Characterization of polymers in plastic packagings irradiated with thermal neutrons.

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In this study results of polymer characterization of two plastic packaging irradiated with thermal neutrons, as well as of their inorganic element content are presented. This assessment is of interest in the investigations of chemical element migration by radiometric method. Plastic samples were irradiated with neutrons from IEA-R1 nuclear reactor and they were analyzed by Differential Scanning Calorimetry (DSC) and Infrared Spectroscopy (FTIR), the results were compared with those obtained for non irradiated samples. Element concentrations were determined by Neutron Activation Analysis (NAA). DSC and FTIR results of irradiated plastics showed degradation and modification in the crystalline and amorphous regions. NAA results indicated the presence of As, Cd, Cr, Co and Sb in plastic packaging.

Introduction

Nowadays plastics are widely used in food packagings. These packagings that are used in direct contact with the food might to contaminate them, so in Brazil, to safeguard the consumer health, the National Health Surveillance Agency (ANVISA) regulated the food products packaging material constituents as well as the element that could migrated to the packaging content [1].

Conventional methods for chemical migration analysis involve element extraction into food-simulating liquids (FSL) and subsequent determination by conventional spectroscopic methods [2]. In the case of radiometric method of migration, the exposure of the sample to the migration is carried out with plastics irradiated with neutrons.

Several studies [5, 6] have shown that depending on the radiation, characteristics and type of the polymers, their degradation and cross-linking may occur. Therefore it is of great interest to verify if neutron irradiation affects the structure of plastics and consequently in the migration of element.

The polymers of packagings have been characterized either by FTIR [3], which is a quick method, however not sensitive to impurities below 1% or by DSC [4].

In the present current investigation the irradiated and non irradiated samples were characterized by FTIR and DSC and the determination of inorganic components was performed by NAA.

Experimental

The analyzed plastic samples were packagings of juice (J) and soft drink (SD). In order to evaluate the radiation effect on the polymers samples, they were irradiated at the IEA-R1 nuclear reactor, for 3 minutes and for 16 h under a thermal neutron flux of 10^{12} n cm^{-2} s^{-1}. The DSC and FTIR analyses were carried for irradiated and non irradiated samples. The polymer identification were carried out about 10 months of decay time in order to avoid the handling of radioactive material.

In the NAA, the gamma ray radiation measurements of samples and standards were performed using a hyperpure Ge detector coupled to a gamma ray spectroscopy. The radioisotopes identification was done by gamma-rays energies and half-lives and the element concentrations were calculated by comparison method.

For FTIR analyses, the irradiated and non irradiated samples were hot-pressed, except for sample of juice 960-minutes irradiated, which was pyrolized. A Nicolet Magna IR 550 series II FTIR spectrophotometer was used. DSC analyses were carried out using a Seiko EXC STAR 6200 calorimeter.

Results and discussion

DSC and FTIR Results

The results of DSC and FTIR analysis indicated high-density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) as the polymers of juice and soft drink packaging, respectively. DSC analysis also showed for the juice packaging sample of HDPE, that both melt temperature (Tm) and heat of fusion (ΔHm) decrease with neutron irradiation time (Table 1), demonstrating that irradiation by neutrons causes modification in the crystalline regions of the polymer, which indicates the samples, underwent structural degradation, a common phenomenon in polymers exposed to radiation [9]. In the case of soft drink packaging sample of PET, no significant variations have been observed between thermal properties of the

irradiated and non irradiated sample, indicating PET is more resistant to short-time irradiation than HDPE.

Table 1 - Variation of samples thermal properties with irradiation time.

Sample	Irradiation time (min)	Tm (°C)	Tg (°C)	ΔHm (J/g)
J0	0	130.5	-	44.2
J3	3	129.8	-	42.0
J960	960	122.9	-	37.5
SD0	0	243.4	71.8	8.5
SD3	3	243.0	70.8	8.9

Comparison between FTIR spectra of the non irradiated HDPE sample and that irradiated for 3 minutes shows the appearance of a band at 1718 cm^{-1} for the latter sample. This band can be attributed to the presence of carbonyl groups, indicating that short-time irradiation leads to oxidative degradation of polyethylene [7], corroborating DSC results. FTIR spectrum of the sample irradiated for 960-minutes, compared to the 3-minutes irradiated sample, shows additional bands at 1642, 992, 966 and 909 cm^{-1}, indicating the presence of trans-vinylene double bonds likely brought about by C-H bond scission[8]. The 1642 cm^{-1} may be attributed to C=C vinyl stretch vibration, the 992 cm^{-1} and 966 doublet to $=CH_2$ out-of-plane twist (typical vibration of trans double bonds) and the 909 cm^{-1} to $=CH_2$ out-of-plane bend.

Oxidative degradation evidence using FTIR is not indicated for comparison between the non irradiated and irradiated sample of PET, since this polymer contains C=O groups in its structure.

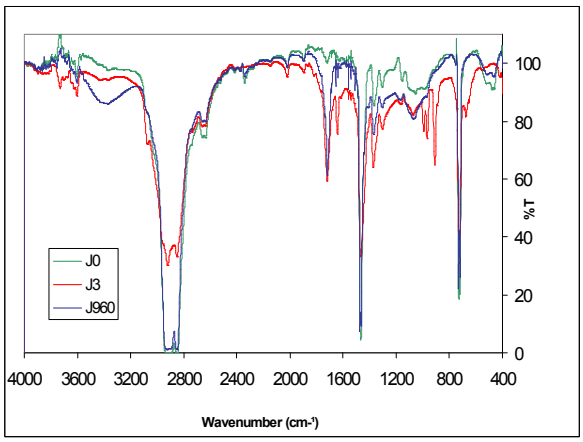

Figure 1 – FTIR spectra of the juice packaging samples non irradiated, 3-minutes irradiated and 960-minutes irradiated.

NAA Results

Results of elemental analysis, from Table 2, show that As, Cd, Co, Cr e Sb are present in plastic packagings analized. The juice packaging presented these elements in low concentrations but, the soft drink packagings presented the high concentrations of Co and Sb. The element Sb derives from the catalyst used in plastic processing. The Co concentration present in soft drink packaging sample induced high activity of ^{60}Co with half life of 5.24 years. Consequently this sample irradiated for 960-minutes could not be measured by DSC and FTIR techniques.

Table 2 – Elemental composition of packagings samples, ng g^{-1} obtained by NAA.

Element	Contend of packaging	
	Juice	Soft drink
As	7.0 ± 0.8	ND*
Cd	160 ± 29	ND
Co	9.6 ± 0.1	1960 ± 30
Cr	377 ± 13	ND
Sb	35.3 ± 0.4	185030 ± 1730

*ND- not detected)

Conclusions

DSC results indicate that the HDPE samples, irradiated for 3 and 960 minutes showed decrease in T_m and ΔHm with irradiation time, due to oxidative degradation of plastic which was confirmed by FTIR analyses.
FTIR analyses also showed that long-time irradiation may cause C-H bond scission.
As to the PET sample not irradiated, the polymer showed to be more resistant to short-time irradiation exposure of 3-minutes.
NAA results showed that food packagings plastics may contain toxic elements and they can constitute a source of food contamination.

Acknowledgments

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