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Gamma Radiation Effects On Random Copolymers Based On Poly(Butylene Succinate) For Packaging Applications

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Abstract

Within the context of new bioplastic materials, poly(butylene succinate) (PBS) and four novel poly(butylene/thiodiethylene succinate) random copolymers (PBS-PTDGS), in sheets as well as in films, were exposed to gamma radiation, in air and in water, and their behaviour along with the effect on their biodegradability was investigated. The molecular weight data obtained from Gel Permeation Chromatography indicate that the sensibility to radiation increases with the amount of sulphur-containing co-unit (TDGS). At 200 kGy the average molecular weight of PBS film halves, while for P(BS60TDGS40) the residual molecular weight is about 20%. The calculated intermolecular crosslink G_x and scissioning G_s yields confirmed that degradation is predominant over crosslink for all the aliphatic systems. As shown by thermal analyses, gamma radiation affects the thermal properties, leading to an increased crystallinity of the systems, remarkable for PBS, and lower decomposition temperatures. Variations of crystallinity with the increasing absorbed dose were confirmed also by PALS analyses. Water contact angle measurements revealed post-irradiation wettability alterations that could positively affect polymer biodegradability. In particular, when irradiated in water at 100 kGy PBS film exhibits a water contact angle decrease of about 17%, indicating an enhanced wettability. After degradation in compost, changes in the surface morphology were observed by means of SEM and sample weight losses were determined, at different extent, according to the irradiation environment. Interestingly, after 52 days in compost PBS films, both pristine and irradiated in air at 25 kGy, showed a residual weight of about 60%, while the ones irradiated in water at 25 kGy of about 44%. Experimental data confirmed that gamma irradiation could represent a viable treatment to enhance biodegradation in compost of PBS and PBS-based copolymers.

Keywords

Poly(butylene succinate), biodegradable polymers, PBS copolymers, degradation in compost, gamma irradiation, radiation-induced modifications.

1. Introduction

During the last 60 years, polymers have started to substitute natural materials in every aspect of life. Their outstanding properties have led them to find many uses in areas as diverse as household appliances, packaging, construction, medicine, electronics, automotive and aerospace components (Hamad et al., 2013). More than one third of plastic production involves disposable materials, which become wastes within one year from manufacture. The increasing plastic pollution issue, due to the extremely long durability of the traditional fossil-based plastic, has risen the necessity to substitute materials with biodegradable ones and to optimize the use and disposal of conventional plastic. Among the class of new biodegradable polymers, poly(Butylene Succinate) (PBS), polycaprolactone (PCL) and poly(Lactic Acid) (PLA) have attracted considerable interest, due to their economically competitiveness. In particular, PBS is an aliphatic biodegradable polymer commercially available since 1993, under the trade name of Bionolle® (Showa Denko). It is characterized by interesting physical and mechanical properties, good processability and biodegradability (Ichikawa and Mizukoshi, 2012). Recently, great efforts have been made to tailor its properties and many works have been published on PBS-based copolymers and composites for different kinds of applications (Gigli et al., 2016; Soccio et al. 2012; Siracusa et al, 2015; Jamaluddin et al. 2016; Supthanyakul et al. 2016; Bautista et al. 2016). In particular, the modification of PBS with different amounts of thiodiethylene glycol has been investigated in terms of structural, thermal and mechanical properties, together with surface wettability, permeability to oxygen and carbon dioxide and biodegradation in a previous literature work. (Genovese et al, 2016). However, radiation resistance of PBS-based copolymers has still to be investigated, because it is expected that copolymerization strongly modifies also such property. Indeed, it is well known that the widespread radiation processing on polymers can induce modifications of their physical, chemical and mechanical properties (Clough, 2001; Chmielewski et al., 2005; Makuuchi and Cheng, 2012). Gamma radiation leads to the formation of very reactive intermediates that include excited states, ions and free radicals resulting in the rearrangement and in the formation of new bonds (Dole, 1973; Woods and Pikaev, 1994). The ultimate effects of these reactions are the formation of oxides products, grafts, crosslinking and scissioning of the main side chains (Güven, 2003). PBS, with its aliphatic chemical structure, is expected to show a lower radiation resistance in comparison with polymers containing aromatic rings (Sasuga et al., 1985; Prasad et al., 2011), even if it is known to be a crosslinkable polymer under suitable irradiation conditions. Some literature works widely described such topic and pointed out as irradiation could affect the biodegradation rate of the polymeric material. Suhartini et al. (2002) showed that electron beam irradiation of PBS in the presence of polyfunctional monomers up to 100 kGy leads to increased gel fraction and heat stability, which results in a slower biodegradation rate. Similarly, Mitomo et al. (1999) demonstrated that, after enzymatic degradation, the weight loss of irradiated PBS is lower than pristine PBS, due to crosslinking, which retards erosion. Similar studies have been conducted also on other interesting biodegradable polymers. Since PLA is often treated with a sterilization process for food and pharmaceuticals preservation, Benyathiar et al. (2016) has recently reported about the positive effect of irradiation by gamma and electron beam on compostability of PLA. However, the effects of irradiation on the degradation of biodegradable polymers have not been yet extensively studied.

The present work aims to investigate the behaviour under irradiation of four poly(butylene/thiodiethylene) succinate random copolymers (P(BS$_x$-TDGS$_y$), containing amounts of thiodiethylene succinate (TDGS) co-units ranging from 10 to 40% and widely investigated in a previous literature work (Genovese et al, 2016). Due to the interesting potentialities of such copolymers, the effects of ionizing radiations on their properties and especially on their biodegradation have been considered. In particular, the effect of irradiation in water has been analyzed, in order to assess the positive effect of such irradiation environment in enhancing polymer degradability, as similarly reported in literature works concerning polyethylene (Matsui et al., 2002; Billamboz et al., 2010). The chemical structure of the two comonomeric units are reported in Figure 1.

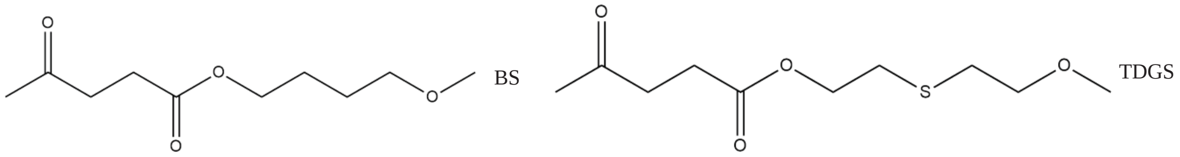

Figure 1. Structures of BS and TDGS comonomeric units.

2. Experimental

Poly(butylene succinate) (PBS) and poly(thiodiethylene glycol succinate) (PTDGS) were synthesized according to the two-stage polycondensation procedure, as previously reported (Genovese et al., 2016). Polymers in form of powder were molded in 1-mm sheets, 200-µm and 40-µm films by using a hydraulic power press. The samples were irradiated by means of a Co-60 source with a dose rate of 2.5 kGy/h in air at absorbed doses ranging from 50 to 500 kGy. A second irradiation campaign up to 100 kGy was performed with the samples plunged into a fixed amount of deionized water. Successively, the irradiated materials were fully characterized by Gel Permeation Chromatography (GPC), Differential Scanning Calorimetry (DSC), Thermogravimetric analysis (TGA) and Positron Annihilation Lifetime Spectroscopy (PALS). The surface properties were investigated by water contact angle measurements (WCA) and scanning electron microscopy (SEM). The degradation after irradiation was evaluated by disintegration tests based on the ISO-20200 standard method.

2.1 Molecular weight

Molecular weight data were obtained by GPC at 30 °C using an 1100 Hewlett Packard system equipped with a PL gel 5m MiniMIX-C column (250 mm/4.6 mm length/i.d.). A refractive index detector was employed. In all cases, chloroform was used as eluent with a 0.3 mL min^{-1} flow and sample concentrations of about 2 mg mL^{-1} were applied. Polystyrene standards in the range of molecular weight 2000–100000 were used. Data were collected by HP Chemstation A.05.04 and elaborated with GPC Calculator 7.6 software. The measurements have been carried out in triplicate.

2.2 Thermal properties

Thermal properties were evaluated by means of a Mettler Toledo DSC 822e instrument calibrated with high purity standards (indium and zinc). Samples (c.a. 10 mg, 200-μm film or 1-mm sheet) were encapsulated in aluminum pans and heated to about 20 °C above fusion temperature at a rate of 20 °C/min (first scan) under nitrogen flux. For each sample, two heating and cooling cycles were performed. 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 phenomenon. The melting enthalpy per unit mass (ΔH_m) was calculated from the area of the DSC endothermic peak. In addition, thermo-gravimetric analyses were performed under nitrogen atmosphere using a Perkin Elmer TGA 4000 apparatus (gas flow: 30 mL/min) up to 850°C at 10°C/min heating rate. The temperature of initial decomposition (T_0), identified with T_{onset}, and the temperature of the maximum degradation rate (T_{max}) were determined.

2.3 Positron Annihilation Lifetime Spectroscopy

Several 1-mm thick samples of the considered PBS-based polymers were cut in squares of about 1 cm^2 and analyzed by means of PALS to get information about the free volume features. The β^+ source, ^{22}Na with an activity of about 0.3 MBq, was sealed between two Kapton® foils (7.5 μm thick) and sandwiched between two sheets of the investigated polymers. The samples thickness of 1-mm was enough to stop all the injected positrons. The lifetime spectra of the positrons annihilating in the specimen were collected by means of 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. LT program (Kansy, 1996) was used to deconvolve the spectra into three components allowing the determination of the lifetimes and the relative intensity.

2.4 Surface wettability

The wettability of polymer films was evaluated by means of static water contact angle measurements. First, the films surface was properly washed with 70% ethanol aqueous solutions and then dried overnight in a sealed desiccator. Contact angle analyses were performed using an optical contact angle apparatus (OCA 15 Plus – Data Physics Instruments GmbH, Filderstadt, Germany) equipped with a video measuring system and the software SCA 20 (Data Physics Instruments GmbH, Filderstadt, Germany) was used for data acquisition. Measurements were performed at ambient conditions by recording the side profiles of deionized water drops for image analysis. For each sample, ten measurements were performed. Image analysis was carried out with a Drop Shape Analysis software. The data reported correspond to the average value.

2.5 Polymer surface morphology

Inspection of the morphology of degraded films was conducted by using a field emission scanning electron microscope (FE-SEM) working in high vacuum Zeiss Supra 40 equipped with the GEMINI column. Film samples were glued on aluminium stabs with carbon tape and images were acquired under vacuum.

2.3 Disintegration experiments

The rate of disintegration was determined by a procedure based on the ISO-20200 standard method. Prior to degradation tests, each specimen was placed under vacuum to constant weight and then weighted to obtain the initial mass. Then each specimen was mixed with a weighted amount of mature compost and then incubated at 58°C. For all the incubation period, humidity was maintained at 90% of the water holding capacity of the system. The disintegration test lasts at minimum 45 days, but it can be extended up to 90 days. After the incubation period, samples were sieved at 2 mm, accurately washed by dipping in water and finally dried under vacuum to constant mass. The disintegration in compost is evaluated on visual appearance and by SEM investigations of the samples and then quantified by the determination of the samples weight loss. It is worth noting that, according to the standard method applied, the material can be defined disintegrable if the residual weight is under 30% after 45 days. To check the test effectiveness, multiple reference samples of Mater-Bi®, a compostable material produced by Novamont, were considered. All the tests have been performed in duplicate.

3. Results And Discussion

Physical characterization

PBS and PBS-PTDGS copolymers films and sheets were irradiated in air atmosphere by means of a gamma-ray source. As result of the gamma irradiation, samples irradiated above 200 kGy showed an increased embrittlement. The residual number-average molecular weight values (M_n res%) of pristine and irradiated PBS and copolymers samples are reported in Figure 2 together with the polydispersity index (PDI).

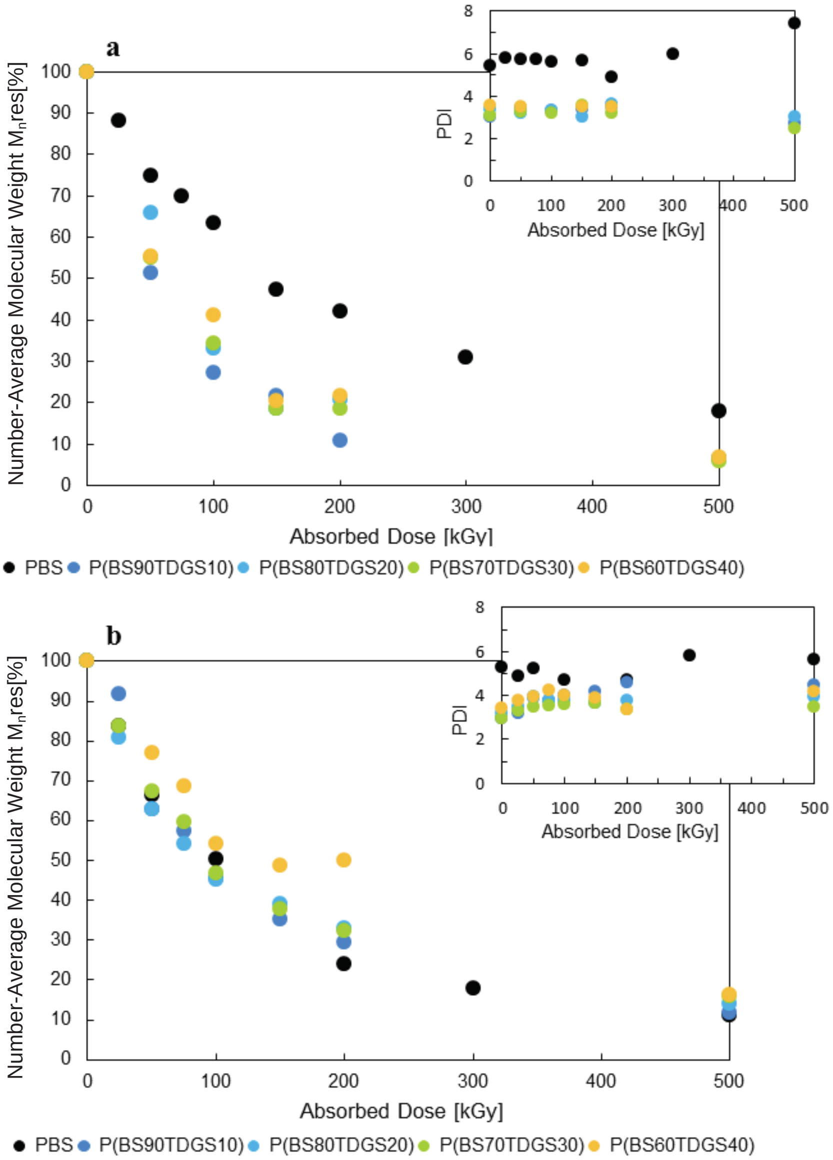

Figure 2. GPC results: residual number-average molecular weight [M_n res%] and polydispersity index (PDI) as a function of the absorbed dose and sample thickness 200 µm (a) and 1 mm (b).

When polymers are submitted to high energy radiation, contrasting radio-induced phenomena are observed, with a dominant effect of cross-linking or of chain scission. By using the molecular data, the yields of intermolecular crosslink

G_x and scissioning G_s were calculated according to the following formulas (O'Donnell, 1991; Olejniczak, 1991; Charlesby, 1960) and reported in Table 1:

$$\frac{1}{M_w} = \frac{1}{M_{w,0}} + \frac{1}{2}(G_s - 4G_x)D_x \cdot 1.038 \cdot 10^{-7} \qquad (1)$$

$$\frac{1}{M_n} = \frac{1}{M_{n,0}} + (G_s - G_x)D_x \cdot 1.038 \cdot 10^{-7} \qquad (2)$$

where, $M_{w,0}$ and $M_{n,0}$ are respectively the weight average and number average molecular weight of non-irradiated samples and M_w and M_n the corresponding values at the dose D_x expressed in kGy.

Table 1 – Yields of chain scission Gs and crosslinking Gx of polymer samples as a function of the absorbed dose and sample thickness.

Polymer	Dose (kGy)	1 mm			200 µm		
		G_s	G_x	G_s/G_x	G_s	G_x	G_s/G_x
PBS	25	1.90	0.23	8.14	1.50	0.32	4.67
	50	2.60	0.44	5.89	1.84	0.35	5.24
	100	2.46	0.37	6.66	1.57	0.28	5.55
	200	3.98	0.63	6.33	1.82	0.29	6.35
	500	4.17	0.74	5.61	2.53	0.51	5.00
P(BS90TDGS10)	50	3.51	0.62	5.68	4.10	0.88	4.67
	100	3.27	0.65	4.99	4.86	0.71	6.80
	200	3.23	0.57	5.64	6.65	0.81	8.20
	500	3.20	0.57	5.61	10.24	1.30	7.87
P(BS80TDGS20)	50	3.91	0.65	6.01	6.75	0.54	12.49
	100	3.35	0.62	5.36	2.69	0.25	10.81
	200	3.32	0.52	6.45	5.39	0.62	8.74
	500	2.76	0.41	6.82	5.18	0.69	7.51
P(BS70TDGS30)	50	3.34	0.48	6.91	7.72	0.78	9.90
	100	3.00	0.51	5.87	4.89	0.62	7.91
	200	3.34	0.45	7.50	5.62	0.64	8.76
	500	3.07	0.40	7.73	6.53	0.75	8.70
P(BS60TDGS40)	50	3.09	0.39	7.88	8.76	0.52	16.73
	100	1.85	0.38	4.93	4.39	0.53	8.28
	200	2.50	0.42	5.93	3.95	0.52	7.62
	500	1.46	0.22	6.58	5.05	0.71	7.08

The results highlighted some differences between the homopolymer and the copolymers series as well as between films and sheets. For PBS films, M_n strongly decreases with increasing the absorbed dose displaying a change of slope at 150 kGy (see Figure 2). The initial radiation doses resulted in a drastic decrease in M_n, attributable to the rupture of long polymeric chains in shorter segments causing the massive formation of alkyl free radicals within both the amorphous and crystalline region. Both the ionization and excitation mechanisms are expected to be operative in the chain scission of polar polyester chains, with the anionic path being well defined on the base of pulse radiolysis studies and the EPR identification of the intermediates (Ayscough and Oversby, 1972). For absorbed doses in the range 100-200 kGy, the main scission mechanism could become hydrogen abstraction, mainly at the favored sites adjacent to the ester group, which implies a less pronounced effect on the decrease of molecular weight, as shown in Figure 2. Moreover, with further increasing the absorbed dose (above 200 kGy) a relative increase of cross-linking with respect to chain scission could take place, corresponding to a decrease of the G_s/G_x ratios (see Table 1). Anyway, G_s/G_x ratios higher than 4 confirm chain scission as the dominant mechanism even at higher doses. Chain branching arisen from cross-linking or radicals recombination also leads to a less uniform distribution of chain length as suggested by the increasing trend of PDI values for absorbed doses higher than 150 kGy (see Figure 2). This kind of behavior was already observed and reported in literature for PLA polymer (Gupta and Deshmukh, 1982; Loo et al., 2005).

Concerning the copolymers, one can see that by introducing TDGS units, M_n decreases faster with the absorbed dose than PBS films (M_n is more than halved over 100 kGy) showing the same change in slope at 150 kGy (Figure 2). The attitude of sulfur to expand its valence shell coupled with a lower ionization potential and the weakness of the C-S bond (Chatgilialoglu and Guerra, 1993) are the base for justifying the profound effects observed following the insertion of the thioether function in the polymer chains. By considering the electron scavenging properties of the ester groups and the lower ionization energy of the thioethers, it is reasonable to assume that the latter groups are suited to act as scavengers of positive charges giving the $S^{+\cdot}$ cation radicals, whose existence has been assessed by matrix EPR spectroscopy (Quin et al., 1987). Within this hypothesis, charge neutralization should afford the necessary excitation energy for the chain scission via the splitting of the weakest C-S bond.

The results observed for copolymers can be ascribed also to the different crystallinity degree of the copolymers with respect to PBS, as evidenced by DSC results reported in Table 2. In particular, copolymerization with the introduction of C-S linkages in the polymer chains leads to a reduction of the crystallinity degree. According to the principles of radiation chemistry, radiation energy is deposited uniformly in matter, leading to radicals formation in both the crystalline and amorphous regions. However, the radicals reaction paths after irradiation are different in the two regions (Loo et al., 2005). In the crystalline region, polymeric chains are more oriented and closely packed and this characteristic favors radicals recombination and limits oxygen diffusivity, resulting in the dominant formation of alkyl free radicals, that can recombine each other, with respect to peroxyl free radicals. In this view, it is not surprising that the introduction of heteroatoms along the polymer chains strongly affects the stability towards ionizing radiations (Chatgilialoglu and Guerra, 1993; Chatgilialoglu, 1990; Sevilla et al., 1988). The same considerations could be inferred by the G_s values. At the highest absorbed doses, for all the copolymers films, crosslinking and chain scission balance each other, as indicated by the more modest M_n decrease and by the constant PDI values. In fact, at high radiation doses, alkyl free radicals are more numerous than peroxyl free radicals, due to the limited oxygen diffusion inside the polymer, and they are more likely to recombine or cross-link in the crystalline and amorphous regions respectively (Carlsson and Chmela, 1990).

Thick samples have been analyzed and a lower degradation was observed due to the limited oxygen permeation in the bulk of the sample (Figure 2). In the case of copolymers, M_n decreases at a lesser extent with respect to films, moreover the PDI values show a slight increase. This observation is coherent with the less oxidative conditions that favor the formation of alkyl free radicals and crosslinking via quaternary carbon atoms. On the contrary, the degradation observed in PBS sheets appears to be incoherent with the behavior of the corresponding films, since samples with higher thickness resulted to be more degraded, and the M_n decreases at the same extent of copolymers sheets. This unexpected behavior has not been yet clearly explained. It can be inferred that in PBS primary and secondary peroxy radicals are formed, which undergo mutual coupling with disproportionation to alcohols and carbonyls instead of alkoxy radicals according to the Russell mechanism (Russell, 1957). The lack of formation of alkoxy radicals, which are efficient generators of carbon radicals via H abstraction, will enhance the inhibition effect of oxygen with respect to branching and crosslinking reactions. Further studies are clearly needed to clarify the nature of the degradation of the primary radiolytic products and the lifetime of the species involved to better explain the behavior of the PBS sheets. For the copolymers, the very complex mechanism of the reaction of oxygen with sulfur radicals must be considered. Starting from the oxygen addition to thioyls, giving the unstable peroxyl intermediates $RSOO_{\cdot}$, whose existence has been definitely assessed by EPR, several sulfur/oxygen species are reported to be formed as the sulfinyl radicals ($R\text{-}S_{\cdot}(=O)$), the sulfonyl radicals ($RS_{\cdot}O_2$), the sulfonyl peroxyl radical ($RSO_2OO_{\cdot}$) and other species arising from oxygen addition to sulfuranyl and disulfide dimer radicals (Sevilla et al., 1988; Black et al., 1988). The oxygen/sulfur species do not show significant reactivity with respect to H abstractions, but may play a role in radical couplings thus contributing sulfur containing groups, like sulfones, to the polymer structure. The low reactivity of the sulfur/oxygen species suggest that the inhibition of the crosslinking and branching reactions by oxygen should not be significantly depressed with respect to PBS.

Table 2 - Thermal data, obtained by DSC in 200 µm films, as a function of the absorbed dose.

Dose		**[kGy]**	**0**	**50**	**100**	**200**	**500**
PBS	**T_g**	**[°C]**	-34	-34	-36	n.d.	n.d.
	T_m	**[°C]**	115	114	115	112	110
	ΔH_m	**[J/g]**	56	65	67	70	79
P(BS90TDGS10)	**T_g**	**[°C]**	-36	-35	-34	n.d.	n.d.
	T_m	**[°C]**	107	105	105	105	105
	ΔH_m	**[J/g]**	80	79	82	81	113
P(BS80TDGS20)	**T_g**	**[°C]**	-36	-35	-38	-38	n.d.
	T_m	**[°C]**	98	100	96	94	94
	ΔH_m	**[J/g]**	48	55	57	59	93
P(BS70TDGS30)	**T_g**	**[°C]**	-37	-35	-38	-39	n.d.
	T_m	**[°C]**	88	89	90	90	85
	ΔH_m	**[J/g]**	43	43	51	63	98
P(BS60TDGS40)	**T_g**	**[°C]**	-36	-36	-37	-36	-39
	T_m	**[°C]**	73	75	74	76	75
	ΔH_m	**[J/g]**	50	49	55	73	85

n.d.: not detectable

Although the interaction of radiations takes place uniformly in the whole polymer mass, the distribution of the radiolytic intermediates and the radiation damage are concentrated in the amorphous regions. DSC data for 200 µm films, showing a monotonic increase of ΔH_m for PBS, P(BS80TDGS20) and P(BS70TDGS30) and an increase above 200 kGy for the other copolymers (see Table 2), seem to suggest that the effect of irradiation in the amorphous phase of the polymer begins through a chain scission mechanism. Shorter chains orient themselves easier, producing an increase in the relative fraction of the crystalline regions. In the crystalline phase, because of the restraint to molecular motion, chain scissions are hindered by the high probability of the back reactions, radicals and radical ions cannot easily reach their lowest energy configuration and bimolecular interactions between not neighbor reactive centers are prevented. Consequently, phenomena of charge, energy and free valence migration take place toward the amorphous sites, which act as traps where a major part of the radiation damage is concentrated. Therefore, in the crystalline region, irradiation acts by creating defects, which generate less perfect crystallites due to chain segments recombination. This affects the melting temperature, which tends to decrease as observed in PBS and in some copolymers. For the sake of completeness, the experimental uncertainty due to DSC measurement of temperature does not exceed a few tenths of a degree centigrade. Moreover, the thermograms show a distortion of the melting peak and in some cases the formation of a little second melting peak towards lower temperatures, together with a similar cold crystallization peak. A few calorimetric traces concerning P(BS80TDGS20) at various irradiation doses are shown in Figure 3 as an example.

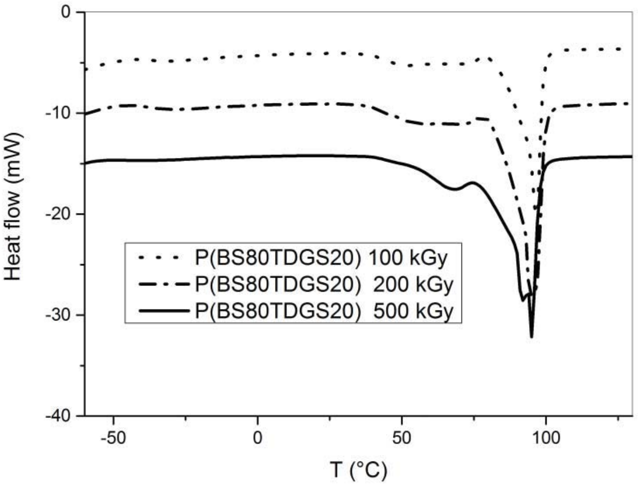

Figure 3 – DSC curves of P(BS80TDGS20) at different irradiation doses. Graphs were shifted for the sake of clarity.

The effect of the irradiation on the thermal stability of the samples under study was evaluated by thermogravimetric analysis. From the TGA curves shown in Figure 4, it can be noticed that in all cases the weight loss takes place in one step; in addition, TGA curves moved to lower temperature as absorbed dose increased. Such variations are in agreement with the observed reduction of molecular weight, due to the degradation of polymer chains into shorter segments with lower decomposition temperatures.

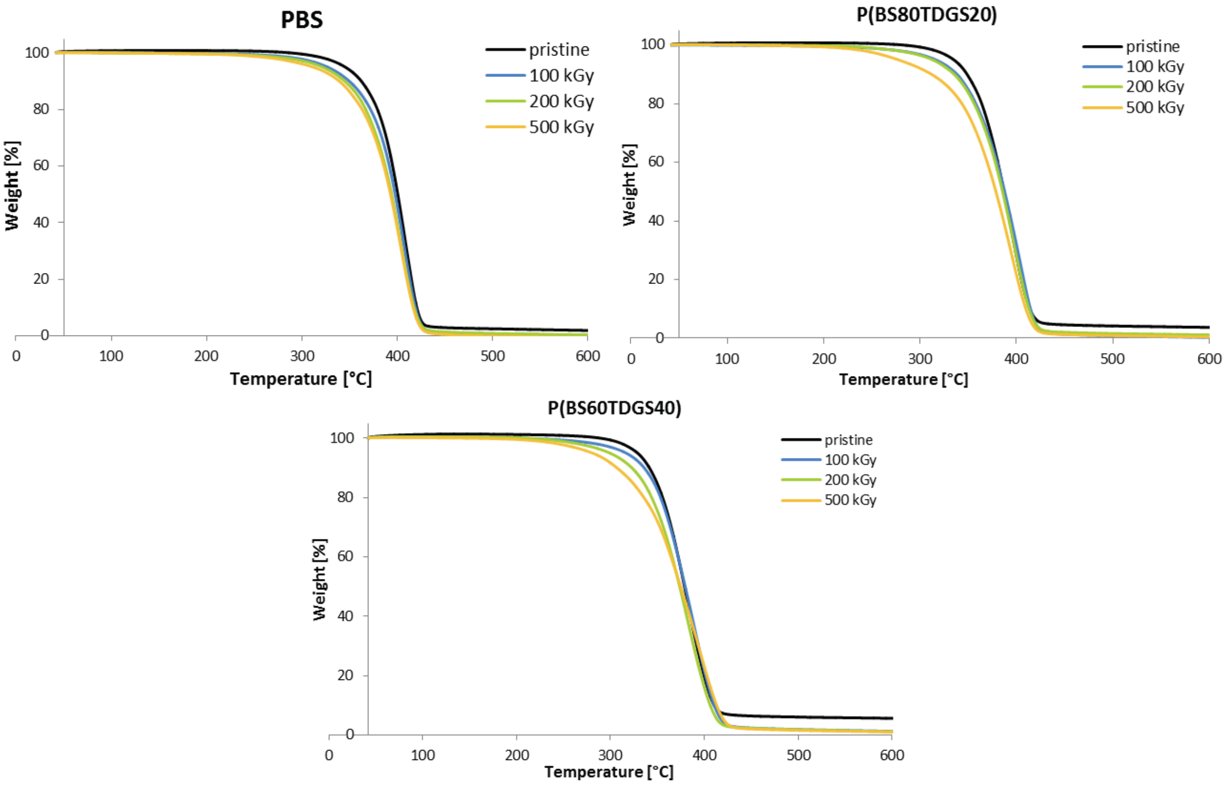

Figure 4. Thermogravimetric curves of PBS, P(BS80TDGS20) and P(BS60TDGS40) as a function of the absorbed dose (200 μm films).

The effect of the irradiation environment on the polymer modifications was also considered. According to the original observation by Charlesby (1960), the irradiation of polymers in water solutions greatly increases the crosslinking yield because of the obliteration of the direct radiolysis effects and its substitution with the reactions of species (OH and H radicals) with great affinity for H abstraction. A somewhat different situation applies in the present case, since the systems are far from being dilute water solutions and direct radiolysis effects on the polymers are still important. It can be envisaged that the Charlesby effect be significant only at the surface. GPC results of PBS and P(BS70TDGS30) samples irradiated in water up to 100 kGy are reported in Figure 5. Limited to the few samples treated, PBS films did not show significant differences in M_n with respect to films irradiated in air, while PDI values slightly increase. Differently, for P(BS70TDGS30) films a lower decrease of M_n can be seen along with increasing PDI values.

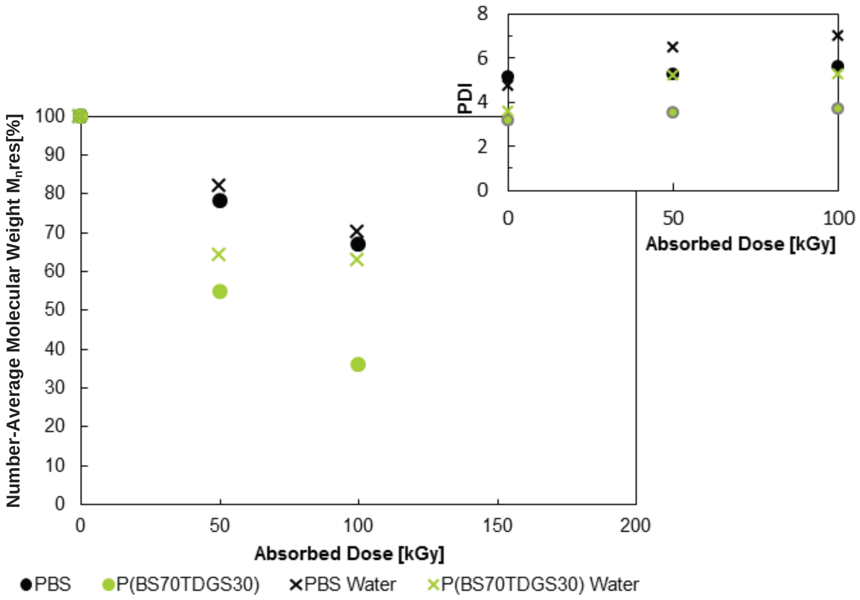

Figure 5. GPC results on 200 µm films: residual number-average molecular weight [M_n res%] (a) and polydispersity index (b) as a function of the absorbed dose and irradiation environment.

During irradiation, water undergoes the most of radiation damage, leading to the formation of free radicals, that can recombine each others, according to the following stoichiometry (Sharpatyi, 2006):

$$H_2O - \backslash\!/\!\backslash\!/\!\backslash\!\rightarrow [0.28]\,{}^{\cdot}OH + [0.27]e^{-}_{aq} + [0.06]H^{\cdot} + [0.07]H_2O_2 + [0.27]H_3O^{+} + [0.05]H_2 \qquad (3)$$

The most reactive radiolytic species are the oxidizing hydroxyl radical (HO·) and the reducing aqueous electron (e^-_{aq}), produced in approximately equal amounts. Under the aerated conditions used in the irradiation experiments, the aqueous electrons produced could be scavenged by the oxygen dissolved in solution, resulting in the formation of the superoxide radical ion (${}^{\cdot}O_2^-$). Superoxide radical ions can react with hydrogen ions (H^+) to form hydroperoxy radicals ($HO_2^{\cdot}$). Both the superoxide radical anions and hydroperoxy radicals lead ultimately to the formation of hydrogen peroxide that may act as an oxidizing agent. The reactive intermediates due to the direct water radiolysis can react with the polymer and its radicals mainly at the surface. The action of hydroxyl radicals could be the abstraction of hydrogen atoms from the polymeric chain bringing about the formation of alkyl radicals, which can produce oxygenated functions by reacting with water, oxygen or other radiolysis products. Therefore, with respect to irradiation in air, this could lead to a lower decrease of molecular weight, but to more relevant surface modifications that could affect polymers wettability and result crucial for facilitating microbial attack during the degradation process in compost. Moreover, the presence of sulfur in the polymer chains, and thus of the sulphur radicals, is a source of most significant changes in the mechanisms described above. In water solutions, the sulphur cation radicals ($S^{+\cdot}$) are reported to undergo deprotonation, yielding α-carbon radicals. Moreover, there are evidences from both EPR and pulse radiolysis studies that such cation radicals have the tendency to add to sulfur of neighbor thioether groups, giving the dimer cation-radicals. Chain splitting in the copolymers may also result from the charge neutralization of the latter species (Petersen et al., 1978; Monig et al., 1987). The oxidation of a variety of organic sulfides by hydroxyl radicals in aqueous solutions has been already reported in a number of studies by means of pulse radiolysis, showing the formation of a sulfuranyl intermediate, which can address different reversible pathways (Gilbert et al., 1973; Davies et al., 1984). Unfortunately, up to now, these considerations could not be validated by the qualitative infrared spectroscopic analyses performed. Indeed the FTIR-ATR investigations on both 200 and 40-µm films of PBS and copolymers did not highlight the formation of any new functional groups.

In order to investigate the free volume structure of the irradiated samples, several PALS measurements were performed. 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 in the macromolecular matrix that undergoes structural changes when exposed to physical factors such as ionizing radiation (Misheva, 2009, Mariani et al., 2007; Ravasio et al., 2007), environmental degradation (Brambilla et al., 2003) or crosslinking reactions in copolymers (Salgueiro et al., 2007)). PALS measurements allowed us to get insights on the free volume of the material, 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 unstable atom named positronium (Ps), which is 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 is due to the annihilation of ortho-positronium atom (o-Ps), the sublevel with parallel spins, into the holes present in the amorphous zones, therefore, it is used to probe the free-volume hole dimension (Wang and Jean, 1988). Indeed, o-Ps interacts with the electrons belonging to the cavity where Ps is trapped; its lifetime comes from the annihilations of the positron with one of such ‘external’ electrons in a relative singlet state (‘pickoff’ process) (Jean, 1995). This involves a correlation between o-Ps lifetime and the sizes of the cavity, which can be cast in a quantitative form by suitably modeling the trapping site. A longer o-Ps lifetime τ_3 is found in bigger holes because the lower electron density surrounding Ps reduces the probability of Ps annihilation. By assuming a spherical geometry a relationship between o-Ps lifetime τ_3 and the mean radius R of holes results, known as Tao-Eldrup equation (Tao, 1972; Eldrup et al., 1981):

$$\boldsymbol{\tau_3 = \tau_0\left[1 - \frac{R}{R+\delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\delta R}\right)\right]^{-1}} \qquad (4)$$

where, δR=1.66 Å is an empirical parameter and τ_0 (= 0.5 ns) is the annihilation lifetime of o-Ps in the presence of a high electron density. Although more complex topologies can be envisaged (Consolati et al., 2005), in this work we considered the simplest (spherical) approximation for the holes. Cavities show a distribution of sizes, due to the disordered character of the amorphous zone. This involves a distribution of o-Ps lifetimes, which is supplied from the analysis of annihilation lifetime spectra. Holes size distribution is obtained through a simple mathematical treatment of the distribution of lifetimes (Consolati, 2002). Table 3 reports centroid R and second moment σ of the normalized holes size distribution, as obtained from the PALS measurements. PBS and copolymers do not display significant variations of the distribution parameters as the absorbed doses increase by taking into account the experimental uncertainties (4% for the centroid and 15% for the second moment). Ionizing radiation induces a rearrangement of the broken chains that causes an increase of crystallinity of the samples. Although the hole sizes of our copolymers do not undergo significant variations with respect to the pristine samples, however, their number density decreases due to the diminution of the amorphous zones. This is evidenced by the decrease of o-Ps intensity as shown in Table 3. Indeed, the normalized amount of o-Ps yield, as measured by the corresponding intensity I_3, is correlated to the number density of holes, which are found only in the amorphous zones of the polymer. Therefore, any change of crystallinity influences I_3. In conclusions, PALS measurements are in perfect agreement with calorimetric results.

Table 3 – PALS results on 1 mm samples: intensity of o-Ps decay (I_3), correlated mean radius (R) of nanoholes and relative dispersion (σ) as a function of the absorbed dose. Uncertainties of I_3 is evaluated to be 5%.

	Dose	**[kGy]**	**0**	**100**	**200**	**500**
PBS	**I_3**	**[%]**	21.2	19.8	19.6	19.0
	R	**[nm]**	0.42	0.39	0.41	0.41
	σ	**[nm]**	0.10	0.10	0.10	0.10
P(BS90TDGS10)	**I_3**	**[%]**	21.4	20.2	19.2	17.2
	R	**[nm]**	0.41	0.40	0.39	0.40
	σ	**[nm]**	0.10	0.10	0.09	0.09
P(BS80TDGS20)	**I_3**	**[%]**	21.8	20.8	19.8	18
	R	**[nm]**	0.40	0.39	0.38	0.39
	σ	**[nm]**	0.09	0.09	0.08	0.08
P(BS70TDGS30)	**I_3**	**[%]**	22.4	21.1	19.9	18.3
	R	**[nm]**	0.41	0.39	0.38	0.38
	σ	**[nm]**	0.10	0.09	0.08	0.08
P(PB60TDGS40)	**I_3**	**[%]**	22.1	21.6	20.1	18.7
	R	**[nm]**	0.40	0.41	0.37	0.38
	σ	**[nm]**	0.09	0.10	0.08	0.08

Surface modifications

Water contact angles (WCA) measurements were performed on PBS and copolymers films irradiated both in air and in water, in order to investigate radiation-induced modifications of the polymers surface and its effect on their wettability, being this parameter strictly related to the microorganisms capability to attack polymer surface. The contact angle of PBS films (around 90°) did not change when the homopolymer is irradiated in air, while seems to decrease when the sample is irradiated in water, of about 8% at 50 kGy and 17% at 100 kGy. This could be an evidence of the homopolymer surface modification caused by the reactive species generated after irradiation in water, as discussed before. Differently, in both the irradiation conditions, the wettability of PBS-based copolymers increases with the absorbed doses, especially in air. For example, as reported in Table 4, the contact angle for pristine P(BS70TDGS30) is 81° ± 3°, and it decreases to 69° ± 2° after treatment at 100 kGy in air, and to 75° ± 2° when irradiated at the same dose in water, in accordance with GPC results, that evidenced higher M_n decrease for the sample irradiated in air. Scanning electron microscopy has been used to study the surface of polymers after irradiation at different absorbed doses, without evidencing relevant macroscopic modifications.

Table 4. Water contact angles vs absorbed dose for PBS and copolymers 200 μm films irradiated in different conditions.

Sample	Irradiation environment	Contact angle [°]		
		Pristine	50 kGy	100 kGy
PBS*	air	90 ± 3	89 ± 2	95 ± 3
	water		83 ± 3	75 ± 2
P(BS90TDGS10)	air	84 ± 2	80 ± 1	77 ± 1
P(BS80TDGS20)	air	83 ± 3	74 ± 2	72 ± 1
P(BS70TDGS30)	air	81 ± 3	73 ± 2	69 ± 2
	water		78 ± 3	75 ± 2
P(BS60TDGS40)*	air	83 ± 2	85 ± 1	70 ± 3
	water		77 ± 3	74 ± 2

* as film of 40 μm thickness

Radiation effects on biodegradation

The results obtained by the physical and chemical characterization of the PBS-based copolymers allowed us to address the composting experiments. The surface wettability enhancement observed after exposure to radiation, along with the decrease of molecular weight, suggest polymer modifications that should favor the attack by microorganisms and thus degradation. However, results from disintegration tests provided different indications. After 52 days of incubation, the reference Mater-Bi® samples are completely destroyed, confirming the validity of the tests, and the same was observed for the copolymer with the highest TDGS co-unit percentage (40%), both pristine and irradiated in air. The degree of disintegration determined for the PBS-based copolymers appeared to be very high with respect to PBS, indicating that the introduction of sulphur atoms along the polymer chains deeply affects microbial attack. As shown in Figure 6, the P(BS70TDGS30) and P(BS80TDGS20) samples displayed an increasing degradation with increasing the absorbed dose. As an example, the pristine samples of P(BS70TDGS30) showed a residual weight of about 35% (see Figure 6), while those irradiated in air at 100 kGy of about 10%. PBS as well as P(BS90TDGS10) copolymers showed a completely different behaviour: when irradiated at 100 kGy in air both samples appeared to be more resistant to degradation. Coherently with the increase of crystallinity suggested by the DSC results (increase of ΔH_m) and further confirmed by means of PALS results (decrease of I_3), the broken molecular chains are still hard to be destroyed by microorganisms. As previously reported by Yoo and Im (1999) and confirmed by other studies (Gigli et al., 2012), the initial stage of the degradation process consists in the hydrolytic scission of the ester bonds within the amorphous region: the molecules are loosely packed and they are more susceptible to the attack by degrading agents. According to the collected results, it seems that a decreasing residual weight with increasing the absorbed dose was observed in the PBS-based copolymers with a percentage of TDGS unit ≥ 20%. This behavior is associated with a similar M_n decrease, an increase of ΔH_m, corresponding to an increase of cristallinity, and a decrease of the water contact angle, corresponding to an increase of hydrophilicity. Contrarily, in PBS and P(BS90TDGS10) samples, at 100 kGy the residual weight increases, so that the samples resulted to be more resistant than the pristine ones. Despite M_n decreases at different extent, crystallinity changes only in PBS and hydrophilicity only in the P(BS90TDGS10), a similar degradation in compost was obtained. The higher crystalline portion of such samples, further increased by radiation, is hardly attacked by microorganisms and thus lower weight losses are observed. The overall behavior of the homopolymer and the copolymer with the lowest TDGS content can be explained on the basis of the different radiation effects balance each other in the system.

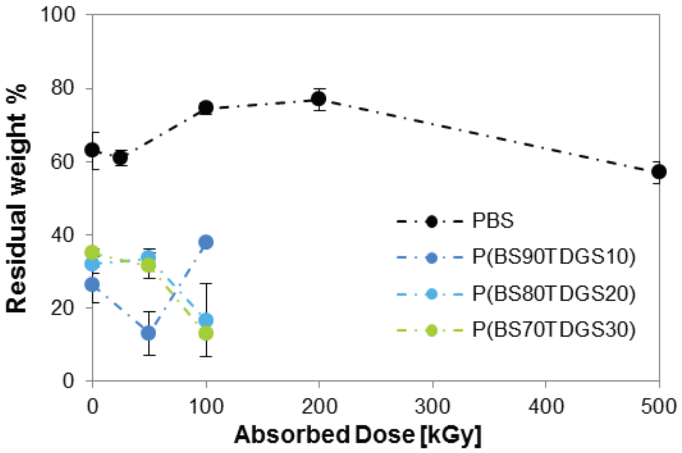

Figure 6. Residual Weight % as a function of the absorbed dose for 200 µm films of PBS and P(BSxTDGSy) copolymers irradiated in air after 52 days in compost.

Biodegradation experiments carried out on PBS and its copolymers irradiated in water proved the potential effectiveness of the radiation treatment. Indeed, after 52 days in compost, pristine PBS showed a residual weight of 62%, while PBS irradiated in air at 100 kGy resulted to be more resistant (residual weight 77%, after 52 days). On the contrary, PBS films irradiated in water at 25 and 100 kGy exhibit a residual weight of about 44% and 40%, respectively. For P(BS70TDGS30) copolymer, irradiation in water at 100 kGy implied only a slight improvement in biodegradation with respect to the treatment in air at the same absorbed dose, coherently with the observed M_n and wettability changes. Disintegration tests performed with the samples irradiated at the highest doses (500 kGy) encountered some difficulties in the polymer recovery during the composting experiment, due to the sample brittleness induced by radiation. Furthermore, the morphology of the polyester films, was analyzed by Scanning Electron Microscopy before and after the composting tests. First of all, SEM images, reported in Figure 7, highlighted surface modifications in agreement with weight loss measurements. Comparing the SEM analyses of the pristine PBS samples before and after composting, only a slight attack of the samples surface can be noted (Figure 7). With increasing the absorbed dose, erosion and cracks start to appear. Clear evidences of degradation can be observed in the SEM images of PBS samples irradiated in water, already at low absorbed doses. In addition, Figure 7 shows also SEM micrographs for the copolymer P(BS70TDGS30), for which in general surface morphological changes are much more evident. In particular, erosion, cracks and holes are already present in the pristine sample after incubation in compost and become even more evident in the samples irradiated in air, especially at 50 kGy. Concerning the P(BS70TDGS30) films irradiated in water, those ones treated at 50 kGy present erosion and big holes, while at 100 kGy the surface is smooth with small holes. The smooth surface revealed by SEM for samples at 100 kGy after compost results from the complete erosion of the superficial layer by microorganisms, leading to an apparently less damaged surface but a lower residual weight.

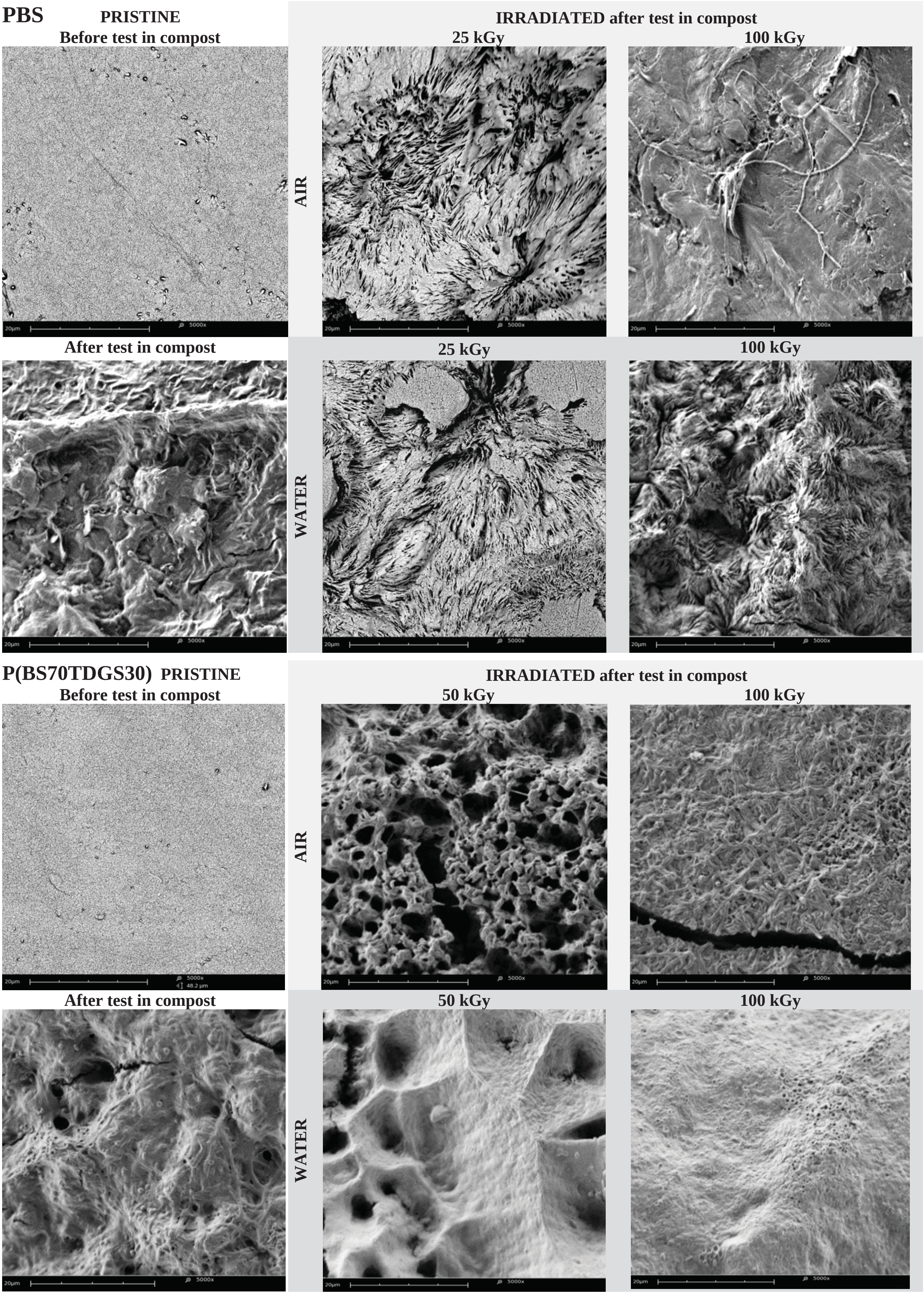

Figure 7. SEM photographs of pristine and irradiated PBS and P(BS70TDGS30) 200 µm films after 52 days of degradation in compost.

4. Conclusions

The need of new plastic materials that are appropriate for specific technological applications and that fulfill sustainability criteria has addressed the research efforts towards different solutions with a common goal, the reduction of environmental pollution due to plastic accumulation. The present research work contributes to this scenario by investigating the behavior under gamma irradiation of new PBS-based random copolymers containing thioether linkages, interesting for their processing properties, and by assessing how gamma radiation can affect the polymer degradability in compost. As expected, aliphatic copolyesters proved to be very sensitive towards radiation, in particular the higher the amount of sulphur-containing co-unit (TDGS), the higher the sensibility. In general, for both PBS and copolymers gamma irradiation modifies polymer crystallinity and wettability and, consequently, their degradation rate in compost. Interestingly, a relevant difference was observed in the experiments where PBS was irradiated in solution rather than in air. Indeed, while PBS irradiated in air at 100 kGy resulted to be more resistant than the pristine one, PBS irradiated in water at the same absorbed dose degraded faster. The obtained results highlighted that gamma irradiation under suitable conditions could be considered a viable treatment to enhance biodegradation in compost of slow degrading polymers.

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