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Effect of ionizing radiation on the properties of PLA packaging materials

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Abstract. Poly(lactic acid) (PLA) is attractive as a substitute for classical polymer packaging material due to its biodegradability and sufficient mechanical and barrier properties. Presented research was focused on the changes of basic mechanical parameters after ionizing irradiation performed with doses in the range of 2.5–25 kGy, commonly used in radiation sterilization and preservation of foods. Two commercial available PLA packaging films were tested. The influence of radiation dose on the mechanical properties – tensile strength and elongation were determined using standardized methods. Radiation resistance of PLA is sufficient for packaging applications. The investigations of gas products of radiolysis of PLA have been made by gas chromatography after electron beam (EB) irradiations.

Key words: packaging materials • radiation modification of polymers • radiation sterilization • packaging films • poly(lactic acid) (PLA)

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Introduction

PLA is fully biodegradable polymer with properties similar to widely used polymers derived from petrochemicals. Due to its physical and chemical properties, PLA gives an opportunity to replace some amounts of petroleum-based packaging material by an environment-friendly substitute [8]. The unique blend of physical properties of PLA makes it well suited for a broad range of packaging applications including high-value films, rigid thermoformed containers for food and beverage, coated papers and boards and other packaging applications. This is a packaging material with significantly reduced greenhouse gas emissions to combine performance with environmental benefits [6, 9].

In particular, an idea has appeared to apply PLA as packaging material predicted for radiation sterilization. For example, as packaging for food subjected to radiation treatment. Irradiation induces reduction of losses due to spoilage and deterioration and control of the microbes and other organisms that cause food-borne diseases. The applied doses were from 0.07 to 70.00 kGy. Studies on insect disinfestations included quarantine treatment and elimination of food-borne parasites, the doses applied being 0.07–1.00 kGy. Reduction of pathogenic microbes in fresh and frozen meat, poultry and seafood were performed with doses 3.00–7.00 kGy. Sterilization of packaged meat, poultry and their products which are shelf stable without refrigeration were performed with doses 25.00–70.00 kGy) [10].

The processes related to irradiation of petroleum-based polymers are well known [1]. According to the possible application of biodegradable polymers for

irradiated products, it is important to understand also the influence of radiation on their properties. As mechanical properties of such packaging are of the highest importance, the effect of irradiation on these properties should be known.

Gas chromatography appeared to be an appropriate method for examination of the resistance of polymers to ionizing radiation. This is because the low yield of gaseous products *G* (μmol/J) shows their high resistance to irradiation. Ionizing radiation is a unique form of energy that induced chemical reactions in polymers at ambient and lower temperatures causing production of a wide spectrum of low molecular weight compounds with gaseous products included. In the radiolytic decomposition at room temperature (RT) hydrogen is the main constituent of the gas phase above any hydrogen bearing material, including polymers. Radiation processing, e.g. radiation sterilization by an EB or gamma radiation causes additional oxidation of polymers already during irradiation as well as oxidation by O_2 after irradiation, in regard to a chain mechanism [3]. The uptake of oxygen corresponds to this process. A small amount of other gaseous products (a like CH_4, CO) are formed probably due to degradation processes occurring within multi-ionization spurs, which are localized in the site of decomposition of comparatively high amount of energy. Our previous works have shown the advantage of determination of radiation yield of hydrogen and oxygen in the evaluation of degree of radiolysis of polymers applying gas chromatography [2].

The aim of the present work was to determine the resistance of some selected commercial films PLA to radiation treatment. The changes of mechanical properties (tensile strength and elongation at break) of the PLA films subjected to ionizing radiation were tested. The content of H_2, CH_4, CO and O_2 were also determined using gas chromatography.

Experimental

Materials

Two commercially available biodegradable materials were tested. Both of them were purchased as thin films dedicated to use as packaging. Confirmation of the biodegradability of the used materials are the certificates DIN CERTCO (Germany) (Table 1).

Irradiation

The irradiation took place at the Institute of Nuclear Chemistry and Technology (INCT) in Warsaw. Irradiation with gamma rays was carried out with the samples predicted for mechanical tests in a gamma cell "Issledovatel" with a ^{60}Co source (dose rate 0.389 $Gy \cdot s^{-1}$). The samples were irradiated using four doses of radiation: 2.5, 5, 10 and 25 kGy. Irradiation with EB was carried out with the films predicted for gas chromatography. Irradiations were done with electron linacs "Elektronika" 10/10 (10 MeV, 10 kW). Samples for chromatographic studies were irradiated in small bottles, volume 3.5 ml, closed with rubber septa. Average doses of EB were 0.5, 20 and 60 kGy. All polymers were irradiated in air at RT.

Before tests of mechanical properties, the irradiated materials and reference non-irradiated materials were stored at RT in air for 24 h.

Mechanical properties

Two basic mechanical parameters: tensile strength and elongation at break were determined according to the standard procedure using a Universal Testing Machine (Model 5565. Instron Co.) [5]. Samples (150 mm in length and 15 mm in width) at RT with 50 mm/min crosshead speeds were used for the measurement. Ten independent samples for each measurement point were tested. Tensile strength and elongation at break was determined.

Gas chromatography

A gas chromatograph type GC 2014 by Shimadzu, equipped with a thermal conductivity detector and a column packed with molecular sieves 5 A was used for the analyses of the gaseous products: hydrogen, oxygen, methane and carbon monoxide. The data were acquired by the program CHROMAX. The carrier gas was argon of purity 99.99%, the calibration gas was hydrogen of purity 99.99%. Operations were done with syringes vol. 10, 25 and 500 μL. The column was heated at 40°C for the analysis of H_2, O_2, CH_4, and of CO at 120°C. The detector worked at 120°C. The rate of flow of carrier gas was 10 mL/min.

Table 1. Specification of tested materials

Parameter	BIOMAT	SWIRL
Producer	Pro-Tech Biologische und Technische Produkte GmbH	Melitta Haushaltsprodukte GmbH & Co KG
Thickness (μm)	37	28
Basis weight (g/m^2)	45	34
Biodegradability	biodegradable compostable	biodegradable compostable
No. of DIN CERTCO certificate	7P0094	7P0002
Certification standard	DIN EN 13432:2000-12	DIN V 54900-1:1998-10 DIN V 54900-2:1998-09 DIN V 54900-3:1998-09

Table 2. Results of Anova analysis. Statistical significance p of effect of material and radiation dose on the foil parameters

Parameter	p Values for variability factor		
	Foil type	Dose	Foil type x dose interaction
Tensile strength MD*	0.0003	0.3809	0.0005
Tensile strength TD**	0.0000	0.0000	0.0000
Elongation MD	0.0000	0.0000	0.0000
Elongation TD	0.0307	0.0294	0.0006

*MD – machine direction.
**TD – transverse direction.

Table 3. Effect of radiation dose on mechanical properties of the foil types

Tensile strength (MPa)	Material	Dose (kGy)	Mean ± SD	Elongation at break (%)	Material	Mean ± SD*
Machine direction	BIOMAT	0.0	23.8 ± 0.9a	Machine direction	BIOMAT	448 ± 34e
		2.5	25.1 ± 2.0ab			195 ± 10ab
		5.0	23.7 ± 1.3a			351 ± 57c
		10.0	25.5 ± 1.7ab			383 ± 51cd
		25.0	24.8 ± 1.1a			422 ± 46de
	SWIRL	0.0	26.0 ± 0.8ab		SWIRL	204 ± 8ab
		2.5	24.9 ± 2.5a			181 ± 19a
		5.0	27.4 ± 1.4b			236 ± 23b
		10.0	25.7 ± 1.5ab			185 ± 12a
		25.0	24.9 ± 1.8a			216 ± 39ab
Transverse direction	BIOMAT	0.0	15.9 ± 0.9A	Transverse direction	BIOMAT	745 ± 84E
		2.5	14.2 ± 2.1A			587 ± 78AB
		5.0	15.5 ± 1.8A			654 ± 89C
		10.0	14.0 ± 2.7A			603 ± 134CD
		25.0	15.8 ± 2.3A			685 ± 89DE
	SWIRL	0.0	19.3 ± 2.1B		SWIRL	628 ± 32AB
		2.5	22.0 ± 1.1C			677 ± 59A
		5.0	19.6 ± 1.2BC			603 ± 13B
		10.0	14.8 ± 1.9A			606 ± 59A
		25.0	18.5 ± 0.7B			585 ± 50AB

* Mean of 10 measurement ± SD. Identical letters within the columns indicate statistically homogeneous groups according to the Tukey test.

Statistical analysis

Variance analysis Anova and Tukey tests at a significance level of $p \leq 0.05$ were used for the statistical analysis of the results of mechanical test. The Statistica ver. 9 was applied for the calculations.

Since there is no critical limits in absolute figures for mechanical parameters of the foils, all the data obtained were converted into standardized values using the formula:

$$Z = \sum_{1}^{n} (X_i - X_m) / \mathrm{SD} \quad (1)$$

where: X_i – result of i measurement; X_m – mean value of parameter measured; SD – standard deviation, n – number of measurements.

As all the absolute values measured were converted into unit less figures and, therefore, all the parameters might be evaluated jointly. For unit less Z value, the critical limits are always ±3 and this means that the all converted values, remaining at a distance below –3 or above +3 from the mean = 0 indicate a significant damage of irradiated foil [7].

Results and discussion

Mechanical properties

Significance of the effect of radiation dose, foil type and foil parameters are shown in Table 2.

From Table 2 it occurs that only for the tensile strength in machine direction effect of the dose was insignificant, since p value = 0.3809 and remained above 0.05. Since the foil type and the interaction of the foil type and dose value was statistically significant for all cases, the effect of dose should be discussed separately for each experimental factor.

It was rather difficult to find a functional dose – effect relationship for the data in Table 3, and this can be seen in Figs. 1 and 2.

From the figures it appears that it would be rather difficult to outline the formulas between the dose and measured parameters. This leads to the conclusion that radiation energy randomly causes some type of disorder in the structure of the foils tested. However, this conclusion has to be associated with information regarding the extent of disorder, that means the effect

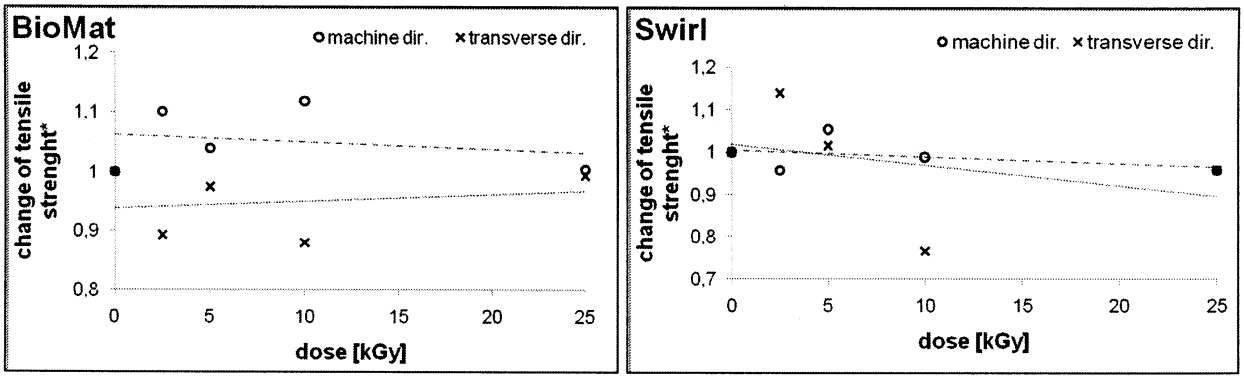

Fig. 1. Dose-effect relationship for tensile strength of the foils.

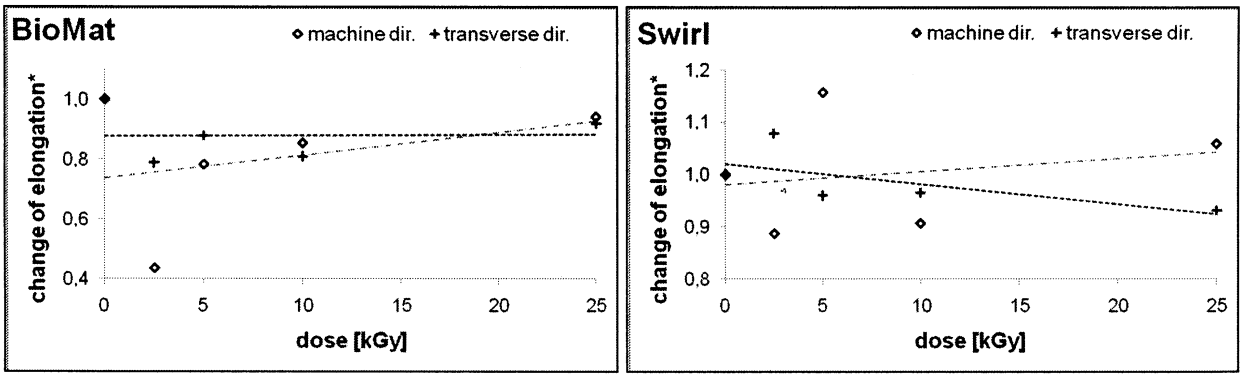

Fig. 2. Dose-effect relationship for elongation at break of the foils.

remains within the critical limits $\pm 3Z$ standardized values. Figure 3 presents the distribution of Z values for BIOMAT and SWIRL foil.

In most cases Z values are positioned within the limit of $\pm$ 3Z. This means that the foil structure disorder after irradiation was of statistical nature. Only in the case of

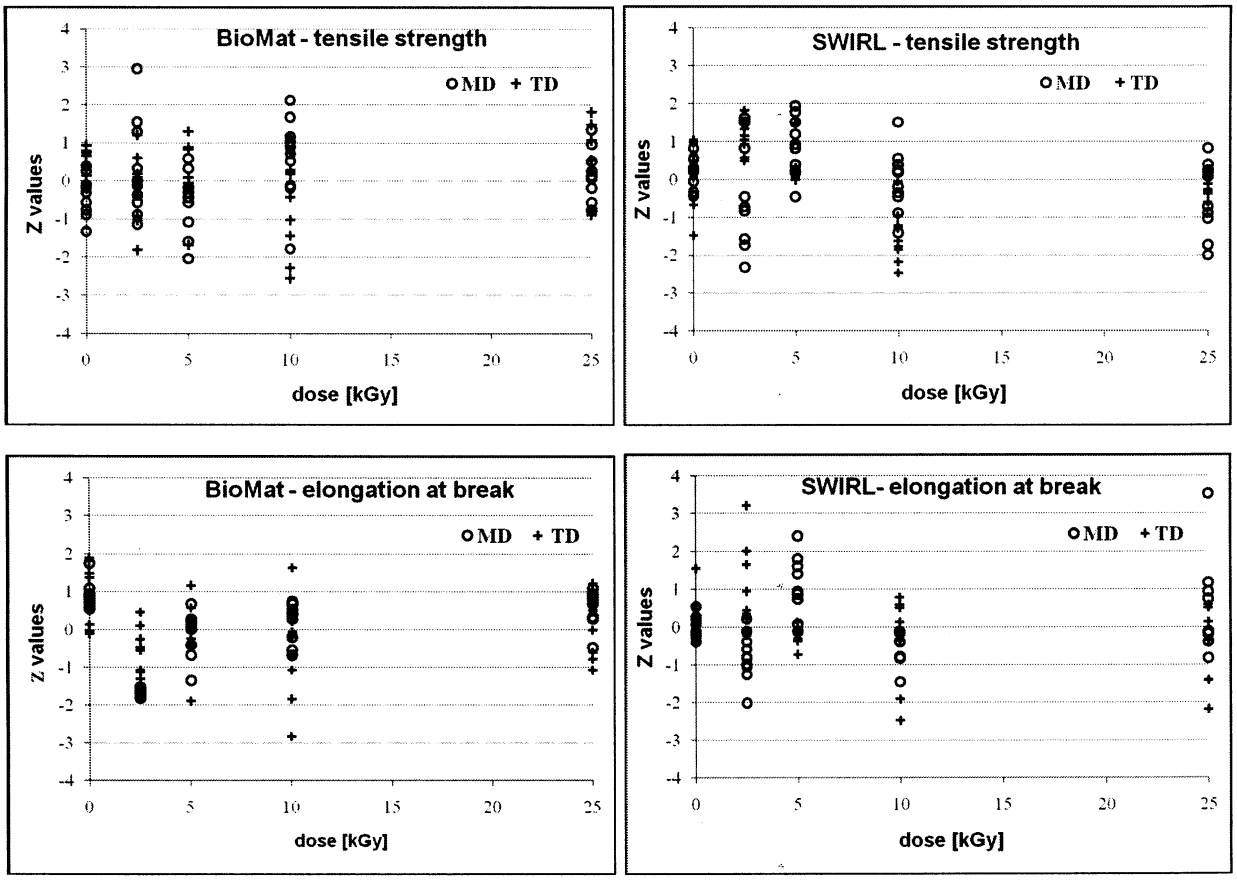

Fig. 3. The distribution of Z values of mechanical parameters measured.

Table 4. Radiation yield of hydrogen, oxygen, carbon monoxide and methane (average values for doses 0.5, 20 and 60 kGy)

Gas products of radiolysis	Radiation yield of gaseous products (μmol·J^{-1})	
	BIOMAT	SWIRL
H_2	0.28	0.26
O_2	–0.40	–0.38
CO	0.018	0.016
CH_4	0.0012	0.0010

the SWIRL foil a slight change of elongation after irradiation may be expected, since two *Z* values are above +3*Z*, but this did not depend on the dose value.

Gaseous products of radiolysis

In the present experiment hydrogen was released immediately, whereas the determination of methane demanded gentle heating of the vessel in the case of thick films of the material, before sampling from the gas phase of the vessel was done. Carbon monoxide was determined after aeration during subsequent lapses of time.

Radiation yields of gaseous products are relatively constant in the full range of applied doses 0.5–60 kGy, although the curve of hydrogen yields vs. the dose, with a visible lower yield seen at the beginning of the curve. It was similar to the typical curve obtained in the case of the majority of commercial polymers [4].

The gaseous product yields were relatively low, Table 4. In fact, the average hydrogen yield obtained in the case of PLA was lower than in the case of polypropylene or polyethylene.

Conclusion

The tested materials could be submitted to ionizing irradiation with doses below 25 kGy without significant changes of mechanical properties. Formation of H_2, CO and CH_4 as well as O_2 uptake resulting in radiolysis processes of PLA are smaller than the yields or uptake of those gases involved in polyethylene and polypropylene under similar conditions. This indicated good resistance of PLA to radiation treatment. In fact, the application of PLA films as packaging of product irradiated with a dose below 25 kGy seems to be possible. Further tests including more parameters as ageing problem and wider spectrum of PLA-based materials are, however, necessary for better evaluation of the PLA applicability.

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