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FTIR ANALYSIS OF IRRADIATED FOOD-GRADE PVC FILMS

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RESUMO:

Este trabalho teve como objetivo investigar a influência da radiação ionizante (raios gama e elétrons acelerados) em doses comerciais de 1, 2 e 4 kGy nas propriedades ópticas de filmes de PVC usados em embalagens de alimentos. FTIR foi executado na faixa entre 4000 – 400 cm-1 através de leitura direta dos filmes de PVC.A formação de polienosfoiavaliada por espectrofotometria no comprimento de onda de 400 nm. FTIR das amostras irradiadas demonstraram reduções das absorbâncias das bandas referentes às bandas das ligações carbono-hidrogênio (metileno) e carbono-cloro, sugerindo reações de cisão das moléculas do PVC devido às reações de dehidrocloração.A formação de polienos demonstrou aumento nas amostras irradiadas devido às reações de cisão nos filmes de PVC. Este fato confirma as reações deradiólise do polímerodecorrente dos raios gama ou elétrons acelerados.

Palavras-chave: poli (cloreto de vinila), embalagem de alimentos, radiação gama, feixe de elétrons.

ABSTRACT:

This work aimed to investigate the influence of ionizing radiation (gamma radiation and accelerated electrons) at commercial doses of 1, 2 and 4 kGy on optical properties of PVC films used as food packaging. FTIR was carried out for range of 4000 to 400 cm-1 by direct measurement. Polyene formation was measured with spectrophotometry at wavelength of 400 nm. FTIR of irradiated samples reveals reduction of absorbance of carbon-hydrogen (methylene) and carbon-chloride bands suggesting PVC scission due to dehydrochlorination reactions. Furthermore, polyene formation demonstrated increase on irradiated samples because of scission reactions on food-grade PVC films. This observation confirms polymeric radiolysis mechanisms promoted by gamma-rays or accelerated electrons.

Keywords: poly(vinyl chloride), food packaging, gamma radiation, electron beam.

Poly (vinyl chloride) (PVC) is a low-cost thermoplastic polymer with a broad spectrum of properties (Vinhaset al., 2004a;Vinhas et al., 2004b;Colombani et al., 2007) such as its mechanical performance, goodprocessability and vast versatility due to plasticizers incorporation (Rodolfo Jr & Mei, 2007). PVC has many applications from long-term and short-term uses as materials for food packaging, medical devices and advanced engineering (Labed, Obeid &Ressayre, 2013).

Nowadays, the use of ionizing radiation (gamma radiation and accelerated electrons) was established in order to assure food decontamination andsterilization of packaging materials(Haji-Saied, Sampa&Chmielewski, 2007; Zygouraet al., 2011a). In addition, radiation could be applied to promote chemical modifications on polymers due to cross-linking reactions, improving performance of polymeric materials (Rouif, 2004; Rouif, 2005; García-Castañedaet al., 2010). Besides its uses, the effects of gamma radiation and accelerated electrons on poly (vinyl chloride) must be well comprehended to estimate radiolysis pathways and evaluate scission/cross-linking ratio reactions (Colombaniet al., 2007).

Although interactions between gamma radiation or accelerated electrons and polymers could differ according to irradiation parameters such as dose, dose rate, atmosphere and films thickness, the main reactions on polymer surface are due to Compton effects (Woo & Sandford, 2002). So, the aim of this work was to investigate the effects of commercial doses

(1 to 4 kGy) of gamma-rays and accelerated electrons on optical properties of food-grade PVC films with FTIR/UV-VIS analysis.

METHODS

Food-grade poly (vinyl chloride) packaging films were commercial product acquired from Dispafilm do BrasilLtda (Guarulhos, São Paulo, Brazil). Films were composed by PVC resin and additives (plasticizers and stabilizers). Samples “as received” were stored in desiccators for 48 h, at room temperature with controlled moisture (30-35 %) and tests were executed subsequently.

Square specimens of food-grade PVC films (A = 100 cm2) were supported on a stainless-steel board (5 mm inch) to avoid folding and guarantee uniform distribution of ionizing radiation on films surfaces.The irradiation was performed on both irradiators, a 60Co gamma source, model Gamma Cell 220 Excel, MDS Nordion (Toronto, Canada), (1,17 and 1,33 MeV)or an electron beam industrial irradiator (10 MeV) at room temperature and air atmosphere with commercial radiation doses of 1, 2 and 4 kGy.

The Fourier transform infrared spectroscopy (FTIR) was recorded using a Thermo Scientific Nicolet model IS50 infrared spectrometer at a resolution of 4 cm^{-1}. The spectra were obtained on the wavenumber range of 4000-400 cm^{-1} with number of scans equal to 32. The bands assignments were made for PVC/additives and the behaviour of main bands were analysed in order to evaluate chemical modifications on irradiated samples.

For polyene quantification, the absorption of the unirradiated and irradiated PVC specimens was measured at VARIAN UV-VIS model 100 Conc at wavelength of 400 nm at room temperature and controlled humidity (20 ± 0.5°C and 30-35%, respectively). The tests were executed on five different regions of irradiated samples.The statistical analysis of data were executed on Graphpad Prism version 5.0, using one-way analysis of variance (ANOVA) ($p < 0.05$).

RESULTS AND DISCUSSION:

The FTIR spectra main absorption bands of functional groups and vibrational modes of PVC and additives are given in Table 1.

Table 1: Main absorption bands assignments of functional groups for PVC and additives.

Band assignment	PVC Wavelength (cm^{-1})	Additives Wavelength (cm^{-1})	Functional Group
Asymmetric stretching	2958	2958	CH_3
Asymmetric stretching	2928	2928	CH_2
Symmetric stretching	2855	2855	CH_3
Symmetric stretching	2818	2818	CH_2
Symmetric stretching	-	1728	C=O
Stretching	-	1620	C=C (aromatic)
Stretching	-	1600	C=C (aromatic)
Stretching	-	1580	C=C (aromatic)
Stretching	1539	-	Bending CH_2
Stretching	-	1462-1460	C-O-C and CH_2Scissoring
Angular deformation	1426	-	CH_2-Cl
Angular deformation	1380	-	CH_3
Angular deformation	1335	-	CH_2
Out of plane angular deformation	1256	1256	Cl-CH and C-O-C
In plane angular deformation		1120	C-H aromatic
In plane angular deformation	-	1074	C-H or C-C aromatic
Out of plane trans deformation	960	-	Cl-CH
Stretching	694	-	C-Cl
Stretching	636	-	C-Cl

Table 1 demonstrated bands assignments for FTIR spectra typically related to PVC and plasticizers groups. The main characteristics absorption bands for the polymer are in accordance with data found for many authors for pureand plasticized polymer (Zhu et al., 2008; Coltro, Pitta e Madaleno, 2013; Reddeppaet al., 2013; Wuet al., 2014;Nadimicherlaet al., 2015). FTIR of food-grade PVC films showed peaks for C-H bond stretching for CH_3 and CH_2 groups between 3000-2800 cm-1, angular deformation for CH_2-Cl bond at 1426 cm-1, deformation of methyl and methylene groups between 1380-

3000-2800 cm-1, angular deformation for CH2-Cl bond at 1426 cm^{-1}, deformation of methyl and methylene groups between 1380-1335 cm^{-1}, out of plane angular deformation of Cl-CH bond at 1256 cm-1, deformation trans out of plane of CH-Cl bond at 960 cm-1 and two stretching vibrational modes for C-Cl bond at 694 and 636 cm^{-1}. So, the monitoring of chemical bonds between carbon and chlorine atoms (CH-Cl, CH_2-Cl and C-Cl) could be an useful tool to predict the stability of PVC films towards electron beam or gamma radiation. Furthermore, analysis of C-H methylene stretching could indicate deprotonation reactions on polymeric chains generating HCl and polyene polymeric chains (Vinhas et al., 2003).

Furthermore, FTIR spectra reveals bands assignments of additives as bands at 1728 cm^{-1} (most intense) related to C=O bond, peaks between 1700-1500 cm^{-1} for C=C bond for aromatic plasticizers,vibrational modes for C-O-C bond at 1256 cm^{-1}, C-H and C-C bonds vibrational modes at range of 1150-1000 cm^{-1}.

The FTIR spectra of unirradiated and irradiated (electron beam or gamma radiation) for food-grade PVC films are illustrated on Figure 1. No significant changes were observed on main characteristics peaks for samples treated with accelerated electrons (Figure 1a) or gamma-rays (Figure 1b) on commercial radiation doses up to 4 kGy. In order to assure a better resolution of main characteristics bands, FTIR spectra of unirradiated and irradiated food-grade PVC films were evaluated on bands assignments for C-H, CH-Cl, CH_2-Cl and C-Cl bands, respectively (Figures 2-5).

The C-H, CH-Cl, CH_2-Cl and C-Cl absorption peaks (Figures 2-5) showed decrease for carbon-hydrogen and carbon-chloride bounds. This fact is related to scission reactions promoted by gamma-rays or accelerated electrons because of interactions between ionizing radiation and electrons because of interactions between ionizing radiation and electrons located on polymer surface, due to Compton or photoelectric effects. The Compton or photoelectric effects leads to activation of radiolysis mechanisms characterized by scission reactions of poly (vinyl chloride) and additives chains bounds.The decrease in the intensity of C-H stretching (CH3 and CH2 groups) is an indicative of deprotonation reactions which leads to hydrochloric acid and polyene formation as termination radiolysis products of poly (vinyl chloride) (Vinhas et al., 2003).

Furthermore, the decrease on absorbance observed (figures 2-5) has a more regular pattern of reduction on specimens irradiated with gamma-rays in comparison with electron beam irradiation. So, energy differences between ionizing radiation sources could be responsible for alterations on FTIR spectra especially on low radiation doses.

However, when radiation dose is increased the analytical response noted on carbon-chloride absorption peaks demonstrates a similar pattern of modifications on poly (vinyl chloride) films.

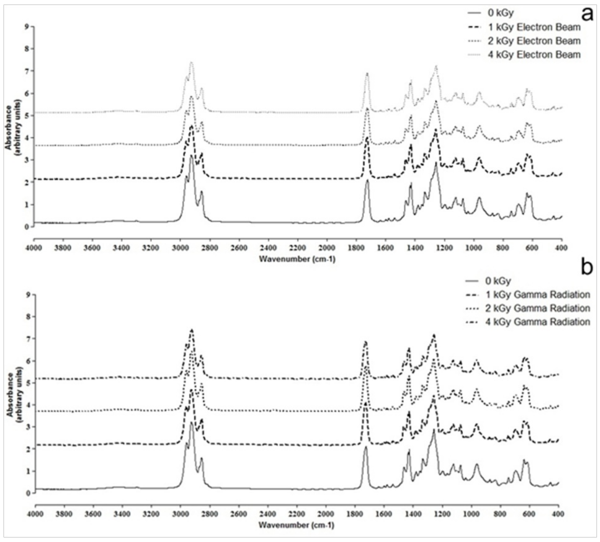

Figure 1.FTIR spectra for unirradiated and irradiated food-grade PVC films. Legend (a) accelerated electrons; (b) gamma-rays.

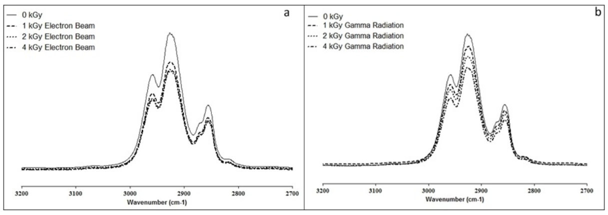

Figure 2. Absorption peaks for C-H (CH3 and CH2 groups) for unirradiated and irradiated food-grade PVC films. Legend: (a) accelerated electrons; (b) gamma-rays.

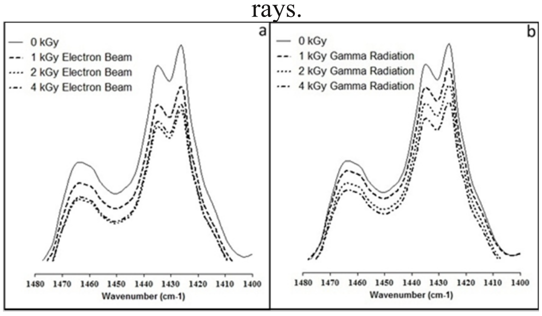

Figure 3. Absorption spectra for CH2-Cl bound at 1426 cm-1. Legend (a) accelerated electrons; (b) gamma-rays.

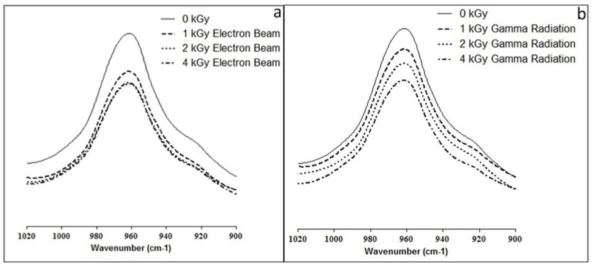

Figure 4.Absorption spectra for CH-Cl angular deformation at 1256 cm-1. Legend (a) accelerated electrons; (b) gamma-rays.

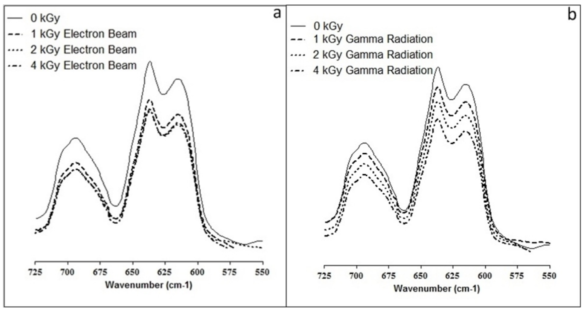

Figure 5. Absorption spectra for stretching vibrational modes for C-Cl bond at 694 and 636 cm-1. Legend (a) accelerated electrons; (b) gamma-rays.

Figure 6 reveals that polyene formation is increased on irradiated samples (4 kGy of electron beam irradiation) ($p < 0,05$) in comparison with unirradiated samples, formation.

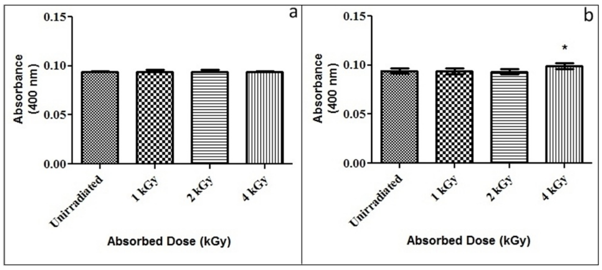

Figure 6.Absorbance for polyene quantification at 400 nm. Legend: (a) gamma-rays; (b) electron beam.

The polyene formation during treatment with ionizing radiation for PVC packaging materials is related by many authors (Baccaro et al., 2003; Vinhas et al., 2003; Vinhas et al., 2004a). Double bounds formation occurs by dehydrochlorination of PVC, which causes progressive yellowish of irradiated samples with increase of absorbed radiation dose (Baccaro et al., 2003; Laverne et al., 2008). The yellowish of food packaging materials could affect the acceptance of irradiated foodstuff by consumers due to reduction of transparence of stretch PVC films.

CONCLUSION

Irradiation with gamma-rays and accelerated electrons at commercial doses up to 4 kGy could promote scission of poly (vinyl chloride) used as food packaging materials. This behaviour is due to radiolysis mechanism promoted by ionizing radiation when interacting with PVC based polymeric materials. The results showed that FTIR/spectrophotometry could be employed to estimate dehydrochlorination process on PVC films.

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