

## MECHANICAL AND THERMAL PROPERTIES OF COMMERCIAL MULTILAYER PET/PP FILM IRRADIATED WITH ELECTRON-BEAM

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### ABSTRACT

The effects of electron-beam irradiation on mechanical and thermal properties, for one commercial flexible food packaging multilayer structure, were studied. The laminated poly(ethylene terephthalate) (PET)/ polypropylene (PP) structure was irradiated up to 60 kGy, using a 1.5 MeV electron beam accelerator, at room temperature in the presence of air. Mechanical properties showed significant changes ( $p < 0.05$ ). In addition, the DSC analysis, after treatment, showed that the fusion enthalpy and crystallinity of the PET/PP structure components presented significant changes ( $p < 0.05$ ) with the electron-beam radiation doses applied. It was observed an increase in PP crystallinity while the PET crystallinity decreases. Such decrease in PET crystallinity indicates the predominance of a cross-linking process on the irradiated PET layer; responsible for the increase in some mechanical properties of the studied film.

### 1. INTRODUCTION

Treatment with ionizing radiation, particularly electron-beam radiation, is a promising approach to the controllable property modification 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, in order 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 [1, 2].

The use of multilayer laminated or coextruded flexible packaging structures is rising in food packaging industries because such materials provide various desirable properties, such as barrier to gases, water vapor, organic compounds and UV light, mechanical strength, puncture resistance, heat sealability, machinability and relatively low cost. All these advantageous aspects cannot be provided by one single material. Most laminated or

coextruded 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), polyethylene terephthalate (PET) and polyamide (PA), when a medium oxygen barrier properties is desirable [3]. In the present study, the changes in mechanical and thermal properties of a commercial multilayer structure used in food packaging, after electron-beam irradiation up to 60 kGy, were evaluated.

A variety of techniques was used to evaluate such changes, e.g. tensile testing for information about changes in tensile strength and elongation at break, evaluation of the material penetration resistance and, also, thermal analysis (DSC) for information on the modification in crystallinity, melting temperature and enthalpy of the packaging materials. The degree of crystallinity is a very important parameter to evaluate the effects of ionizing radiation on polymer packaging materials. The degree of crystallinity and the morphology of the materials have profound effects on their optical, mechanical, barrier, thermal, and chemical resistance properties. It also defines other physical characteristics, such as the stability in different processes [4-7].

## 2. EXPERIMENTAL

Samples of the PET/PP laminated structure, comprising 12  $\mu\text{m}$  of PET, 3  $\mu\text{m}$  of laminating adhesive and 25  $\mu\text{m}$  of PP, were irradiated up to 60 kGy, using an electrostatic accelerator (Dynamitron II, Radiation Dynamics Inc., 1.5 MeV energy, 25 mA current and 37.5 kW power), at room temperature, in the presence of air, and dose rate of 11.22 kGy/s. Irradiation doses were measured using cellulose triacetate film dosimeters "CTA-FTR-125", from Fuji Photo Film Co. Ltd. The thermal analysis, i.e. differential scanning calorimetry (DSC) analysis, was carried out on four weighed samples with  $3.0 \pm 1.0$  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 for each component of the multilayer structure was determined per gram of material. Considering that the crystallinity percentage variation ( $\Delta\tau$ ) is directly related with the material fusion heat, the ( $\Delta\tau$ ) of the structure components, as a function of the electron-beam radiation dose, was calculated by the following equation:

$$\Delta\tau = \frac{\Delta H_m - \Delta H_m^*}{\Delta H_m} \cdot 100 \quad (1)$$

where,

$\Delta H_m^*$  is the melting enthalpy of the irradiated sample

$\Delta H_m$  is the initial melting enthalpy of the non-irradiated sample.

The mechanical properties were determined using an INSTRON Testing Machine model 5564. The tensile tests were carried out according to ASTM D 882-91 [8] and the penetration resistance based on ASTM F 1306-90 [9].

The differences between results for irradiated and non-irradiated structures were then evaluated statistically by one-way ANOVA, using BioEstat software (version 5.0, 2007, Windows 95, Manaus, AM, Brazil). Significance was defined at  $p < 0.05$ .

### 3. RESULTS AND DISCUSSION

#### 3.1. Differential Scanning Calorimetry

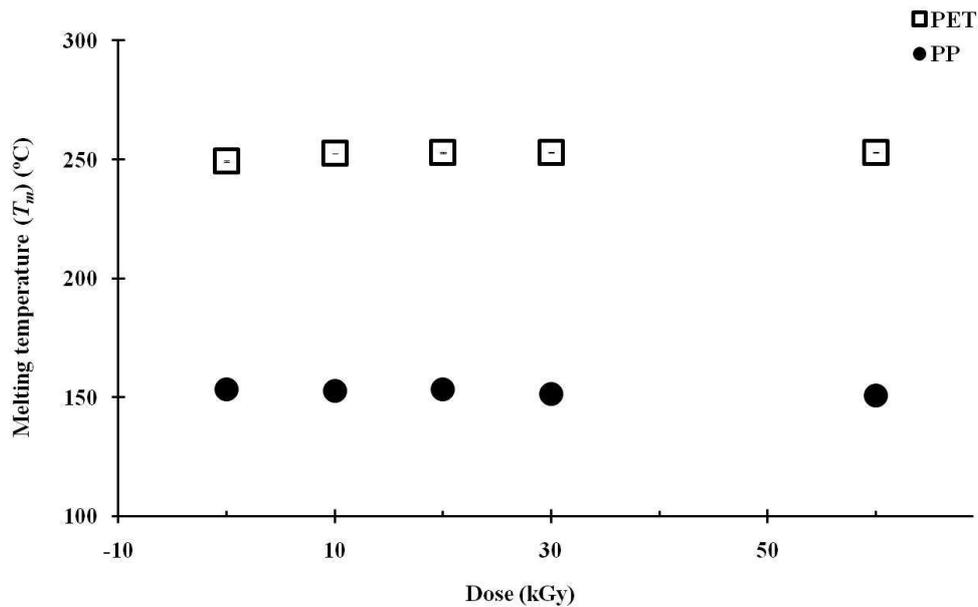
The results of the DSC analysis for the PET/PP structure are summarized in Table 1. The results presented in Table 1 are averages calculated from the data obtained by DSC analysis. The standard deviation for DSC analysis was less than 10 % for all tests. As it can be seen, there were significant differences ( $p < 0.05$ ) for  $T_m$ ,  $\Delta H_m$ , and consequently, crystallinity percentage variation of the structure.

**Table 1. Effect of electron-beam irradiation on thermal properties of PET/PP structure**

DOSE (kGy)	PET/PP									
	PET					PP				
	$T_m$ (°C) <sup>a</sup>	$T_m$ S. D. <sup>b</sup>	$\Delta H_m$ (J/g) <sup>c</sup>	$\Delta H_m$ S. D. <sup>d</sup>	$\Delta\tau$ (%) <sup>e</sup>	$T_m$ (°C) <sup>a</sup>	$T_m$ S. D. <sup>b</sup>	$\Delta H_m$ (J/g) <sup>c</sup>	$\Delta H_m$ S. D. <sup>d</sup>	$\Delta\tau$ (%) <sup>e</sup>
0	249.24	0.37	3.07	0.49		112.45	0.32	27.82	2.11	
10	252.48	0.04	2.65	0.85	7.87	112.84	0.21	30.01	1.17	-13.68
20	252.82	0.25	2.77	0.55	0.98	112.41	0.35	27.76	1.44	-9.77
30	252.99	0.20	2.58	0.23	2.4	112.12	0.80	28.10	0.56	-15.96
60	252.95	0.22	2.19	0.69	4.94	111.95	0.38	29.20	1.43	-28.66

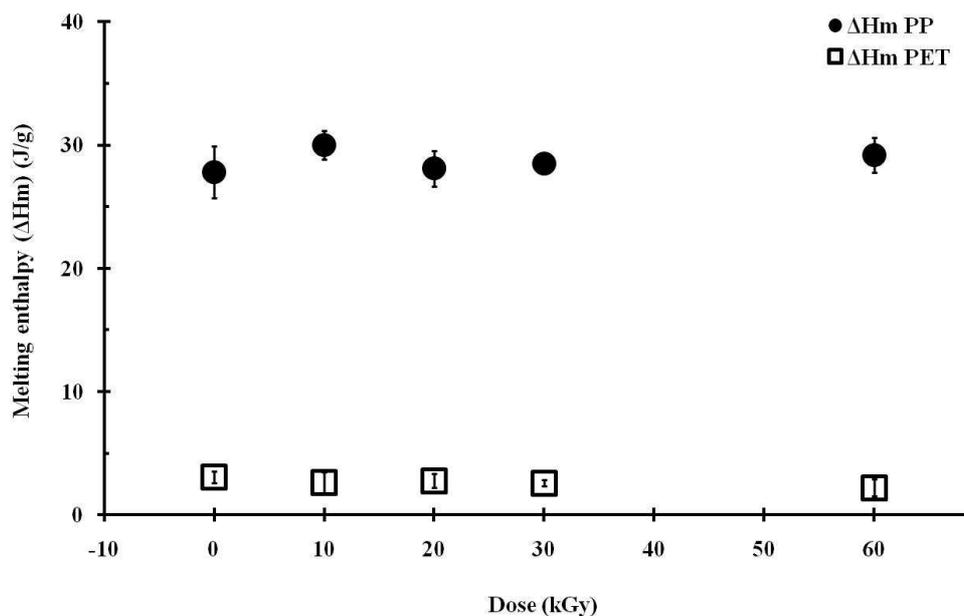
a. Melting Temperature; b. Melting Temperature Standard Deviation; c. Melting Enthalpy; d. Melting Enthalpy Standard Deviation; e. Crystallinity percentage variation.

Fig. 1 shows the melting temperature average results ( $T_m$ ) for the PET and PP layers of the structure, as a function of electron-beam irradiation. As it can be seen, the irradiated PET layer  $T_m$  increased ca. 3 °C, while the PP layer  $T_m$  decreased by 3 °C, as the radiation doses increased (Fig.1).



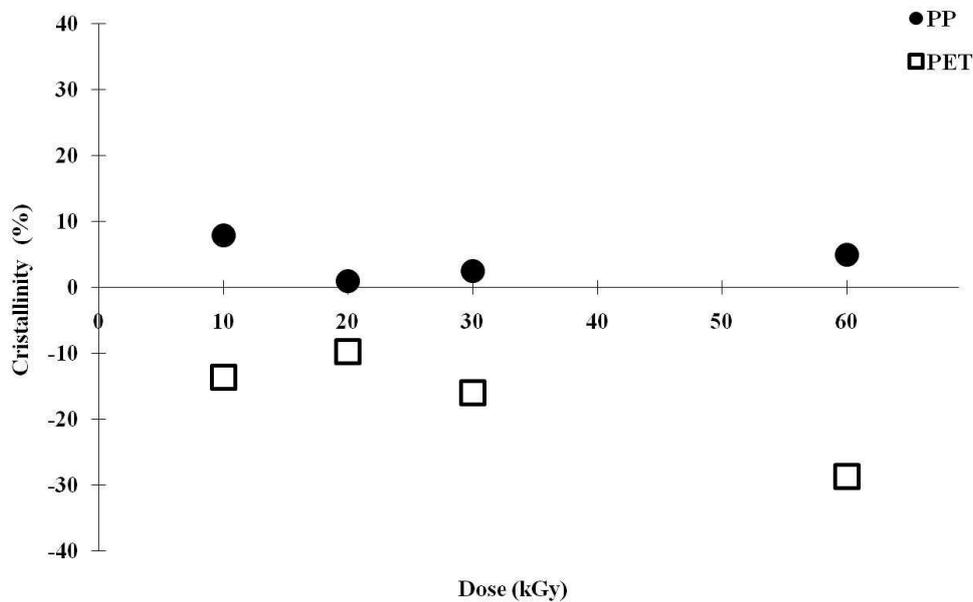
**Figure 1. Melting temperature for PET and PP layers of the structure, as a function of electron-beam irradiation.**

Fig. 2 shows the melting enthalpy average results ( $\Delta H_m$ ) for the PET and PP layers of the structure, as a function of electron-beam irradiation. As it can be seen, the values of the irradiated PET  $\Delta H_m$  were 9 – 28 % lower than the original PET  $\Delta H_m$  (non-irradiated samples), while the irradiated PP  $\Delta H_m$  showed a maximum increase of 8 %, at 10 kGy, and a minimum of 1 %, at 20 kGy.



**Figure 2. Melting enthalpy for PET and PP structure layers, as a function of electron-beam irradiation.**

The structure crystallinity percentage variation results ( $\Delta\tau$ ), as a function of electron-beam dose are shown in Fig. 3. As it can be seen, the ( $\Delta\tau$ ) of the PET layer showed significant decrease of 10 – 29 %. On the other hand, Fig. 3 showed small but significant increase of 1 - 8 % in PP layer crystallinity compared with original PP layer crystallinity ( $p < 0.05$ ).



**Figure. 3 Crystallinity percentage variation ( $\Delta\tau$ ) for the PET and PP structure layers, as a function of electron-beam irradiation.**

### 3.2. Mechanical properties tests

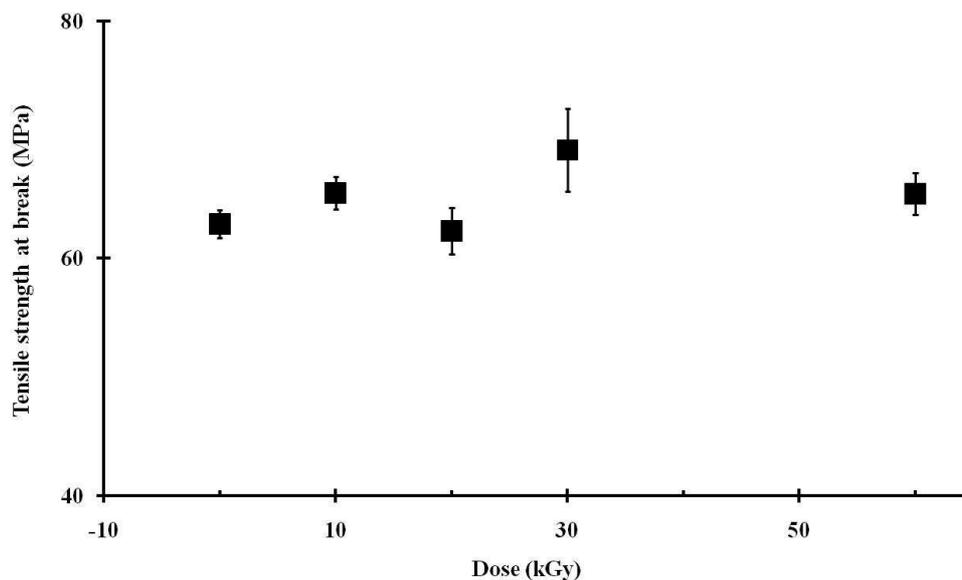
The results of the mechanical properties tests for the PET/PP structure are summarized in Table 2. The results presented in Table 2 represent the average of the data obtained by mechanical properties tests. The standard deviations for mechanical properties tests were less than 10 % for all tests.

**Table 2. Effect of electron-beam irradiation on some mechanical properties of PET/PP structure**

Dose (kGy)	PET/PP					
	T (MPa) <sup>a</sup>	T S.D. <sup>b</sup>	E (%) <sup>c</sup>	E S.D. <sup>d</sup>	P (N) <sup>e</sup>	P S.D. <sup>f</sup>
0	62.89	1.16	188.01	4.10	5.03	0.03
10	65.50	1.36	196.29	3.77	6.24	0.46
20	62.31	1.96	198.73	4.03	4.97	0.02
30	69.14	3.48	198.59	6.55	6.65	0.20
60	65.43	1.78	178.02	6.87	6.30	0.04

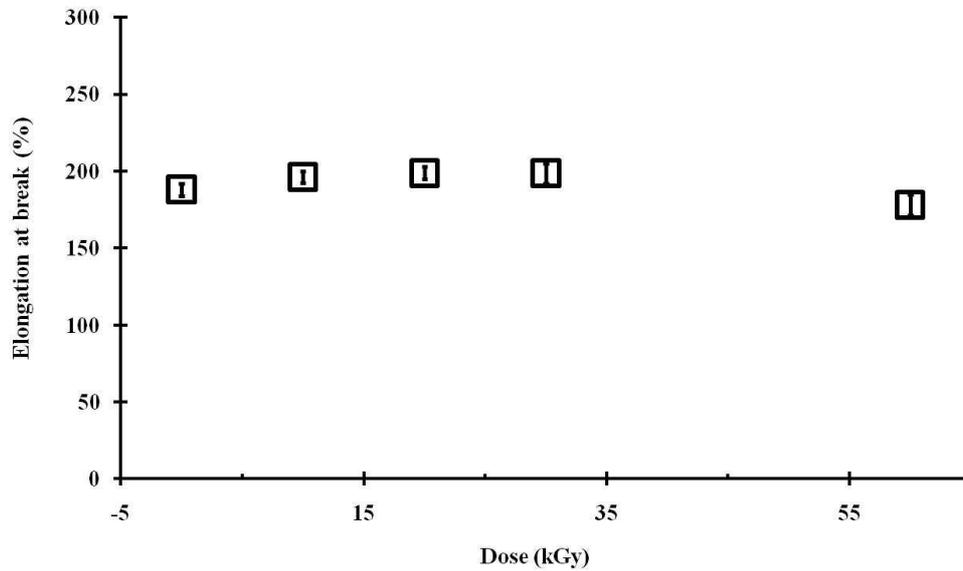
a. tensile strength at break; b. tensile strength at break Standard Deviation; c. elongation at break; d. elongation at break Standard Deviation; e. penetration resistance; f. penetration resistance Standard Deviation.

The tensile strength at break data, as a function of electron-beam irradiation for the structure PET/PP are given in Fig. 4. As it can be seen, there were significant increases ( $p < 0.05$ ) up to 10 % in tensile strength at break.



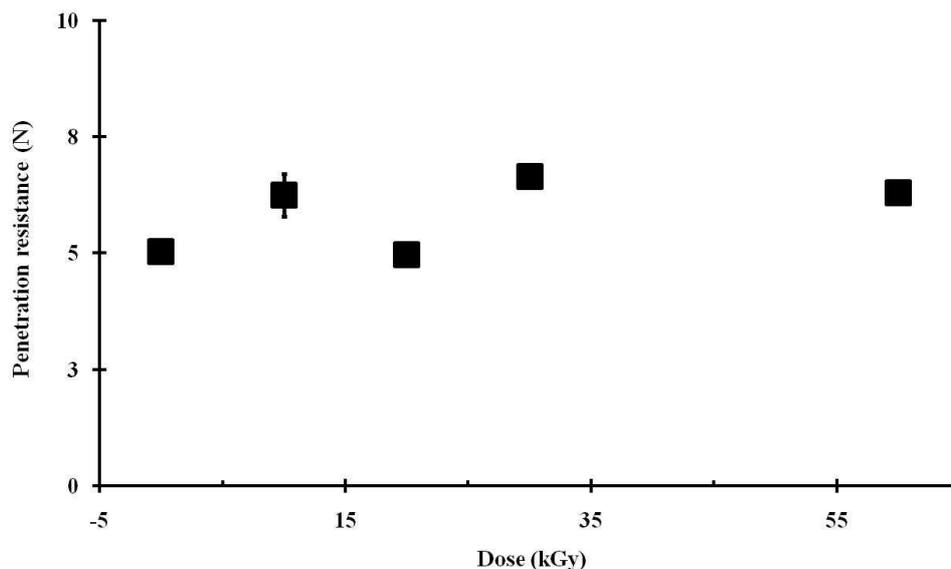
**Figure 4. Tensile strength at break, as a function of electron-beam irradiation for the structure PET/PP.**

The results of the percent elongation at break, as a function of electron-beam irradiation for PET/PP, are presented in Fig.5. In terms of elongation at break, the structure showed an increase ( $p<0.05$ ) ca. 5 %, at 10 - 30 kGy and a reduction ca. 5 %, at 60 kGy.



**Figure 5. Elongation at break, as a function of electron-beam irradiation for PET/PP structure.**

Fig. 6 presents the penetration resistance, as a function of electron-beam irradiation for PET/PP structure. The results showed significant differences ( $p<0.05$ ) in the penetration resistance of the film for all dose ranges studied. As it can be seen, the original penetration resistance of the film increased up to 32 %, as a result of the radiation doses applied.



**Figure 6. Penetration resistance, as a function of electron-beam irradiation for the structure PET/PP.**

The mechanical and thermal properties results showed that concurrent cross-linking and scission effects in the molecular structure, of each material layer, will result in more or less significant changes of these properties in the final packaging. Gains of the tensile strength at break of the irradiated PET/PP can be directly related to an increase of the amorphous phase of the PET layer due to, probably, the predominance of cross-linking process on irradiated PET chains, as the PET layer is the major responsible for the tensile strength of the structure PET/PP. On the other hand, the changes in the molecular structure, responsible for an increase in PP layer  $\Delta H_m$  and, consequently, of its crystalline phase after irradiation, can be responsible for the changes in elongation at break and for penetration resistance performances of the irradiated PET/PP.

#### 4. CONCLUSIONS

Results showed that electron-beam radiation doses up to 30 kGy, in the conditions studied in this work, led to better mechanical properties and significant changes in the thermal characteristics of the film components, suggesting cross-linking predominance for the PET layer polymeric chains, and an increase of the PP layer crystalline phase. A decrease in PET crystallinity indicates increase of its amorphous phase due to, probably, the predominance of a cross-linking process on the irradiated PET layer; and it can be responsible for the increase in some mechanical properties of the studied film. The increase in the PP crystallinity observed in this work reduces the mobility of the PP amorphous chains and can lead to more efficient molecular orientation and a fall in permeation rates, since a rise in molecular organization makes the diffusivity of a liquid or gas more difficult in the polymeric structure. To confirm these results, future analyses, such as X-ray diffractometry, gas/vapor transmission and TG, may be made. Regarding the mechanical performance, the advantageous results found can be of interest for commercial applications.

## ACKNOWLEDGMENTS

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