NUKLEONIKA 2008;53(Supplement 2):S141–S144

TECHNICAL NOTE

Mechanical and thermal properties of commercial multilayer flexible plastic packaging materials irradiated with electron beam

**Vitor M. Oliveira,
Beatriz R. Nogueira,
Angel V. Ortiz,
Esperidiana A. B. Moura**

Abstract. The effects of electron-beam irradiation on mechanical and thermal properties were studied for two commercial multilayer structures of flexible food packaging. Both the laminated poly(ethylene terephthalate) (PET)/low-density polyethylene (LDPE) and the coextruded LDPE/polyamide(PA)/LDPE structures were irradiated up to 120 kGy using a 1.5 MeV electron beam accelerator, at room temperature in the presence of air. Mechanical properties showed significant changes ($p < 0.05$), specially in sealability that was severely affected. Changes in mechanical properties were discussed in relation to the eight day and the six month period after irradiation. In addition, the DSC analysis six months after treatment showed that the fusion enthalpy of the PET/LDPE structure components increase for the LDPE from 10 kGy and decrease for the PET up to 120 kGy ($p < 0.05$). On the other hand, the LDPE/PA6/LDPE presented increase in the LDPE and PA up to 120 kGy, except for LDPE at 10 and 15 kGy and PA at 5 kGy doses ($p < 0.05$). The effects of irradiation were less severe for the LDPE/PA6/LDPE than for the PET/LDPE. The electron-beam irradiation did not show advantageous results that could be of interest for commercial applications for the film industry, but brings important information about the packaging behavior for food producers who may decide to use irradiation as a form of cold pasteurization of their packed products.

Key words: electron-beam radiation • multilayer packaging materials • mechanical properties • thermal properties

V. M. Oliveira, B. R. Nogueira, E. A. B. Moura✉
Radiation Technology Center,
Nuclear and Energy Research Institute
(IPEN-CNEN/SP),
2242 Prof. Lineu Prestes Ave., 05508-000 São Paulo,
SP, Brazil,
Tel.: +55 11 3133 9883, Fax: +55 11 3133 9765,
E-mail: eabmoura@ipen.br

A. V. Ortiz
Unipac Embalagens Ltda,
Rua Arnaldo Magniccaro 521, 04691-060, São Paulo,
SP, Brazil

Received: 27 October 2008
Accepted: 3 February 2009

Introduction

Treatment with ionizing radiation, particularly, electron-beam radiation is a promising approach to the controllable modification of the properties of polymeric flexible packaging materials, in order to adjust their physicochemical, mechanical, optical, barrier and other properties. In recent years, electron-beam radiation has been efficiently applied in the flexible packaging industry to promote cross-linking and scission of the polymeric chains to improve specific material mechanical properties. On the other hand, ionizing radiation can also affect the polymeric material itself leading to a production of free radicals. These free radicals can in turn lead to degradation and or cross-linking phenomena, with release of gases, discoloration, changes in mechanical, thermal and barrier properties, degradation and leaching of polymer additives into solvents [4, 7]. The use of the multilayer laminated or coextruded structures of flexible packaging is rising in food packaging industries because such materials provide various desirable properties such as barrier to gases, water vapor, organic compounds and UV, mechanical strength, puncture resistance, heat sealability, machinability and relatively low cost, that one single material by itself is not able to provide. Most laminated or coex-

truded multilayer structures of flexible food packaging are based on polyolefins (low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), biaxially oriented polypropylene (BOPP) [5]. Other very common polymeric layers in multilayer structures of food packaging industry are based on polyethylene terephthalate (PET), polyamide (PA) if a medium oxygen barrier properties is desirable, and ethylene vinyl alcohol copolymer (EVOH) when a higher oxygen and aroma barrier and excellent organoleptic properties are necessary [6]. In the present study, the changes in mechanical and thermal properties of the commercial multilayer structures used in food packaging, after electron-beam irradiation up to 120 kGy, were evaluated. A variety of techniques were used to evaluate such changes, e.g. thermal analysis (DSC) for information on the modification in melting temperature and enthalpy of the packaging materials; tensile testing for information about changes in tensile strength and elongation at break of the materials and penetration and sealability resistance testing.

Experimental

Two commercial multilayer structures, commonly used in dry food packaging, were chosen for the present study: i) PET (12 μm)/LDPE (120 μm) film, 132 μm thick, a very common multilayer laminate structure and ii) LDPE (40 μm)/PA6 (50 μm)/LDPE (70 μm film, 160 μm thick, representative of a medium oxygen barrier coextruded flexible packaging. Although both structures use LDPE, different grades of the material were used by the packaging producer in each structure. The materials were irradiated up to 120 kGy using a 1.5 MeV electrostatic accelerator (Dynamitron II, Radiation Dynamics Inc., 1.5 MeV energy, 25 mA current and 37.5 kW power), at room temperature, in air, dose rate 11.22 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters "CTA-FTR-125" from Fuji Photo Film Co. Ltd. Preliminary studies had indicated that irradiation doses over 120 kGy affected sealing strength of the material severely, resulting in a film that could not be used as food packaging when sealing was required. Consequently, these higher doses are of no interest in this study. The thermal analysis, i.e. differential scanning calorimetry (DSC) analysis, was carried out on structures six month after irradiation. DSC analysis of the structure materials were performed on four weighed samples with 3.0 ± 1.0 mg of the irradiated and non-irradiated structure materials, through the use of a differential scanning calorimeter, DSC 50 (Shimadzu, Japan). Samples were heated from 25 to 300°C, at a heating rate of 10°C/min (in a nitrogen atmosphere). The heat of fusion of the multilayer structures components was determined per gram of the material. The mechanical properties tests were carried out on structures initially eight days after irradiation and six month later, in order to consider post irradiation effects. The tensile tests were carried out according to ASTM D 882-90 [1], the penetration resistance based on ASTM F 1306-90 [2] and sealability resistance according to ASTM F 88-00 [3]. Mechanical properties were determined using an INSTRON Testing Machine model 5564 and a sealing packaging machine Mical model SE 450. For the determination of the material mechanical properties of the non-irradiated structures, and for each applied dose, six samples in the same size and thickness, obtained randomly, were assayed. The difference between the results for irradiated and non--irradiated structures was than evaluated statistically by ANOVA using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at $p < 0.05$.

Results and discussion

The results of the DSC analysis for melting temperature (T_m) and enthalpy (ΔH_m) of the multilayer structure materials are summarized in Table 1. The results presented in Table 1 represent the average values calculated from the data obtained by DSC analysis. The standard deviation for DSC analysis was less than 10% for all tests. As it can be seen, there were significant differences ($p < 0.05$) of the T_m and ΔH_m of the film structures. The LDPE layer T_m, for both irradiated structures changed, for PET/LDPE layer at 75 kGy T_m decreased to 3.5°C. The PET layer T_m increased by 5°C, increasing the radiation doses; the PA layer T_m decreased by 5°C, increasing the radiation doses. On the other hand,

Table 1. Effect of irradiation on thermal properties of multilayer structures

Dose (kGy)	PET/LDPE				LDPE/PA6/LDPE			
	LDPE		PET		LDPE		PA6	
	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m (J/g)
0	119.25	11.55	249.24	3.07	112.45	22.44	219.38	7.95
5	120.43	8.93	250.04	2.63	111.78	23.02	218.18	7.86
10	118.62	15.03	252.48	2.65	112.84	21.96	218.87	11.59
15	118.79	15.30	253.80	2.64	112.27	22.22	218.05	9.32
20	118.86	16.96	252.82	2.77	112.41	22.70	218.50	8.61
25	118.02	16.30	252.82	2.55	111.31	23.85	216.81	10.43
30	119.46	15.32	252.99	2.58	112.12	22.74	217.62	8.46
45	119.05	15.86	253.44	2.72	111.50	24.42	216.91	8.59
60	118.50	14.87	252.95	2.19	111.95	25.78	216.39	8.83
75	115.71	12.86	251.42	2.14	111.19	29.74	215.28	10.77
90	118.71	15.07	253.64	1.88	111.26	34.00	215.28	8.50
105	118.64	15.80	254.06	2.33	111.38	31.38	214.07	9.69
120	118.38	15.56	253.25	1.76	111.89	24.29	213.45	8.72

Table 1 shows an increase in LDPE layer ΔH_m for both structures, except for PET/LDPE at 5 kGy and LDPE/PA/LDPE at 10 and 15 kGy ($p < 0.05$). After electron-beam irradiation, the increases of the LDPE layer ΔH_m in absolute values were up to 47% for PET/LDPE and up to 51% for LDPE/PA/LDPE. The PA layer ΔH_m irradiated increased up to 46%, except at 5 kGy ($p < 0.05$). The PET layer ΔH_m decreased up to 57%. The tensile strength at break average data are given in Fig. 1. As can be seen, the structure tensile properties increased or decreased in the different timeframes, as a result of the doses applied, presenting significant differences ($p < 0.05$). The PET/LDPE tensile strength presented a 10% maximum decrease, eight days after irradiation and an increase lower than 7%, six months after irradiation. For LDPE/PA/LDPE, the tensile properties showed a 22% maximum increase eight days after irradiation, but six months after irradiation presented increases by 11–22% and decreases by 7–27% (Fig. 1), as a result of the doses applied. Figure 2 shows the average results of the percent elongation at break tests. The elongation properties of the structures irradiated showed significant differences ($p < 0.05$). However, the percent elongation at break of the PET/LDPE, showed increases by 16–43% six months after irradiation, while the LDPE/PA/LDPE presented increases between 8–17% on some radiation doses and a large decrease by 24% at doses range 25–75 kGy (Fig. 2). The penetration resistance test average results of the structures are given in Fig. 3. The PET/LDPE penetration resistance basically was not affected by irradiation, since that showed a slightly increase between 1–2% and decreases by 5–10% eight days after irradiation, but was not affected by radiation

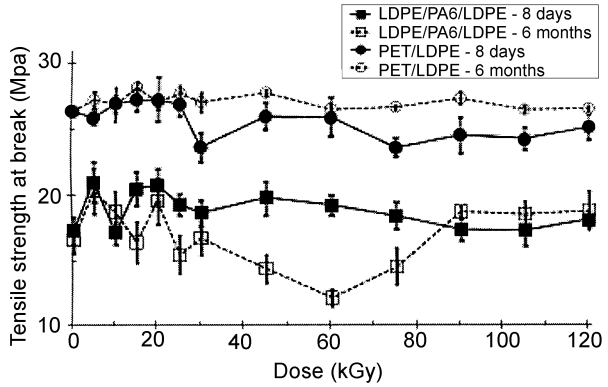

Fig. 1. Tensile strength at break as a function of electron-beam radiation dose for the examined structures.

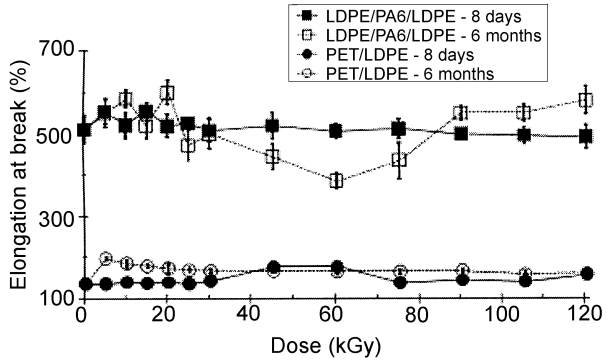

Fig. 2. Elongation at break as a function of electron-beam radiation dose for the examined structures.

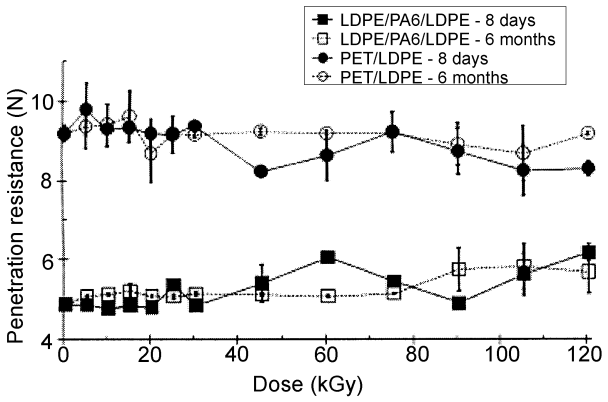

Fig. 3. Penetration resistance as a function of electron-beam radiation dose for the examined structures.

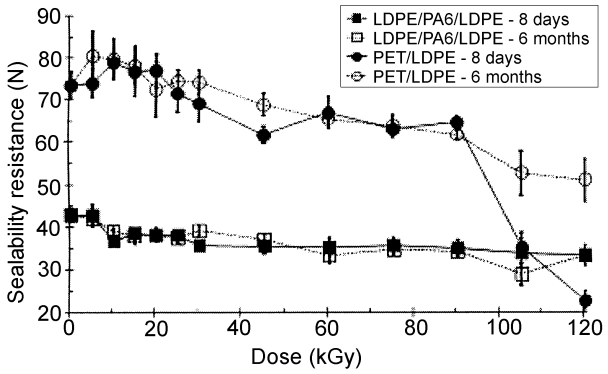

Fig. 4. Sealability resistance as a function of electron-beam radiation dose for the examined structures.

doses six months after irradiation ($p < 0.05$). For the LDPE/PA/LDPE there were significant increases ($p < 0.05$) eight days after radiation doses of 60 and 120 kGy and six months after irradiation increased by 4–20%, increasing the radiation doses. The sealing properties average data are given in Fig. 4. The PET/LDPE showed loss of sealability from of 45 kGy, with reduction between 9–70% eight days after irradiation, and 6–30% six months after irradiation. For LDPE/PA/LDPE, the loss of sealability was 10–22% eight days after irradiation and 9–32% six months after irradiation. The standard deviation was less than 10% for all the mechanical properties tests carried out on structures.

Conclusions

In general, results showed that electron-beam irradiation, for the dose range studied, led both to increases and decreases of ΔH_m, depending on the studied packaging component. The concurrent cross-linking and scission effects in the molecular structure of each material, added to the initial packaging industrial structure, will result in more or less significant changes in the mechanical and thermal properties of the final packaging, depending on the dose. For example, results showed an increase of the LDPE and PA layers ΔH_m for almost radiation doses applied. Changes in the molecular structure, responsible for an increase in ΔH_m of LDPE/PA/LDPE, affected the mechanical characteristics of structure, especially penetration resistance that increased, according to the radiation doses. Comparison

of both structures also leads to the conclusion that the mechanical properties of the PET/LDPE were more deteriorated by irradiation than LDPE/PA/LDPE, except in terms of sealing properties, which showed a great loss for both irradiated structures, with a higher degree of loss for the PET/LDPE. Concluding, for the structures and doses studied, the electron-beam irradiation did not show advantageous results that could be of interest for commercial applications for the film industry, but brings important information about the packaging behavior for food producers who may decide to use irradiation as a form of cold pasteurization of their packed products.

Acknowledgment. The authors wish to thank Carlos Gaia da Silva and Elizabeth S. R. Somessari for performing the EB irradiations and Unipac Embalagens Ltda. for the support provided in this work.

References

1. American Society for Testing and Materials (1996) Standard test methods for tensile properties of thin plastic sheeting. ASTM D 882-91
2. American Society for Testing and Materials (1994) Standard test method for slow rate penetration resistance of flexible barrier films and laminates. ASTM F 1306-90
3. American Society for Testing and Materials (2000) Standard test method for sealability resistance of flexible barrier films and laminates. ASTM F 88-00
4. Buchalla R, Schuttler C, Bogl KW (1993) Effect of ionizing radiation on plastic food packaging materials: a review. Part 1. Chemical and physical changes. J Food Prot 56:991–997
5. Goulas AE, Riganakos KA, Kontominas MG (2003) Effect of ionizing radiation on physicochemical and mechanical properties of commercial multilayer coextruded flexible plastics packaging materials. Radiat Phys Chem 68:865–872
6. Kim KB, Sung WM, Park HJ, Lee YH, Han SH (2004) Hydrophobic properties of ethylene-vinyl alcohol copolymer treated with plasma source ion implantation. J Appl Polym Sci 92;4:2069–2075
7. Riganakos KA, Koller WD, Ehlermann DAE, Bauer B, Kontominas MG (1999) Effects of ionizing radiation on properties of monolayer and multilayer flexible food packaging materials. Radiat Phys Chem 54;5:527–540