



ELSEVIER

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Effect of gamma irradiation on poly(butylene naphthalate) based polyesters

I. Malavasi^a, G. Consolati^b, F. Quasso^b, M. Soccio^c, M. Gigli^c, M. Negrin^{a,*}, E. Macerata^a, F. Giacobbo^a, N. Lotti^c, A. Munari^c, M. Mariani^a^a Department of Energy, Politecnico di Milano, Piazza L. da Vinci, 32, 20133 Milano, Italy^b Department of Aerospace Science and Technology, Politecnico di Milano, Piazza L. da Vinci, 32, 20133 Milano, Italy^c Department of Civil, Chemical, Environmental, and Materials Engineering, Università di Bologna, Via Terracini, 28, 40131 Bologna, Italy

HIGHLIGHTS

- Gamma irradiation of polyesters with different number of aromatic rings was studied.
- Effect of gamma radiation on PBN, PDEN, PTDEN, PDET, and PTDET was investigated.
- Irradiated polymers were studied by GPC, DSC and PALS.
- Introduction of heteroatoms decreases polymers radiation resistance.
- Presence of double aromatic ring confers a higher stability with increasing doses.

ARTICLE INFO

Article history:

Received 3 October 2015

Received in revised form

27 November 2015

Accepted 30 November 2015

Available online 1 December 2015

Keywords:

Naphthalate-based polyesters

Heteroatom-containing polyesters

Gamma irradiation

Positron Annihilation Lifetime Spectroscopy

Differential Scanning Calorimetry

Gel Permeation Chromatography

ABSTRACT

The present work investigates the effect of gamma radiation on the properties of three naphthalate-based polyesters, i.e. poly(butylene naphthalate) (PBN), poly(diethylene naphthalate) (PDEN) and poly(thiodiethylene naphthalate) (PTDEN). In addition, the analogous terephthalate-based polymers of PDEN and PTDEN, i.e. poly(diethylene terephthalate) (PDET) and poly(thiodiethylene terephthalate) (PTDET), are also investigated, in order to check the effect of a lower number of aromatic rings. All the polymers, irradiated in air at different absorbed doses, were characterized by several techniques. The data obtained indicate that all the polymers, except PBN, show a decrease of molecular weight with the dose increase. The thermal behavior and the morphology confirm the previous results and show that the higher the crystallinity degree and number of aromatic rings, the higher the radiation resistance. The introduction of heteroatoms decreases the ability of a polymer to crystallize due to a reduction of polymer chain symmetry, thus worsening their radiation resistance.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Polymers have been key enablers for innovation. Nowadays, they find many uses in fields as diverse as household appliances, packaging, construction, medicine, electronics, automotive and aerospace components (Hamad et al., 2013). Among these large varieties of environments, polymers could undergo ionizing radiation, such as during sterilization and treatments in nuclear medicine (Güven, 2009). It is well known that radiation processing on polymers can induce modifications of their physical, chemical and mechanical properties: ionizing radiation has been

extensively used to enhance and alter the polymer properties. The polymer-gamma radiation interaction leads to the formation of very reactive intermediates in the form of excited states, ions and free radicals that result in the rearrangement and in the formation of new bonds. The ultimate effects of these reactions are the formation of oxides products, grafts, crosslinking and scissioning of the main side chains, which is also called degradation (Güven, 2003). Conventional polymers are often treated with additives to avoid UV or solar radiation degradation and to give certain desired properties for a specific application. By selecting the proper polymeric material resistant to gamma radiation, it can be ensured that the critical elements of material performance are not compromised during its application, thus reducing the use of additives (OECD, 2004). Polymers containing aromatic rings, such as the

* Corresponding author.

E-mail address: maddalena.negrin@polimi.it (M. Negrin).

most widely used poly(ethylene terephthalate) (PET), as well as those having a higher number of aromatic rings, such as poly(ethylene naphthalate) (PEN), display a higher radiation resistance than the analogous containing aliphatic groups (Woods and Pikaev, 1994; Prasad et al., 2011). In addition it was demonstrated that a bigger number of aromatic rings reduces the radiolytic degradation effect (Buttafava et al., 2005). Butylene glycol-based polymers are widely used in electrical insulation because of their high breakdown strength, high resistivity and low dielectric loss, and they are widely used in aerospace electronics, electric engineering and medical equipment. Therefore much research regarding the influence of radiation on polymeric materials have been done for both crosslinking and degradation reaction. Du et al. (2007) have shown that dielectric properties are improved by irradiation for butylene glycol-based polymers containing more combined phenyls in the main chain. Their good stability for lower doses of gamma irradiation allow their sterilization. Aliev et al. (2006) showed that PBT radiation degradation is effective at doses of 2.5 MGy. Soccio et al. (2007) showed that the introduction of heteroatoms along PBT polymer chain can influence its properties. Naphthalate moieties along the polymer backbone were found to have outstanding results: various properties such as stiffness, strength, thermal stability, barrier to oxygen, carbon dioxide, water vapor and gasoline, UV absorption cut-off have been improved. Nevertheless, naphthalates are more expensive (Lin, 2008). This affects their production volumes and limits their application. Otherwise, polyesters based on alkylene ether glycols can present potential compostability, favored by the presence of ether-linkages that increase the hydrophilic character of the polymer, facilitating its dissolution under environmental conditions. However, their radiation resistance has yet to be investigated.

The present work aims to verify the role of the aromatic rings and the crystallinity on the radiation resistance of PBN-based polymers by investigating the effect of gamma radiation on three naphthalate-based polyesters, i.e. poly(butylene naphthalate) (PBN), poly(diethylene naphthalate) (PDEN) and poly(thiodiethylene naphthalate) (PTDEN) (Soccio et al., 2007). PDEN and PTDEN differ from PBN for the introduction in the glycol sub-unit of an ether–oxygen and sulfur atom, respectively. In this view, the effects induced by gamma irradiation in air at absorbed doses up to 1 MGy on the polymer chemical structure have been characterized in terms of molecular and thermal properties. In addition, the analogous terephthalate poly(butylene terephthalate) (PBT)-based polymers of PDEN and PTDEN, i.e. poly(diethylene terephthalate) (PDET) and poly(thiodiethylene terephthalate) (PTDET) have been also studied (Fig.1).

2. Experimental

Synthesized polymers (Soccio et al., 2007) in form of powder (purity higher than 99.98%) were molded in films of 1 mm thickness

by using a power press equipped with two cast-iron plates activated by an hydraulic ram. The press was protected by two Teflon layers to avoid the sticking of the polymers to the metal plates. The 1 mm thick films were cut into 1 cm² squares. The polymers were irradiated by means of Co-60 gamma rays with a dose rate of 2.5 kGy/h in air at the absorbed doses ranging from 100 to 1000 kGy. Successively, the treated materials have been fully characterized by Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC) and the free volume features were investigated by Positron Annihilation Lifetime Spectroscopy (PALS).

2.1. GPC analyses

In order to determine the molecular weight, 2 mg/mL solution of each sample were analyzed by gel permeation chromatography at 30 °C using a 1100 HO Series system with an UV spectrometer (at 254 nm wavelength) as detector, equipped with PL gel 5 μ MiniMIX-C column (250/4.6 length/i.d., in mm). A mixture of chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (CHCl₃/HFIP) (95/5 v/v) was used as diluent with a 0.3 mL/min flow rate. A molecular weight calibration curve was obtained with several monodisperse polystyrene standards in the range of molecular weight 2000–100,000. Data were collected by HP Chemstation A.05.04 and elaborated with GPC Calculator 7.6 software.

2.2. DSC measurements

Calorimetric measurements were carried out by means of a Mettler Toledo DSC 822e instrument calibrated with high purity standards (indium and zinc). Samples (c.a. 10 mg) were encapsulated in aluminum pans and heated to about 20 °C above fusion temperature at a rate of 10 °C/min (first scan). Two heating and cooling cycle were performed for each sample. The glass transition temperature (T_g) was taken as the inflection point of the heat capacity increment Δc_p associated with the glass-to-rubber transition. The melting temperature (T_m) was determined as the peak value of the endothermic phenomena in the DSC curve. The specific heat increment (Δc_p), associated with the glass transition of the amorphous phase, was calculated from the vertical distance between the two extrapolated baselines at the glass-transition temperature. The heat of fusion (ΔH_m) was calculated from the area of the DSC endothermic peak.

2.3. Positron Annihilation Lifetime Spectroscopy analysis

The β^+ source, consisting of a carrier free ²²NaCl with an activity of 0.3 MBq, was sealed in two Kapton[®] foils (7.5 μ m thick), and sandwiched between two samples of the investigated polymers. The thickness of the samples was enough to stop all the positrons injected. The lifetime spectra of the positrons annihilating in the specimen were collected by a standard fast–fast coincidence time spectrometer, having a resolution of about 250 ps.

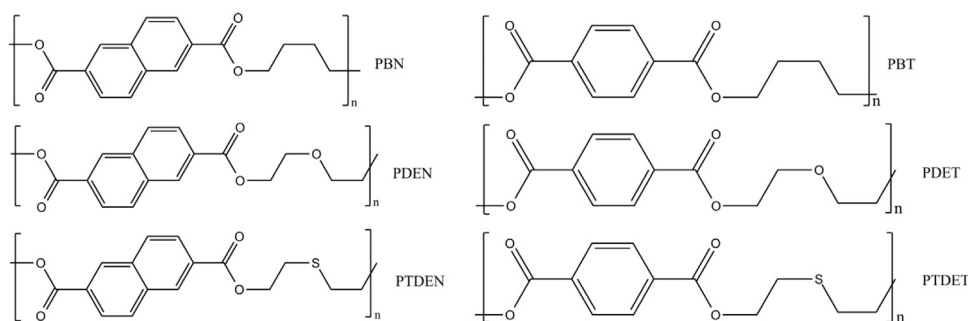


Fig. 1. Structures of the investigated polyesters and of the well-known PBT.

Download English Version:

<https://daneshyari.com/en/article/1891019>

Download Persian Version:

<https://daneshyari.com/article/1891019>

[Daneshyari.com](https://daneshyari.com)