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# XPS analysis of PE and EVA samples irradiated at different $\gamma$ -doses

Samuel Dorey<sup>a,\*</sup>, Fanny Gaston<sup>a,b,c,\*\*</sup>, Sylvain R.A. Marque<sup>c,d</sup>, Benjamin Bortolotti<sup>e</sup>,  
Nathalie Dupuy<sup>b</sup>

<sup>a</sup> Sartorius Stedim FMT S.A.S, Z.I. Les Paluds, Avenue de Jouques CS91051, 13781 Aubagne Cedex, France

<sup>b</sup> Aix Marseille Univ, CNRS, IRD, Avignon Université, IMBE UMR 7263,13397, Marseille, France

<sup>c</sup> Aix Marseille Univ, CNRS, ICR, Case 551, 13397 Marseille Cedex 20, France

<sup>d</sup> Vorozhtsov Novosibirsk Institute of organic chemistry Office 312, 9 Prospect Academican Laurentiev, 630090 Novosibirsk, Russia

<sup>e</sup> STMicroelectronics Rousset SAS, ZI Rousset, Avenue Celestin Coq, 13106 Rousset Cedex, France

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## A B S T R A C T

The principal plastic materials used for the fluid contact and storage in the biopharmaceutical industry are mainly made up of semi-crystalline polymers, polyolefins, PVC, Siloxane and PET. The polyethylene (PE) and the polypropylene (PP) are often used as fluid contact in multi-layer materials like films. As one sterilisation way of single-use plastic devices used in medical and pharmaceutical fields can take place via  $\gamma$ -irradiation, the effect of sterilization on plastics must be investigated. The irradiation process leads to the production of radicals, which can generate changes in the polymer structure and on the polymer surface. It is well known that the presence of oxygen with free radicals precede the generation of peroxide species so called ROS (reactive oxygen species) which are highly reactive. The purpose of this work is to investigate the  $\gamma$ -rays impact on the surface of PE (polyethylene) and EVA (polyethylene vinyl alcohol) based films when ionized at different doses. X-ray Photoelectron Spectroscopy (XPS) was applied to determine the surface compositions of the polymers to highlight the different chemical moieties generated during the  $\gamma$ -irradiation process and to monitor the potential presence of the ROS.

### Keywords:

$\gamma$ -irradiation

Polyethylene

Polyethylene-vinyl acetate

XPS

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## 1. Introduction

The principal plastic materials used for the fluid contact and storage in the biopharmaceutical industry are mainly made up of semi-crystalline polymers, polyolefins, PVC, Siloxane and PET. The polyethylene (PE) and the polypropylene (PP), which belong to the family of polyolefins, enter mainly in the manufacture of one-layer films, covers, stoppers and are more and more used as fluid contact in multi-layer materials like films. As one sterilisation way of single-use plastic devices used in medical and pharmaceutical fields can take place via ionizing radiation [1,2], the effect of sterilization on plastics (i.e. the polymers and their additives) must be investigated. Irradiation processing such as  $\gamma$ -irradiation of plastic single-use medical devices may affect chemical and physical properties of the plastic materials [3,4]. The irradiation process leads to the production of radicals, which can generate changes in the polymer structure and on the polymer surface [5]. It is well known that

the presence of oxygen with free radicals precede the generation of peroxide species so called ROS (reactive oxygen species) which are highly reactive. Multilayer films could be the predominant elements to constitute flexible plastic bags which can contain proteins or other active pharmaceutical ingredients (API). The modification of the film surface properties and some by-products thereof, can thus lead to the modification of sensible proteins prone to oxidation [6,7] due to the presence of ROS. Surprisingly the presence of peroxide is always reported by indirect methods either using enzyme, or colorimetry, dyes, etc. [8–16].

In parallel, high-energy irradiation leads to a succession of chemical reactions, which ultimately lead to either an increase or a decrease in the molecular weight of a polymer. The initial processes which occur when a high-energy photon interacts with an organic polymer are reasonably well established and do not depend essentially on the chemical structure of the material. However, these primary processes lead to a cascade of further reactions, the nature of which depends sensitively on the nature of the polymeric material.

In the evaluation of radiation resistance of plastics, changes in the physico-mechanical, thermal, optical, physico-chemical, and other properties need to be investigated [17]. It should be noted that radiation does not affect the properties of all polymers in the same way, or to the same level, and when selecting a polymer for

a particular application the effect of irradiation should be considered. The purpose of this work is to investigate the  $\gamma$ -rays impact on the surface of several lots of commercial PE (polyethylene) and EVA (polyethylene vinyl acetate) based films when ionized at different doses. Contact angle measurements and XPS (X-ray photoelectron spectroscopy) methods can be used to analyse surface properties of PE and EVA [18–20]. X-ray photoelectron spectroscopy (XPS) was applied as well to determine the surface compositions of the EVA copolymers [21–23]. In this current study, film surface analysis is performed by XPS to highlight the different chemical moieties generated during the  $\gamma$ -irradiation process and to monitor the potential presence of the ROS.

## 2. Materials and methods

### 2.1. Film samples

The two multilayer films studied in this work are: PE film and EVA film. The PE film has the following structure: PE/EVOH/PE, with a thickness of about 400  $\mu\text{m}$ . The EVA film sample is composed of ethylene vinyl acetate (EVA) and ethylene vinyl alcohol (EVOH): EVA/EVOH/EVA, with a thickness of about 360  $\mu\text{m}$ . Two batches of EVA film and three batches of PE film are investigated. For the sake of clarity, the results of the third lot of PE film are not described as it displays very similar results.

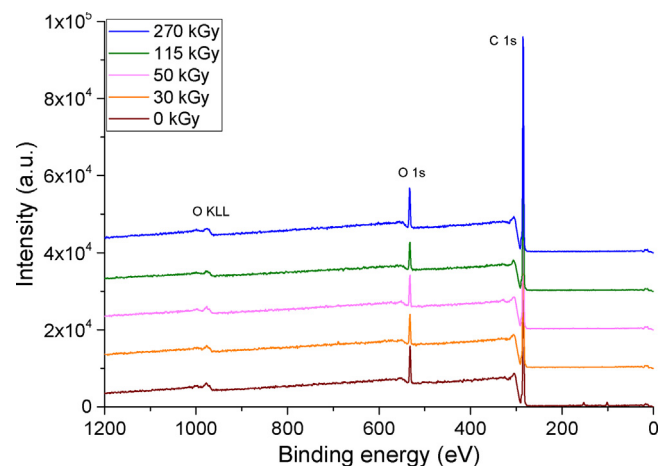
### 2.2. $\gamma$ -Irradiation

All film samples of PE and EVA films have been prepared in specific packaging (PE) to be irradiated at room temperature in a  $^{60}\text{Co}$   $\gamma$ -source providing a dose rate of 8–13 kGy/h, as given by Synergy Health company (Marseille, France). The samples have been  $\gamma$ -irradiated at doses of 30 ( $\pm 1$ ), 50 ( $\pm 1$ ), 115 ( $\pm 2$ ) and 270 ( $\pm 5$ ) kGy. A sterilization cycle corresponds approximately to 25 kGy. Desired dose is obtained by several sterilization cycles, including a non-controlled waiting time in non-controlled storage conditions between each cycle. The impact of the  $\gamma$ -irradiation is assessed from modifications occurring between irradiated samples and non-sterilized samples, which correspond to 0 kGy samples in the document.

### 2.3. XPS

The XPS spectra were carried out with a Kratos Axis Nova spectrometer using a monochromatic Al K(alpha) source (15 mA, 15 kV). XPS can detect all elements except hydrogen and helium, probes the surface of the sample to a depth of 5–10 nanometres, and has detection limits ranging from 0.1 to 0.5 atomic percent depending on the element.

The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f $^{7/2}$  line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p $^{3/2}$  line of metallic copper. The Kratos charge neu-



**Fig. 1.** XPS spectra of EVA film at different absorbed doses. Only XPS spectra recorded on batch 1 are presented as they are identical to batch 2.

tralizer system was used on each samples. The effectiveness of the charge neutralization was tuned by monitoring the Full Width at Half Maximum of the C 1s peak of adventitious carbon. The quantifications are calculated from relative sensibility factors (RSF) from each element, given by the manufacturer. Measurements are performed with a precision of 5% for the major elements and 10% for the minor elements.

Survey scan analyses were carried out with an analysis area of 300  $\times$  700  $\mu\text{m}$ , a pass energy of 160 eV and a dwell time of 100 ms. High resolution analyses were carried out with an analysis area of 300  $\times$  700  $\mu\text{m}$ , a pass energy of 10 eV and a dwell time of 500 ms. Spectra have been charge corrected to the main line of the carbon 1s spectrum (adventitious carbon) fixed at 284.8 eV.

Spectra were analysed using CasaXPS software (version 2.3.16).

## 3. Results and discussion

### 3.1. EVA film

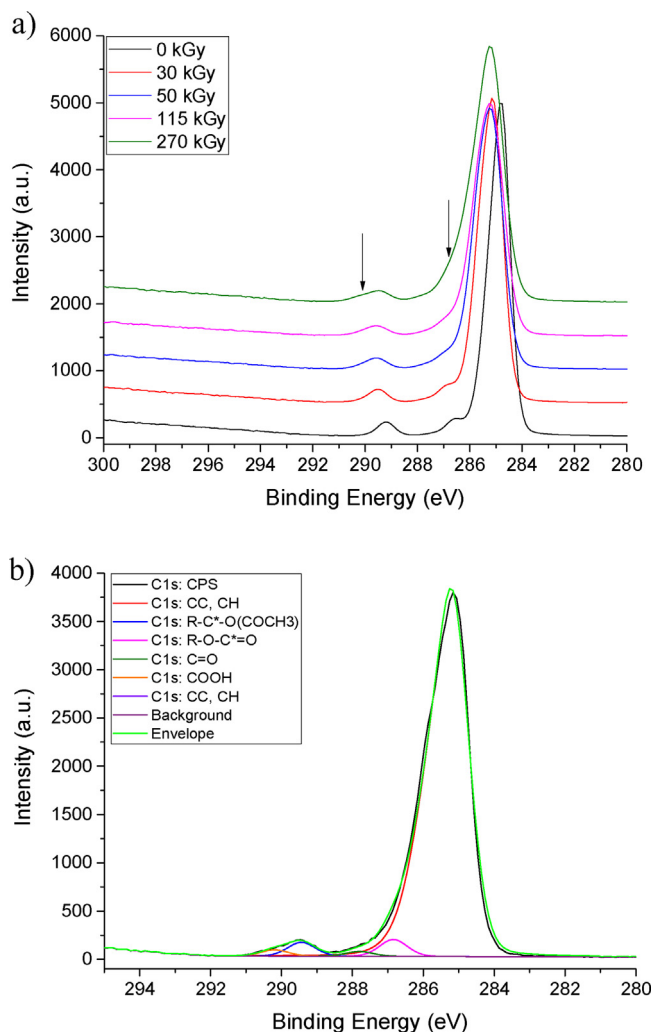
**Fig. 1** shows the surface XPS spectra for pristine EVA film and  $\gamma$  ray-irradiated films at different irradiation doses. All spectra point out the presence of oxygen and carbon atoms and no other element has been found above the detection limit. According to the literature [24,25], the peak at approximately 285 eV is assigned to C1s photoelectrons likely corresponding to C–C, C=O, and O–C=O bonds on the surface of sample. The presence of O1s at 532 eV in the pristine sample is directly attributed to the presence of the ester moiety in the EVA polymer. After irradiation, it is clearly observed in the XPS spectra that the O1s peak intensity decrease with  $\gamma$ -irradiation doses up to 50 kGy and increase afterwards. The peak O1s assigned to the presence of C–O or C=O 24, points out surface changes as oxidation during irradiation under air condition. To estimate change in oxygen content in the surface of the EVA film upon

**Table 1**  
Percentage of carbon and oxygen in EVA film after different irradiation doses.

Irradiation dose (kGy)	Relative composition			Relative composition		
	batch 1			batch 2		
	C 1s (% Atomic Concentration)	O 1s (% Atomic Concentration)	Ratio O/C	C 1s (% Atomic Concentration)	O 1s (% Atomic Concentration)	Ratio O/C
0	92.9	7.1	7.6%	94.1	5.9	6.3%
30	94.3	5.7	6.0%	94.2	5.8	6.1%
50	94.1	6.0	6.4%	94.3	5.7	6.0%
115	94.0	6.0	6.4%	93.6	6.4	6.8%
270	93.1	6.9	7.4%	92.9	7.1	7.6%

**Table 2**  
Assignment of the peaks detected in C1s XPS spectra 26–32 and Variation of the different chemical moiety relative concentration according to the  $\gamma$ -irradiation doses. Carbon marked with an asterisk is the target one when several carbons are written.

Assignment of the peaks detected in C1s XPS spectra											
Binding energy	285.2 eV	286.8 eV	287.8 eV	289.2 eV	290.2 eV						
Assignment	CC, CH	R-O-C*=O	C=O	R-C*-O(COCH <sub>3</sub> )	COOH						
Chemical forms relative concentration (%)											
Batch number		1	2	1	2	1	2	1	2	1	2
$\gamma$ -irradiation doses (kGy)	0	92.8	92.7	3.3	3.4	0.4	0.4	3.3	3.4	0.2	0.1
	30	92.9	92.7	3.1	3.3	0.5	0.6	3.0	3.3	0.5	0.2
	50	92.8	92.8	2.9	3.1	0.8	0.6	2.8	3.1	0.7	0.4
	115	93	92.7	2.9	2.8	0.7	1.0	2.6	2.8	0.8	0.7
	270	92	92.5	3.2	2.7	0.9	1.3	2.6	2.7	1.2	0.9



**Fig. 2.** a) C1s XPS spectra of EVA film irradiated at different  $\gamma$ -doses, b) example of decomposition of the C1s spectrum recorded on sample irradiated at 270 kGy.

irradiation, the level of oxidation was further quantitatively calculated and is shown in Table 1. With an increase of absorbed doses, the level of surface oxidation changes gradually (Table 1, Table 2 and Figs. 2 and 3).

Fig. 2a shows the C1s XPS spectra of EVA films irradiated with different  $\gamma$ -doses. According to the literature [20,22,24,26–32], one major peak at 285 eV is attributable to  $-\text{CH}_2-$  groups in expected environments (Table 2). Two minor peaks at 289 eV and 286.6 eV are assigned to the ester  $-\text{COOR}$  species. This peak is expected in the fresh film because of the acetate moiety in the pristine polymer. On

closer scrutiny, a small peak on the high binding energy side of the CH peak is apparent. Upon curve fitting (Fig. 2b), this small peak is situated at 287.8 eV and is ascribed to carbonyl  $\text{C}=\text{O}$  species [26,27]. For the irradiated surfaces, a chemical shift in the C1s spectra has occurred, which indicates that oxygen containing compounds are produced. Carboxyl groups are formed on the EVA surfaces through the bond scission by the irradiation of  $\text{O}_2$  monomer ions with a fingerprint at 290 eV affording a broadening of the peak at 289 eV as well. The 290 eV peak intensity due to  $-\text{COO}$  groups produced by the EVA degradation grows in intensity during  $\gamma$ -ray exposure (Table 2).

All moiety creations and modifications observed in C1s XPS spectra are corroborated likewise with the O1s XPS spectra (Fig. 3a). Curve fitting allows highlighting thereof all the different chemical moieties during C1s XPS spectra decomposition (Fig. 2b). An increase of the  $\gamma$ -irradiation dose causes an increase of generation of ketones, aldehydes and acids directly related to the degradation of the ester groups from the EVA polymer. This observation agrees with other results obtained using ATR-FTIR technics [33]. Unfortunately, hydro(gen) peroxides have not been detected.

The relative contents of CC and CH are stable up to 270 kGy, informing us that the polymer structure is not deteriorated. Acetate group decreases and acid groups increase with the  $\gamma$ -doses whatever the lots. The  $\text{C}=\text{O}$  and COOH relative contents evolve simultaneously. One may presume that the acetate moieties is transformed into carboxyl moieties. No peroxide has been detected, whereas peroxide must be the root cause of the generation of carboxyl moieties.

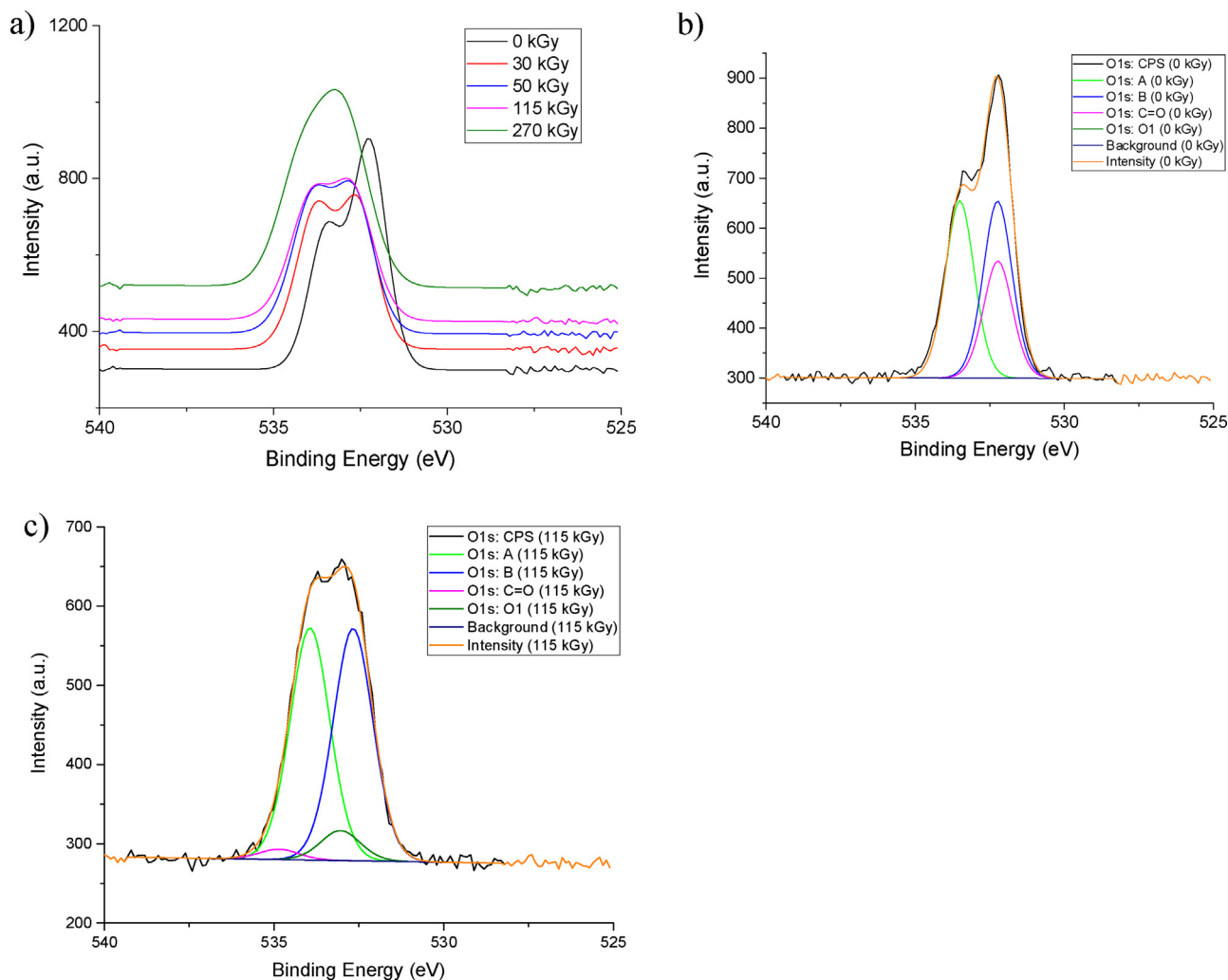
### 3.2. PE film

Radiation effect on the surface of PE film from three batches was studied by XPS spectra; results on one batch are presented and discussed as they are strictly identical for other batches. Fig. 4 shows the surface XPS spectra for pristine film and  $\gamma$  ray-irradiated films at different irradiation doses. All spectra indicate the presence carbon atoms and some of them exhibit the presence of oxygen atoms. The peak at approximately 285 eV is assigned to C1s photoelectrons and the peak at 532 eV is assigned to O1s photoelectrons [22,24,26–30]. The absence of O1s at 532 eV in the pristine sample directly indicates that there no oxidation occurred during thermal processing of the PE film.

The relative elemental composition between carbon and oxygen is given in Table 3.

The relative contents of C are stable up to 115 kGy and decrease slightly at 270 kGy, informing us that the polymer structure is not deteriorated.

Fig. 5a shows the C1s XPS spectra of PE films irradiated with different  $\gamma$ -doses. One single peak at 284.8 eV is ascribed to  $-(\text{CH}_2)_n-$  [22,34–36]. For the irradiated samples, a chemical shift in the C1s



**Fig. 3.** a) O1s XPS spectra of EVA film irradiated at different  $\gamma$ -doses, b) example of decomposition of the O1s spectrum recorded on the non- irradiated (NS) sample, c) example of decomposition of the O1s spectrum recorded on the irradiated sample at 115 kGy. Direct decomposition of oxygen O 1s spectra cannot be done clearly.

**Table 3**  
Percentage of carbon and oxygen in PE film after different irradiation doses.

$\gamma$ -irradiation dose (kGy)	Relative composition			
	Batch 1		Batch 2	
	C 1s (% Atomic Concentration)	O 1s (% Atomic Concentration)	C 1s (% Atomic Concentration)	O 1s (% Atomic Concentration)
0	100	0	100	0
30	100	0	99.9	0.1
50	99.9	0.1	99.8	0.2
115	99.5	0.5	99.4	0.6
270	98.1	1.9	98.4	1.6

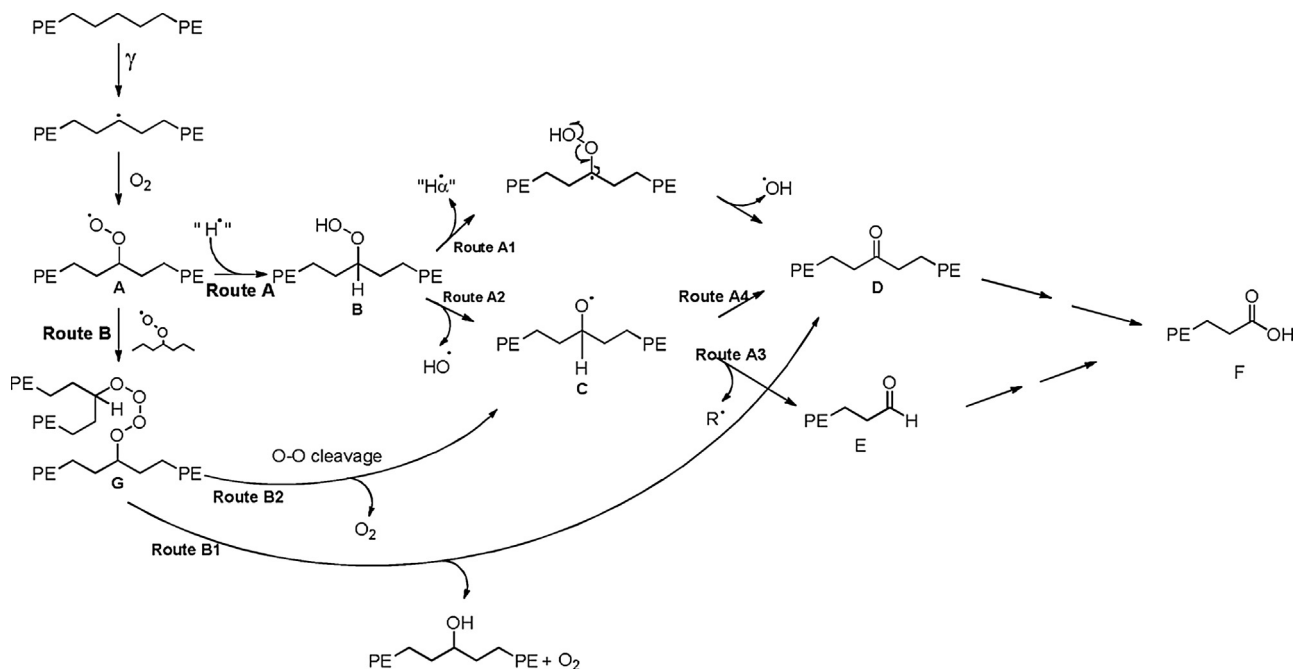
spectra has occurred, which indicates that oxygen containing compounds are produced [37]. On closer scrutiny, a small shoulder on the high binding energy side of the CH peak is apparent. Upon curve fitting (Fig. 5b), this small peak is at  $\sim 285.2$  eV and may be ascribed to C–O(H) species [38], or to  $sp^2$  carbons [39]. In another paper, decomposition of the C1s spectra of LDPE samples leads to Csp<sup>2</sup> at  $\sim 284.9$  eV, and to Csp<sup>3</sup> at 285.2 eV [40].

Due to the overlapping of some O1s components, all moiety generations and modifications observed in C1s XPS spectra do not directly fit with the O1s XPS spectra (Fig. 6). Carboxyl groups are formed on the PE surfaces through the bond scission by the irradiation of O<sub>2</sub> monomer ions. An increase of the  $\gamma$ -irradiation dose causes an increase of oxygenated compounds while distinguishing

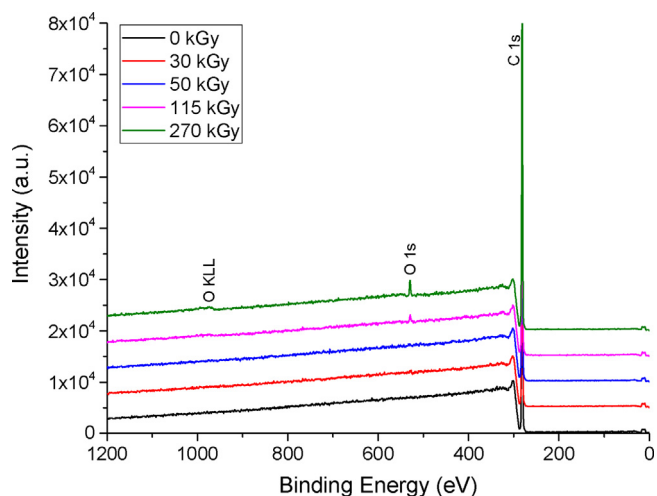
between ketones, aldehydes and acids is not directly possible by curve fitting due to the weak peak intensities. This indicates the oxidation occurs in a weak proportion in a PE film supporting previously reported results [41]. Besides no hydro(gen) peroxide has been detected.

### 3.2.1. Formation mechanisms of oxygenated species

Several mechanisms are considered to account for the formation of oxygenated species. Some of mechanisms proposed in Scheme 1 are reported in the literature [42–44]. Carboxylic acid is generated through a manifold based on alkylperoxyl radical. Interestingly, the formations of ketone and aldehyde are involved in routes A3, A4,



**Scheme 1.** Routes describing the formation of oxidized products.

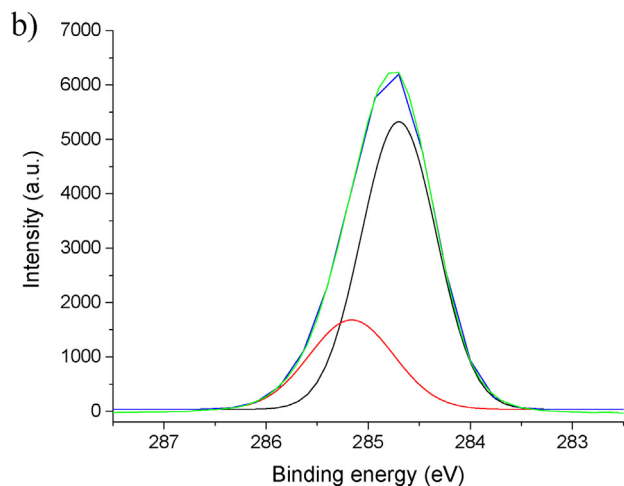
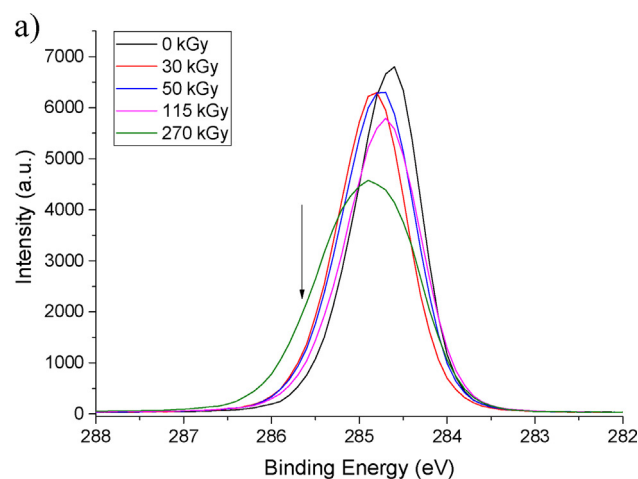


**Fig. 4.** XPS survey spectra of PE film at different absorbed doses. Only one batch is represented as others are identical.

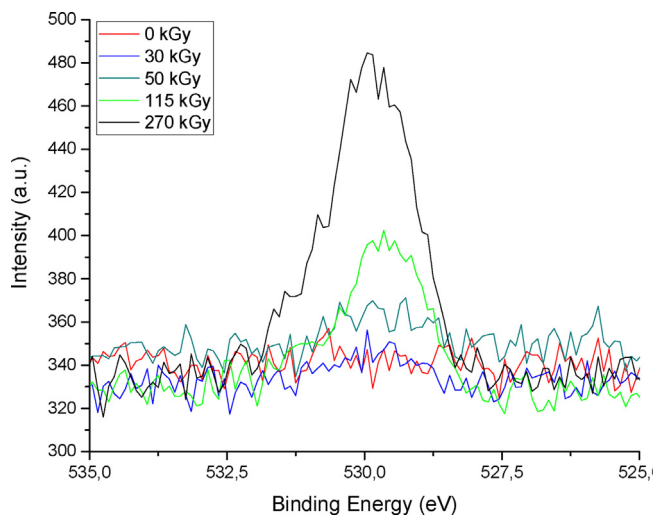
**B**, which may account for the non-symmetrical peak observed in Fig. 5a.

The alkyl radicals are obtained after  $\gamma$ -irradiation of PE, which are scavenged by the molecular oxygen to afford an alkylperoxy radical **A**. The **intermediate A** abstracts a H-atom from its surrounding to afford the hydroperoxide **B** or it reacts by intermolecular coupling to afford a tetra-oxide **G**.

The **intermediate B** reacts either by the fragmentation of the peroxidic bond (**route A2**) with loss of hydroxyl radical and formation of alkoxy radical **C** [42], or by the H-atom abstraction (**route A1**) at the  $\alpha$ -position of hydroperoxy group (Bond Dissociation Energy,  $BDE(\text{CH}_3\text{CH}_2\text{COOH}) \sim 406 \text{ kJ mol}^{-1}$ ) affording hydroperoxyalkyl radical. Then the latter fragments into the ketone **D** and a hydroxyl radical [42–44]. Abstraction (**route A4**) of the H-atom at  $\alpha$ -position of the oxyl radical **C** ( $BDE(\text{C}_2\text{H}_5\text{CH}(\text{O})\text{CH}_3) \sim 49 \text{ kJ mol}^{-1}$ ) may occur to afford the ketone **D**. More likely to occur is the  $\beta$ -fragmentation of **C** (**route A3**,  $BDE(\text{CH}_3\text{CH}_2-\text{CH}(\text{CH}_3)\text{O}^\bullet) \sim 18 \text{ kJ mol}^{-1}$ ) releasing an aldehyde



**Fig. 5.** a) C1s XPS spectra of PE film irradiated at different  $\gamma$ -doses, b) example of decomposition of the C1s spectrum recorded on sample irradiated at 50 kGy.



**Fig. 6.** O1s XPS spectra of PE film irradiated at different  $\gamma$ -irradiation doses.

(E) and an alkyl radical. The ketone **D** and the aldehyde **E** could be further oxidized into carboxylic acids **F**.

In parallel to the **route A**, the **intermediate A** reacts also by self-coupling (**route B**) to afford the tetra-oxide **G**, which collapses either in ketone **D** and alcohol [45] (**route B1**) or by O–O bond cleavage releasing O<sub>2</sub> in the intermediate radical **C** (**route B2**) [46].

#### 4. Conclusion

In the evaluation of the  $\gamma$ -rays impact on PE (polyethylene) and EVA (polyethylene vinyl alcohol) films when ionized at different doses, changes in the physico-chemical features on surface have been investigated by XPS (X-ray Photoelectron Spectroscopy) to highlight the different chemical moieties generated during the  $\gamma$ -irradiation process.

In the EVA film, the chemical groups corresponding to the carboxylic acids and aldehyde/ketones increase with the  $\gamma$ -irradiation dose. The acetate moiety decreases on film surface when increasing  $\gamma$ -irradiation due to the lysis of the acetate group of the EVA polymer in profit to the carboxylate, aldehyde/ketones moieties. The shift of the C1s and O1s peaks indicates as well an oxidation of the film surface occurs. After all, it seems the highest dose investigated in that paper, i.e. 270 kGy, leads as well to the cleavage of carboxylates.

In opposite, the XPS analysis of the PE film does not reveal a high content of oxygen when  $\gamma$ -irradiating the samples. Asymmetric shapes of C1s and O1s peaks linked to weak intensity in XPS spectra on PE films do not allow clearly identifying the generated chemical groups. Previous study suggests that carboxylic acids and aldehyde/ketones are generated<sup>41</sup>. The films surface study investigated by XPS did not allow detecting the hydro(gen) peroxides generated during the  $\gamma$ -irradiation process. Nevertheless, the hydro(gen) peroxide(s) must be present to induce oxidation of the polyolefin chains leading to the generation of the oxygenated species.

The radiation does not affect the properties of all polymers in the same way, or to the same degree, even though polymers investigated here are all polyolefin based. It means the effect of irradiation should be considered when selecting a polymer for a particular application. However, the extent of the modifications issued by  $\gamma$ -rays should be seen as minor as new chemical moieties mainly brought by oxygenated species represent <1% of the pristine moieties present after the plastics production. A stabilisation of the oxidised specie moieties on film surface would indicate

that hydro(gen) peroxide has wholly reacted guarantying an inert film surface.

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