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Radical detection and electron-spin resonance (ESR) monitoring in polymer materials irradiated with gamma and X-rays: Polyethylene and polypropylene

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Abstract

When ionizing radiations interact with polymers, free radicals are generated and are known to be the initiating species for the modification in materials. Monitoring and identifying free radicals after irradiation allow assessing the impact of X-rays and gamma rays on materials. A comparative study has been performed on materials made from polypropylene and polyethylene after irradiation by the two irradiation technologies. Electron spin resonance (ESR) signal has been monitored up to 380 days when signal was still present. ESR signals, concentration profiles, and kinetics were observed after X-rays and gamma rays.

KEYWORDS

electron spin resonance (ESR), gamma rays, polymers materials, sterilization, X-rays

1 | INTRODUCTION

Commercial polypropylene (PP) and polyethylene (PE) materials were selected to compare interaction outputs between X-rays and gamma rays with matter. Both materials are known for their good mechanical and thermal properties¹ and are widely used in biopharmaceutical applications.² Among sterilization technologies for medical and biopharmaceutical devices, radiation remains one

of the most widespread technics and especially the use of gamma irradiation.^{3,4} Indeed, Cobalt 60 (⁶⁰Co) is presently the main source of radiation used for the sterilization of single-used plastic systems in biopharmaceutical industry accounting for 40%–45% of the global market in 2020. According to the current health context, a strong growth of products volume is intended for the pharmaceutical industry in the coming years and questions concerning gamma sterilization capacity are arising.⁴

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Thus, to guarantee the continuity of the production activities of these systems, alternative methods of radiation sterilization based on machine sources to complement gamma rays must be developed.² X-rays sterilization is considered as one possible technology which could absorb this market growth as proven by growing research on gamma rays and X-rays equivalency.⁵⁻⁸

X-ray and gamma rays exhibit very similar features as both are photons but produced from different sources.⁸ Gamma rays refer to the production of photons by radioactive disintegration, whereas X-rays are produced with electron accelerator through conversion of electron energy into photons via Bremsstrahlung effect.⁹ Their energy deposition profiles (i.e., dose profile) are very similar while in some cases,⁷ X-rays irradiation can achieve a slightly better dose uniformity because of the higher photon energy present in X-rays spectrum. For these two irradiation technologies, delivered dose rates are very different (in the order of 1–2 kGy h⁻¹ for gamma rays and 12 kGy h⁻¹ for X-rays). Indeed, photons will generate secondary electrons through pair creation, Compton diffusion or photoelectric effect. These electrons will deposit their energy along their track in the matter. An energy of 10–500 eV can be deposited in a volume of the order of a cubic nanometer, which leads to the generation of free radicals in spurs.^{10,11} When ionizing radiations interact with polymers, free radicals are generated. Free radicals are well known to be the starting point of modification, and several studies have investigated free radical in PP and PE through mechanical properties, Fourier Transform Infrared (FTIR), Gas Chromatography-Mass Spectroscopy (GC-MS), and electron spin resonance (ESR) (i.e., crosslinking, chain scission, and radiation oxidation).¹²⁻¹⁶

The energy of the source particles we are considering, that is, gamma and X photons, ranges between ~0.1 and ~7 MeV. The minimum energy required to create ionization is approximately 100 eV, which is 1000 to 70,000 times less than the energy of the source particles.⁷ When these source particles collide with matter, such as a device to be sterilized, they trigger a cascade of photons and electrons. The number of particles increases while the energy per particle decreases as the cascade progresses. As the average energy per particle decreases, the number of ionizations proportionally increases.⁷ This continues until the energy per particle falls below the energy needed to ionize an atom. At this point, the remaining energy is deposited in the matter as heat. The aim is to determine if there is a variation in the radicals generated when radiation from the two sources interacts with the products. If no differences are observed, it can be inferred that irradiated materials will exhibit similar behavior irrespectively of the radiation source.

Most generated radicals react very quickly when they exhibit sufficient mobility in matter. Others could be quite stable, especially in the crystalline phase and sometime in the amorphous phase of semicrystalline polymers, and, therefore, can be measured from minutes to days/weeks after irradiation.¹⁷ ESR is a very powerful method to identify the type of radicals formed during irradiation and to monitor their quantity and decay after irradiation.^{18,19} The effects of irradiation on PP and PE have been extensively studied by ESR.^{13,20-22} However, very few studies have compared the effects of these irradiations on polymers. Free radical quantity and identification of radicals after irradiation help assess similarities on material impact between X-rays and gamma rays.

There are thousands of commercially available polymer grades potentially suitable for healthcare products, making it impractical to test them all. Consequently, we have selected several samples from these commercial polymer grades for our study. Our ESR study reveals that the type of radicals generated is dependent on the polymer type, although additives may also produce superimposed signals. Furthermore, while the qualitative data may vary based on the specific plastic recipe, this does not impact the decay kinetics. By testing a wide range of polymers, we can confirm that the interaction between photons and matter is consistent across all polymer grades when exposed to gamma and X-rays. Our sample size, representing the most commonly used plastics, will yield results that can be confidently extended to other polyolefins.

The ESR signals of formulated polymers are complex and change over time, depending on the conditions in which they are stored. The challenge in ESR spectroscopy lies in identifying the pure substances within a spectrum that displays a mixture of many species. To address this, a curve resolution analysis, specifically the SIMPLE-to-use Self-modeling Mixture Analysis (SIMPLISMA)²³⁻²⁶ method, was employed. This method allows for the mathematical extraction of the pure signals from a complex mixture of several compounds, such as polymers and additives. It also provides their concentration profile. Importantly, this method does not require any prior knowledge about the system under study or any assumptions about the number of species present.

In this study, we investigated the effects of gamma and X-rays on 22 materials. These materials were either made of PP, PE, and thermoplastic elastomer (TPE), or composed of mixtures of these. ESR analyses were conducted on each material over a period of 380 days after irradiation. The aim was to monitor using ESR the free radicals generated after gamma and X-ray irradiations on each class of polymers.

2 | MATERIALS AND METHODS

2.1 | Sample

The samples investigated in this article are PP, TPE, and PE of various types: high-density polyethylene (HDPE),

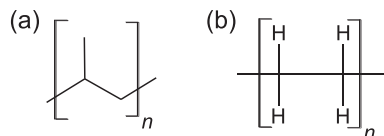


FIGURE 1 Chemical structure of (a) polypropylene and (b) polyethylene.

low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE),^{15,27-29} and multilayer films. Their chemical structure is depicted in Figure 1, and Table 1 displays their properties: density and melting flow rate.

2.2 | Irradiations

2.2.1 | Gamma ray irradiation

Irradiation with gamma rays produced from ⁶⁰Co sources was performed at Ionisos, Dagneux, France, at a dose rate of 1–2 kGy h⁻¹. The samples were packed in craft boxes at room temperature. This together with the adapted

TABLE 1 Commercial of nonirradiated PP, TPE, and PE samples (density and MFI) and postirradiation features (C_{\max}^a and $t_{1/2}^a$).

Polymers	Identification number	Density (g·cm ⁻³)	MFI (g·10 min ⁻¹) ^b	C_{\max} gamma (spin g ⁻¹)	C_{\max} X-ray (spin g ⁻¹)	$t_{1/2}$ gamma (days)	$t_{1/2}$ X-ray (days)
PP	1	0.9	2.1	7·10 ¹⁶	3·10 ¹⁶	≈24	≈19
	2	0.9	18	8·10 ¹⁶	3·10 ¹⁶	≈23	≈27
	3	0.9	35	7·10 ¹⁶	5·10 ¹⁶	>380	>380
	4	0.9	10	8·10 ¹⁶	4·10 ¹⁶	≈24	≈26
TPE	5 ^c	0.9	n.a. ^d	6·10 ¹⁶	3·10 ¹⁶	≈25	≈31
	6	0.9	n.a. ^d	n.a. ^d	1·10 ¹⁶	n.a. ^d	<120
HDPE	7	0.960	7.6	1·10 ¹⁷	9·10 ¹⁶	≈13	≈12
	8	0.953	26	2·10 ¹⁶	2·10 ¹⁶	≈14	>60
	9	0.954	0.25	2·10 ¹⁶	3·10 ¹⁶	≈33	≈31
	10	0.953	6.6	8·10 ¹⁵	1·10 ¹⁶	>60	>60
	11	0.962	13	5·10 ¹⁶	6·10 ¹⁶	≈22	≈15
LLDPE	12	0.925	1.9	n.d. ^e	n.d. ^e	n.d. ^e	n.d. ^e
LDPE	13	0.923	22	n.d. ^e	n.d. ^e	n.d. ^e	n.d. ^e
	14	0.922	0.33	5·10 ¹⁶	6·10 ¹⁶	n.a. ^d	n.a. ^d
	15	0.924	n.a. ^d	n.d. ^e	n.d. ^e	n.d. ^e	n.d. ^e
	16	0.920	1.5	n.d. ^e	n.d. ^e	n.d. ^e	n.d. ^e
	17	0.922	n.a. ^d	n.d. ^e	n.d. ^e	n.d. ^e	n.d. ^e
	18	n.a. ^d	n.a. ^d	n.d. ^e	n.d. ^e	n.d. ^e	n.d. ^e
	19	n.a. ^d	n.a. ^d	n.a. ^d	n.a. ^d	n.a. ^d	n.a. ^d
	PE/EVOH/PE ^f	20	n.a. ^d	n.a. ^d	4·10 ¹⁶	5·10 ¹⁶	≈24
EVA/EVOH/EVA ^f	21	n.a. ^d	n.a. ^d	1·10 ¹⁶	1·10 ¹⁶	n.d. ^e	n.d. ^e
PE/EVOH/PA/PET ^f	22	n.a. ^d	n.a. ^d	9·10 ¹⁶	1·10 ¹⁷	≈40	≈44

Abbreviations: EVA, ethylene-vinyl acetate; EVOH, ethylene vinyl alcohol; HDPE, high-density polyethylene; LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; LOD, limit of detection; MFI, melt flow index; PA, polyamide; PE, polyethylene; PET, polyethylene terephthalate; TPE, thermoplastic elastomer.

^a C_{\max} : maximum concentration of radicals measured and $t_{1/2}$: half lifetime of radicals.

^bMFI: 190°C × 2.16 kg⁻¹ for PE samples and 230°C × 2.16 kg⁻¹ for PP samples.

^cSample 5 is commercially available from Sartorius, that is, Tuflux[®] TPE.

^dn.a.: not available.

^en.d.: not detected, LOD < 3 × 10¹⁵.

^fMultilayer films proprietary of Sartorius. 20, 21, and 22 are commercially available as S80 (PE/EVOH/PE), S71 (EVA/EVOH/EVA), and S40 (PE/EVOH/PA/PET).

packaging of plastic parts in thin craft boxes provides a good treatment uniformity.

Targeted dose was $50 \text{ kGy} \pm 10\%$. Dosimetry has been realized using alanine pellet and AerEDE Dosimetry software (Aerial, France) by placing dosimeters in cardboard box volume.

2.2.2 | X-ray irradiation

X-ray irradiation has been performed at Aerial-CRT on Feerix facilities. This facility is based on a Rhodotron (TT300-IBA) and delivers X-ray beams. In this study, 7-MV X-rays have been obtained from the conversion of 7 MeV electrons in a tantalum target. Irradiation has been performed with a vertical scan and a horizontal translation of products. This, together with the adapted packaging of plastic parts in thin craft boxes, provides good treatment uniformity. The average dose rate was about 12 kGy h^{-1} .

Targeted dose was $50 \text{ kGy} \pm 10\%$ maximum which was verified by placing dosimeters in cardboard box volume. Dosimetry has been realized using alanine ESR dosimetry system with AerEDE software as well. Dose measurements performed are traceable to an international standard through appropriate calibration.

2.3 | ESR measurements

ESR measurement has been performed on a Magnetech MS5000X ESR spectrometer from Bruker, Switzerland with ESR studio controlling software. Samples have been prepared from irradiated dog bones or from irradiated material parts. Little pieces have been cut to be introduced in a glass probe of 4.2 mm of inner diameter. A height of about 4 cm and a sample mass of 100 to 200 mg were used.

All signals have been observed in the range of 322 to 340 mT magnetic field, corresponding to organic radicals. In this case, a subtraction of the ruby signal of the spectrometer has been performed. Spectra have been recorded with a modulation of 0.2 mT, 60 s of sweeping time, and a single scan.

Kinetics have been performed till the fading of the signal, over more than 1 year, and have been stopped earlier when the signal was too weak because of fading. Measurement days (D) are the following: D9, D15, D30, D60, D120, D180, and D380. For X-ray samples, D1 has been measured additionally. This wasn't possible with gamma irradiated samples because of delay caused by shipment. The intensity of the peaks was normalized with the sample mass, to use them in the chemometrics

processing data. Total number of spins was directly calculated in ESR studio software. Only spin $\frac{1}{2}$ is considered which could be verified later with SIMPLISMA analysis.

The LOD and the limit of quantification (LOQ) are defined as follows:

$$\text{LOD} = \text{background signal}(\text{average of 10 measurements}) + 3 \times (\text{background standard deviation}).$$

$$\text{LOQ} = \text{background signal}(\text{average of 10 measurements}) + 10 \times (\text{background standard deviation}).$$

The background signal depends on the range of measurement. For the range 322–340 mT, the average signal was 1×10^{15} spins $\pm 2 \times 10^{14}$ spins. Obtained LOD and LOQ are, respectively, 2×10^{15} and 3×10^{15} spins. For the range 300–360 mT, a subtraction is realized for signal quantification, so that the background has been subtracted to another background of another day, obtain LOD and LOQ are, respectively, 3×10^{15} and 7×10^{15} spins. Each measurement is compared with the LOD and LOQ before normalization by the sample mass, and data are not reported in figures when inferior to LOD.

To obtain the variance of measurement for ESR signal a repeatability study has been realizing both on irradiation and measurement. 3×3 samples of the PE/EVOH/PE material (n°21) have been irradiated to 50 kGy in X-rays during three different irradiation sessions to generate a total number of nine samples for analyses in ESR. Measurement has been performed 1 day after irradiation, and the standard error of 11.4% was assessed.

Simulation of ESR spectra were performed with Pepper, a part of EasySpin program,³⁹ based on Matlab 7.14 (R2012a).

2.4 | Curve resolution method (SIMPLISMA)

The method used for self-modeling mixture analysis is the SIMPLISMA method described in the literature.^{24-26,30-32} This method is used for self-modeling mixture analysis by resolving mixture data into pure component signal and concentration profiles without the help of prior information about the mixture. In the case of plastics, it's always a mixture of polymers and additives. SIMPLISMA will consider as "pure" either a mono-material or a mixture that evolve in the same way after irradiation.²³ When the radicals have the same kinetic trend, the same *g*-factor, and same concentration profile, this tool is unable to differentiate the characteristics of

TABLE 2 Test for equivalency techniques measured with radical concentration in (2,2,6,6-tétraméthylpipéridin-1-yl)oxy (TEMPO) references.

Concentration range applicability (spin g ⁻¹)	Number of tests	Standard deviation	Six-sigma variation	Ratio lower limit ^a	Ratio upper limit ^a
$1.5 \times 10^{16} < \text{concentration} < 10^{17}$	8	4.6×10^{15}	112%	0.1	2.2
$10^{17} \leq \text{concentration} < 10^{18}$	8	9.7×10^{15}	50%	0.4	1.6
concentration $\geq 10^{18}$	8	2.2×10^{17}	21%	0.7	1.3

^aRatio limit: mean \pm 3 standard deviations.

different components. SIMPLISMA analysis is based on least squares optimization to determine the pure signal that has received the contributions from only one component. To properly handle noise, peak shift, and instrument drift, user interaction is required.²⁴

The fitting of the SIMPLISMA results is calculated using the relative residual sum of squares (RRSSQ), square sum between the calculated and the original spectra. The number of species is incrementally increased until the reconstructed signal reaches 90% of the experimental signal. The SIMPLISMA procedure was performed with Matlab 7.14 (R2012a).

2.5 | Equivalency criteria

To evaluate the difference between gamma and X-ray irradiated samples, three criteria are defined: ESR pattern (type of radical), radical amount, and radical shelf life. The ESR signal (qualitative criterion) show the same signal shape at the same magnetic field for both gamma and X-ray irradiated samples highlighting the same type of radical (s). For the quantitative criterion, close amount for both gamma and X-ray irradiated samples are observed when concentration detected is higher than the LOQ (i.e., $>2 \times 10^{16}$ spin g⁻¹). Depending on the concentration measured, the equivalency is claimed when the ratio $[\text{Radicals}]_{\text{X-rays}}/[\text{Radicals}]_{\text{gamma}}$ is above the lower limit and below the upper limit (Table 2). These limits depend on the spin concentration range, as obtained after repeatability evaluation (cf. number of testing in Table 2). Regarding the shelf life criterion, the radical concentration should show the same kinetic decrease overtime for both gamma and X-ray irradiated samples.

2.6 | Storage condition

After irradiation and between measurements, samples were stored in a temperature and hygrometry-controlled environment (T: 22°C \pm 2°C and RH: 45% \pm 15%) in UV-free light.

3 | RESULTS

3.1 | Polyethylene

Different types of PE were analyzed: HDPE, LLDPE, and LDPE. The ESR signals for the LLDPE and LDPE samples couldn't be included in the quantitative study and processes by SIMPLISMA because they exhibit a too short lifetime, with concentrations rapidly fading under the LOD. The absence or the weak signal obtained for the LLDPE, and LDPE samples can be accounted by their low degree of crystallinity. The radicals can easily self-terminate as their mobility is higher in LDPE and LLDPE than in HDPE because of the higher amorphous phases in LDPE and LLDPE.³³

Samples 20,21, and 22 (Table 1) are multilayer films with a contact layer of PE or EVA and with an embedded EVOH (ethylene vinyl alcohol) layer. These multilayer films have been intensively investigated and represent our reference materials.^{3,17,23} The ESR signal of PE was not detected in these samples and the signal recorded is attributed to the EVOH[•] species.¹⁷

3.1.1 | Qualitative studies

Figure 2 displays the ESR signal of a HDPE at 9 days (Figure 2a) and 60 days (Figure 2b) after gamma and X-rays irradiations. Similar signals are observed for other samples and reported in Figure S1. There is no ESR signal in nonirradiated samples. These multiple signals afford a g-value of 2.003 corresponds to alkyl radicals which are ascribed to a mixture of superimposed signals of alkyl, allyl, and polyenyl radicals (Figure 3) according to the literature.^{22,34-39} The multiplet signal changed overtime into a single line which is ascribed to the polyenyl radicals, as highlighted by signal at 60 days (Figure 2b). No change in the g-value is observed. Whatever the irradiation technology, ESR signal displayed the same pattern (Figures S1 and S2 in Supporting Information).

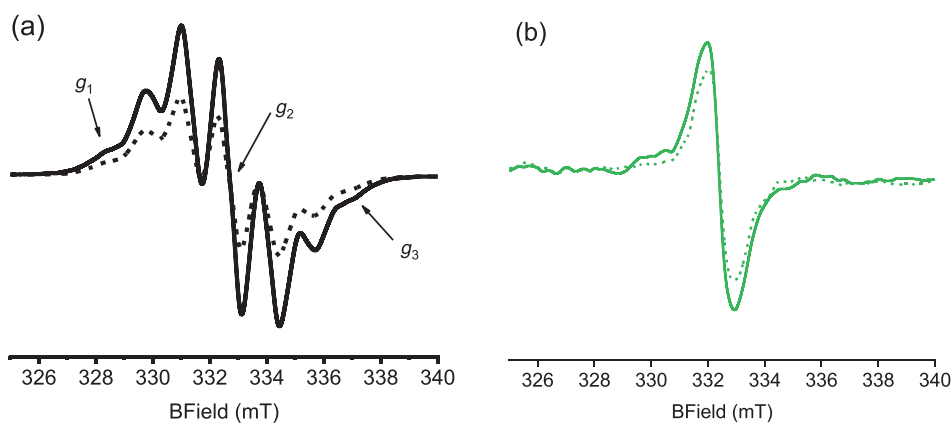


FIGURE 2 (a) Electron spin resonance signal of HPDE-7, 9 days after gamma (full line) and X-rays (dotted line) irradiation corresponding to a mixture of allyl, alkyl, and polyenyl radicals. $g_1 = 2.021$, $g_2 = 2.003$, and $g_3 = 1.985$. (b) Signal of high-density polyethylene-7, 60 days after gamma (full line) and X-rays (dotted line) irradiation corresponding to a polyenyl radicals. [Color figure can be viewed at wileyonlinelibrary.com]

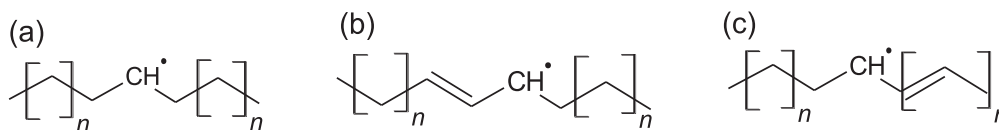


FIGURE 3 Structure of (a) alkyl radical, (b) allyl radical, and (c) polyenyl in high-density polyethylene.

3.1.2 | Quantitative studies

Kinetics of all PEs are displays in Supporting Information (Figure S2). The equivalence tests were further applying on the quantitative ESR results between gamma and X-ray irradiated samples. The equivalency is claimed when the ratio $[\text{Radicals}]_{\text{X-rays}}/[\text{Radicals}]_{\text{gamma}}$ is in between the limits summarized in Table 2. The ratio is 0.8 for HPDE-7 9 days after irradiation for instance. The ratios for the other HPDEs are available in Table S1 in SI. For all HDPEs being irradiated with X-ray and gamma rays, the nature and quantity of radicals generated is equivalent.

3.1.3 | SIMPLISMA analysis

Given that ESR spectra are the superimposition of spectral contributions from various species present in the materials, we applied the SIMPLISMA treatment. This was carried out for the 26 spectra recorded over 380 days for gamma-irradiated samples and the 26 spectra recorded over the same period for X-ray samples, in order to separate each signal. This interactive method,²⁶ known as self-modeling mixture analysis, is used to resolve mixture data into pure spectra that are comparable with those of the mixture species. This is done without any prior information about the mixture. The method also provides associated concentration profiles, representing the relative contribution of each species in the mixture. The ability of SIMPLISMA curve resolution is to detect the wavenumbers or B field, with the highest intensity variations in the data set and it is these wavelength

regions which will be most characteristic of each component in the mixture. It is applied for the analysis of FTIR and ESR,^{24,40} and it is especially efficient in analyzing spectra containing both sharp and broad bands.^{41,42}

Its concept is based on the determination of pure variables (e.g., a wavelength, a wavenumber in spectroscopic terms) that have contributions from only one component. By identifying the least correlated wavenumbers, which exhibit the largest variations, a ‘pure variable’ is defined. This is a wavenumber at which the contribution of an individual component to the spectral intensity is at its maximum, whereas the contributions from other components are minimal. Consequently, the intensity of the pure variable can be considered proportional to the contribution or relative ‘concentration’ of that corresponding individual component in the mixture. Once the pure variables have been determined through interaction with the maximum ratio (referred to as ‘purity’) of standard deviation to mean intensity of each spectrum, the original dataset can be resolved into pure components and their contributions in the original mixture spectra. The SIMPLISMA algorithm has been described in detail elsewhere.^{24,25} The results obtained from SIMPLISMA when applied to time evolving ESR data sets are pure kinetic and spectral profiles of the radicals present in the studied polymer. Resolved spectral profiles can be used to identify these radicals by comparing them with those reported in the work by Paul et al.⁴³ or by ESR spectra simulations (Figure 5). Afterward, the time profiles give the kinetic information of each radical and a description of the full-time-dependent process. For curve resolution methods, Abou Fadel et al.⁴⁰ use SIMPLISMA and then MCR-ALS. The main interest of MCR-ALS is to impose constraints,

such as the nonnegativity on the concentration profiles. As all the profiles obtained in this work are positive, there is no interest presently in constraining and simplifying the digital part.

The SIMPLISMA procedure shows that the ESR signal is decomposed into three signals corresponding to three radicals species as given by $g = 2.003$: a signal ascribed to alkyl radical with $a_H = 2.152$ mT (Figure 4a), a signal ascribed to allyl radical with $a_H = 1.324$ mT (Figure 4b), and a signal corresponding to polyenyl radical mainly (Figure 4c) with some residual alkyl and allyl radical. To account for the variation in the data set (RRSSQ = 5%), three reconstructed signals are sufficient to avoid overfitting (decrease of the RRSSQ in Table S2 and their concentration profile in Figure S3).

Figure 4d shows the superimposition of the signal of alkyl (blue dotted line), allyl (red dotted line), and polyenyl radicals (black solid line). It's clear that the starred bands are because of the combination of signals of these radicals.

To complete the interpretation of the SIMPLISMA treatment, an ESR spectra simulation was performed with EasySpin. The signal provided may contain some combination of signals issued from the different radical species. Hence, the signals given by EasySpin simulation of allyl radicals match significantly with the signal given by SIMPLISMA (Figure 5). The differences are likely due to presence of alkyl and polyenyl radicals. Interestingly,

SIMPLISMA affords an easy way to analyze several tenth of spectra. That so, it is possible to pinpoint two experiments displaying “pure” signals of allyl and alkyl radicals which are nicely modeled using EasySpin (see Figure S4). Therefore, SIMPLISMA is an efficient approach to decipher quickly species observed in the sample.

Same approach was performed for alkyl and polyenyl radicals, a nice agreement was observed for polyenyl radicals (see Figure S4). For alkyl radicals a good agreement

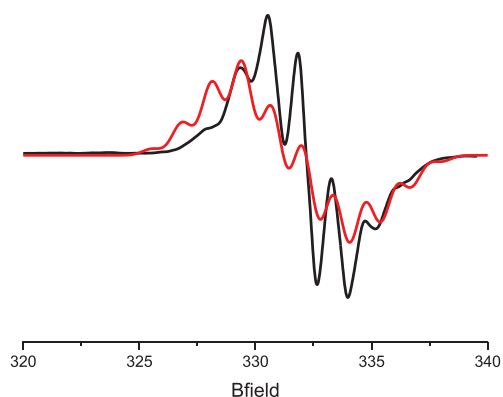


FIGURE 5 Signal of allyl radical (red line) simulated with EasySpin and (black line) reconstructed with SIMPLISMA treatment. [Color figure can be viewed at wileyonlinelibrary.com]

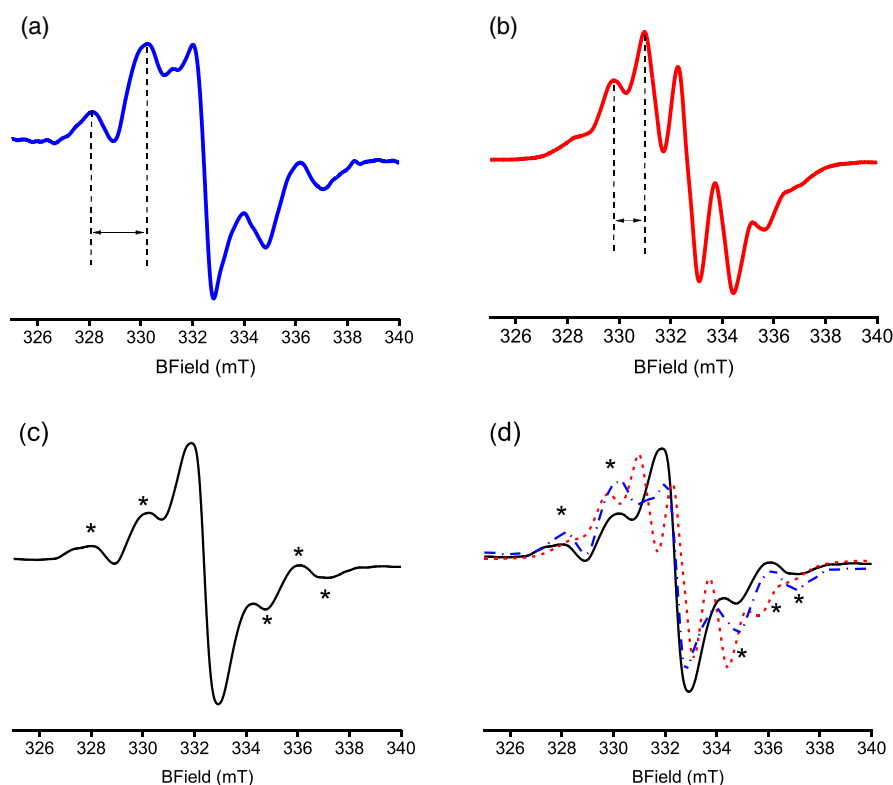


FIGURE 4 “Pure” signal reconstructed with SIMPLISMA analysis displays (a) alkyl radicals ($a_H = 2.152$ mT), (b) allyl radical ($a_H = 1.3236$ mT), (c) polyenyl radical, and (d) the superimposing of signals (a–c). Stars indicate alkyl and allyl radicals, blue dotted line represents alkyl radicals and red dotted line represents allyl radicals. [Color figure can be viewed at wileyonlinelibrary.com]

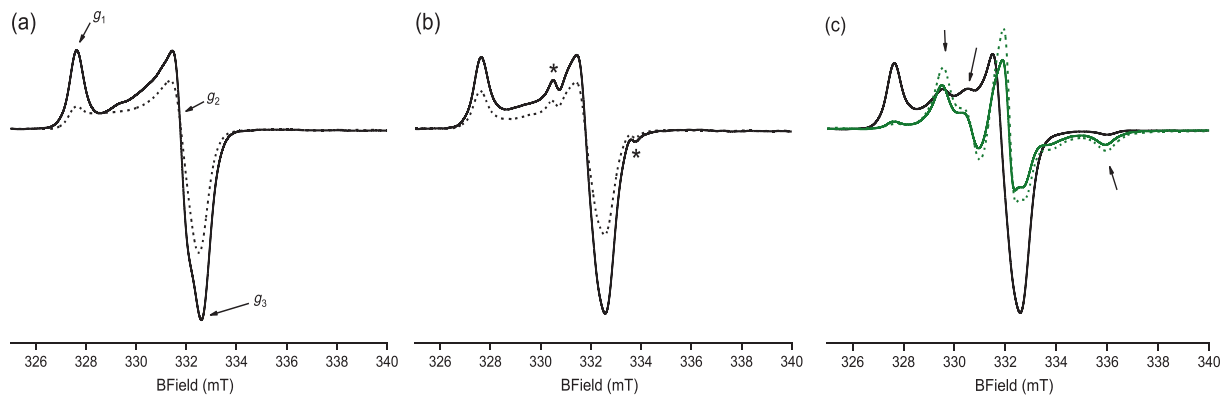


FIGURE 6 Electron spin resonance signal of polypropylene (PP) samples after gamma (full line) or X-rays (dotted line) irradiation at various times after irradiation: (a) PP-2 at day 9 corresponding to a peroxy radical. $g_1 = 2.0339$, $g_2 = 2.0087$, and $g_3 = 2.0036$. (b) Thermoplastic elastomer-5 at day 9 corresponding to a mixture between a peroxy radical and an unidentified radical (stars). (c) PP-3 at 9 days (back line) and 60 days (green line) arrows highlight nitroxide peaks (see SIMPLISMA analysis section). [Color figure can be viewed at wileyonlinelibrary.com]

was observed despite the presence of signal of allyl radicals.

Hence, whatever the irradiation technology, for all the analyzed PE samples, only HDPEs exhibit ESR signals 9 days after irradiation. Radicals (nature and quantity) generated in PE samples irradiated with gamma or X-rays are equivalent.

3.2 | PP and TPE

3.2.1 | Qualitative studies

There is no ESR signal in nonirradiated samples. ESR Signals of PP-2, PP-3, and TPE-5 are displayed in Figure 6 after gamma and X-ray irradiations at various times. Similar signals are observed for other PP and TPE samples and reported in Figure S5. The TPE samples (samples 5 and 6 in Table 1) signals (Figure 6b) mainly correspond to the signal observed in PPs (Figure 6a). The g factor of the major radicals observed in Figure 6 is 2.015 ascribed to a peroxy radical ($\text{RO}_2\bullet$, $g = 2.015$) (Figure 7a) according to the literature.^{44,45} Interestingly, a nonidentified radical is observed for TPE-5 (stars in Figure 6b) with a signal superimposed to the signal of peroxy radical. More puzzling is the significant signal of side product (arrows in Figure 6c) observed with the peroxy signals for sample 3. Upon aging up to 60 days after irradiation (Figure 6c) this signal is persistent and becomes the main signal. The g -value of 2.004 is ascribed to a nitroxide, which is a radical side product. Indeed, sample 3 is loaded with hindered-amine light stabilizers (HALS) which are prone to afford the signal of nitroxide (Figure 6b,c).

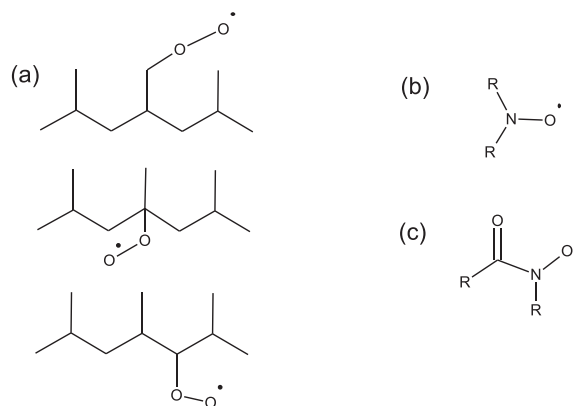


FIGURE 7 (a) Possible structures of the peroxy radicals formed. (b) Structure of nitroxide radicals, and (c) structure of acyl nitroxide.

Taking into account the structure of PP, several peroxy radicals are possible (Figure 7a) and cannot be distinguished. For PP-3, because of the presence of HALS, the presence of amines may quench the oxidation processes by scavenging radicals to generate many side products such as highly persistent nitroxide (Figure 7b) or acyl nitroxide (Figure 7c).

3.2.2 | Quantitative studies

Figure 8 displays ESR signal evolution overtime for PPs postirradiation, showing the decay of the signal of the peroxy radical. Figure 9 plots radicals concentration measured by ESR at different times postirradiation. Whatever the irradiation technology, most PPs and TPEs exhibit similar trends in term of ESR signals, radical

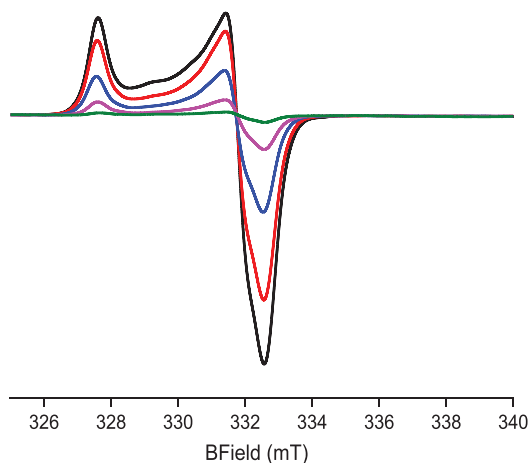


FIGURE 8 Monitoring of electron spin resonance signal for polypropylene-4 after gamma irradiation and measured at 9 days (black line), at 15 days (red line), at 30 days (blue line), at 60 days (pink line), and at 120 days (green line). [Color figure can be viewed at wileyonlinelibrary.com]

decay kinetics, concentration profiles, except for PP-3 (Figure 9a–e). Sample 6 couldn't have been measured after gamma irradiation (Figure 9f). All samples present a similar radical concentration decay and no more significant ESR signal is detected 120 days after irradiation, except for PP-3 (Figure 9c). ESR measurements were stopped at that stage. This comment holds for both for X-rays and gamma irradiated samples. For PP-3, assuming the oxidation of HALS by RO_2^\bullet radicals, the plateau observed after 60 days denotes the full consumption of RO_2^\bullet species as for other samples. For all PP samples being irradiated with X-ray and gamma rays, the quantity of radicals generated is equivalent (Table S3 in Supporting Information).

3.2.3 | SIMPLISMA analysis

The SIMPLISMA treatment was applied to the 23 spectra recorded over 380 days for gamma-irradiated samples

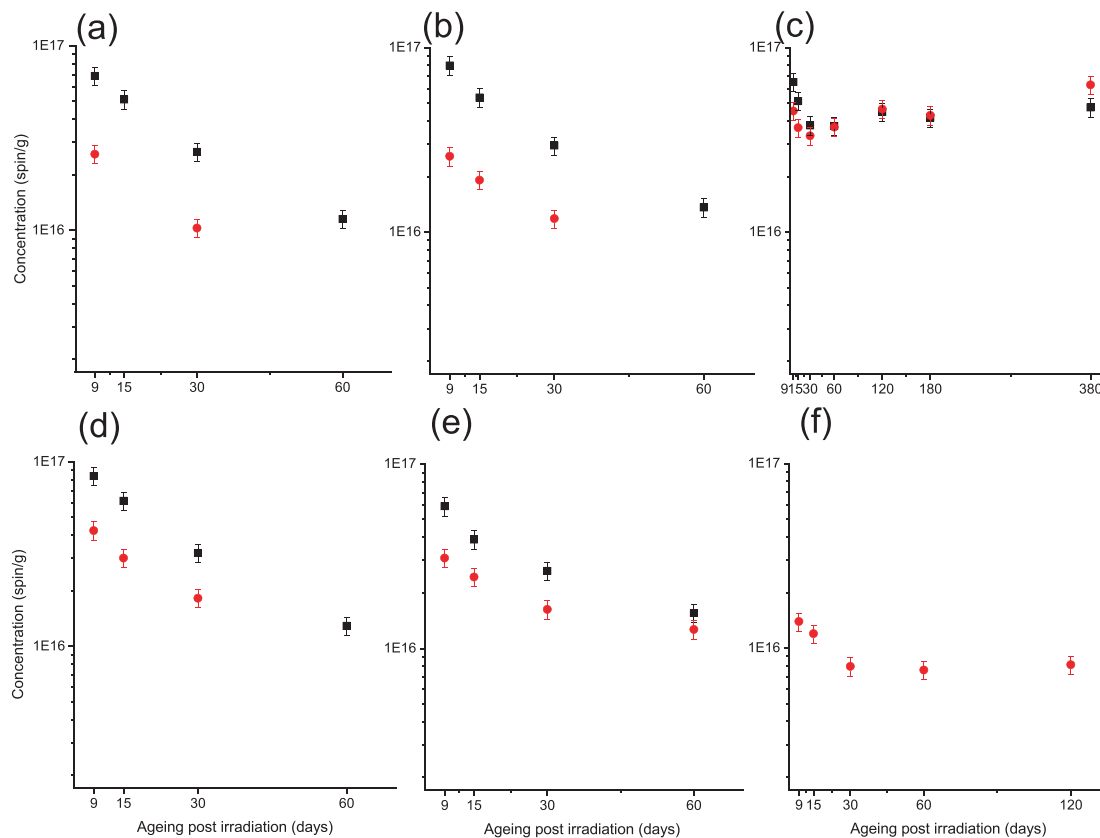


FIGURE 9 Kinetics studies monitoring of the concentration of radicals for each polypropylene (PP) and thermoplastic elastomer (TPE) samples recorded by electron spin resonance as concentration (spin g^{-1}) versus aging post irradiation (days). (a) PP-1. (b) PP-2. (c) PP-3. (d) PP-4. (e) TPE-5. (f) TPE-6. Red circles correspond to samples irradiated by X-rays and black squares are samples irradiated by gamma rays. [Color figure can be viewed at wileyonlinelibrary.com]

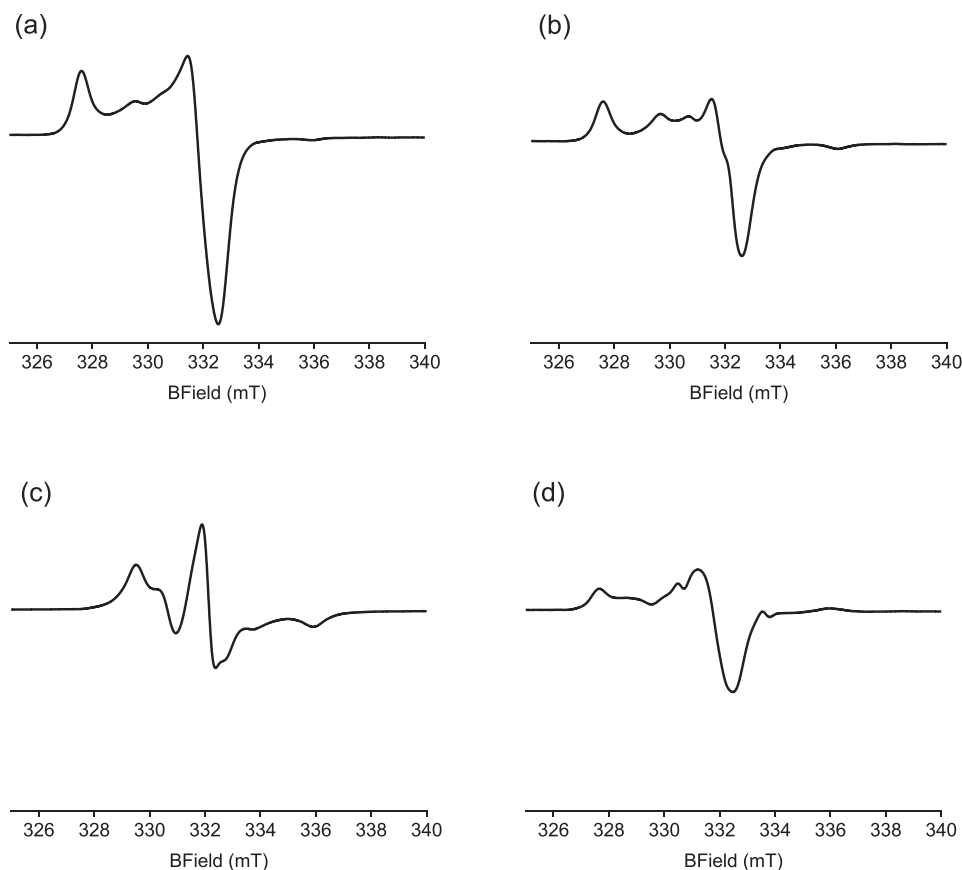


FIGURE 10 “Pure” signals reconstructed with SIMPLISMA analysis displays peroxyl radical (a) in mobile and (b) in nonmobile phase. (c) “Pure” signal of nitroxyl radical. (d) “Pure” signal of a mixture of peroxyl and unidentified radicals.

and the 36 spectra recorded over the same period for X-ray samples, in order to separate the signal of each species. The changes in the data set (59 ESR spectra) are nicely described by four species affording different kinetics (RRSSQ is <9%) (decrease of the RRSSQ in Table S4). These four signals are assigned: two for peroxyl radicals (Figure 10a,b), one for the nitroxide (Figure 10c) and last one for the mixture of peroxyl radical and the unidentified radical observed in TPE-5 (Figure 10d). The concentration profiles of peroxyl radicals, nitroxide radicals, and the mixture of radicals are obtained for each irradiation technology at different aging after processing data with SIMPLISMA (Figure S6 in Supporting Information). In SIMPLISMA, absolute concentration cannot be determined because the signal intensity of pure radicals is unknown.

Peroxyl radicals in Figure 10a decayed faster than the ones in Figure 10b. PP exhibits two phases: amorphous and crystalline.^{46,47} We hypothesize that the mobility of polymers is higher in the amorphous phase than in the crystalline phase,³³ which favors termination reactivity. Therefore, we attribute the signal in Figure 10a to peroxyl radicals in the amorphous phase of PP, and the signal in Figure 10b to peroxyl radicals in the crystalline phase of PP. Signal in Figure 10c is a mixture of peroxyl and nitroxyl radicals present in the sample 3. The concentration profiles

display that the absolute concentration of nitroxide increases with aging post-irradiation (Figure S6 in Supporting Information).

4 | CONCLUSION

Given the vast number of commercially available polymer grades that could be utilized in healthcare products, it is not feasible to test them all. As such, we have chosen a selection of samples from these commercial polymer grades for our investigation. Our ESR study indicates that the type of radicals produced is contingent on the specific polymer, though additives may also generate overlapping signals. Additionally, while the qualitative data might fluctuate depending on the precise plastic composition, this does not influence the kinetics of decay. By examining a broad spectrum of polymers, we can affirm that the photon-matter interaction remains consistent across all polymer grades when subjected to gamma and X-rays. Our sample set, which encompasses the most frequently used plastics, will produce findings that can be confidently applied to other polyolefins.

Both groups of studied polymers generate featured radicals independently of the photon irradiation technologies. In sharp contrast to LDPE and LLDPE, the HDPE

samples display strong ESR signal after both gamma and X-ray irradiation, related to their density and their crystallinity. For all HDPE samples, alkyl, allyl, and polyenyl radicals are observed, and differentiated with their coupling constants. The results obtained with the SIMPLISMA treatment and the ESR simulation with EasySpin are correlated. For PP samples, similar ESR signal was observed for all samples attributed to a peroxy radical. The radical nature depends first of all on the polymer family and second on some specific recipes. For one sample, nitroxide radical was identified because of nitrogen containing additives. A curve resolution analysis (SIMPLISMA) allows identifying peroxy radicals. Among 22 different materials subjected to this work, divided in two groups (PE and PP), no significant differences of ESR signals have been observed between gamma and X-ray irradiation. There is no significant difference in amount and kinetics for the free radicals generated from PE and PP despite the generated radicals are different. No quantitative relationship was found between different the radiation source induced radicals and the material shelf life. The aim was to determine if there is a variation in the radicals generated when radiation from the two sources interacts with the products. If no differences are observed, it can be inferred that irradiated materials will exhibit similar behavior irrespectively of the radiation source. The similar ESR signals, kinetics, radical concentration profiles with both gamma and X-rays on PP and PE provide evidence about the same radiation interaction with condensed matter in link with theoretical physical considerations.⁷

AUTHOR CONTRIBUTIONS

Blanche Krieguer: Data curation (equal); formal analysis (equal); investigation (equal); methodology (equal); project administration (equal); software (equal); validation (equal); visualization (equal); writing – original draft (equal). **Sylvain R. A. Marque:** Conceptualization (equal); data curation (equal); formal analysis (equal); investigation (equal); methodology (equal); project administration (equal); software (equal); supervision (equal); validation (equal); visualization (equal); writing – review and editing (equal). **Samuel Dorey:** Conceptualization (equal); data curation (equal); funding acquisition (lead); investigation (equal); methodology (equal); project administration (equal); resources (lead); software (equal); supervision (equal); validation (equal); visualization (equal); writing – review and editing (equal). **Nathalie Dupuy:** Conceptualization (equal); data curation (equal); investigation (equal); methodology (equal); project administration (equal); software (equal); supervision (equal); validation (equal); visualization (equal); writing – review and editing (equal). **Fabien Girard:** Conceptualization

(equal); data curation (equal); investigation (equal); methodology (equal); project administration (equal); software (equal); supervision (equal); validation (equal); visualization (equal); writing – review and editing (equal). **Nina Girard-Perier:** Data curation (equal); investigation (equal); project administration (equal); software (equal); validation (equal); visualization (equal); writing – review and editing (equal). **Florent Kuntz:** Data curation (equal); investigation (equal); project administration (equal); software (equal); validation (equal); visualization (equal); writing – review and editing (equal). **Nicolas Ludwig:** Data curation (equal); formal analysis (equal); investigation (equal); project administration (equal); software (equal); validation (equal); visualization (equal); writing – original draft (equal).

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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