

Radiation-Induced Oxygen Scavenging Activity in EVOH Copolymers

Amparo López-Rubio,¹ José María Lagarón,¹ Tomoyuki Yamamoto,² Rafael Gavara¹

¹Packaging Laboratory, Institute of Agrochemistry and Food Technology, 46100 Burjassot, Spain

²Central Research Laboratory, The Nippon Synthetic Chemical Industry Company Limited, Osaka 567-0052, Japan

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ABSTRACT: Oxygen scavenging capacity has been observed for the first time in an ethylene-vinyl alcohol (EVOH29, i.e., 29 mol % of ethylene) copolymer as a consequence of electron beam irradiation at doses of 30 and 90 kGy. This oxygen blocking activity is thought to arise from the reaction of oxygen with the free radicals formed during the irradiation process and it has been observed to be dependent of the irradiation dose, i.e., the higher the dose, the longer the time the polymer is able to react with oxygen. The characterization of the irradiated polymeric samples has been carried out through DSC and FT-IR and the oxygen transmission rate has been measured as a function of time and compared with the properties of the nonirradiated material. A

drop in the melting point and in the enthalpy of fusion and broader peaks were observed after irradiation, which indicated changes in the morphology of the copolymer. Through FT-IR, a slight decrease in the crystallinity of the irradiated EVOH29 was observed at the highest irradiation dose and several bands arise which correspond to the formation of degradation products such as aldehydes and ketones after irradiation. Those radiolysis compounds were identified through gas chromatography coupled to mass spectroscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2676–2682, 2007

Key words: barrier; electron beam irradiation; structure-property relations; oxygen scavenging; crystallinity

INTRODUCTION

Irradiation of prepackaged foodstuffs using gamma and electron beam radiation is gaining ground as a method of food preservation. Although widely used in the US, the commercialization of irradiated products in many European countries is rather limited due to strict regulations concerning the labeling of the food products and to the lack of information given to consumers about the harmlessness of irradiated food over consumers' health.

To enhance the protection offered by irradiation, foodstuffs are usually prepackaged in flexible packaging materials prior to the treatment and, in that way, subsequent recontamination by microorganisms is prevented. Moreover, this technique is also being used for the sterilization of flexible packages utilized later on in aseptic packaging technology.¹

The advantages of this technique include the following:

It can be used at room temperature and, therefore, the nutritional characteristics of the food products are maintained;

The treatment offers a reliable sterilization;

The operation is safe and relatively easy; and

The irradiation dose and dose rate can be easily controlled.²

However, irradiation also presents a number of limitations:

The irradiation doses allowed for food sterilization cannot inactivate enzymes and, thus, it is necessary to use it in combination with heat, for example, to achieve a complete stabilization of food products;

The irradiation is not capable of inactivating viruses and microbial toxins and, therefore, in certain applications it cannot totally assure food safety.³

Irradiation can induce organoleptic changes, especially in fatty products. For example, the irradiation in milk is not feasible because doses of 0.5 kGy provoke aroma alterations.⁴

Because of the variability of the food products, it is difficult to standardize the treatment.^{5,6}

As a consequence of irradiation, radiolysis products from the packaging materials may be liberated to the inner package atmosphere and affect the sensory properties and even the safety of prepackaged food products.⁷

Correspondence to: R. Gavara (rafael.gavara@iata.csic.es).

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Concerning this last aspect, plastics are affected in various ways when exposed to high-energy radiation. The polymer chains may exhibit scission, cross-linking,⁸ free radical production,^{9,10} formation of gases and low molecular weight radiolysis products,¹¹ discoloration and formation of unsaturated bonds.¹² The dominant effect depends on the particular material, additives used in the plastic, radiation dose and irradiation conditions.¹³

Obviously, physical and chemical changes in plastics as a result of irradiation are of prime importance since they can affect the quality of the packaged food products. Probably because of the lack of information, there are limited number of polymers approved under current regulatory standards of the United States Food and Drug Administration (USFDA) to be irradiated together with the food products.¹⁴ USFDA states that any dietary constituent is below the threshold of regulation (TOR) if it occurs at less than 0.5 ppb in the diet,¹⁵ and it has been demonstrated that all the radiolytic and nonradiolytic products of ethylene-vinyl alcohol (EVOH) copolymers are within this TOR (safe limit),¹¹ so in principle, this confirms the safety of irradiated EVOH as a food contact material. EVOH copolymers are widely used as high barrier layer in multilayer food packaging structures due to their outstanding properties and very low permeability to oxygen and food aromas. The formation of radiolysis compounds as well as the changes occurred as a consequence of irradiation in the structure and properties of these materials have been already studied. However, to the best of our knowledge, the radiation-induced oxygen scavenging activity that these copolymers show has not been described before.

The aim of this article was, therefore, to study the potential structural modifications that explain the curious behavior observed in EVOH copolymers as a consequence of electron beam irradiation.

EXPERIMENTAL

Materials

A commercial grade of an ethylene-vinyl alcohol copolymer containing a 29 mol % of ethylene in the copolymer composition (Soarnol[®] D2908, EVOH29) was supplied by the Nippon Synthetic Chemical Industry (Nippon Gohsei, Osaka, Japan). The films of two different thicknesses (approximately 10 and 60 μm) were shipped individually vacuum packaged in aluminum bags to keep their properties after irradiation as constant as possible. Nonirradiated samples were also supplied for the sake of comparison.

Methods

Irradiation

The monolayer films of 10 and 60 μm of EVOH 29 were irradiated using an electron beam at doses of 30 and 90 kGy. Irradiation was carried out at room temperature in the presence of air with an Electrocurtain CB250/15/180L (Eye Graphics, Tokyo, Japan) in the Central Research Laboratory (Nippon Gohsei, Japan) with an acceleration voltage of 200 KV and an irradiation current of 1.4 mA. Irradiation doses were measured using an Eye Graphics method.

Oxygen transmission rate

Oxygen transmission rate (O_2TR) measurements were performed in an OX-TRAN[®] 2/20 (Lippke, Neuwied, Germany) at a temperature of 45°C and 0% RH. High temperature assays were carried out to increase the permeability of the EVOH films and, thus, be able to measure it with higher certainty, given the very high barrier character of these materials with 29 mol % of ethylene content. The values shown are the average of at least three samples.

Differential scanning calorimetry

DSC experiments were carried out in a Perkin-Elmer DSC-7 calorimeter (Wellesley, MA). The heating and cooling rate for the runs was 10°C/min, being the typical sample weight around 4 mg. Calibration was performed using an indium sample. All tests were carried out, at least, in duplicate to confirm the repeatability of the results. The temperature range of the assays was from 50°C to 200°C. From the thermograms, the melting temperature was determined from the maximum of the endotherm. Three films were analyzed per sample.

Fourier transform infrared spectroscopy

Transmission FT-IR experiments were recorded with a Bruker Tensor 37 equipment (Ettlingen, Germany) with 4 cm^{-1} resolution and 4 s as typical acquisition time. The samples, previously vacuum-dried, were placed into the measuring chamber which was continuously purged with a high flux of N_2 to maintain a constant dry and inert environment.

Gas chromatography/mass spectrometry

The identification of organic compounds released by the irradiated films when exposed to air was carried out by gas chromatography coupled to mass spectrometry. Film samples of about 10 cm^2 were introduced in a glass vial closed with a mininert valve

(Supelco, Belafonte, PA) and kept at room temperature during 10 days. Some samples were stored in air and others were stored in nitrogen by purging the vial atmosphere with a high flow stream of this gas. The volatile compounds released from the film in the vial headspace were analyzed by gas chromatography sampling with a solid phase microextraction (SPME) device. The SPME system was introduced in the vial through the mininert port and the 65 μm PDMS/DVB fiber (Supelco, Belafonte, PA) was exposed to the vial headspace during 20 min. Then, the fiber was introduced in the injection port of a G1800A GC/MS (Agilent Technologies, Palo Alto, CA) where the volatile compounds were thermally desorbed and identified by comparison with the Wiley 138K Mass Spectral Database software (John Wiley New York, NY) and posterior verification with pure aldehydes and ketones supplied by Sigma (Barcelona, Spain) and used without further purification. The chromatographic conditions were as follows: injector temperature, 220°C; helium flow rate, 1 mL/min; GC-mass spectrometer interface temperature, 280°C; initial oven temperature, 40°C during 3 min; first temperature ramp at 3°C/min to 60°C; second ramp at 10°C/min; final temperature, 250°C for 5 min. The GC was equipped with a TRB-Meta X5 capillary column (30 m, 0.32 mm internal diameter, 0.25 μm film thickness; Teknokroma, Barcelona, Spain). Mass spectra were obtained by electron impact at 70 eV, and data were acquired across the range 34–400 *uma*.

RESULTS AND DISCUSSION

Oxygen scavenging capacity of irradiated EVOH

Despite the extensive characterization of the effects of irradiation over polymeric materials, to the best of our knowledge, there has not been any previous report about the induced capacity of oxygen scavenging in EVOH copolymer which, specially in the case of plastics for food packaging applications (EVOH copolymers are used as high-barrier materials for oxygen-sensitive products) is of paramount importance.

This oxygen scavenging phenomenon of the irradiated EVOH29 was observed by placing the polymeric film samples in the OX-TRAN immediately after opening the aluminum bags supplied. The oxygen transmission rate (O_2TR) of the materials was recorded as a function of time until equilibrium was reached. Figure 1 shows the O_2TR evolution of the irradiated films in comparison with the nonirradiated polymer. In this case, as the thickness of the film samples analyzed is identical (10 microns), O_2TR values can be directly compared. From this figure it can be observed that the oxygen transmission

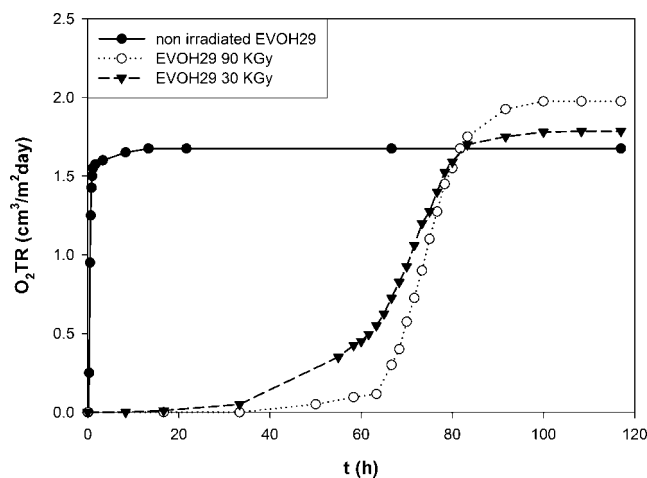


Figure 1 Oxygen transmission rate curves of EVOH29 nonirradiated and irradiated at 30 and 90 kGy.

rate of the EVOH29 irradiated at 90 kGy is close to zero during the first 50 h and, in the case of the copolymer irradiated at 30 kGy, the passage of oxygen is “blocked” during more than 30 h.

However, the equilibrium permeability of the irradiated films is higher (about 18% and 7% for the films irradiated at 90 and 30 kGy respectively) than that of the nonirradiated specimen and, therefore, it seems that the oxygen scavenging induced capacity is directly related with changes in the polymeric structure, because the higher the irradiation dose applied to EVOH, the longer the time the polymer blocks oxygen and, concurrently, the higher the equilibrium permeability attained.

After measuring their oxygen scavenging capacity, the irradiated films were exposed to dry nitrogen and a new O_2TR experiment was initiated. Figure 2 shows the first and second tests run on a sample irradiated at 90 kGy. In the second experiment, the curve profile, instead of reflecting the oxygen blocking capacity, was similar to that shown by the nonirradiated sample, although the final transmission rate was identical to that observed in the first experiment.

From the second run curve, it is possible to determine the diffusion coefficient (D) by curve fitting to the Pasternak’s solution to the Fick’s laws with the boundary conditions of the permeation experiment¹⁶:

$$\frac{F(t)}{F(\infty)} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{\ell^2}{4Dt}} \sum_{n=1,3,5}^{\infty} \exp\left(-\frac{n^2 \ell^2}{4Dt}\right)$$

where F is the transmission rate at any time (t) and at equilibrium (∞), and ℓ is the film thickness. Considering that the permeability coefficient is the product of D times the solubility coefficient (S) as defined by Henry’s law, it is possible to characterize the oxygen transport properties through the irradiated sam-

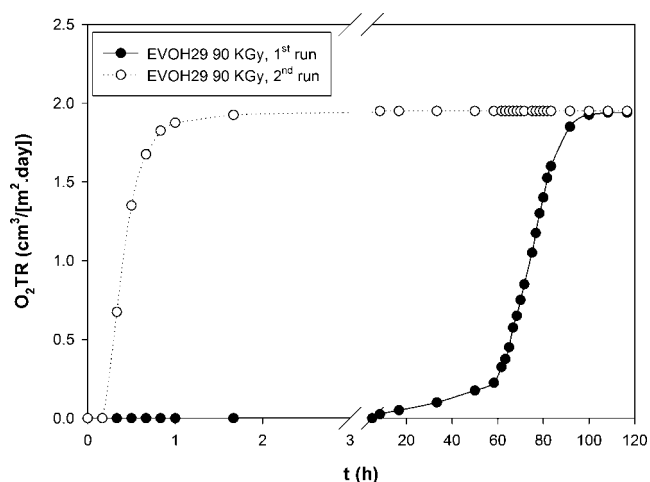


Figure 2 Oxygen transmission rate curves of EVOH29 irradiated at 90 kGy obtained immediately after opening (1st run), and once the scavenging effect is exhausted (2nd run).

ple. Table I lists the values of the three coefficients for a nonirradiated EVOH29 film and that of a copolymer film irradiated at 90 kGy with the oxygen scavenging capacity exhausted.

As can be observed, the irradiation slightly decreases the solubility to oxygen of the polymer but significantly increases the oxygen diffusion coefficient through the film. This last parameter appears to be the main responsible of the observed increment in O_2TR , and therefore in the permeability coefficient.

In Figure 2, the area limited by the two curves (the oxygen scavenging film and that with this capacity exhausted), the O_2TR at equilibrium and the baseline can be an indirect measurement of the oxygen scavenging capacity of the film. For the 90 kGy irradiated film, this capacity has been estimated in about $5 \text{ cm}^3/\text{m}^2$ of film.

Thermal and structural variations as a consequence of irradiation

If the crystalline polymeric phase is affected by the irradiation treatment, it is expected that the thermal characteristics also change. Both the nonirradiated

TABLE I
Oxygen Permeability (P), diffusion (D), and solubility (S) coefficient values for nonirradiated and irradiated EVOH29 films

	Nonirradiated	Irradiated 90 kGy
D (m^2/s)	$(8.0 \pm 0.4) \times 10^{-15}$	$(11.0 \pm 0.6) \times 10^{-15}$
Permeability ($\text{m}^3 \text{ m}/\text{m}^2 \text{ s Pa}$)	$(1.94 \pm 0.05) \times 10^{-21}$	$(2.43 \pm 0.07) \times 10^{-21}$
S ($\text{m}^3/\text{m}^3 \text{ Pa}$)	$(2.42 \pm 0.20) \times 10^{-7}$	$(2.21 \pm 0.18) \times 10^{-7}$

and the irradiated copolymer samples were temperature scanned and the thermograms obtained are collected in Figure 3. The first heating runs of the three samples analyzed (upper curve of each experiment) display a rather broad melting endotherm but the maximum of the peak is displaced towards lower temperatures in the irradiated samples (the higher the dose used during irradiation, the lower the melting point). For the sake of clarity, the DSC parameters (melting and crystallization temperatures, enthalpies of fusion and crystallization and peak width) obtained for the different experiments are showed in Table II.

From Figure 3 it is apparent that there are induced structural changes and, moreover, that those morphological modifications caused by irradiation are irreversible. Again, the effects prove to be dose-dependent as, for example, the crystallization temperature range is more extended after irradiation and if comparing between both treatments, the higher dose, i.e., 90 kGy, shows the broadest crystallization peak.

In Table II the dose-dependent irreversible morphological changes induced by irradiation are clearly discernible. From the second heating rate it is observed that the higher the irradiation dose, the lower the melting point and the enthalpy of fusion and the broadest the melting peak. That is, as the irradiation dose is increased the crystallinity appears to decrease and the crystals formed appear to be more heterogeneous.

Among the previously commented chemical reactions that arise after irradiation, the formation of free radicals has been observed to be the predominant

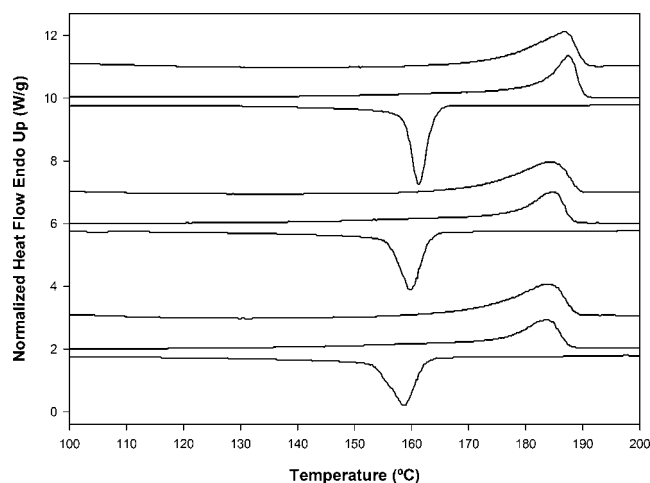


Figure 3 DSC thermograms of (from up to down): nonirradiated, irradiated at 30 kGy and irradiated at 90 kGy EVOH29 films (with the scavenging capacity exhausted). The three runs of each experiment are showed together in the figure, being the upper one the first heating run. Data have been offset for clarity.

TABLE II
DSC Parameters of Nonirradiated, Irradiated at 30 kGy,
and Irradiated at 90 kGy EVOH29 films^a

	Nonirradiated	Irradiated at 30 kGy	Irradiated at 90 kGy
First heating run			
T_m (°C)	187.00	184.00	183.83
ΔH_f (J/g)	70.84	74.06	76.47
Peak width (°C)	16.23	17.25	15.80
Cooling run			
T_c (°C)	161.30	159.80	158.80
ΔH_c (J/g)	-70.67	-69.56	-67.86
Peak width (°C)	5.32	7.57	8.97
Second heating run			
T_m (°C)	187.53	184.87	183.70
ΔH_f (J/g)	74.03	70.79	67.39
Peak width (°C)	8.07	11.16	12.41

^a T_m , melting point; T_c , crystallization temperature; ΔH_f , enthalpy of fusion; ΔH_c , enthalpy of crystallization.

path responsible for the structural changes in polymers irradiated with electron beam.¹⁷

The potential structural modifications responsible for the changes in thermal properties observed were studied through FT-IR spectroscopy. Previous infrared studies were made on irradiated EVOH, but as a part of a multilayer packaging structure² and, in that case, no significant changes were observed between the nonirradiated and irradiated IR spectra.

In Figure 4, FT-IR spectra in the range 900–1800 cm^{-1} of EVOH29 nonirradiated and irradiated at 30 and 90 kGy are represented.

The spectra have been normalized to the intensity of the 1333 cm^{-1} band for comparison purposes. From this figure, two remarkable changes are observed. First of all, from previous studies¹⁸ it is known that the band at 1140 cm^{-1} in the spectra of EVOH copolymers can be related with their crystallinity, in a way that an increase in that band indicates an increase in the molecular order of the materials. Figure 4(b) shows an enlargement of this range in which the decrease in the crystallinity band is hardly discernible in the case of EVOH29 irradiated at 30 kGy, but for the copolymer irradiated at 90 kGy, a clear fall of the 1140 cm^{-1} band is observed, indicating a loss of crystallinity due to the high-dose irradiation treatment.

The second important change is a new band arising at around 1700 cm^{-1} in both irradiated EVOH spectra. This band probably corresponds to the formation of degradation products, such as aldehydes and ketones. In fact, the C=O stretching mode of both aldehydes and ketones generates IR bands in the range 1680–1750 cm^{-1} . Those bands have been also observed at high irradiation doses in LDPE, and have been described to arise from the interaction of oxygen with free radicals of the polymer.¹⁹ It would

be, therefore, expectable that as oxygen molecules interact with the free radicals formed during the irradiation process, the intensity of this spectral range increase. The confirmation of this hypothesis was carried out with the 60 μm EVOH29 specimens that were measured in the transmission mode to get the absolute absorbance in the range of interest.

Figure 5 shows the evolution of this range with time for a sample of EVOH29 irradiated at 90 kGy.

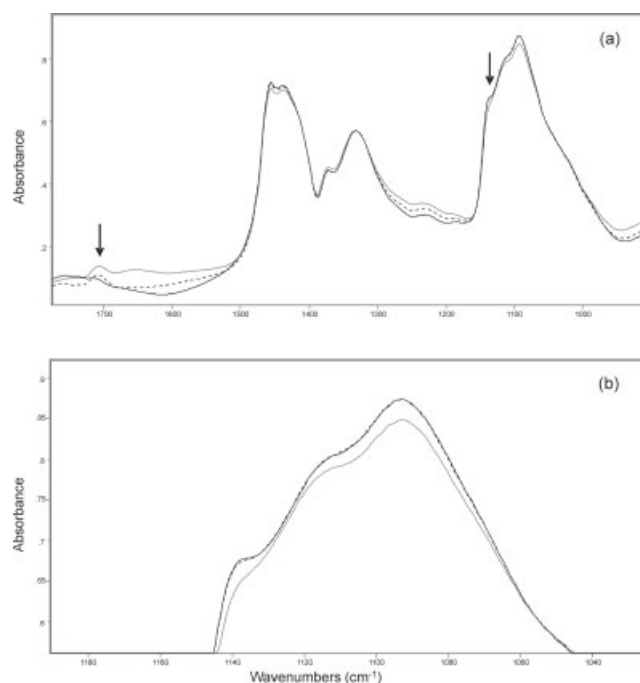


Figure 4 (a) FT-IR spectra of EVOH29 dry (continuous black line), irradiated at 30 kGy (dashed black line) and irradiated at 90 kGy (gray line) in the range 900–1800 cm^{-1} . (b) Enlargement of the “crystallinity band” range.

To obtain the figure, the sample was recorded immediately after opening the vacuum sealed aluminum bag and during 1 week of storage in air. Between measurements it was stored mounted on the sample holder (to avoid changes in sample thickness or optical path) in a desiccator to keep the film dry.

From observation of Figure 5, the intensity of this spectral range increases with time as oxygen reacts with the free radicals of the sample. However, this increase is rather small, indicating that most of the free radicals have already reacted with oxygen.

The formation of these compounds was further confirmed by gas chromatography coupled to mass spectrometry. Figure 6 shows the chromatograms obtained following the methodology described in the experimental section. The figure compares the chromatograms obtained for an irradiated sample stored in air and that for a sample stored in nitrogen. A similar experiment was also carried out with a non-irradiated sample to identify the compounds which desorption is caused just by the irradiation process or the posterior oxygen scavenging effect. No relevant peaks were obtained from the nonirradiated samples (results not shown). However, in the case of the irradiated sample, a number of volatile compounds were detected. As can be seen in Figure 6, several linear aldehydes and ketones were identified as radiolysis compounds. The difference between these results and those observed by Kothapalli and Sadler¹¹ could be easily explained by the different methodology used. They extracted the radiolysis compounds from the EVOH samples with liquid solvents used as food simulants, while in this work only volatile compounds released by the film in the vial headspace and trapped by the SPME fiber were analyzed. Another relevant feature is that in the absence of oxygen, the release of compounds is highly reduced. This result appears to confirm that these compounds are produced by reaction of oxygen molecules with the radicals present in the irradiated

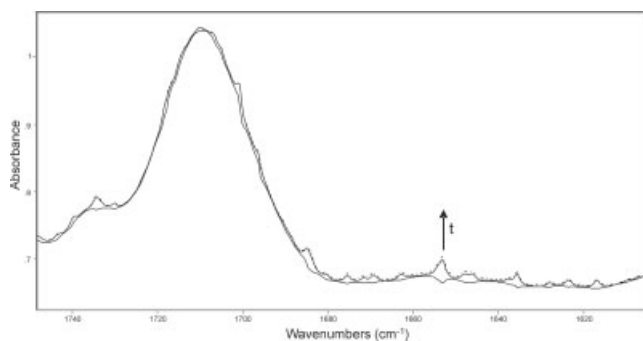


Figure 5 FT-IR spectra in the range 1600–1750 cm^{-1} of an EVOH29 (60 microns thick) measured at various times after irradiation. The arrow indicates the formation of new degradation products as a function of time.

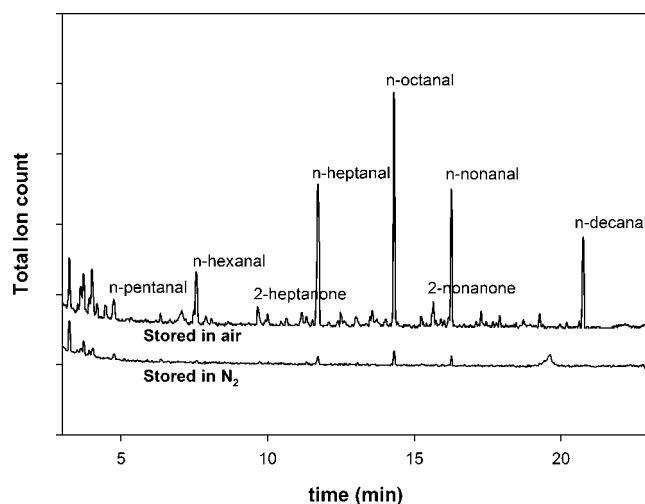


Figure 6 Gas chromatograms highlighting the most relevant volatile compounds, released by an EVOH29 film irradiated at 90 kGy, using the experimental conditions described in the experimental section and after storage in air (top) and in nitrogen (bottom).

films. Although the amounts of these released volatiles were not quantified, their headspace concentration should be very small since no GC peaks were observed from the direct injection of 1 mL of the vial headspace gas.

From a food packaging application point of view, the e-beam irradiation of EVOH-containing structures produce the desired reduction of microbial contamination, and an oxygen scavenging activity which might be of great interest for the packaging of oxygen-sensitive products. As a consequence of oxygen adsorption, the EVOH films release aldehyde and ketone degradation substances, although it is highly unlikely that the release of reduced quantities of these compounds might alter the flavour of the packaged food.

CONCLUSIONS

Oxygen scavenging capacity has been observed for the first time in an ethylene-vinyl alcohol copolymer as a consequence of electron beam irradiation at doses of 30 and 90 kGy. This oxygen blocking activity is thought to arise from the reaction of oxygen with the free radicals formed during the irradiation process, which results in the release of several ketones and aldehydes volatile compounds. After exhaustion of this capacity the irradiated films are slightly more permeable to oxygen as a consequence of faster oxygen diffusion. The results obtained by DSC and FTIR showed that irradiation resulted in a reduction in the crystallinity percentage of the EVOH films and changes in their chemical structure, both effects being responsible of the slight increase in permeability values.

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