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γ-Irradiation effects on polyethylene terephthalate studied by positron annihilation lifetime spectroscopy

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Abstract

Structural changes in commercial polyethylene terephthalate subjected to γ-irradiation were investigated by means of differential scanning calorimetry, viscosity measurements and positron annihilation lifetime spectroscopy. Irradiated samples show a lower molecular weight and increased crystallinity, which are attributed to chain scissions of the macromolecules. Positron results support such an interpretation and supply an estimation of the average sizes of the free volume holes and of the defects in the crystalline regions of the polymer. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Differential scanning calorimetry; Irradiation effects; Polyethylene terephthalate

1. Introduction

Radiation methods are successfully used for polymerisation, for polymer modification [1], for degradation, for biomaterials [2], for the radiation treatment of food products, for the solution of ecological problems [3] and many other applications [4]. The radiation processing is a useful technology to induce suitable modifications of materials. In particular, it is a very important way to generate or to improve new properties in materials as well as new means of production.

On the other hand the combined action of ionising radiation and oxygen on polymers may rapidly lead to a severe deterioration of the polymer properties. The resulting effects are strongly dependent on the chemical structure of the polymer. The radiation damage and the oxidative degradation cause chemical changes in the polymer structure with build up of a variety of new functional groups as carbonyls, carboxyls, esters, hydroxyls, unsaturations; furthermore, chain scissions and cross-links are also often induced. These changes cause severe deterioration of the polymers, which shows up very early, with consequent decay of important properties such as electrical insulation power, transparency and hydrorepellency. The polymer degradation induced by radiation is a prompt way to simulate the aging of polymeric materials and to study their radiation stability or the change of chemical, physical and mechanical properties in view of their future applications.

In the present paper we will focus on the changes of physical properties of polyethylene terephthalate (PET) induced by gamma irradiation. PET is a polymer which shows a good resistance to radiation due to the aromatic groups that are effective at dissipating the energy of the ionising radiation. In fact, a severe damage is achieved only for doses higher than 30 MGy [5]. At lower doses, minor effects are expected. In this connection, we decided to investigate radiation effects for doses up to 1 MGy by using macroscopic techniques (DSC and viscosity) as well as an atomic method, positron annihilation lifetime spectroscopy (PALS). PALS is a relatively simple technique which can probe the properties of the free volume holes in a non-destructive way [6]. It is based on the fact that some of the positrons injected into the material under investigation are trapped in regions with reduced electron density where they may form a bound positron–electron system, positronium (Ps). According to the different spin orientation of the two particles we distinguish the Ps ground state into *para*-Ps (*p*-Ps) and *ortho*-Ps (*o*-Ps). *p*-Ps is scarcely influenced by the environment; on the contrary, *o*-Ps interacts with the surrounding electrons belonging to the cavity where *o*-Ps is trapped ('pickoff' process). A correlation between *o*-Ps lifetime and the sizes of the cavity comes out, which can be

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Table 1
Physical properties of the investigated PET

Density (25 °C)[a]	1.38×10^3 kg m^{-3}
Dielectric constant (25 °C, 50 Hz)[b]	3.3
Dielectric strength (25 °C, 50 Hz)[c]	2.8×10^8 V m^{-1}
Specific heat (25 °C)	1.32 J g^{-1} K^{-1}
Tensile modulus[d]	3.8×10^9 Pa

[a] ASTM D 1505-63T.

[b] ASTM D 150-65T.

[c] ASTM D 149-64 (500 V s^{-1} rate of rise).

[d] ASTM D 882-64T Method A (100% elongation per minute).

cast in a quantitative form by suitably modelling the trapping site [7,8]. Furthermore, since Ps formation is favoured in the free volume present in the amorphous regions of the polymer, a correlation between Ps intensity and free volume fraction can also be expected.

In this paper we will show that comparison among the different techniques offers a coherent interpretation of the physical changes occurring in PET after irradiation.

2. Experimental

2.1. Irradiation source

The polymer was a commercial PET by DuPont in form of films (thickness 25 μm). Some physical properties are listed in Table 1. It was irradiated using a gamma-emitting source of ^{60}Co at the Pavia University (Italy), with absorbed dose rate of 0.30 Gy s^{-1} to give absorbed dose values up to 1.1 MGy.

2.2. Differential scanning calorimetry (DSC)

Thermal transitions and melting heat ΔH_m of pristine and irradiated PET were determined by DSC with a Mettler TA 822 instrument (indium calibrated), with heating/cooling runs between 293 and 573 K, at a heating/cooling rate of 10 K min^{-1}. The glass transition temperature T_g was evaluated as transition midpoint of the trace.

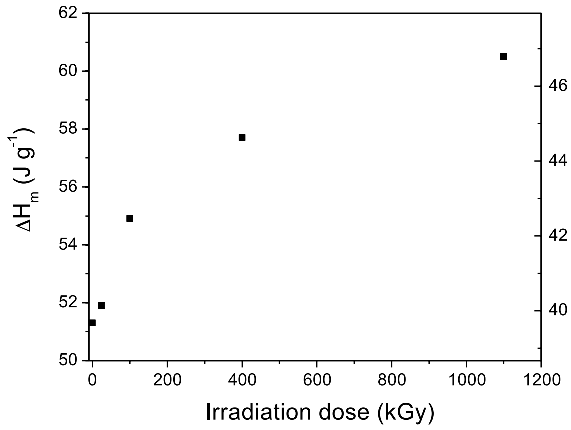

Fig. 1. Melting heat ΔH_m versus the irradiation dose in the investigated PET samples. The right *y*-axis shows the corresponding crystallinity (%).

2.3. Viscosity measurements

Solution viscosity measurements were performed in order to get information on the molecular weight changes induced by γ-irradiation. The polymer dilute solution viscosity can be correlated with the molecular weight of the dissolved polymer molecules. The viscosity ratios (relative viscosity) $\eta_r = \eta(c)/\eta(0)$, of pristine and of two PET samples irradiated at different doses were measured at three different polymer concentration (c). The intrinsic (η_{int}) and the inherent viscosity (η_{inh}) were also determined. The polymers were dissolved in a 50% (w/w) solution of 1,1,2,2 tetrachloroethane and phenol. The measurements were carried out with a Ubbelohde Viscosimeter at 308 ± 0.1 K. The determinations of the viscosity were carried out according to Standard ASTM D 2857-70. Viscosity average molecular weight M was estimated from dilute solution viscosity measurements, according to the Mark–Hawkin relationship ($\eta_{int} = KM^a$), assuming for K and a the values of virgin PET [9].

2.4. Positron lifetime spectroscopy

The positron source consisted of a droplet of ^{22}Na from a carrier-free neutral solution (activity: 0.3 MBq), dried between two Kapton foils (thickness 1.08 mg cm^{-2}), which were afterwards glued together. Care was taken to confine the glue at the edge of the foils, thus preventing the glue from reaching the region interested to annihilation. The source was inserted within two identical layers of a specimen in a typical ‘sandwich’ configuration; the thickness of the specimens—formed by stacking several sheets of the same sample—was sufficient to stop all the injected positrons. Positron annihilation lifetime spectra were collected through a conventional coincidence set-up, having a resolution of about 240 ps. All the measurements were performed at room temperature. Each spectrum contained about 5×10^6 counts. At least three spectra for each dose were collected. Deconvolutions were carried out through the computer code LT [10], with a suitable correction for the positrons annihilated in the Kapton.

3. Results and discussion

DSC measurements show a glass transition temperature T_g, a melting temperature T_m and a corresponding melting heat ΔH_m. Average values of T_g and T_m are 348 ± 4 and 528.7 ± 0.9 K, respectively. The ΔH_m values are shown in Fig. 1. The increase in the melting heat corresponds to an increase in crystallinity in the irradiated specimens. It can be calculated from the values of ΔH_m of the irradiated PET, since the melting heat for an ideal sample (100% crystalline)

Table 2
Viscosity data for pristine PET as well as for two irradiated samples

Absorbed dose (Gy)	c (g dm^{-3})	η_r [a]	η_{inh} [b] (dm^3 g^{-1})	η_{int} [c] (dm^3 g^{-1})	M [d] (g mol^{-1})
0	1.279	1.079	0.0723	0.0758	21 794
	2.557	1.177	0.0637		
	4.476	1.306	0.0596		
100	1.279	1.083	0.0622	0.0678	19 023
	2.557	1.157	0.0571		
	4.476	1.242	0.0485		
1100	1.279	1.065	0.0490	0.0495	12 962
	2.557	1.105	0.0399		
	4.476	1.204	0.0411		

[a] $\eta_r = \dfrac{\eta(c)}{\eta(0)}$.

[b] $\eta_{inh} = \dfrac{\ln \eta_r}{c}$.

[c] $\eta_{int} = \lim_{c\to 0} \eta_{inh}$.

[d] $M = 0.82\sqrt{\dfrac{\eta_{int}}{2.1\times 10^{-5}}}$.

is known to be 129.3 J g^{-1} [11]. The results are also shown in Fig. 1. This is in agreement with the results of the viscosity measurements, carried out in the pristine specimen as well as in two irradiated samples and listed in Table 2. The average molecular weight M which decreases at increasing irradiation dose can be considered as a consequence of the scission of the macromolecules induced by gamma irradiation. The reduced molecular weight accounts for an increase in molecular mobility, thus allowing an easier arrangement in crystalline structures. Similar behaviour is observed in PET also when molecular weight reduction is the result of different chain scission mechanisms, such as for example hydrolysis [12] or photodegradation [13]. Such a change in the polymer morphology should be accompanied by a decrease in the free volume. In order to investigate this point we carried out positron annihilation measurements.

Positron annihilation lifetime spectra were initially deconvoluted into four free components; the results are listed in Table 3. The shortest component is attributed to decays from *p*-Ps. The second component is ascribed to decays of the free (that is, not bound) positrons. The two longest components come from *o*-Ps decay. Although it is generally assumed that Ps is formed in the amorphous regions of the polymers, a contribution to the *o*-Ps component from defects present in the crystalline zones should also be taken into account [14]. For this reason we analysed the positron spectra into four components, according to analogous findings in other semicrystalline polymers [14–16]. The third component is attributed to annihilations of *o*-Ps trapped in crystalline defects; the longest component is due to *o*-Ps annihilated in the free volume holes. According to the data listed in Table 3, τ_4 is quite constant for the various samples. Concerning τ_3, it does not show a particular trend with the irradiation dose; however, the data shows rather large uncertainties. In order to get more precise information we tried to analyse the lifetime spectra by fixing the intermediate component to its average value; however, this procedure did not significantly reduce the scattering of the two intensities I_3 and I_4. Furthermore, τ_4 still remained almost constant, which means that the average sizes of the free volume holes do not change with the irradiation dose. Then the lifetime spectra were re-analysed by fixing the two longest lifetimes to their average values; Fig. 2 shows the intensities I_3, I_4 and their sum found with this procedure. The behaviour of the two intensities versus the irradiation dose is opposite and these results can be understood on the basis of the previous discussion. Indeed, the increase in crystallinity with the

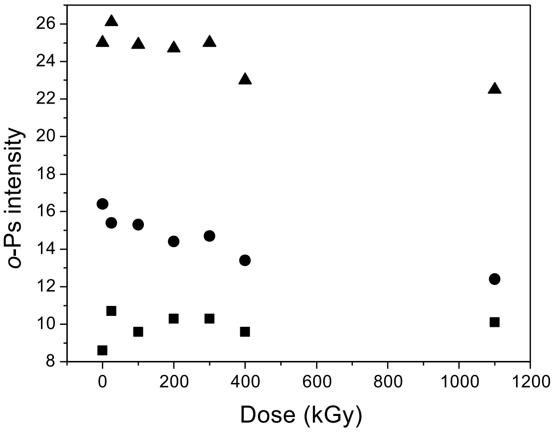

Fig. 2. *o*-Ps intensities versus the irradiation dose. Squares: I_3. Circles: I_4. Triangles: $I_3 + I_4$. Data obtained from lifetime spectra analysed by fixing the values of τ_3 and τ_4.

Table 3
Positron annihilation lifetime data. Analysis into four components without constraints

Dose (kGy)	τ_1 (ns)	I_1 (%)	τ_2 (ns)	I_2 (%)	τ_3 (ns)	I_3 (%)	τ_4 (ns)	I_4 (%)
0	0.16 ± 0.03	14 ± 2	0.35 ± 0.01	60 ± 3	0.99 ± 0.08	12 ± 4	1.84 ± 0.04	14 ± 2
25	0.14 ± 0.02	9 ± 1	0.33 ± 0.01	62 ± 3	0.75 ± 0.07	14 ± 3	1.79 ± 0.05	15 ± 2
100	0.17 ± 0.03	13 ± 2	0.36 ± 0.01	60 ± 4	0.76 ± 0.08	11 ± 4	1.80 ± 0.04	16 ± 1
200	0.15 ± 0.03	12 ± 2	0.41 ± 0.01	62 ± 3	0.78 ± 0.08	9 ± 3	1.75 ± 0.05	17 ± 2
300	0.18 ± 0.02	13 ± 2	0.34 ± 0.01	60 ± 3	0.73 ± 0.09	12 ± 4	1.77 ± 0.04	15 ± 2
400	0.16 ± 0.03	15 ± 3	0.36 ± 0.01	66 ± 2	0.98 ± 0.08	9 ± 3	1.88 ± 0.06	10 ± 1
1100	0.13 ± 0.03	8 ± 1	0.33 ± 0.01	67 ± 3	0.77 ± 0.07	14 ± 5	1.76 ± 0.03	11 ± 2

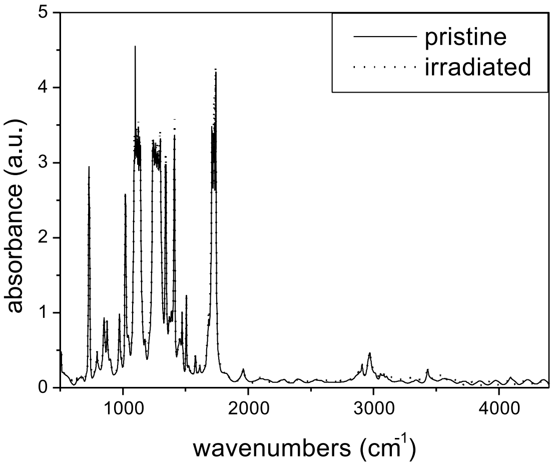

Fig. 3. FTIR spectra for pristine and irradiated (1100 kGy) PET samples.

irradiation dose reduces the available free volume; Ps formation in the amorphous phase is also reduced and the corresponding intensity I_4 decreases. Furthermore, I_3, the *o*-Ps intensity related to the crystalline phase, shows a moderate increase with the irradiation dose. Since the polymer becomes more compact at increasing crystallinity, it is expected that the total *o*-Ps intensity ($I_3 + I_4$) decreases at higher doses, as it is indeed observed.

PALS results in polymers should be discussed by taking into account the possibility that the positron source can induce radiation damage. Such effects can be considerable at low temperatures [17,18]. In the case of the data here shown we did not observe systematic variations in the longest components intensities in the various subsequent runs concerning a given γ-irradiation dose. Therefore, we do not consider radiation effects from the positron source of primary importance in order to interpret our measurements, according to the data shown in fig. 4 of Ref. [19], obtained through a positron source whose activity was comparable to ours.

According to our data the mean values of the *o*-Ps lifetimes in the crystalline defects and in the free volume holes are, respectively, 0.82 and 1.80 ns. We can transform these data into average sizes of the free volume holes and of the defects in the crystalline regions using the Tao–Eldrup semiempirical equation [7,20]: the cavity hosting Ps is assumed to be a spherical void with effective radius R. Such a Ps trap has a potential well with finite depth; however, for convenience of calculations one usually assumes the depth as infinite, but the radius increased to $R + \Delta R$, ΔR (1.66 Å [7]) being an empirical parameter which describes the penetration of Ps wave function into the bulk. The electron density is supposed to be zero for $r < R$ and constant for $r > R$. The relationship between *o*-Ps lifetime τ (ns) and radius R (Å) is as follows:

$$\tau = 0.5\left[\frac{\Delta R}{R+\Delta R} + \frac{1}{2\pi}\sin\left(2\pi\frac{R}{R+\Delta R}\right)\right]^{-1}. \qquad (1)$$

We get $R = 2.66$ Å for the free volume holes and 1.33 Å for crystalline defects. Of course, these values should be interpreted only as rough estimations, since holes are irregularly shaped.

A decrease in intensity could also be due, in principle, to chemical reactions between Ps and products of radicalic reactions taking place during the irradiation of the sample. A possible inhibition of Ps would manifest as a reduced intensity. In order to investigate this last point we carried out FTIR measurements in pristine PET as well as in the sample irradiated at 1.1 MGy. FTIR spectra for the two samples are shown in Fig. 3. There is no evidence for the formation of oxidated species in such an amount to justify reactions with Ps. Furthermore, such a chemical reaction should also give rise to a quenching of Ps lifetime, which in fact is not observed.

4. Conclusions

Gamma irradiation of PET induces changes in its morphology which can be interpreted—according to DSC and viscosity data—as chain scissions with reduction of the average molecular weight and increased crystallinity. Positron annihilation results confirm this conclusion, since the increase in crystallinity appears as a decrease in Ps intensity. Furthermore, PALS adds microscopic information, supplying an estimation of the average sizes of free volume holes as well as of defects in the crystalline regions. Average sizes of the free volume holes do not display significant changes with the irradiation dose. Anyway, an unambiguous interpretation of positron data required a further investigation with FTIR spectroscopy, in order to exclude possible alternative processes which are able to induce analogous variations in the positron parameters.

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