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ORIGINAL PAPER

Effect of Gamma Irradiation on Fully Aliphatic Poly(Propylene/Neopentyl Cyclohexanedicarboxylate) Random Copolymers

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Abstract

The widespread use of conventional petrochemical-based plastics and their low biodegradability led to a growing pollution issue. Among the class of the aliphatic polyesters, poly(propylene/neopentyl cyclohexanedicarboxylate) [P(PCExNCEy)] random copolymers combine promising physical–chemical properties and biodegradability features but they are characterized by slow degradability. The effect of gamma radiation on both chemical-physical properties and compostability was evaluated by several techniques on different samples irradiated in air at absorbed doses up to 500 kGy and in water or under oxidative atmosphere up to 100 kGy. According to the results obtained, exposure to radiation significantly affects polymer molecular weight and hydrophilicity, while crystallinity remains unaltered and biodegradability is only slightly influenced. In particular, among the different irradiation environments used, irradiation in water seems to favor the polymer degradation in compost.

Keywords Aliphatic polyesters · Random copolymers · 1,4-Cyclohexanedicarboxylic acid · Gamma irradiation · Compostability

Introduction

Plastic pollution is one increasing issue due to the large amount of wastes that has been accumulating in the environment, caused by the long durability of conventional petrochemical-based plastics. In particular great concern has risen recently about the health and environmental effects caused by microplastics and their additives consumed by marine microorganisms that finally enter the food web [1–3]. Consequently, new synthetic materials more ecofriendly have been studied [4], but the high production costs along with the poorer properties limit their introduction in the market. Aliphatic polyesters containing 1,4-cyclohexylene rings have attracted considerable attention as they combine the features of biodegradability with physical and chemical properties comparable with some of the most extensively used polymers, like LDPE, PP, etc. [5]. In addition, it was proved that the presence of an aliphatic ring along the polymer backbone confers high melting temperature, good thermal stability, good resistance to weather, heat, light and moisture, and interesting mechanical properties still maintaining biodegradability [6]. Different studies concern the effects of the introduction of 1,4-cyclohexylene rings into the polyester chains as a replacement of the aromatic moieties to increase the degradability [7–12, 9, 10, 11, 12]. Moreover, Commereuc et al. [12] showed that aliphatic cyclic units degrade after exposure to long UV degradation times.

Nowadays polymers could be exposed to radiation during their lifetime, e.g. for gamma sterilization. Ionizing radiation treatment of polymer materials can affect the polymer itself modifying its physical, chemical and biological properties due to its ability to cause crosslink or scission and oxidation of a wide range of materials [13]. It is well known that polymers containing aliphatic structure are sensible to

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radiations [14, 15] but there are no systematic studies on the radiation induced effects in aliphatic polyesters containing cyclohexylene rings. The ionizing radiation effects on cyclic compounds lead to carbon-hydrogen bond breakage and, in the case of cyclohexane, the resulting molecular radicals disproportionate and the H atom mainly combines or undergoes H abstraction [16, 17].

The potential compostability is a key factor for the employment of new materials as packaging. The treatment with gamma radiation could facilitate the biodegradation of polymers by inducing its oxidative fragmentation [18–20]. The biodegradability of polyesters, due to the presence of hydrolysable ester bonds, depends on several factors but high molecular weights could extend the timescale of degradation. Although aliphatic polyesters are already characterized by the presence of many functional groups that assure the complete degradation under microbial attack, the kinetic of this process could be extremely slow, depending on many environmental factors such as temperature, humidity, pH and solar energy. The degradation process could be optimized and fastened but no attempts to exploit pre-irradiation for promoting biotreatment of these polyesters have been apparently made so far.

In this framework, the present research work focused on the evaluation of the effect of gamma radiation on chemical-physical properties of fully aliphatic poly(propylene/neopentyl cyclohexanedicarboxylate) [P(PCE_xNCE_y)] random copolymers, reported in Fig. 1, whose general properties have been already presented in a previous paper [21]. The good processability of these polymers makes them good candidates for film applications, such as packaging, in which the materials can be treated with radiation before use and become waste in a short period. In this perspective, the experimental activities were addressed to investigate if a radiation treatment of the polymer in an environment promoting oxidative degradation could represent an effective pre-treatment for improving their biodegradation by inducing suitable structural modifications. For this purpose, samples were irradiated in air, oxygen atmosphere and water at absorbed doses up to several hundreds of kGy and then fully characterized by different analytical techniques.

Materials and Methods

Materials, Samples Preparation and γ-Irradiation

Poly(propylene cyclohexanedicarboxylate) and poly(neopentyl glycol cyclohexanedicarboxylate) homopolymers (PPCE and PNCE) and poly(propylene/neopentyl cyclohexanedicarboxylate) random copolymers [P(PCExNCEy)] were synthesized according to the two-stage polymerization procedure previously reported by using *trans*-1,4-dimethylcyclohexane dicarboxylate (DMCE, 99%) [21]. Polymers, in form of powder, were molded into 1 mm thickness sheets and 200 μm thickness films by first heating at 30 °C above the melting temperature and holding for 4 min and then increasing the molding pressure to 2 ton m^{-2}. The molds were immediately quenched at room temperature. Irradiation was carried out with a Co-60 gamma source with a dose rate of 2.5 kGy h^{-1}, allowing uniform exposure. Each sample was treated in air at adsorbed doses up to 500 kGy. A second irradiation campaign was performed plunging the samples into a fixed amount of deionized water or in oxygen atmosphere by applying absorbed doses up to 200 kGy. Finally, samples were 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). Possible chemical changes were studied by infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR). The degradation after irradiation was evaluated by disintegration tests based on the ISO-20200 standard method.

Molecular Weight

The weight average molecular weight (M_w) and number average molecular weight (M_n) were determined at 30 °C using a 1100 Hewlett Packard system equipped with a PL gel 5 m 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

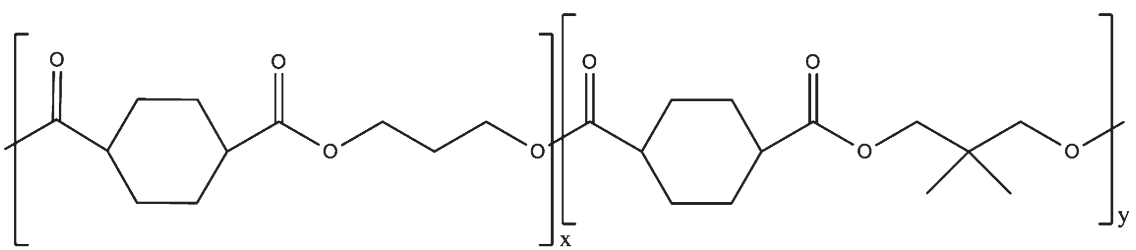

Fig. 1 Chemical structure of poly(propylene/neopentyl glycol cyclohexanedicarboxylate), P(PCExNCEy)

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sample concentrations of about 2 mg mL^{-1} were applied. The calibration was done using 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. The measurements have been carried out in triplicate.

Thermal Properties

A Mettler Toledo differential scanning calorimeter (DSC 822e) calibrated with high purity standards (indium and zinc) was used to evaluate thermal properties. Samples (c.a. 5 mg, 200-μm film or 1-mm sheet) were encapsulated in aluminum pans and heated to about 20 °C above melting temperature at a rate of 20 °C min^{-1} (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, thermal stability of the polymers was studied using a Perkin Elmer TGA 4000 apparatus in nitrogen atmosphere (gas flow: 30 mL min^{-1}) at a heating rate of 10 °C min^{-1} up to 850 °C. The temperature of initial decomposition (T_{id}) and of the maximum degradation rate (T_{max}) were determined.

Positron Annihilation Lifetime Spectroscopy

A conventional fast–fast coincidence time spectrometer with a time resolution of 250 ps was used for PALS measurements, in order to investigate the free volume features of the samples. The positron source (^{22}Na, activity 0.3 MBq) was deposited in an envelope of two Kapton® foils (7.5 μm thick) and sandwiched between two samples of the investigated polymers. The samples thickness was enough to stop all the injected positrons. Three spectra of about 5×10^6 counts were collected for each polyester at room temperature. LT program [22] was used to analyze the spectra into three components allowing the determination of the lifetimes and the relative intensities.

Surface Characterization

In order to investigate the radio-induced modifications of polymers surface, chemical changes of polymer backbone, wettability and surface morphology were examined as a function of the absorbed dose.

FTIR analyses were carried out with a Nicolet Nexus FTIR spectrometer on pristine and irradiated samples of PPCE and P(PCE80NCE20). This apparatus was set up with a single bounce ATR probe made in silicon, which allows the analysis of the surface of the polymer over the 4000–700 cm^{-1} wavenumber range. The ATR system is equipped with a load cell which allows to control the contact pressure of the ATR probe on the sample. Furthermore, a glass slide was placed between the load cell and the sample ensuring better contact between the film and the crystal, thus allowing the same depth to be analyzed for each sample. The penetration depth of IR light (1700 cm^{-1}) into the sample was estimated to be about 0.5 μm. The infrared spectra were recorded after an accumulation of 32 scans with a resolution of 4 cm^{-1}. To make easier comparison, each spectrum was baseline corrected and the intensity of the whole spectrum was normalized to the reference peak at 1721 cm^{-1}, corresponding to the C=O stretching vibration.

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

SEM images of polymers films were acquired using a field emission scanning electron microscope (FE-SEM) working in high vacuum Zeiss Supra 40 equipped with the GEMINI column. Images were acquired under vacuum by gluing films on aluminum stabs with carbon tape.

Disintegration Experiments Under Simulated Composting Conditions

The disintegration experiments were performed on pristine and irradiated PPCE and P(PCE85NCE15) samples, following a procedure based on the ISO-20200 standard method. First, the initial mass of each sample was assessed placing it under vacuum to constant weight. Then, a weighted amount of mature compost was added to each specimen in a suitable vial and incubated at 58 °C for different periods, maintaining humidity at 90% of the water holding capacity of the system. The disintegration tests lasted from a minimum of 45 days up to 90 days. After the incubation period, samples were sieved at 2 mm, accurately washed by dipping in aqueous sodium dodecyl sulphate solution (2%) and finally dried under vacuum to constant mass. The disintegration in compost was evaluated on visual appearance and quantified by the determination of the samples weight loss. Further indications could be

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deduced by SEM investigations. 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.

Results and Discussion

Physical Characterization

Sample irradiation was performed with a Co-60 gamma-ray source in air atmosphere on both films and sheets of PPCE and PPCE–PNCE copolymers. Some physical changes were observed in samples irradiated above 200 kGy, such as embrittlement. Figure 2 shows the residual number-average molecular weight percentage values (M_n[%]) of PPCE and copolymers samples, together with the polydispersity index (PDI), as a function of the absorbed dose. The number-average molecular weight (M_n) of pristine samples ranges from about 25,000 to 23,000 g mol^{-1} for PPCE and its copolymers with increasing the NCE co-unit percentage. In general, M_n strongly decreases with increasing the absorbed dose and PDI index increases. In the case of films, the residual number-average molecular weight exhibits the same trend for all the samples, characterized by a change of slope just sketched beyond 150 kGy. As shown in Fig. 2 (*top*), at 200 kGy the M_n is almost halved and at 500 kGy the M_n[%] is around 20–30%. Lastly, no appreciable copolymerization effect has been evidenced in the composition range $0 < X_{NCE} < 0.2$.

As expected, due to the different permeation of oxygen within the sample, a lower degradation is observed in the case of sheets with respect to films. The decrease of molecular weight is almost linear with the absorbed dose, displaying a even less noticeable change of slope over 150 kGy (see Fig. 2, *bottom*), linked to the increase of PDI. At 500 kGy the M_n[%] is around 30–40%.

The decrease of molecular weight is the result of two competing phenomena, cross-linking and chain scission, induced by exposure to high energy radiation. By using the molecular data, the yields of intermolecular crosslink G_x and scissioning G_s were calculated according to the following formulas [23–25]:

$$\frac{1}{M_w} = \frac{1}{M_{w,0}} + \frac{1}{2}\left(G_S - 4G_x\right)D_x \times 1.038 \times 10^{-7} \quad (1)$$

$$\frac{1}{M_n} = \frac{1}{M_{n,0}} + \left(G_S - G_x\right)D_x \times 1.038 \times 10^{-7} \quad (2)$$

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.

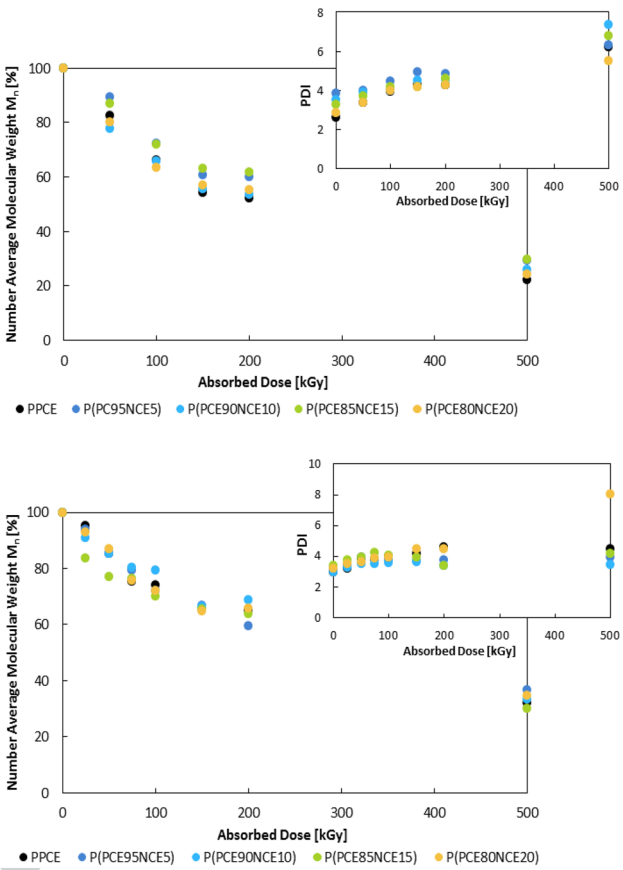

Fig. 2 GPC results: residual number-average molecular weight percentage (Mn[%]) and polydispersity index (PDI) as a function of the absorbed dose and sample thickness: 200 µm (top) and 1 mm (bottom)

According to the values reported in Table 1, the G_s/G_x ratios are slightly higher than 4, without a clear trend with the absorbed dose, suggesting that chain scission is predominant and causes the M_n decrease despite crosslink is present. Chain branching arisen from cross-linking or radicals recombination 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 Fig. 2). This kind of behavior was already observed and reported in literature for poly(alkylene dicarboxylate)s [26, 27]. Even if no further M_n reduction can be clearly observed with increasing NCE content, the presence of neopentyl glycol units could represent a weak point inside the copolymer structure, more prone to cleavage than propanediol subunit, and the recombination of radicals originated from the NCE unit could be limited by the presence of methyl groups and their steric hindrance. Moreover, the G_s/G_x ratios are slightly higher for films with respect to sheets, because of the lower oxygen permeation and thus the less oxidative conditions in the latter that favor crosslink.

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Table 1 Yields of chain scission G_s and crosslinking G_x of polymer samples as a function of the absorbed dose and sample thickness

Polymer	Dose	1 mm			200 μm		
		G_s	G_x	G_s/G_x	G_s	G_x	G_s/G_x
PPCE	50	1.78	0.39	4.57	3.93	0.79	4.94
	100	1.83	0.38	4.75	3.45	0.72	4.80
	150	1.86	0.42	4.41	3.38	0.69	4.90
	200	1.42	0.32	4.44	2.70	0.54	5.02
	500	2.29	0.54	4.25	3.68	0.76	4.87
P(PCE95NCE5)	50	1.80	0.40	4.50	1.34	0.25	5.43
	100	2.02	0.44	4.61	2.24	0.45	4.99
	200	1.83	0.43	4.29	1.93	0.39	4.95
	500	1.89	0.46	4.09	2.80	0.57	4.90
P(PCE90NCE10)	50	2.01	0.34	5.84	3.26	0.61	5.39
	100	1.54	0.29	5.30	2.95	0.52	5.71
	200	1.37	0.29	4.73	2.49	0.48	5.22
	500	2.47	0.57	4.33	3.40	0.74	4.60
P(PCE85NCE15)	50	3.23	0.84	3.85	1.78	0.42	4.21
	100	2.28	0.55	4.10	2.25	0.50	4.53
	200	1.51	0.38	3.98	1.80	0.40	4.49
	500	2.47	0.59	4.17	2.74	0.60	4.58
P(PCE80NCE20)	50	1.72	0.48	3.59	2.61	0.58	4.50
	100	2.07	0.46	4.50	3.01	0.67	4.50
	200	1.47	0.38	3.86	2.12	0.46	4.62
	500	2.06	0.49	4.20	3.19	0.63	5.03

Radiolytic Degradation Mechanism

The radiolytic behavior of PPCE–PNCE copolymers can be inferred by studies conducted on the sub-units present in their structure. The radiolytic mechanism of simple carboxylic acids and esters proceeds via ionic and free radicals major pathways leading to a complex mixture of end products which include carboxylic acids, alcohols, CO, CO_2, H_2 and hydrocarbons [28–30]. The radiolytic behavior of the ester functional groups $R_2CH–(C(=O)O)–CH_2–$ in the polymers and copolymers under study is suggested to proceed through electron capture and electron loss events, leading to the formation of anionic and cationic radicals:

$$R_2CH{-}C(=O)O{-}CH_2{-} + \gamma \rightarrow\rightarrow R_2CH{-}(C(=O)O)^{-\cdot}, \; R_2CH(C(=O)O)^{+\cdot}CH_2 \quad (3)$$

The anionic radicals, $R_2CH–(C(=O)O)^{-\cdot}$, proceed through chain scission according to the following reactions:

$$R_2CH{-}(C(=O)O)^{-\cdot}{-}CH_2 \rightarrow R_2CH{-}C(=O)O^{-} + {-}CH_2^{\cdot} \quad (4)$$

$$R_2CH{-}(C(=O)O)^{-\cdot}{-}CH_2 \rightarrow R_2CH{-}C^{\cdot}(=O) + {-}CH_2O^{-} \quad (5)$$

$$R_2CH{-}C^{\cdot}(=O) \rightarrow CO + {>}CH^{\cdot} \quad (6)$$

The cationic path instead envisages intramolecular and intermolecular H transfer according to the following reactions:

$$R_2CHC(=O^{+\cdot})O{-}CH_2{-} \rightarrow R_2CH(C(=OH^{+})OCH^{\cdot}{-} \quad (7)$$

$$R_2CHC(=O^{+\cdot})O{-}CH_2{-} + R_2CH{-}C(=O)O{-}CH_2 \rightarrow R_2CH{-}(C(=OH^{+})O{-}CH_2{-} + R_2C^{\cdot}{-}C(=O)O{-}CH_2{-}\,(a), R_2CH{-}C(=O)O{-}CH^{-}(b), {-}CH_2{-}CH^{\cdot}{-}{-}CH\,R_2(c), \; R_2CH{-}CH^{\cdot}{-}CH2{-}\,(d) \quad (8)$$

The H abstractions may not be restricted at the sites bearing the weakest C–H bonds (radicals a and b) but they may also take place at secondary C–H bonds within the propylene (radicals c) and cyclohexane (radicals d) sections being favored by the eventual juxtaposition of reacting centers in neighboring chains (intermolecular) or through the attainment of suited ring configurations (intramolecular).

Despite GPC results did not clearly show that with increasing the NCE percentage chain scission increases over crosslinking, as compared to PPCE homopolymer, the neopentyl units in the PNCE homopolymer could display a higher cationic and excitation contributions to chain scission according to the following reaction:

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$$R_2CH_2{-}C(=O)O{-}[CH_2C(CH_3)_2CH_2{-}]^{+\cdot} \rightarrow {-}CH_2{-}C(=O)O{-}CH_3 + [CH_2{=}C(CH_3)CH_2{-}]^{+\cdot} \quad (9)$$

The electron loss events localized in the neopentyl moiety may have a role in prompting also the homolytic chain scissions at the quaternary carbon following charge neutralization and decomposition of the excited intermediate:

$$-CH_2-C(=O)O-[CH_2C(CH_3)_2CH_2-]^{+\cdot} + e^- \rightarrow -CH_2-C(=O)O-[CH_2C(CH_3)_2CH_2-]^{\times}$$

$$-CH_2-C(=O)O-[CH_2C(CH_3)_2CH_2-]^{\times} \rightarrow -CH_2-C(=O)OCH_2^{\cdot} + {}^{\cdot}C(CH_3)_2)CH_2-$$

In the solid polymer, bimolecular encounters via mass diffusion are severely restricted, however charges migration by electron hopping between neighboring centers may occur even at the lowest temperature, as observed by EPR measurements. A number of charge neutralization reactions could be proposed leading to some of the expected major stable end products:

$$R_2CH{-}C(=OH^+)OCH_2{-} + R_2CH{-}(C(=O)O)^{-\cdot}{-}CH_2{-} \rightarrow H + 2\,R_2CH{-}C(=O)O{-}CH_2{-} \quad (10)$$

$$R_2CH{-}C(=OH^+)OCH_2{-} + R_2CH{-}C(=O)O^- \rightarrow R_2CH{-}C(=O)OH + R_2CH{-}C(=O)OCH_2{-} \quad (11)$$

$$H + R_2CH{-}C(=O)O{-}CH_2{-} \rightarrow R_2C^{\cdot}{-}C(=O)O{-}CH_2{-}, \quad R_2CH{-}C(=O)O{-}CH^{\cdot}{-} + H_2 \quad (12)$$

$$-CH_2-O^- + R_2CH-C(=OH^+)OCH_2- \rightarrow -CH_2-OH + R_2CH-C(=O)O-CH_2- \quad (13)$$

The migration of free spins via a sequence of H abstractions between reacting centers lying within a critical distance is the basic mechanism allowing crosslinking and branching to take place in the solid matrix during and after the irradiation.

Radicals of type $R_2C^{\cdot}$–C(=O)O–CH_2– (a) are suited to abstract hydrogen only from neighboring equivalent tertiary C–H sites. As consequence, the spin migration is hindered, the species have a longer lifetime and tend to accumulate in the system, as clearly observed by means of matrix EPR measurements in irradiated aliphatic polyesters. A similar description applies, although to a lower extent, to the species of type –OC$H^{\cdot}$– (b) for which spin migration is allowed via thermoneutral (H abstraction at –O–CH_2– sites) and exothermic (H abstraction at R_2CH–C(=O)O–) reactions. A different situation applies instead to the species –CH_2–$CH^{\cdot}$–CHR_2 (c) and R_2CH–$CH^{\cdot}$–CH_2– (d) which are the most active in the spin migration process since they can undergo exothermic or thermoneutral H abstractions with all the C–H bonds in the polymer chains (except for methyl C–H bonds). As a consequence, these species have a shorter lifetime being terminated by coupling (crosslinks) or by conversion to the other radical species. Two different stages can thus be envisaged in the crosslinking process: (i) one taking place during the irradiation and based on the coupling of the "mobile" species (c) and (d) with themselves and with the other species in the system; and (ii) a slower one taking place mostly after the irradiation and during the degradation of the polymer, and based mainly on the coupling of the most stable species (a) and (b). The slower crosslinking stage is likely to be less efficient since it is more exposed to inhibition by oxygen. This scenario points to crosslinking being favored by the greater relative abundance of mobile radicals of type (c) and (d) which in turn implies a greater concentration of methylene groups in the chains. This effect may contribute, together with the better affinity for chain scission, to enhance the G_s/G_x ratio in PNCE with respect to PPCE.

Chain scission radicals –$CH_2^{\cdot}$ are the most reactive species in the polymer system because of the favored enthalpy changes in the H abstractions coupled with the especially large motional amplitude available at the chain ends. These species are of course expected to be the major precursors of branching but they will also contribute to the insource and post irradiation crosslinking processes through the generation of intrachain radicals by H abstraction.

Coupling takes place competitively with disproportionation. The latter mechanism is generally neglected despite the fact that the ratio between the rate constants for the two reaction modes k_d/k_c attains significant magnitudes which increase with increasing the number of β hydrogens available for disproportionation and it is relatively little affected by the change of solvents or temperature [31]. In our polymers, a prominent contribution by disproportionation can be predicted for reaction of tertiary neopentyl radicals –$(CH_3)_2C^{\cdot}$–CH_2–, since k_d/k_c for t-butyl radical is reported to be 2.3. Disproportionation is bound to reduce the crosslinking and branching yields, but a partial compensation effect is expected to develop with increasing the radiation dose following the generation of double bonds. Disproportionation coupled with the cage effect may be expected to enhance the yield of the homolytic chain scissions by reducing the probability of the back reaction. This effect is likely to acquire importance when scissions of C–C bonds at the neopentyl units are involved. As a consequence of the arrangement of the neopentyl hydrocarbon structure to host the electron loss

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centers, additional pathways for chain scission are available in PPCE–PNCE copolymers, based on the radical-cations fragmentation and excited intermediates. A lower yield of reactive radicals suited for carrying on crosslinking is produced due to the smaller number of CH_2 groups in the PNCE chains. With respect to PPCE, the greater affinity of neopentyl type radicals for disproportionation enhances the chain scission probability by hindering the cage back couplings.

Thermal Properties

It is known that the presence of the cyclohexylene ring along the polymer structure confers good thermal stability [10]. Moreover, as already reported, PPCE copolymerization with increasing percentage of NCE unit did not have a negative effect on the thermal properties. The effect of gamma irradiation on the thermal behavior was investigated on 1-mm sheets of PPCE homopolymer and the four copolymers.

The glass transition phenomenon is always slightly evident both in pristine and irradiated samples, due to relatively high degree of crystallinity. The glass transition temperature tends to become lower with irradiation dose in accordance with the molecular weight decrease and does not show a clear trend with NCE unit content (Table 2).

The melting process is characterized by two endothermic peaks, even in the unirradiated samples: the first one, with a lower melting enthalpy, lies between 50 and 60 °C; the second one is characterized by higher temperature and melting enthalpy. This melting behavior is probably due to the existence of crystallites with different shape, dimension and degree of perfection [32]. In the crystalline phase, because of the additional restraint to molecular motion, chain scissions are hindered by the high probability of the back reactions, radicals and radical ions cannot easily attain their lowest energy configuration and bimolecular interactions between non-neighboring reactive centres are prevented. As a consequence, irradiation acts by creating defects which generate less perfect crystallites. The first melting temperature increases with the absorbed dose due to reorganization of the chain segments. The second one decreases both with the dose, caused by chain scission that has taken place during irradiation creating shorter chains with increased ability to re-orientate, and with the NCE unit content as already found [21]. The thermograms of P(PCE90NCE10) as a function of the irradiation dose are reported as an example in Fig. 3. Finally, the melting enthalpy displays a decrease with the dose in the copolymers, with the exception of PPCE, and does not show a regular behavior with NCE unit content. Moreover, calorimetric measurements were performed on pristine and irradiated films of P(PCE95NCE5) and the same changes on the melting temperatures and enthalpy were observed with respect to sheets.

Table 2 DSC thermal data (1st scan) for all the polymers sheets as a function of the absorbed dose

Dose (kGy)	0	75	200	500
PPCE				
T_g (°C)	15	11	12	10
T_m (°C)	52/150	56/144	59/142	60/136
ΔH (J/g)	34	35	38	37
P(PCE95NCE5)				
T_g (°C)	n.d	20	15	18
T_m (°C)	52/143	59/138	58/135	62/129
ΔH (J/g)	43	36	39	31
P(PCE90NCE10)				
T_g (°C)	19	16	17	13
T_m (°C)	53/136	55/132	57/129	60/123
ΔH (J/g)	38	36	36	34
P(PCE85NCE15)				
T_g (°C)	24	20	12	18
T_m (°C)	52/125	58/119	57/117	62/113
ΔH (J/g)	43	36	29	29
P(PCE80NCE20)				
T_g (°C)	17	15	15	12
T_m (°C)	62/120	55/114	57/113	60/109
ΔH (J/g)	32	31	31	30

n.d. not detectable

The thermal stability of the samples under study was investigated by thermogravimetric analysis. From the TGA curves shown in Fig. 4, it can be noticed that in all cases the weight loss takes place in one step at decreasing temperatures with increasing the absorbed dose. T_{max} decreases of about 1.5 and 1% from the pristine sample to that irradiated at 500 kGy for PPCE and P(PCE80NCE20), respectively. The temperature of initial decomposition of pristine PPCE is 392 °C and decreases to 386 °C when irradiated at 500 kGy, and similarly T_{id} decreases from 395 to 391 °C for the copolymer. Such results are in agreement with the molecular weight changes due to the degradation of polymer chains into shorter segments with lower decomposition temperatures.

Positron Annihilation Lifetime Spectroscopy

Exposure to physical factors such as ionizing radiation can lead to modifications of the free volume holes present in macromolecular matrices. In complementing conventional characterization techniques, PALS offers unique insights towards understanding molecular void spaces and microstructure, as well as changes in physical properties, such as gas and vapor permeability. The

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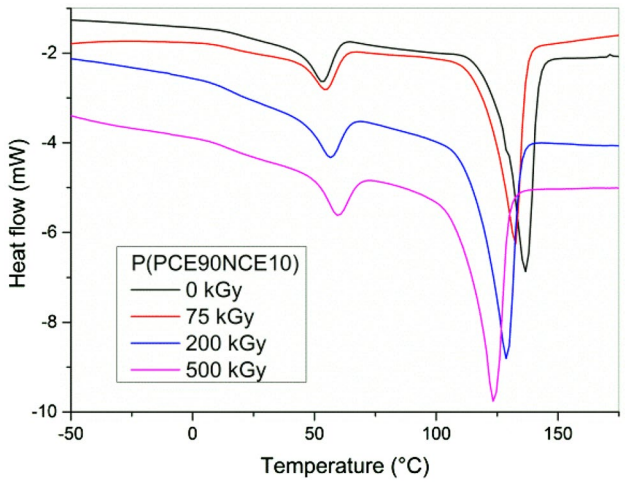

Fig. 3 DSC curves of P(PCE90NCE10) as a function of the irradiation doses

principles of positron annihilation in condensed matter have been extensively discussed elsewhere and here they are only briefly outlined [33, 34]. Positrons from a ^{22}Na source diffuse through the material and may bond with an electron, forming an exotic unstable 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 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. 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 [35, 36]:

$$\tau_3 = \tau_0\left[1 - \frac{R}{R+\delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R+\delta R}\right)\right]^{-1} \quad (14)$$

where $\delta R = 1.66$ 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. 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 [37]. Table 3 reports centroid R and second moment σ of the normalized holes size distribution, as obtained from the PALS measurements. PPCE and copolymers display a small but significant decrease of the centroid of the distribution as the absorbed doses increase. On the other hand, no clear conclusion can be drawn as far as the second moment is concerned by taking into account the experimental uncertainties associated to the two parameters (2% for the centroid and 15% for the second moment). After exposure to ionizing radiation, the rearrangement of the broken chains is partially hindered by the steric hindrance of the methyl groups in the NCE co-unit affecting the sample crystallinity. Table 3 evidences a negative correlation between o-Ps intensity and the dose, which means a decrease in the formation probability of Ps. This could be related to the presence of carbonyl functional groups which increase with the dose. Positrons are attracted by these groups and annihilate with the corresponding electrons thus reducing o-Ps intensity.

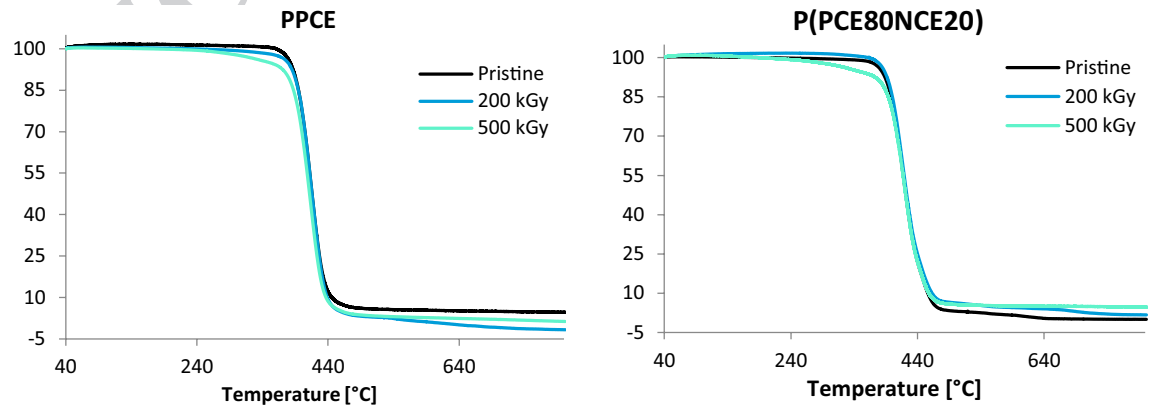

Fig. 4 Thermogravimetric curves of PPCE and P(PCE80NCE20) films at different absorbed doses

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Table 3 PALS results on sheets: intensity of o-Ps decay (I_3), mean radius (R) of holes and relative dispersion (σ) as a function of the absorbed dose

Dose (kGy)	0	100	200	500
PPCE				
I_3 (%)	27.6	26.7	25.4	24.1
R (nm)	0.34	0.33	0.32	0.31
σ (nm)	0.06	0.06	0.05	0.05
P(PCE95NCE5)				
I_3 (%)	28.1	27.2	26.6	24.8
R (nm)	0.33	0.33	0.32	0.32
σ (nm)	0.06	0.06	0.05	0.05
P(PCE90NCE10)				
I_3 (%)	28.1	27.7	26.6	24.8
R (nm)	0.33	0.33	0.32	0.31
σ (nm)	0.06	0.06	0.06	0.05
P(PCE85NCE51)				
I_3 (%)	28.7	27.5	26.6	25.1
R (nm)	0.34	0.31	0.31	0.31
σ (nm)	0.06	0.05	0.05	0.05
P(PCE80NCE20)				
I_3 (%)	29.2	27.7	26.7	25.7
R (nm)	0.33	0.33	0.31	0.33
σ (nm)	0.06	0.06	0.05	0.06

Uncertainties of I_3 are evaluated to be around 5%

Surface Modifications

Since biodegradation in compost is a surface erosion process, it is important to understand in which way irradiation could affect the surface properties of a polymer, in particular those that could favor the microorganisms action, such as wettability. Oxidative degradation induced by radiation could lead to the formation of functional groups that can positively affect the polymer surface wettability. Therefore, possible chemical changes in treated films were qualitatively investigated by FTIR-ATR spectroscopy. To this purpose, the matrix containing the highest percentage of NCE sub-unit [P(PCE80NCE20)] was analyzed and compared with PPCE homopolymer. The FTIR spectra of PPCE did not show structural modifications after irradiation and, for sake of brevity, they are not reported here. Contrary to PPCE, for P(PCE80NCE20) some slight differences are visible in the fingerprint region and for the peak at 1721 cm^{-1}, attributed to the carbonyl stretching vibration. We notice that the carbonyl stretching peak displays several overlapped components: with increasing dose, the component at the highest wavenumber (a) decreases, while the component at the lowest wavenumber (b) increases. This is more evident for the sample irradiated at 500 kGy (see Fig. 5). Such spectral changes have to be associated to chemical modifications related with the formation of carbonyl groups placed in different positions than in the original polymer.

Relevant differences in the polymer wettability were evidenced by water contact angles (WCA) measurements on PPCE and copolymers films irradiated in air. As shown in Table 4, wettability is clearly enhanced only at 500 kGy, coherently with what observed by FTIR analyses. WCA measurements were also acquired for PPCE and P(PCE80NCE20) films at low absorbed doses (25, 50 and 100 kGy), highlighting an increase of even more than 10 degrees with respect to the untreated samples (112 ± 2 for PPCE and 100 ± 2 for P(PCE80NCE20) at 25 kGy). It can be inferred that at such low absorbed doses radiation damage leads to a polymer surface with a hydrophobic character, while proceeding the irradiation such effect is balanced out by oxidation.

Radiation Effects on Compostability

Although aliphatic polyesters could potentially be biodegradable polymers, such characteristic strongly depends on their chemico-physical properties. PPCE and copolymers, despite the fully aliphatic structure and the presence of ester groups, are known to be slow degrading polymers [21]. The presence of the cyclohexylene ring in the polymers backbone confers to the materials under study all the peculiar features that make them suitable for technological applications, but at the same time provides good stability towards degradation in compost. In this perspective, it could be interesting to exploit the oxidative degradation induced by radiation to modify the polymer chemical structure and make it more prone to biodegradation, after the use so that not to affect the polymer performances.

Disintegration tests performed on irradiated PPCE and P(PCE85NCE15) films showed in general the low degree of disintegration of such matrices even at the highest absorbed doses, but also the promising improvement in degradation of the irradiated samples with respect to the pristine ones. As reported in literature, weight losses of about 3% for pristine PPCE and 8% for pristine P(PCE85NCE15) were obtained after 140 days of incubation [21]. In the present work, it was demonstrated that after 45 days of incubation all the pristine samples were barely attacked by microorganisms showing a weight loss under 1%, while samples irradiated at 500 kGy reached a weight loss of about 5% for PPCE and 12% for P(PCE85NCE15). In order to develop a radiation treatment as eco-friendly and cost-effective as possible, attempts were made to try to reach the same degree of disintegration with a lower absorbed dose. In this perspective, disintegration tests were repeated on samples irradiated up to 200 kGy and the test duration was extended

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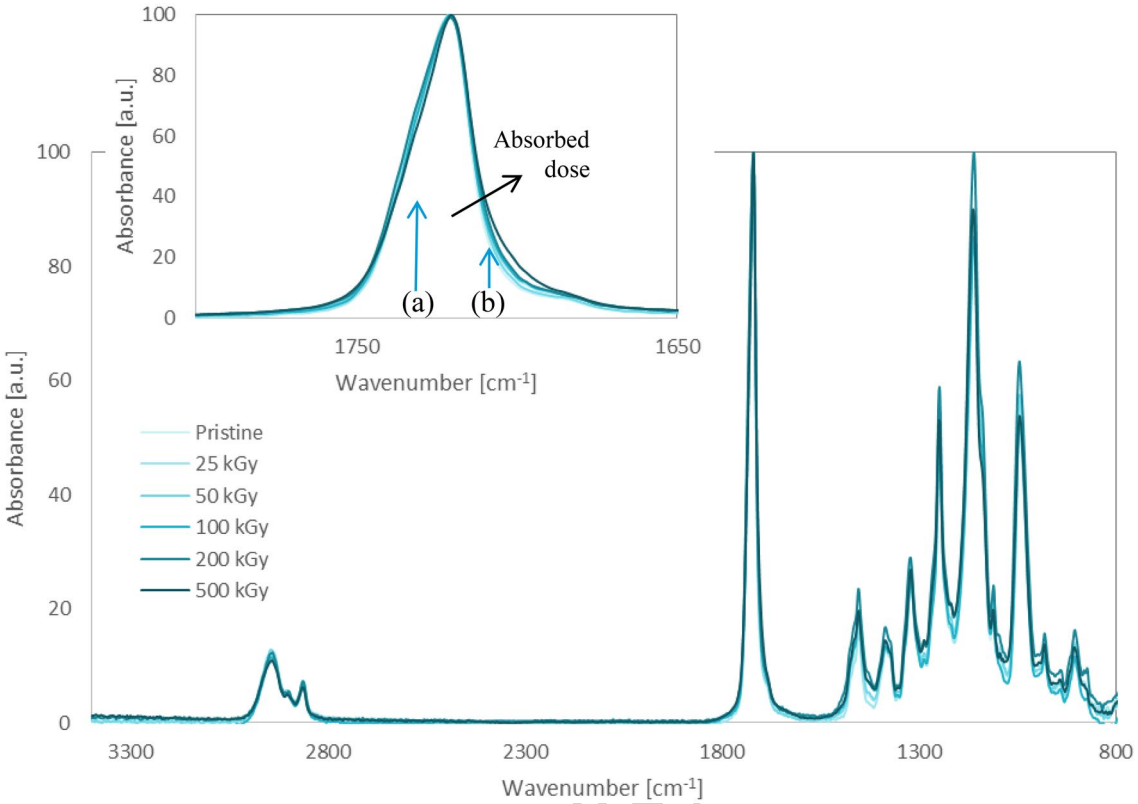

Fig. 5 ATR-FTIR spectra of P(PCE80NCE20) films, pristine and irradiated at absorbed doses up to 500 kGy. The spectra have been normalized such that the intensity of the strongest peak is 100

Table 4 Water contact angles for PPCE and copolymers 200 μm films as a function of the absorbed dose

Polymer	Contact angle (°)		
	Pristine	200 kGy	500 kGy
PPCE	94 ± 3	98 ± 2	87 ± 1
P(PCE95NCE5)	98 ± 2	98 ± 2	88 ± 2
P(PCE90NCE10)	96 ± 2	96 ± 1	87 ± 3
P(PCE85NCE15)	92 ± 1	89 ± 1	85 ± 1
P(PCE80NCE20)	88 ± 2	87 ± 2	74 ± 1

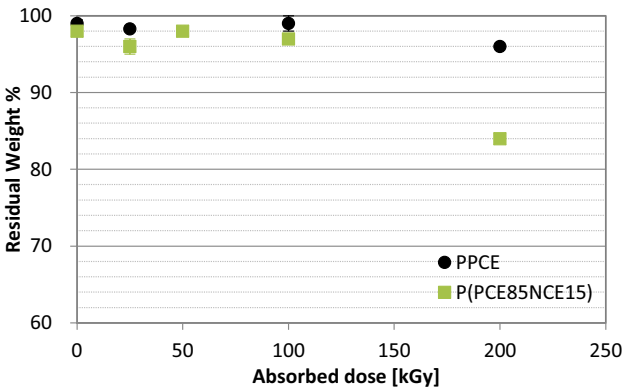

Fig. 6 Residual weight % as a function of the absorbed dose for 200 μm films of PPCE and P(PCE85NCE15) copolymer irradiated in air after 70 days in compost

to 70 and 90 days. As reported in Fig. 6, in comparison with the tests at 45 days, after 70 days the degradation of pristine samples does not show improvements, while PPCE and P(PCE85NCE15) irradiated in air at 200 kGy exhibit a weight loss of about 4 and 16%, respectively. The experiments performed demonstrated that the same result in terms of weight loss was obtained by more than halving the absorbed dose and less than doubling the incubation time. After 90 days in compost no relevant improvements can be reached with respect to 70 days tests.

Morphological modifications of irradiated polymers after composting were investigated by SEM. As an example, SEM micrographs of PPCE and P(PCE85NCE15) films after 70 days of composting are reported in Fig. 7. Micrographs show superficial modifications already at low absorbed doses (25 kGy), mainly as for the copolymer surface is concerned. At higher absorbed doses cracks and holes appear on the surface, whose intensity increases with the irradiation dose,

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leading to a remarkable damage of the surface, especially for the copolymer, that clearly evidence the proceeding of the degradation process. The formation of cracks and holes is faster and more evident for the copolymer with respect to the homopolymer, in accordance with the weight loss measurements.

Effect of Irradiation Environment

In order to maximize the radiation effects on materials, two additional irradiation environments were considered, i.e. water and oxygen atmosphere. As reported in literature, irradiation of polymers in dilute water solutions greatly increases the crosslinking yield because of the obliteration of the direct radiolysis effects and its substitution with the reactions of species ($OH^{\cdot}$ and $H^{\cdot}$ radicals) with great affinity for H abstraction [25]. Previous radiolysis studies on model systems or similar systems, such as low molecular weight alkanes in water [38–41] and hydrophilic polymers in water [42–44] have shown that the $HO^{\cdot}$ radical is the main species responsible for the degradation of these materials. In the present case, direct radiolysis effects on the polymers are still important and the mechanism described by Charlesby can be envisaged being significant only at the surface [25]. During irradiation, the presence of water at the surface of the polymer involves specific radical reactions among the species coming from water radiolysis ($OH^{\cdot}$ and $H^{\cdot}$ radicals) and polymers radicals. It is clear that such reactions could lead to relevant surface modifications that can strongly affect the hydrophilicity of the polymer surface and thus favor its attack by microorganisms. Therefore, some attempts were performed to find the conditions under which such effect is maximized keeping the absorbed dose as low as possible. Moreover, since it is well known that oxygen radicals are very reactive species, irradiation in oxygen atmosphere was attempted in order to try to exploit the most extreme oxidative conditions to modify polymer structure and surface properties.

Given the large number of samples required by such kind of experimental study, investigations on the effect of radiation environment were preliminary conducted only on the homopolymer and two copolymers and at few selected absorbed doses. In particular, the two copolymers with the highest NCE percentage were considered. Figure 8 reports the GPC results for PPCE and P(PCE80NCE20) films irradiated in water and oxygen atmosphere up to 200 kGy and the molecular data for P(PCE85NCE15) films irradiated in water up to 100 kGy. No significant differences were observed in comparison with films irradiated in air. In some cases, irradiation in air seems to be the most effective one in terms of molecular weight reduction. In particular, the oxygen atmosphere at high absorbed doses leads to a lower decrease of M_n[%] with a more homogeneous distribution of chain length (lower PDI values) with respect to irradiation in air.

For PPCE films irradiation at 100 kGy in water led to changes in the thermal properties comparable to those observed after irradiation in air. In the case of the copolymer P(PCE85NCE15), T_m and ΔH_m vary differently when irradiated in water with respect to irradiation in air: at 100 kGy T_m varies from 123 °C in the pristine sample to 122 and 118 °C when irradiated in air and water, respectively, while the melting enthalpy increases from 23 J g^{-1} to 29 and 25 J g^{-1}. The presence of the NCE sub-unit in the copolymer resulted in a higher sensibility to the irradiation environment. The calorimetric curves obtained for PPCE and P(PCE80NCE20) films irradiated in air, water and oxygen at 25 kGy highlighted that, despite the low absorbed dose, crystallinity was enhanced in all the cases.

Up to 100 kGy FTIR-ATR investigations and WCA measurements on PPCE, P(PCE85NCE15) and P(PCE80NCE20) films did not highlight differences between the irradiation environments. As shown in Table 5, it is worth noting that in the case of irradiation in water the increase of the polymers hydrophobic character observed after irradiation in air in the absorbed dose range 25–100 kGy was no more evident, while it is still present in the sample irradiated in oxygen at 25 kGy. (112 ± 2 for PPCE and 100 ± 2 for P(PCE80NCE20) at 25 kGy).

As shown in Fig. 9, the results obtained in the disintegration experiments indicated that irradiation in water at the considered absorbed doses was not significantly effective in enhancing the rate of degradation of the polymers under study. Indeed, after 70 days in compost PPCE and P(PCE85NCE15) samples irradiated in water showed a maximum weight loss of about 4% at 100 kGy, similar to that reached by irradiation in air. The corresponding SEM images show how the degradation process by microorganisms is acting on the polymer surface leading to the appearance of irregular zones. In particular, PPCE surface seems to be consumed more uniformly with hollowed zones, as clearly shown in Fig. 10.

Concerning PPCE degradation irradiation in oxygen as well as the extension of test duration did not imply significant improvements (see Table 6), with respect to the results already presented. Although P(PCE80NCE20) films irradiated at 25 kGy in oxygen showed the same molecular weight decrease observed after irradiation in air and water, no substantial variations of the thermal properties and a worsen wettability, preliminary disintegration tests highlighted a progressive decrease of few percent of the residual weight after 70 and 90 days. As shown in Table 6, P(PCE80NCE20) sample irradiated in water shows the lowest residual weight after 70 days. Disintegration experiments prolonged to 90 days seems to

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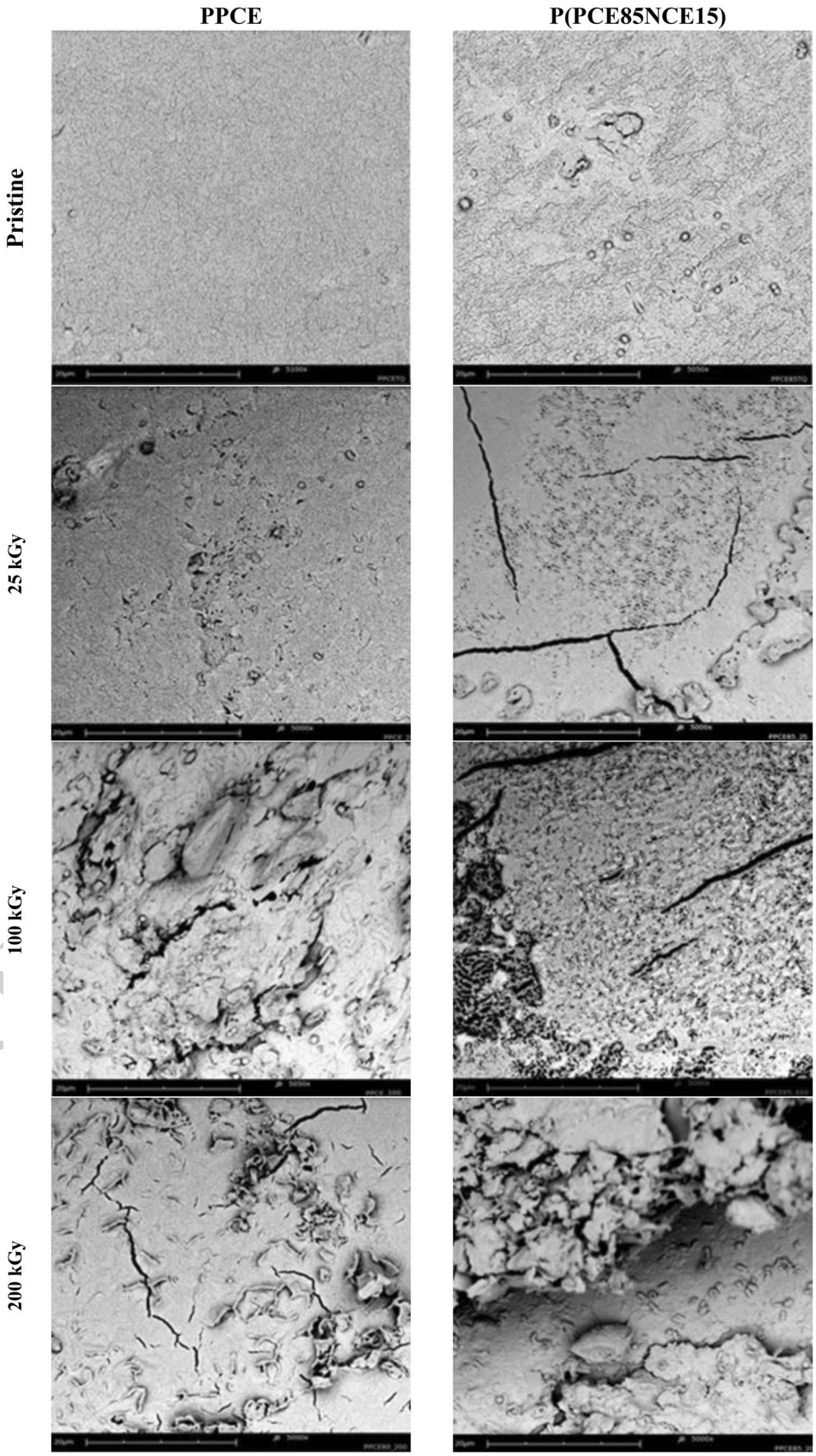

Fig. 7 SEM micrographs of PPCE and P(PCE85NCE15) samples irradiated at 25, 100 and 200 kGy in air and kept for 70 days in compost (magnification ×5000)

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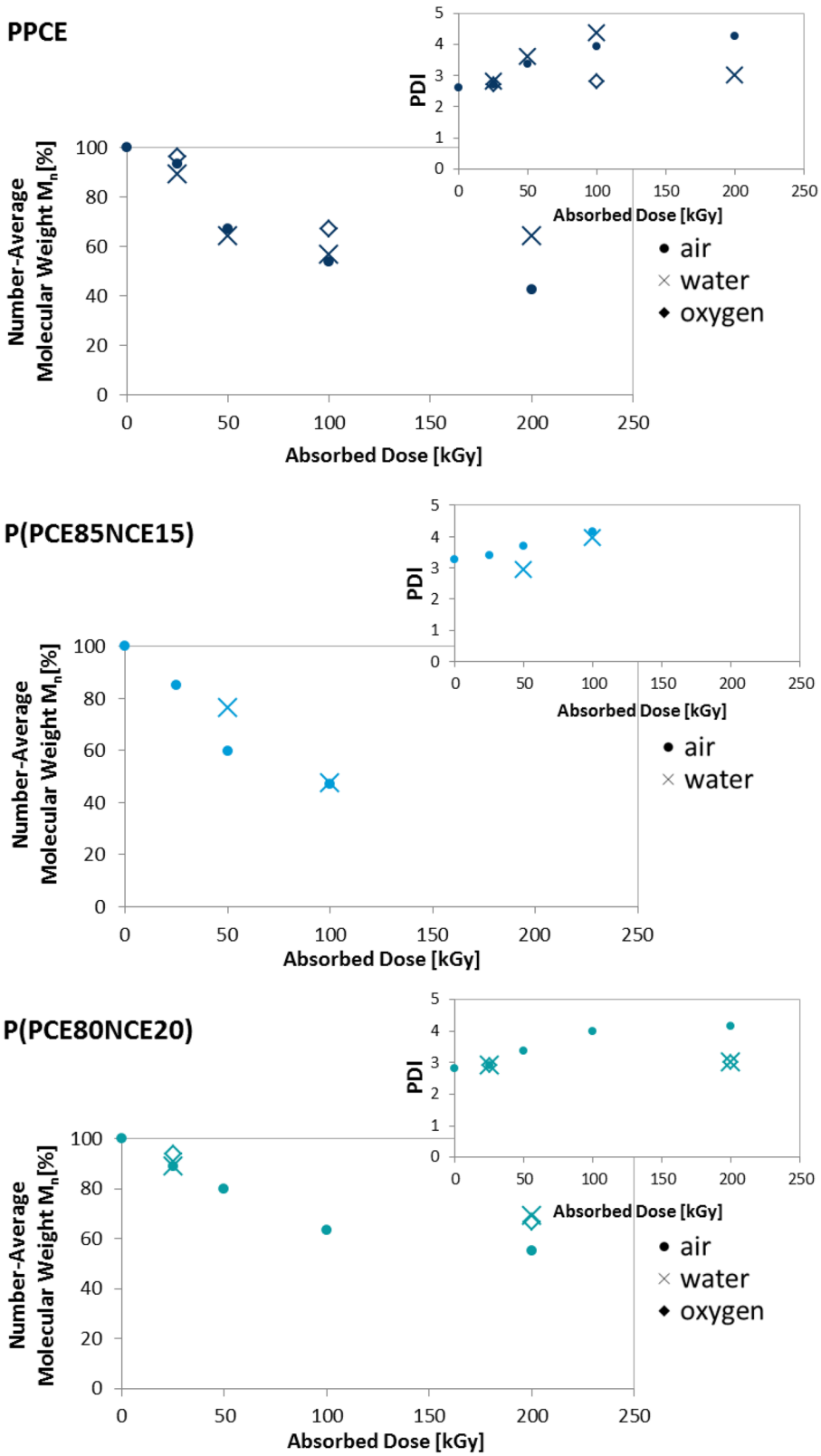

Fig. 8 GPC results on 200 µm films: residual number-average molecular weight Mn[%] and polydispersity index (PDI) as a function of the absorbed dose and irradiation environment

suggest a different disintegration rate among the different irradiation environments. Indeed, while the residual weight of the sample irradiated in water remains constant, that of P(PCE80NCE20) sample irradiated in oxygen decreases.

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Table 5 Water contact angle versus absorbed dose for PPCE and copolymers 200 µm films irradiated in water

Polymer	Contact angle (°)			
	Pristine	25 kGy	50 kGy	100 kGy
PPCE	94 ± 3	101 ± 3	94 ± 1	98 ± 2
P(PCE85NCE15)	92 ± 1	–	98 ± 4	97 ± 7
P(PCE80NCE20)	88 ± 2	89 ± 2	–	85 ± 4

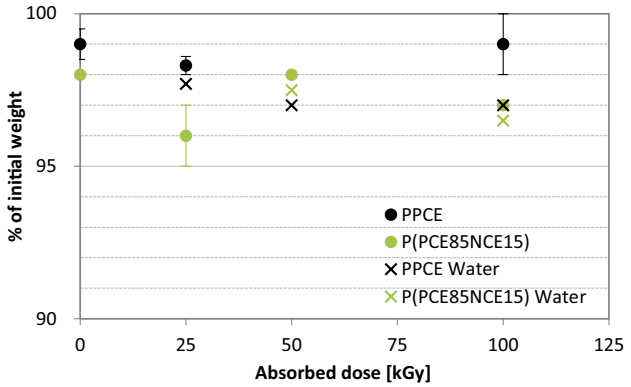

Fig. 9 Residual Weight % as a function of the absorbed dose for 200 µm films of PPCE and P(PCE85NCE15) copolymer irradiated in air and water after 70 days in compost

Despite the small weight losses, some evidences of degradation can be observed for PPCE in the samples irradiated in oxygen and especially in water (see Fig. 11). Interestingly, in P(PCE80NCE20) copolymer small holes appear when the sample is irradiated in air and oxygen, becoming larger if the sample is irradiated in water. The peculiar morphological modifications observed for the samples irradiated in water with respect to the other irradiation environments are coherent with the wettability changes obtained by WCA measurements. This could be an indication that a degradation process, even if slow, has already started in the irradiated samples after 70 days of composting, while the pristine samples surfaces remain practically unchanged. Figure 12 clearly demonstrate the evolution of the degradation process on P(PCE80NCE20) films increasing the incubation period up to 90 days: the sample irradiated in water shows smaller holes uniformly distributed on the surface, while the one treated in oxygen atmosphere exhibits bigger holes inside hollowed areas.

According to the collected results, higher absorbed doses and longer incubation periods should be tested in order to assess the effectiveness of irradiation in water and oxygen.

Conclusions

The present work investigated the behavior under gamma irradiation of new PPCE-based random copolymers, containing cyclohexane unit, whose general properties make them good candidates for biodegradable packaging applications. Indeed, they show good thermal and barrier properties and a slow biodegradation rate. In this perspective, the research activity focused on how gamma radiation can affect the polymer degradability in compost.

Experimental investigations highlighted that exposure to gamma radiation in air mainly affects the polymer

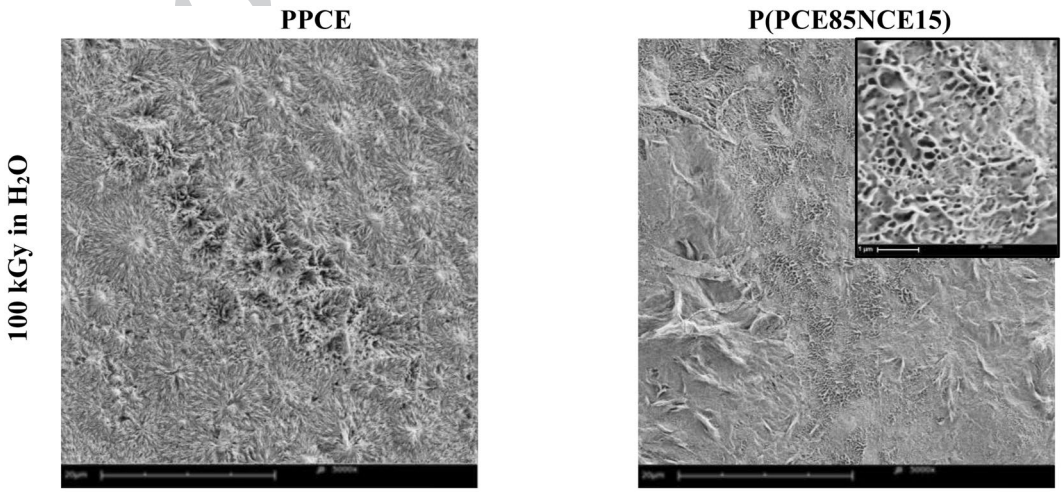

Fig. 10 SEM micrographs of PPCE and P(PCE85NCE15) irradiated at 100 kGy in water and analyzed after 70 days of composting (magnification ×5000, insert ×50000)

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Table 6 Results of disintegration tests (70 and 90 days) on PPCE and P(PCE80NCE20) films irradiated at 25 kGy in the different irradiation environments

Residual weight %				
Incubation period, day	Pristine	Irradiated at 25 kGy in		
		Air	Water	Oxygen
PPCE				
70	99 ± 0.5	98.5 ± 0.5	97.5 ± 0.5	97 ± 0.5
90	99 ± 0.1	97.5 ± 0.5	97.5 ± 0.5	97 ± 0.1
P(PCE80NCE20)				
70	97 ± 1	98.5 ± 0.5	94.5 ± 0.5	97.5 ± 0.5
90	97 ± 1	96.1 ± 0.5	94.5 ± 1	94 ± 2

molecular weight. The radicals formed during irradiation follow mainly a chain scission mechanism causing a decrease of the molecular weight in all the dose range considered. Nevertheless, the treated samples maintained a good thermal stability and exhibited an increased hydrophilicity for absorbed doses above 200 kGy. These findings suggest that the irradiated samples should be more prone to biodegradation. Indeed, despite the relatively short period of incubation considered, SEM images clearly show significant surface changes in the treated samples and irradiation in air at 200 kGy succeeded in enhancing the rate of degradation for P(PCE85NCE15) films: the pristine samples showed a weight loss within 1% after 70 days, while the P(PCE85NCE15) films irradiated at 200 kGy showed a weight loss around 16% over the same incubation time.

In order to enhance the radiation damage, two attempts were performed by considering (i) a more reactive oxygen atmosphere, which favors degradation by oxidation, and (ii) irradiation in solution, which should strongly affect polymer surface. The experimental activities showed that such irradiation environments led to positive effects on the degradation in compost. Indeed, a weight loss of about 6% was obtained on P(PCE80NCE20) films irradiated at 25 kGy in water and oxygen after 70 and 90 days of composting, respectively.

Further experimental investigations are already in progress to demonstrate the effectiveness of irradiation under more oxidative conditions to improve polymers degradation rate in compost.

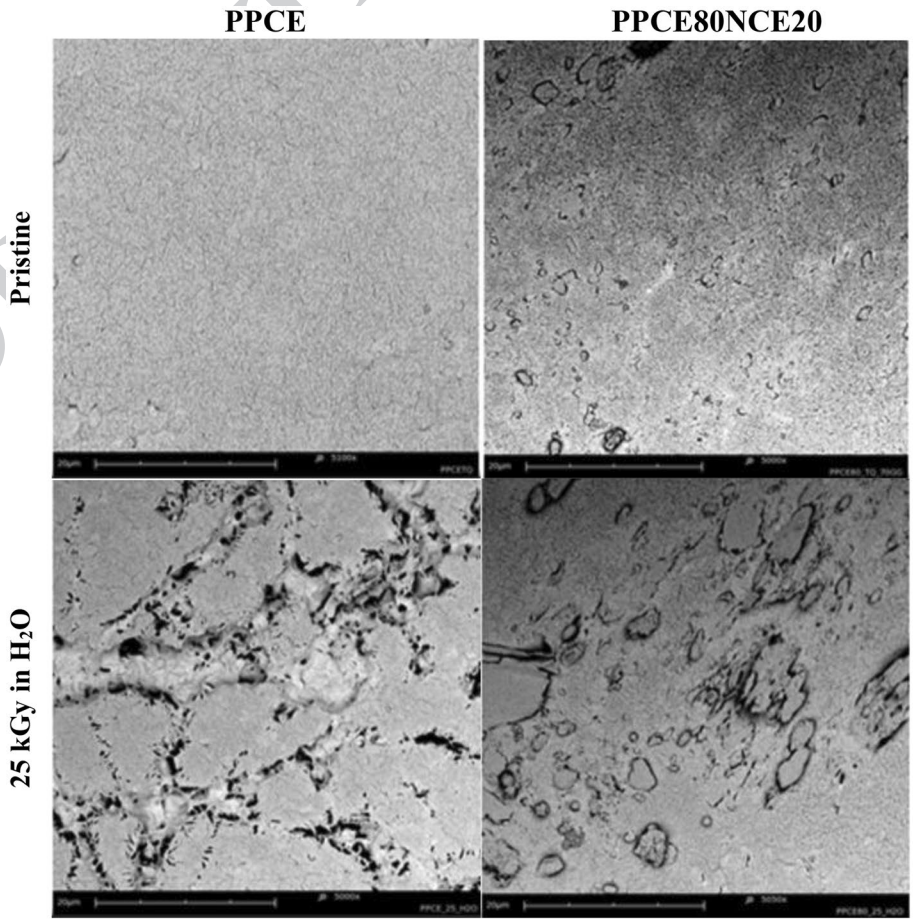

Fig. 11 SEM micrographs of PPCE and P(PCE80NCE20) irradiated at 25 kGy in water after 70 days of composting (magnification ×5000)

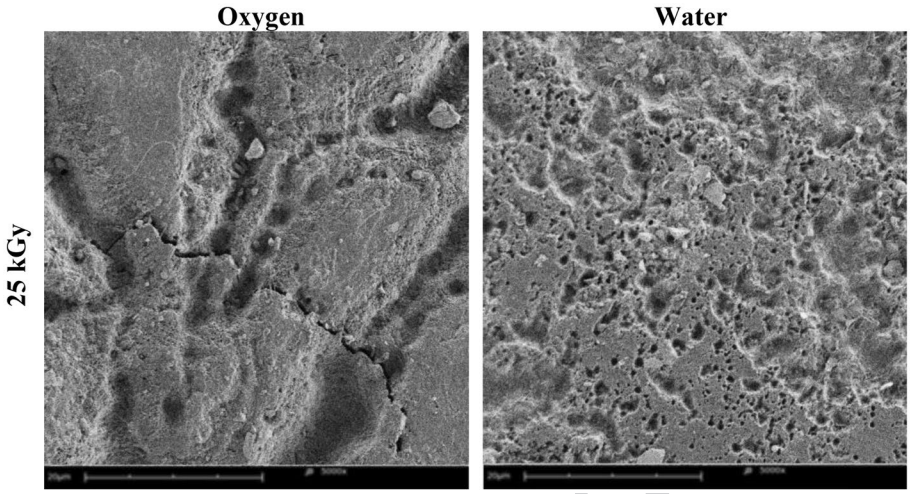

Fig. 12 SEM micrographs of P(PCE80NCE20) irradiated at 25 kGy in different environment and analyzed after 90 days of composting (magnification ×5000)

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