviation of the mean.

3. Results

3.1. UV–vis spectra of non-irradiated fluoropolymers

Fig. 1 shows transmission and absorption optical spectra for the non-irradiated fluoropolymer films studied.

3.2. FTIR spectra of PTFE, FEP and PFA of non-irradiated films

Infrared spectra of non-irradiated PTFE, FEP and PFA samples are shown in Fig. 2. According to the literature the band at 2365 cm^{-1} is a combination band associated with the CF_2 backbone, while the absorption band from 1000 to 1400 cm^{-1} represents the C-F stretching vibration. The band at 1882 cm^{-1} is assigned to carbonyl stretching vibration and at 1793 cm^{-1} is assigned to terminal double bonds in the form of $-CF=CF_2$ in the polymer chain structure [7–10].

3.3. Effects of environmental conditions

The PTEF, FEP and PFA samples were exposed for many days to the laboratory ambient light and to different temperatures between 10 °C and 100 °C. The optical response did not present significant variation (< 5%); therefore, the samples can be manipulated without special care.

3.4. Fluoropolymer films irradiated with ^{60}Co gamma radiation

3.4.1. UV–vis spectra of PTFE, FEP and PFA irradiated films with ^{60}Co gamma radiation

In Fig. 3(a) for FEP and (b) for PTFE and PFA are shown the optical absorption spectra between 190 and 300 nm. It can be seen that optical absorption increases as a function of gamma dose. The dosimetric band wavelengths are 600, 250 and 192/220 nm for PFTE, FEP and PFA films, respectively.

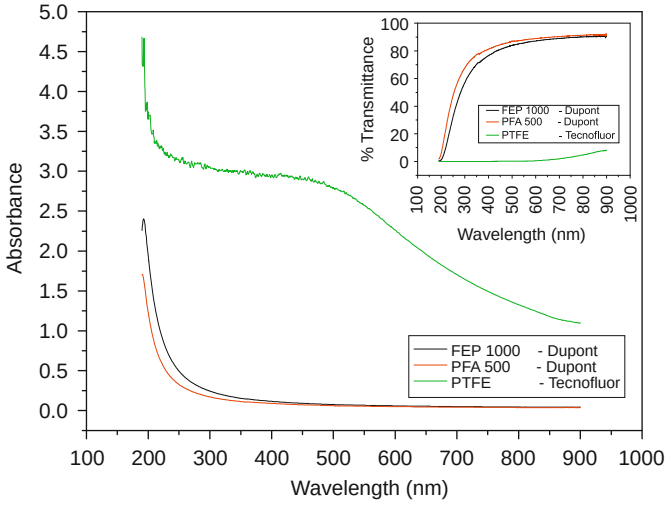

Fig. 1. Light transmission and absorption of non-irradiated fluoropolymer films.

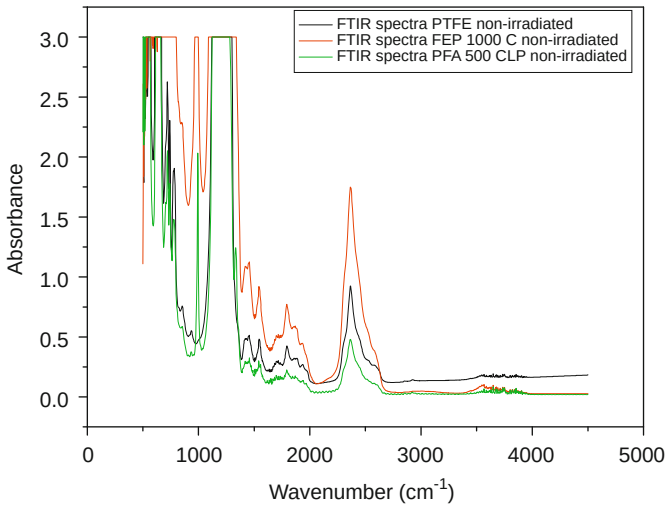

Fig. 2. FTIR spectra of non-irradiated fluoropolymer films.

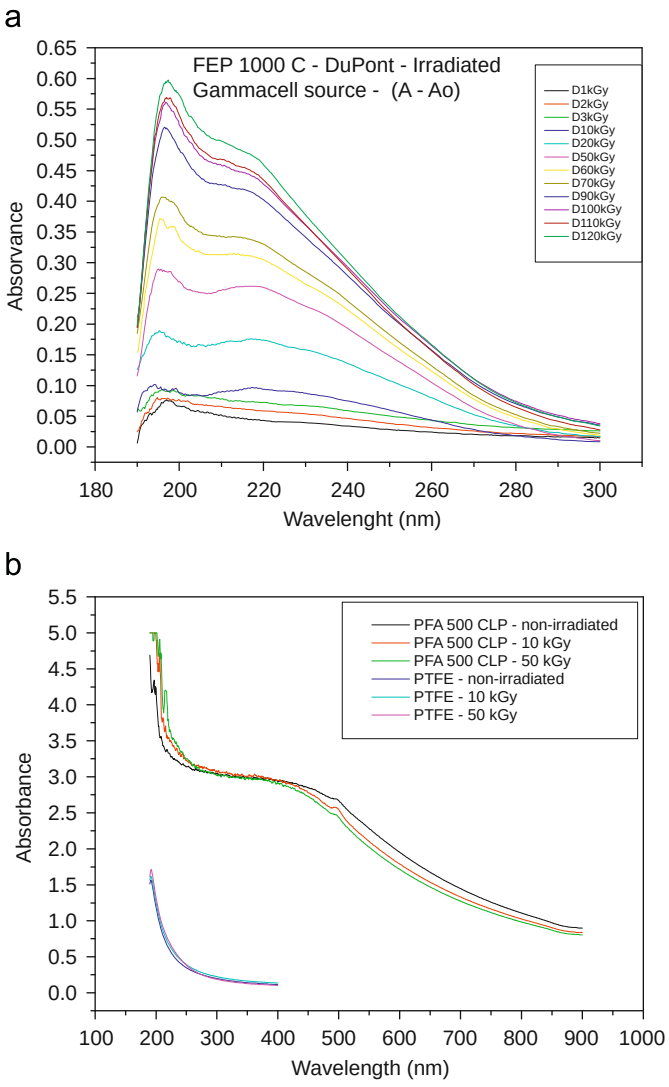

Fig. 3. Absorption spectra of fluoropolymer films irradiated with ^{60}Co gamma radiation.

3.4.2. FTIR spectra of PTFE, FEP and PFA irradiated films with ^{60}Co gamma radiation

The radiation induced changes in the optical absorbance spectra of fluoropolymer films can be observed in Fig. 4(a)–(c) for PTFE, FEP and PFA, respectively. In the studied dose range, only the absorption intensity was noted to vary with the absorbed dose. The appearance of new bands in the spectrum was not observed. The infrared spectra show absorption bands in the 1700–1900 cm^{-1} region typical for oscillations of the double bonds in compounds having fluorine; intensification of absorption was noted to occur at 1699, 1705, 1716, 1734, 1774, 1776, 1796, 1871 and 1887 cm^{-1}, very close to the literature data [7–10].

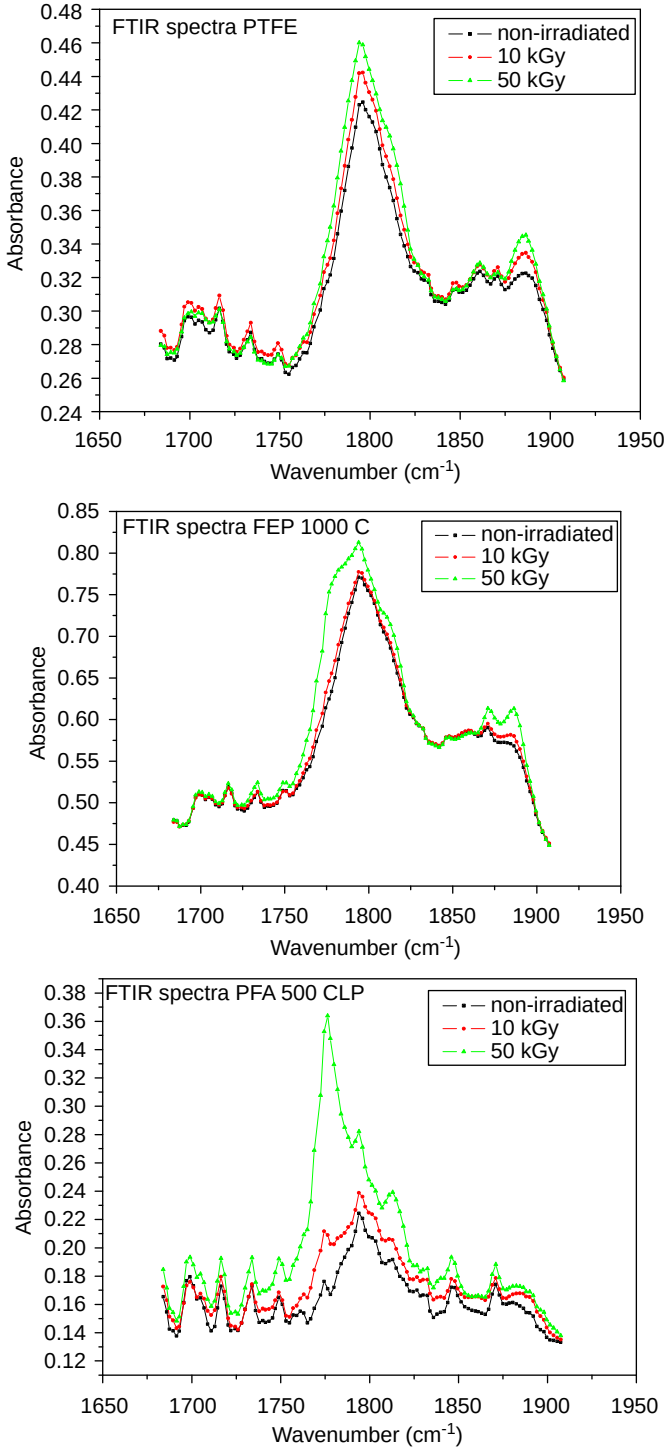

Fig. 4. FTIR spectra of fluoropolymers irradiated with ^{60}Co gamma radiation.

3.4.3. Dose–response curve–spectrophotometric UV–vis analyses

Fig. 5 shows the dose–response curves for FEP and PFA fluoropolymers. A linear dose–response correlation was established. The relationship can be described by the following equation: Absorbance=A+(B × Dose).

3.4.4. Dose–response curve–FTIR analyses

In the FTIR spectra changes were observed in the intensity of the band at 1774 cm^{-1} (PFA 500 CLP) and 1776 cm^{-1} (FEP 1000 C) and these can be correlated with absorbed dose. Fig. 6 shows the dose–response curves for FEP and PFA fluoropolymers. A linear dose–response correlation was established. The relationship can also be described by the previous equation.

4. Conclusions

Radiation induced changes in the optical absorption spectra of the studied fluoropolymer films can be correlated to absorbed

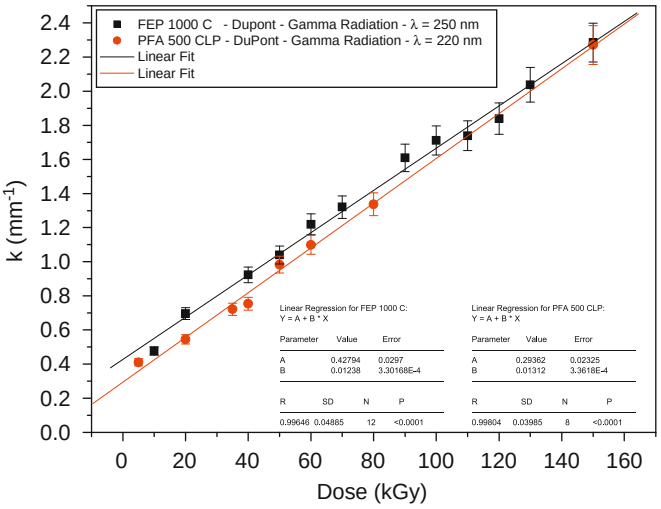

Fig. 5. Dose–response curves–UV–vis absorption analyses of FEP and PFA fluoropolymer films irradiated with ^{60}Co gamma radiation.

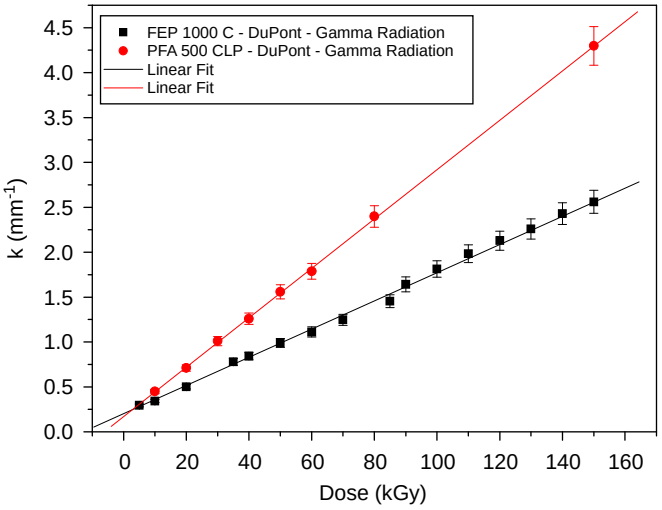

Fig. 6. Dose–response curves and FTIR absorption spectra of fluoropolymer films irradiated with ^{60}Co gamma radiation.

dose. The useful dose range is large and probably this can be extended to absorbed doses higher than 150 kGy.

The UV–vis spectra present a linear correlation between the 600 nm (PTFE), 250 nm (FEP 1000) and 220 nm (PFA 500) peak intensities, which were chosen as being wavelength dosimetric interest for the given gamma doses.

The FTIR spectra show changes in the 1796 cm^{-1} (PTFE), 1774 cm^{-1} (PFA 500) and 1776 cm^{-1} (FEP1000) band intensities that can also be correlated with absorbed dose.

The dosimetric properties can be determined, quantified and related with radiation dose.

The fluoropolymer films present excellent dosimetric characteristics and are promising materials as alternatives in high gamma dose quality control.

Acknowledgements

The authors are thankful to Capes (Coordenação de Aperfeiç oamento de Pessoal de Nível Superior) and CNPq (Conselho Nacional de Pesquisa e Desenvolvimento) for financial support.

References

[1] H. Wilski, Radiat. Phys. Chem. 29 (1987) 1.
[2] S. Ebnesajjad, Fluorconsultants Group LLC. D. Available from: 〈www.FluoroConsultants.com〉 (accessed May 2009).
[3] IAEA TECDOC 1420 2004, Advances in radiation chemistry of polymers, in: Proceedings of a Technical Meeting, Notre Dame, IN, USA.
[4] J.G. Drobny, Technology of Fluoropolymers. second ed., CRC Press, Taylor & Francis Group. Available from: 〈http://www.materialsnetbase.com/books/7158/63170_c000.pdf〉 (accessed May 2009).
[5] S. Ebnesajjad, P.R. Khaladkar, Fluoropolymers Applications in Chemical Processing Industries. PDL Editor of Fluorocarbon Series, PDL Handbook Series. Available from: 〈http://books.google.com.br/books?id=e_E_Pdns8tcC&printsec=frontcover#PPA100,M1〉 (accessed May 2009).
[6] D.W. Clegg, A.A. Collyer, Irradiation Effects on Polymers, Elsevier Applied Science. Available from: 〈http://books.google.com.br〉 (accessed May 2009).
[7] K. Lunkwitz, U. Lappan, D. Lehmann, Radiat. Phys. Chem. 57 (2000) 373.
[8] A.S. Medeiros, L.O. Faria, Nucl. Instr. and Meth. A 587 (2008) 315.
[9] D.J.T. Hill, K.J. Thurecht, A.K. Whittaker, Radiat. Phys. Chem. 67 (2003) 729.
[10] V. Lappan, U. GeiBler, S. Uhlmann, Nucl. Instr. and Meth. B 236 (2003) 413.