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Physical properties of biaxially oriented poly(ethylene terephtalate) irradiated at different temperatures and doses with electron beam

E. Adem [a,*], A. Rubio Hernández-Sampelayo [c], J.E. Báez [d], J. Miranda [a], G.J. Labrada-Delgado [b], A. Marcos-Fernández [c,*]

[a] Instituto de Física, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México D.F., Mexico
[b] Instituto Potosino de Investigación Científica y Tecnológica, Camino a la presa San José 2055, Lomas 4ª secc., 78216 San Luis Potosí, S.L.P., Mexico
[c] Instituto de Ciencia y Tecnología de Polímeros (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain
[d] Department of Chemistry, University of Guanajuato (UG), Noria Alta S/N, 36050 Guanajuato, Gto., Mexico

HIGHLIGHTS

- E-beam produced chain scission and a decrease in molecular weight in PET.
- Melting point decreased and crystallinity increased with the increase in dose.
- Crystallization temperature increased with the increase in absorbed dose.
- Mechanical properties were strongly affected by absorbed dose.
- Irradiation above Tg degraded PET more than irradiation at ambient temperature.

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ABSTRACT

The electron beam irradiation of a biaxially oriented PET film was carried out in air over a range of 50–3000 kGy at different temperatures and a dose rate of 4.48 kGy min^{-1}. The effects of the irradiation at temperatures above and below the glass transition temperature (Tg) on the thermal and mechanical properties were studied. Melting temperature decreased slightly and crystallization temperature and crystallinity increased significantly with the increase in dose, more at higher irradiation temperature, whereas Tg did not show any significant change with dose or temperature. Mechanical properties were adversely affected by irradiation. Stress and strain at break were strongly reduced, more at higher irradiation temperature, and Young's Modulus slightly increased with the increase in dose. The changes in properties were related to the chain scission produced by the electron beam irradiation leading to a decrease in molecular weight.

1. Introduction

Poly(ethylene terephthalate) (PET) is a well established engineering and commodity polymer which has registered an important increasing production trend during recent years. This material has been classified as resistant to radiation (gamma rays), with some damage produced at doses above 1000 kGy and severe damage only at doses above 30,000 kGy (Campbell, 1981). PET film is an authorized packaging material by FDA for use during irradiation of pre-packaged foods at a maximum dose of 10 kGy (Section 179.45(b)) to 60 kGy (Section 179.45(d)). The FDA study concluded that electron beam, gamma rays and X-ray treatments were equivalents in terms of the type and levels of radiolysis products generated during irradiation (Komolprasert, 2007). Some studies on PET demonstrated that measurable amounts of low molecular weight radiolysis products can form even in this very radiation resistant polymer at low doses of up to 50 kGy (Buchalla et al., 2006; Komolprasert et al., 2003).

Most irradiation studies on PET have been done with gamma rays (Aytaç et al., 2007, 2010; Buchalla et al., 2006; Burillo et al., 2002; Buttafava et al., 2002; Komolprasert et al., 2003; Mariani et al., 2007; Prasad et al., 2011; Ravasio et al., 2007; Shaban et al., 1995; Siddhartha et al., 2012) and only a few have been done with electron beam (Aytaç et al., 2010; Burillo et al., 2007; Komolprasert et al., 2003). The doses range in these studies was usually low and only some studies reached doses of 1000 kGy or above (Burillo et al., 2007; Buttafava et al., 2002; Mariani et al., 2007; Ravasio

* Corresponding authors.
E-mail addresses: esbaide@fisica.unam.mx (E. Adem), amarcos@ictp.csic.es (A. Marcos-Fernández).

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et al., 2007; Siddhartha et al., 2012). Ionizing radiation on PET produced mainly chain scission with a decrease in the molecular weight and no evidence of gel formation due to crosslinking (Aytaç et al., 2010; Burillo et al., 2007; Buttafava et al., 2002; Ravasio et al., 2007). By using UV, a shifting to red on the edge of the absorption band was found attributed to the formation of conjugated bonds and other species (Siddhartha et al., 2012) and to the formation of carbonyl and hydroxyl groups by reaction of the radicals produced by the radiation with oxygen (Prasad et al., 2011). However, no evidence of the formation of oxidized species in a significant amount was found by IR by other authors (Buttafava et al., 2002; Ravasio et al., 2007).

The information about the effect of ionizing radiation on the thermal and mechanical properties of PET is scarce. Buttafava et al. (2002) found no effect on the Tg and the melting point and an increase in the crystallinity with gamma rays doses up to 1100 kGy. Burillo et al. (2007) found, for electron beam irradiation of PET up to 15,000 kGy: a decrease in Tg value; a constant value for the melting point and an increase in crystallinity in doses up to 1500 kGy; and, a decrease in the melting point and an increase in crystallinity from 1500 to 15,000 kGy. Thus, both works give contradictory results for the effect of the dose on the Tg value.

The effect on mechanical properties is even less studied, only in two works by Aytaç et al. (2007, 2010), and the results presented for low doses up to 150 kGy concluded that mechanical properties do not change significantly at those doses.

All works in the literature on the irradiation of PET with ionizing radiation have been carried out at ambient temperature, and no studies on the effect of the temperature have been reported.

We present a detailed study on the effect of the irradiation of PET at two temperatures, below and above Tg, within a wide range of doses, up to 3000 kGy, in order to establish clear relationships for the thermal properties and to determine for the first time the detailed effect on the mechanical properties and the effect of temperature.

2. Materials and methods

2.1. Irradiation of the samples

Biaxially oriented PET transparent sheets of approximately $30 \times 30\ cm^2$ and 0.25 mm thickness were received from Goodfellow Cambridge Ltd. (Coraopolis, PA, USA). Type 4 dumbbell test pieces (according to ISO 37) were cut from the sheets. The samples were introduced into polyethylene bags and placed in a holder for heating to different temperatures. The device was designed at the Institute of Physics, UNAM. The samples were irradiated with an electron-beam accelerator, using a Van de Graaff source, 1.3 MeV energy and a beam current of 5 μA at a dose rate of 4.48 kGy min^{-1} and doses from 50 to 3000 kGy in air at ambient temperature and at 100 °C. After mechanical testing, the same samples were used for viscosity measurements and thermal properties characterization.

2.2. Viscosity measurements

Inherent viscosity (η_{inh} in dL g^{-1}) was measured at 30 °C in a hexafluoroisopropanol solution at a concentration of 0.5 g dL^{-1} with a Ubbelohde Viscometer (capillary #1) using the following equation:

$$\eta_{inh} = 2 \ln\left(\frac{t}{t_0}\right)$$

where t_0 is the time to flow through the capillary for the neat solvent and t is the time to flow for the sample solution. Flow times were measured at least seven times, with a calculated error for the mean value of less than 1%.

2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) was carried out using a FEI Helios NanoLab™ 600 DualBeam electron microscope working at an accelerating voltage of 3 kV. A thin layer of gold was sputtered on the sample surface prior to the SEM measurement.

2.4. Thermal properties

Thermal properties were measured in a Mettler Toledo DSC822e instrument. Discs weighting approximately 10 mg were sealed in aluminium pans with perforated cover. Samples were heated at 10 °C min^{-1} from 25 to 280 °C followed by cooling at a rate of −10 °C min^{-1} from 280 to 25 °C. After 5 min at 25 °C, samples were reheated from 25 to 280 °C at 10 °C min^{-1}. All scan were carried out under a constant nitrogen purge. The melting point (Tm) and crystallization temperatures (Tc) are given as the maximum of the endothermic transition and the minimum of the *exo*thermic transition, respectively. Glass transition temperature (Tg) is given as the midpoint of the change in heat capacity. The percent of crystallinity (Xc) was calculated from the endothermic peak area ΔHc by $Xc = (\Delta Hc/\Delta H_0) \cdot 100$, where ΔH_0 is the heat of fusion for 100% crystalline PET (129.3 J g^{-1}) (Wunderlich, 1990).

2.5. Mechanical properties

Tensile properties were measured in a MTS Synergie 200 testing machine equipped with a 1000 N load cell. Type 4 dumbbell test pieces (according to ISO 37) were tested. A crosshead speed of 5 mm min^{-1} was used with an initial gauge length of 20 mm. Strain was measured from crosshead separation and referred to 10 mm initial length. The reported values are the average of at least 4 specimens.

3. Results and discussion

3.1. Poly(ethylene terephtalate) characterization

Prior to irradiation, the PET material was characterized. Cross-polarized optical microscopy showed that the material was crystalline (Fig. S1 in Supplementary information). From a close observation of the images, it seems that the crystals have a certain orientation in the diagonal direction, to the left in the left image and to the right in the right image, due to the biaxial orientation of the sheet. Crystallinity of the sample was confirmed by DSC. When PET was heated (Fig. S2 in Supplementary information), a Tg was found at approximately 71 °C, and at high temperature, above 180 °C, a melting endothermic peak was observed with the maximum at approximately 250 °C. The calculated value of the crystallinity was approximately 38%.

Due to the biaxial orientation of the PET sheet, mechanical properties could be different depending on the direction. For this reason, mechanical properties were measured in the two mutually perpendicular directions of the sheet, that will be called “parallel” and “perpendicular” direction for simplicity. As it can be seen in Fig. S3 in the Supplementary information, mechanical properties were different depending on the direction of measurement. For the “parallel” direction, the values for stress at break and strain at break were 128 ± 3 MPa and 142 ± 9% respectively, and for the “perpendicular” direction 158 ± 6 MPa and 100 ± 11%. This