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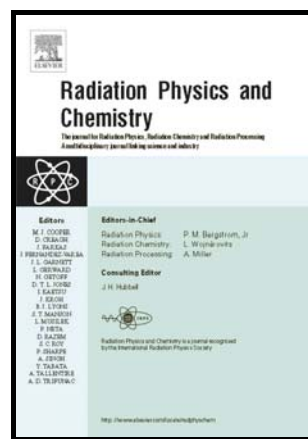
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Abstract

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.

Keywords

Naphthalate-based Polyesters, Heteroatom-containing Polyesters, Gamma Irradiation, Positron Annihilation Lifetime Spectroscopy, Differential Scanning Calorimetry, Gel Permeation Chromatography.

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 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 analogues 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're 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(thiodietylene 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 sulphur 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(dietylene terephthalate) (PDET) and poly(thiodietylene terephthalate) (PTDET) have been also studied (Fig.1).
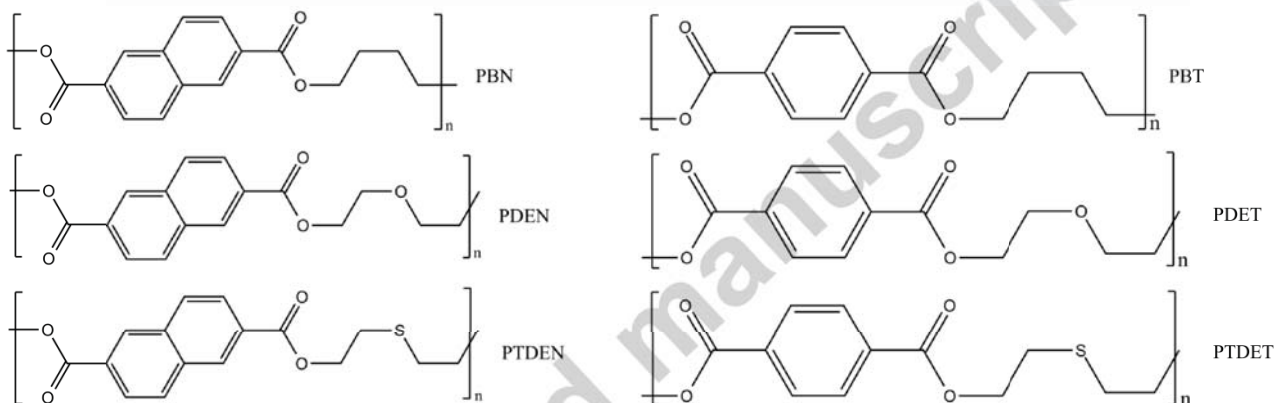

Fig. 1 – Structures of the investigated polyesters and of the well-known PBT.

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 cm^2 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 5µ MiniMIX-C column (250/4.6 length/i.d., in mm). A mixture of chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (CHCl$_3$/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 2000-100000. 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 $^{22}NaCl$ with an activity of 0.3 MBq, was sealed in two Kapton® foils (7.5 μm 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. Three spectra of about $5 \cdot 10^6$ counts were collected for each polyester at room temperature. The spectra were deconvoluted into three components by means of LT program (Kansy, 1996).

3. Results And Discussion

Changes in the molecular weight of the polymers after irradiation were investigated by means of GPC and the results are reported in Figure 2. The pristine samples were characterized by a number average molecular weight of about 19000 g/mol for PBN and PTDEN, and of 27000 g/mol for PDEN, PDET and PTDET. PBN displayed an excellent stability up to 1 MGy due to the interchain reactions, as confirmed by the trend of the polydispersity index. As far as the PBN-based polymers are concerned, the M_n of PDEN and PTDEN slightly decreased till 90% at 1 MGy, indicating that the introduction of heteroatoms along the polymer chain affects the stability towards ionizing radiation. No difference was observed between ether-oxygen and sulphur atoms. The analogous terephthalate-based polymers highlighted a remarkable degradation. PTDET molecular weight decreased to about 75% at 1 MGy, while for PDET, M_n halves at 600 kGy and is reduced to 35% at the highest dose. In general, the trend of the polydispersity index as a function of the absorbed dose is coherent with that of the molecular weight. As expected, polymers with two aromatic rings displayed a better radiation resistance and no significant difference observed by the introduction of O or S atoms along the polymer chains. In the terephthalate-based polymers, having a lower number of aromatic rings, the introduction of an oxygen-atom lead to a greater decrease of the molecular weight with the dose increase with respect to the S-containing polymer.
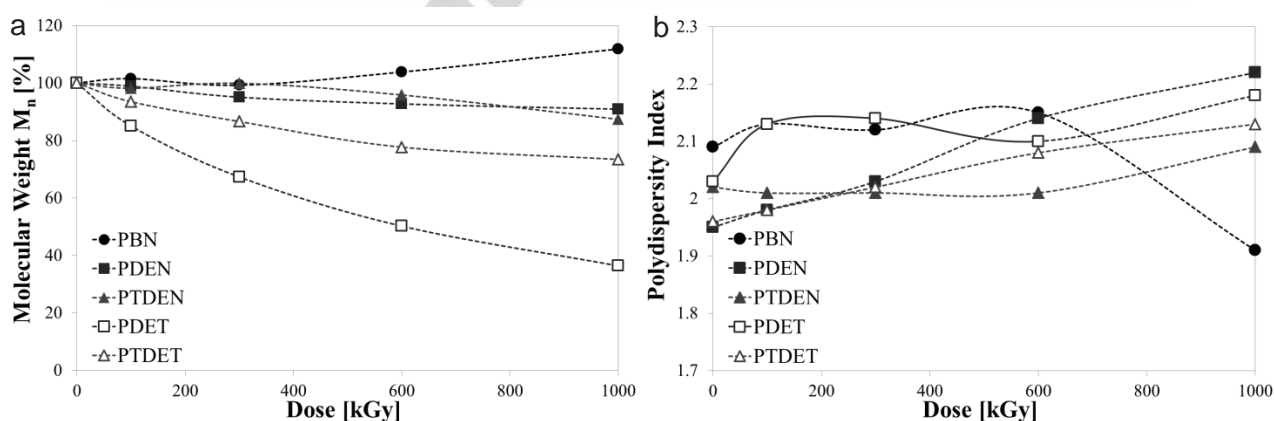
Fig. 2 – Results of the GPC analyses: mean molecular weight [%] (a) and polydispersity index (b) as a function of the absorbed dose.

Both pristine and irradiated polymers were afterwards examined by differential scanning calorimetry and the results are collected in Table 1. From the DSC analyses of the as synthesized samples it can be noted that PBN is the most crystalline material and the introduction of ether and thioether linkages caused a depression of the crystalline fraction, as already reported in the literature (Soccio et al., 2007). The heats of fusion (ΔH_m) and the melting temperatures (T_m) (Fig. 3) of PBN-based polymers decrease for S-containing polymer (PTDEN) and, at a greater extent, for the O-

containing one (PDEN) that showed very low values of ΔH_m. Also the S and O-containing PBT-based polymers displayed a similar behavior as compared to the PBT homopolymer (T_m 226.6°C, ΔH_m 61.8 J/g, (Buttafava, 2005)). DSC analyses of irradiated polymers did not highlight significant variations that could suggest a trend with absorbed dose, notwithstanding the molecular weight decrease observed by GPC.

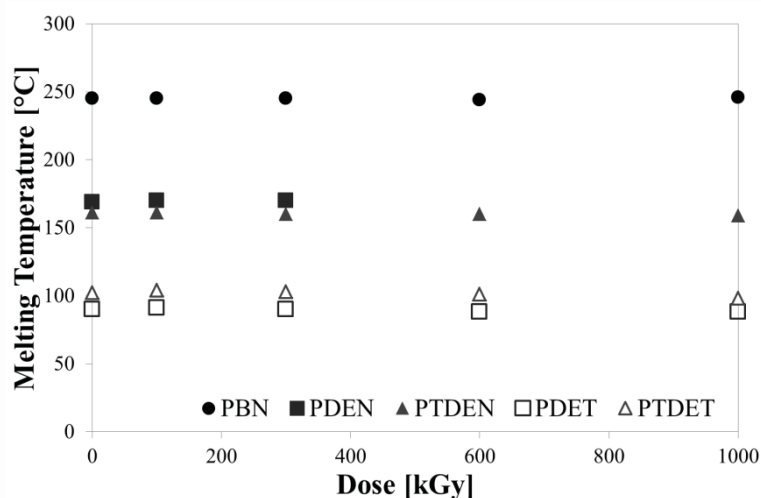Fig. 3 – Melting Temperature [°C] as a function of the absorbed dose.

Table 1 - DSC thermal data for all the polymers as a function of the total absorbed dose.

Dose		[kGy]	0	100	300	600	1000
PBN	T_g	[°C]	n.d.	n.d.	n.d.	n.d.	n.d.
	Δc_p	[J/g·K]					
	T_m	[°C]	245	245	245	244	246
	ΔH_m	[J/g]	38.1	52.3	36.4	30.3	32.2
PDEN	T_g	[°C]	57.9	55.8	57.5	56.5	56.9
	Δc_p	[J/g·K]	0.29	0.14	0.18	0.3	0.35
	T_m	[°C]	169	170	170		
	ΔH_m	[J/g]	0.91	1.07	0.02	-	-
PTDEN	T_g	[°C]	49.4	48.8	47.6	47.9	46.8
	Δc_p	[J/g·K]	0.35	0.3	0.25	0.19	0.29
	T_m	[°C]	161	161	160	160	159
	ΔH_m	[J/g]	12.8	20.0	23.5	13.1	16.8
PDET	T_g	[°C]	21.4	22.9	21.6	21.1	19.8
	Δc_p	[J/g·K]	0.42	0.41	0.41	0.4	0.4
	T_m	[°C]	90	91	90	88	88
	ΔH_m	[J/g]	1.5	0.3	0.4	0.7	0.3
PTDET	T_g	[°C]	17.2	17.3	17.2	17.2	17.0
	Δc_p	[J/g·K]	0.15	0.26	0.19	0.20	0.16
	T_m	[°C]	102	104	103	101	98
	ΔH_m	[J/g]	21.0	20.8	20.3	21.9	22.1

n.d.: not detectable

PALS measurements were performed on the irradiated samples in order to investigate their free volume. It is well known that some physical characteristics, such as permeability, depend on the polymer microstructure and, in particular, on the presence of the free volume holes (pores) in the macromolecular matrix that undergo structural changes when exposed to ionizing radiation (Hill et al., 2006; Misheva, 2009). PALS measurements allow one to get insight on the free volume of the polymer, due to their capability to supply typical sizes of the holes and therefore to foresee changes in gas and vapor permeability. Positrons from [22]Na source diffuse through the material and may bond with an electron, forming an exotic atom named positronium (Ps) which gets trapped in a free volume hole. A typical annihilation time spectrum shows three components, corresponding to the main annihilation channels (para-Ps, free positrons and ortho-Ps). The longest component due to the annihilation of ortho-positronium atom (o-Ps), sublevel with parallel spins, into the holes present in the amorphous zones is used to probe the free-volume hole dimension (Wang and Jean, 1988). These last show a distribution of values, due to the disordered character of the amorphous zone. A longer o-Ps lifetime τ_3 means bigger holes because the lower electron density surrounding Ps reduces the probability of Ps atom annihilation.

Distribution of free volume holes sizes is mirrored by a corresponding distribution of o-Ps lifetimes, characterized by the first two moments (mean lifetime and dispersion). A quantitative correlation between o-Ps lifetime τ_3 and the mean radius of holes in a spherical geometry is known as Tao-Eldrup equation:

$$\tau_3 = \tau_0 \left[1 - \frac{R}{R+\delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R+\delta R}\right) \right]^{-1} \tag{1}$$

where $\delta R=1.66$ Å is an empirical parameter and τ_0 is equal to 0.5 ns (Tao, 1972; Eldrup et al., 1981). Table 2 reports the lifetime data of the o-Ps decays (τ_3), the relative dispersion and intensity and the mean holes radius calculated by using eq. 1, as obtained from the PALS measurements. PBN and polymers containing ether-oxygen linkages have higher values of the mean radius than those containing thioether-linkages. On the other hand, PBT-based polymers display lower τ_3 and σ values than those of PBT (τ_3 1.69 σ 0.39) reported by Buttafava, 2005. The measured radii by PALS do not show significant variations with the absorbed dose. This is very important in view of some applications (e.g. sterilization of medical materials as well as other treatments), the performances of polymers should remain unaltered during irradiation.

Table 2 – PALS measurements: Lifetime τ_3, dispersion σ and intensity I of o-Ps decay and correlated mean radius of nanoholes as a function of the absorbed dose. Uncertainties on the various quantities are evaluated to be 3% (τ_3), 15% (σ) and 5% (I).

	Dose	[kGy]	0	100	300	600	1000
PBN	τ_3	[ns]	1.55	1.51	1.53	1.43	1.48
	σ	[ns]	0.39	0.41	0.36	0.48	0.43
	I	[%]	24.0	24.2	24.2	25.4	24.0
	R	[Å]	2.39	2.35	2.37	2.26	2.31
PDEN	τ_3	[ns]	1.42	1.37	1.29	1.28	1.36
	σ	[ns]	0.41	0.43	0.48	0.49	0.42
	I	[%]	23.8	24.8	26.4	26.9	23.9
	R	[Å]	2.24	2.18	2.08	2.07	2.17
PTDEN	τ_3	[ns]	1.30	1.28	1.21	1.20	1.27
	σ	[ns]	0.47	0.49	0.48	0.50	0.45
	I	[%]	18.1	18.8	19.4	19.2	13.2
	R	[Å]	2.09	2.07	1.97	1.96	2.05
PDET	τ_3	[ns]	1.55	1.59	1.50	1.54	1.51
	σ	[ns]	0.46	0.36	0.48	0.43	0.48
	I	[%]	24.8	22.8	24.6	23.0	23.1
	R	[Å]	2.39	2.44	2.34	2.38	2.35
PTDET	τ_3	[ns]	1.29	1.28	1.28	1.28	1.25
	σ	[ns]	0.50	0.50	0.50	0.49	0.53
	I	[%]	18.7	19.7	19.0	18.2	18.4
	R	[Å]	2.08	2.07	2.07	2.07	2.03

4. Conclusions

The study of polymers radiation resistance is motivated by the growing use of these materials in applications involving ionizing radiations. The present research investigated the effect of gamma irradiation treatment on the structure and the related properties of five aromatic polymers, taking into account the role of aromatic rings and crystallinity degree towards radiation resistance. As expected, aromatic polymers proved to be very stable towards irradiation: the higher the number of aromatic rings, the higher the resistance. The introduction of heteroatoms decreases the ability of a polymer to crystallize, due to a reduction of polymer chain symmetry. This factor, together with the chemical structure, i.e. the presence of ether and thio-ether linkages along the PBN and PBT backbone, caused a worsening of their radiation resistance. By comparing the results obtained for O- and S-containing polymers, it can be evicted that the former show a higher degradation rate. In conclusion, the stability towards ionizing radiations is strictly correlated to the number of aromatic rings, crystallinity and chemical structure.

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Highlights

- Effect of gamma radiation on polyesters with different aromatic density was studied
- Effect of gamma radiation (<1MGy) on PBN, PDEN, PTDEN, PDET, 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