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Use of gamma-irradiation technology in the manufacture of biopolymer-based packaging films for shelf-stable foods

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Abstract

Gamma irradiation is an alternative method for the manufacture of sterilized packaging with increased storage stability and microbiological safety. Biopolymer-based packaging films are a potential solution to many environmental problems that have emerged from the production and accumulation of significant amounts of synthetic polymeric waste. This work was undertaken to verify the effectiveness of low-dose gamma-irradiation in obtaining biopolymer-based packaging films for shelf-stable foods. PHB polyester poly(3-hydroxybutyrate) is an interesting biodegradable polymer that has been intensely investigated as cast and sheet films, with applications in the food industry and medicine. The films obtained are, however, typically brittle, and many scientists have attempted to reduce this brittleness by blending PHB with other polymers.

In the present work, PHB was blended with PEG (polyethyleneglycol) to obtain films by the casting method that were then irradiated at a dose rate of 5.72 kGy/h with a ^{60}Co source. Samples were melted at 200 °C and quenched to 0 °C in order to evaluate film crystallinity levels by differential scanning calorimetry (DSC). DSC analyses were performed with the samples (10 mg) under N_2 atmosphere, heating from −50 to 200 °C (10 °C min^{-1}), cooling from 200 to −50 °C (10 °C min^{-1}); and heating from −50 to 200 °C (10 °C min^{-1}). The thermal and mechanical resistances of the films after irradiation at low doses (5, 10, 20 kGy) are discussed. Water vapour transmission decreased with increasing irradiation dose, indicating that the films' performance as water vapour barrier had improved. Critical loss of the mechanical properties was observed at 40 kGy.

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1. Introduction

Nowadays, one of the most serious environmental concerns is the amount of waste produced and accumulated. Biodegradable edible films based on biopolymers have been developed as interesting solutions to important environmental problems, like, for example, preservation of the surface integrity of food products, restriction of moisture loss, and others [1]. Blends of biopolymers, like starch, gelatin, cellulose derivatives, caseinates, and others have been plasticized with polyols as reported [2–4]. DSC techniques can be used to characterize polysaccharide-, polyalcanoate- and protein-based biopolymer films to which plasticizers are added [1,5]. The films obtained are typically brittle, and many scientists have attempted to reduce this brittleness by processing modifications other than the use of plasticizers. Investigations on PHB polyester poly(3-hydroxybutyrate) as biopolymer with potential applications in the food industry and medicine are a challenge to many scientists. In this study, the application of ionization radiation on PHB in order to promote reduction of film crystallinity was investigated. Furthermore, the thermal stability of the material was evaluated by thermogravimetry (TGA), and specific tests were performed to investigate the behaviour of its water vapour and mechanical properties upon irradiation.

2. Materials and methods

PHB was provided by – Usina da Pedra SP and Polyetilenoglicol (PEG – 300) by Oxiteno. The films were obtained by the casting method on Pyrex trays. PHB was dissolved in chloroform at 60 °C and PEG was added at a final concentration of 5%. The solution was cast into a Pyrex glass mold and the solvent was evaporated to dryness.

Films were irradiated at a dose rate of 5.72 kGy/h (activity: 6917.4 CI) using a ^{60}Co source (Gamma model 220 from Inst. Eng. Atomic, Canada). The thermal properties of the irradiated films were evaluated by differential scanning calorimetry using a DSC 822 from Mettler, Toledo. The samples were melted at 200 °C and quenched to 0 °C. Analyses were performed in a DSC-821 from Mettler, Toledo, under inert N_2 atmosphere; the temperature program used was as follows: heating from −50 to 200 °C (10 °C/min), cooling from 200 to −50 °C (10 °C/min); heating from −50 to 200 °C (10 °C/min). The DSC apparatus was calibrated with In metal (m.p. 156.61 °C; $\Delta H = 28.54\ J\,g^{-1}$). TGA tests were performed in a SDTA-822 thermobalance (Mettler, Toledo), under dynamic nitrogen atmosphere (50 mL min^{-1}) and at a heating rate of 5 °C min^{-1}, using samples of about 30 mg in sapphire crucibles. The films' permeability to water vapour before and after irradiation was determined according to the method of Gontard et al. [6], based on ASTM E96-80 [7]. Tensile strength and percentage elongation were measured on dumbbells using an Instron Universal Testing Instrument operated according to ASTM 1989 (D828-88).

3. Results and discussion

The transparent PHB/PEG (95:5) blend films were flexible in comparison with the brittle pure PHB films. Irradiation was carried out at 5, 10 and 40 kGy. The decomposition temperatures of irradiated films were established as the temperature onset of decomposition and are shown in Table 1. Blend films irradiated at 5 and 10 kGy presented decomposition temperature reductions of 11 and 12 °C, respectively; irradiation at 40 kGy led to a decrease of about 20 °C.

Sample crystallinity was determined on DSC curves (Fig. 1) from the enthalpy ratios (ΔH_0), assuming the enthalpy of 100% crystalline PHB to be 146 J g^{-1} [8]. The DSC results (Table 1) indicate that the blend's crystallization rate and crystallinity decreased with increasing irradiation dose, the films presenting reduced melting and crystallization temperatures. Fig. 1 shows the DSC curves of irradiated samples versus a non-irradiated sample. Glass transition (T_g) was taken as the midpoint of the heat capacity change, and the values show for the blends that, T_g decreased as a function of plasticizer concentration, with practically no influence from irradiation dose (Table 1).

Table 1
Melting and crystallization determinations by DSC of irradiated and non-irradiated pure PHB and PHB/PEG 300/95:5 blend films (irradiation dose range: 5–40 kGy)

	T_g (°C)	T_{m1} °C[a]	T_{m2} °C[a]	T_{c1} °C[a]	1 Crystallization %	Tonset of decomposition (°C)
PHB	5	174	170	91	40	255
Blend	−14	158	157	70	33	256
Blend 5 kGy	−12	165	164	75	30	245
Blend 10 kGy	−14	161	160	70	27	244
Blend 40 kGy	–	198	157	34–74	25	236

[a] T_{m1} – first melting temperature; T_{m2} – second melting temperature, T_{c1} – first crystallization temperature.

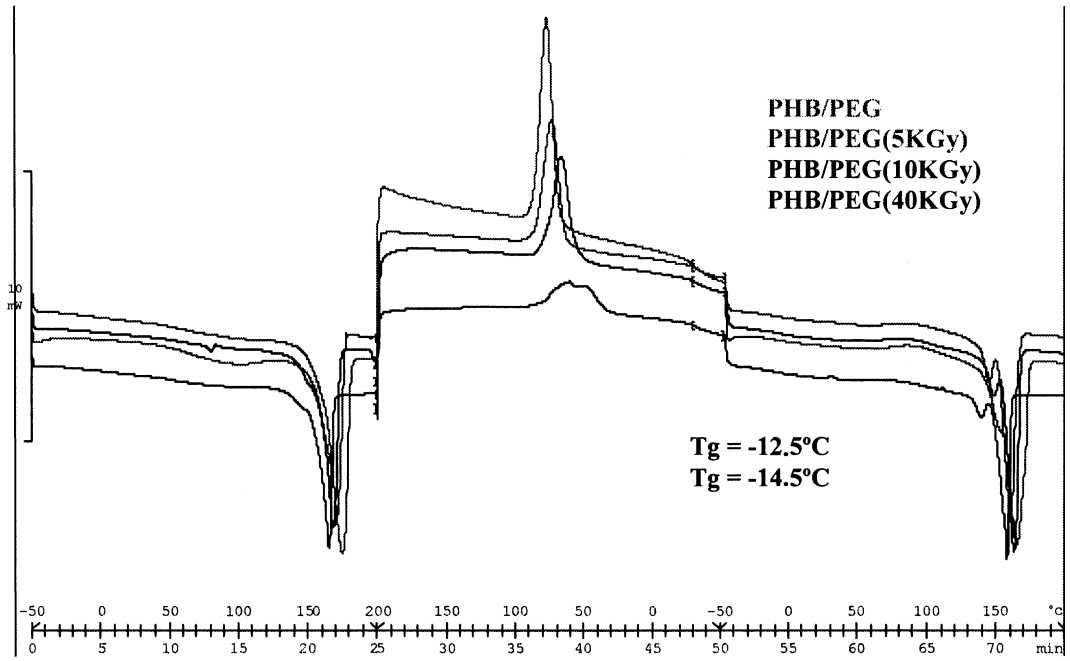

Fig. 1. DSC curves of PHB/PEG (95:5) irradiated and non-irradiated films.

The cold crystallization peak of the blend and pure PHB films shifted to a 1ower re-crystallization temperature when the polymer was irradiated because the crystallization rate is lowered in the non-isothermal crystallization of these samples. Nucleation is hindered and promotes small spherullites formation. Consequently, the flexibility of the blend is enhanced as compared with pure PHB (Table 2).

Upon irradiation, the tensile strength and elongation at break of the blend improved up to 10 kGy, indicating that some cross-linking occurs within the 5–10 kGy dose range. At higher

Table 2
Maximum tension strength and deformation with elongation at break of irradiated and non irradiated pure PHB and PHB/PEG blend films (irradiation dose range: 5–40 kGy)

Strength		
Film	Tension strength (MPa)	Deformation (%)
PHB	4.18	6.00
PHB/PEG 5%	5.27	12.78
PHB/PEG 5% Irrad. 5 KGy	7.70	6.55
PHB/PEG 5% Irrad. l0 KGy	7.90	6.12
PHB/PEG 5% Irrad. 40 KGy	–	–

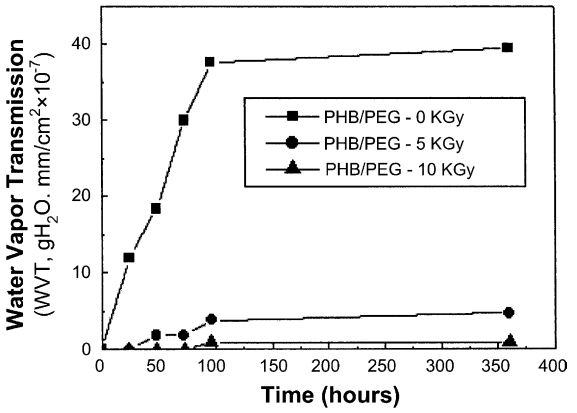

Fig. 2. Water vapour transmission of PHB/PEG irradiated films as compared with a non-irradiated sample.

irradiation doses (40 kGy), testing for the mechanical properties became unfeasible due to degradation of the films.

4. Conclusion

Irradiation of our PHB/PEG blend with ionizing radiation resulted in decreased crystallinity. In this blend, crystallization took longer (shifting of the crystallization temperature to lower values) than in pure PHB probably due to a lower nucleation density. The presence of PEG interferes with the intramolecular interactions within the PHB macrochains; however, upon irradiation, we observed a cross-linking effect up to 10 kGy. Pronounced degradation occurred at higher irradiation doses (40 kGy), with loss of mechanical properties. The vapour barrier property of the PHB/PEG blend was enhanced at low irradiation doses, probably owing to the cross-linking effect that reduced the pore size within the blend structure, thus avoiding the water vapour transmission observed in pure PHB films (Fig. 2).

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References

[1] P.J.A. Sobral, F.C. Menegalli, M.D. Hubinger, M.A. Roques, Food Colloids 15 (2001) 423.
[2] P.J.A. Sobral, E.S. Monterrey-Q, A.M.Q.B. Habitante, J. Therm. Anal. Calorim. 67 (2002) 499.
[3] C.G. Biliaderis, A. Lazaridou, I. Arvanitoyannis, Carbohydr. Polym. 40 (1999) 29.
[4] I. Arvanitoyannis, A. Nakayama, S. Aiba, Carbohydr. Polym. 31 (1996) 105.
[5] D.F. Parra, J.A.R.R. Fusaro, A. Lugão, J. Therm. Anal. Calorim. 79 (2005) 379.
[6] N. Gontard, S. Guilbert, J.-L. Cuq, J. Food Sci. 58 (1993) 206.
[7] ASTM Standard Annual Book of ASTM standards, ASTM, Philadelphia, 1989, p. 730.
[8] P.J. Barham, A. Keller, J. Polym. Sci. 24 (1986) 69.