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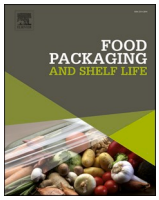

Polylactic acid as a promising sustainable plastic packaging for edible oils

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ABSTRACT

The influence of renewable packaging materials on the oxidative stability of sunflower oil was investigated to evaluate whether they could be used as alternatives to conventional plastics. Two renewable bottle materials, polylactic acid (PLA) and bio-polyethylene (Green-PE) were compared to conventional plastics consisting of virgin and recycled polyethylene terephthalate (PET, r-PET) and regular polyethylene (PE), in a storage study over a period of 56 days. The results showed that the progress of lipid oxidation in PLA was similar to PET and r-PET until day 28, while it was significantly increased in PE and Green-PE. Benzene was detected as the only migration compound in the oil stored in PET and r-PET, with concentrations of 0.153 ± 0.027 μg/g and 0.187 ± 0.024 μg/g after 56 days of storage. The study concluded that PLA could be used as an alternative packaging material for edible oils to replace PET.

1. Introduction

Vegetable oils are one of the most prevalent food products in the human diet and increasing attention is being paid to them due to their importance in the food industry, in nutrition and in human health. Vegetable oils are a source of essential fatty acids as well as of some other minor compounds, such as vitamins, sterols, polyphenols and squalene, to which positive biological effects have been attributed (Gunstone, 2011; Alberdi-Cedeño et al., 2017). Unfortunately, both main and minor compounds naturally present in the oils are susceptible to oxidation reactions which result in a deterioration of their quality and in the formation of a plethora of oxidized compounds (Grüneis et al., 2019; Alberdi-Cedeño et al., 2019). Due to the oxidation of the acyl groups, hydroperoxides are formed, further breaking into secondary and tertiary oxidation compounds (Frankel, 2005; Laguerre et al., 2020; Schaich, 2012). Oxidation is a very complex sequence of transformations. It should be noted that, although there are long-accepted general mechanisms for oil oxidation processes (the classical three stages: initiation, propagation and termination) (Frankel, 2005), the mechanism by which these processes occur is still not fully understood. Moreover, alternative pathways by which the oxidation processes take place have been also described being very different from one case to another, depending on many factors (Schaich, 2012). Thus, the rate of oxidation is influenced by many factors such as the degree of lipid unsaturation, the type and the concentration of oxygen, the temperature as well as light irradiation and the presence and the concentration of minor compounds or molecular species exhibiting either antioxidant or prooxidant activities (Choe & Min, 2006; Pignitter et al., 2014 Martínez-Yusta et al., 2014; Grosshagauer et al., 2019).

Besides these factors, the packaging of vegetable oils is of decisive importance and can affect the final quality of them. Therefore, the choice of the packaging material for such sensitive products is crucial to protect them from lipid oxidation, unwanted biological, mechanical, or physical alterations as well as to prevent contamination of the oil (Shaikh et al., 2021). Several materials, such as glass, metal, and different kinds of plastic films, might be used for packaging. Depending on their O_2 permeability and light transmittance the oxidative stability of the oils and therefore their shelf life and quality may be directly affected (Huyan et al., 2019). Some oils, like extra virgin olive or linseed oils are stored in glass bottles. However, other vegetable oils, such as

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sunflower oil, are stored in transparent plastic containers made of polyethylene terephthalate (PET). Besides PET having good mechanical properties and a low gas permeability to protect the edible oils from being exposed to oxygen, it is also a much lighter material in comparison to glass (Nisticò, 2020). Upon usage PET bottles mostly generate a lot of waste. In 2018, 359 million tons of plastic were produced worldwide, but in Europe only about a third of it was recycled (European Parliament, 2018). Net demand for PET in the EU27 +UK was estimated at 5.1 Mt in 2020, of which 3.0 Mt was supplied from virgin PET production, 1.3 Mt from r-PET production. PET degrades very slowly in nature and can remain for up to 2000 years (Naser et al., 2021). Due to this concern, alternative packaging materials are still being explored. Some alternative packaging materials that can be obtained from renewable food sources, such as corn, potatoes, or sugar cane, are bio-polyethylene (Green-PE) and polylactic acid (PLA) (Naser et al., 2021).

These bioplastics show similar mechanical properties as PET while being more sustainable for the environment. However, they are currently more expensive and are facing several hurdles before they can be considered as a green alternative. One limitation is the need of specific composting utilities for each bioplastic and the lack of research about the migration plastic compounds into food matrices (Rahman & Bhoi, 2021). In the case of PLA, the most promising material from the above-mentioned, lactic acid, lactoyllactic acid and other small oligomers for polylactides have been confirmed as likely migration compounds into food simulants (Ubeda et al., 2019). Polymeric migration has also been confirmed for PE, although the structural identities of compounds that take part of it are not fully elucidated (Katsara et al., 2021). However, it is important to ensure the migration of compounds from these alternative packaging materials remains below the overall migration limit (OML) of 60 mg/kg food (European Union, 2011).

Some studies have investigated the differences in the shelf life and quality of edible oils stored in a variety of plastic packaging materials (Sharma et al., 1990; Tawfik & Huyghebaert, 1999; Ramezani, 2007; Hu et al., 2020). These studies have confirmed high-quality properties of materials such as PET and PE, in regard to parameters such as formation of hydroperoxide in the oils. However, information on other oil oxidation parameters is still unexplored, especially in the case of PLA. Furthermore, these studies applied either accelerated aging conditions, like high temperature, and only studied the effect of conventional plastic packaging materials or films as packaging materials. So far, no data is available regarding the comparison of the effect of conventional plastic materials and renewable and/or biodegradable plastic packaging on the oxidative stability of vegetable oils. It is also relevant to point out that, even though alternative materials such as PLA have been reported to possess a higher oxygen permeability compared to conventional packaging materials such as PET, other properties like thickness, color and light transmittance may impact the progress of the oxidation process in oils, which evidences the need of analyzing the performance of these materials in this regard (Naser et al., 2021).

The aim of the current study was to investigate and compare the effect of the plastic packaging materials PE, PET, recycled PET (r-PET), Green-PE and PLA on the oxidative stability and shelf life of sunflower oil stored at retail and household conditions under cold fluorescent light. Attention was paid to the packaging-induced effects on major and some minor lipid compounds (tocopherols), as well as to the evolution of the lipid oxidation products. Moreover, compounds that migrated from the bottle materials to the oils were analyzed.

2. Materials and methods

2.1. Samples

The study was carried out with sunflower oil acquired from a local supermarket (Vienna, Austria). All the sunflower oil belonged to the same batch. Its composition in acyl groups was determined from ^{1}H NMR spectral data as in previous studies (Guillén & Uriarte, 2012), showing values of 55.45 ± 0.16%, 32.47 ± 0.18% and 12.06 ± 0.27% for linoleic (L), oleic or monounsaturated (O or MU) and saturated (S) acyl groups, respectively. Its composition in tocopherols, determined by High Performance Liquid Chromatography (HPLC) as in previous studies (Fruehwirth et al., 2020), was: 471.4 ± 7.5 mg/kg of α-tocopherol and 76.2 ± 2.0 of mg/kg γ-tocopherol. The sunflower oil was packaged in plastic bottles with a capacity of 250 mL purchased from different manufacturers and made of different plastic materials: polylactic acid (PLA) (NaKu e.U., Wiener Neustadt, Austria), recycled polyethylene terephthalate (r-PET) (Flakado, Mannheim, Germany), polyethylene terephthalate (PET) (Plasticflessen.nl, Zuidbroek, Netherlands), polyethylene (PE) and bio-polyethylene (Green-PE) (H. H. Rotert GmbH & Co. KG, Bad Idburg, Germany). PLA bottles had a thickness of 0.7 ± 0.05 mm and showed clear slight-yellow colors, whereas PET and r-PET bottles were thinner (0.3 ± 0.05 mm) and clear, with no color. PE and Green-PE bottles had the highest thickness (1.0 ± 0.05 mm) and showed a white milky color.

2.2. Chemicals

Methanol (LC-MS Grade), water (LC-MS Grade), acetonitrile (LC-MS Grade), formic acid and isooctane were purchased from Avantor/VWR International Inc. (Radnor, PA, USA). Chloroform, acetic acid, and 0.1 M sodium thiosulfate were obtained from Carl Roth GmbH& CO. (Karlsruhe, Germany) and deuterated chloroform was bought from Eurisotop (Andover, USA). Hexane, 2-propanol, starch, tetrahydrofuran, *p*-anisidine, benzene, α-tocopherol, and γ-tocopherol were acquired from Sigma Aldrich (St. Louis, MO, USA). Rac-Tocol was obtained from Abcam (Cambridge, United Kingdom).

2.3. Study design

About 225.5 ± 0.1 mL of sunflower oil were filled into the plastic bottles (PET, r-PET, PE, Green-PE, and PLA), which ensured that the headspace was the same for all bottles. The bottles were closed with a cap and were stored at room temperature at equal distances from each other in a cabinet, with light conditions as described in a previous study (Pignitter et al., 2014). They were exposed to cold fluorescent light for 12 h per 24 h. Samples were taken after 1, 3, 7, 14, 28 and 56 days, and stored at − 80 ºC until analysis. The experiments were carried out in quadruplicates, which means that sampling of four bottles per material was performed per day. The fresh sunflower oil was analyzed as a control sample.

2.4. Study of the oxidative stability of oil during storage

2.4.1. Proton nuclear magnetic resonance (^{1}H NMR)

^{1}H NMR spectra of the samples were acquired using a Bruker Avance 400 spectrometer operating at 400 MHz. Briefly, 200 μL sample were added to 400 μL deuterated chloroform which contained 0.2% non-deuterated chloroform and a small amount (0.03%) of tetramethylsilane as internal reference. The following acquisition parameters were used as in previous studies (Martínez-Yusta & Guillén, 2014): spectral width 6410 Hz, relaxation delay 3 s, number of scans 64, acquisition time 4.8190 s, and pulse width 90º, with a total acquisition time of 8 min 38 s. The identification and quantification of linoleic acyl groups, hydroperoxy-*Z,E*-conjugated dienes and total hydroperoxides, were performed as reported in previous works (Guillén & Ruiz, 2003; Guillén & Ruiz, 2005; Guillén & Uriarte, 2012; Martínez-Yusta & Guillén, 2014).

To this aim, the concentration of linoleic acyl groups (%L), expressed as molar percentage, was estimated by means of the following equation:

$$\%L = 100(2A_A/3A_B)$$

In this equation, A_A is the area of the signal of *bis*-allylic protons of linoleic acyl groups and A_B is the area of the signals due to the glycerol protons at the *sn*-1 and *sn*-3 positions of triglyceride (TG) (see signal **B** in

Fig. S1).

The concentrations of hydroperoxy-*Z,E*-conjugated dienes and total hydroperoxides, throughout the storage time, were determined by means of the following equations:

$$[Hydroperoxy - Z,E - conjugateddienes] = [(A_a)/(A_B/4)] * 1000$$

$$[TotalHydroperoxides] = [(A_b)/(A_B/4)] * 1000$$

In these equations, A_a is the area of signal **a** corresponding to one of the protons of hydroperoxy-*Z,E*-conjugated dienic systems, A_b the area of the signal **b** corresponding to the proton of the hydroperoxide groups and A_B the area of the protons at *sn*-1 and *sn*-3 positions in the glycerol backbone of TG (see signal **B** in Fig. S1). The concentrations thus determined are given in millimoles per mol of triglyceride (mmol/mol TG).

2.4.2. Peroxide value

The peroxide value (POV) was determined by the method according to Wheeler (1932) with slight modifications. A total of 5 g oil was mixed with 20 mL acetic acid/chloroform solution (3:2 v/v), and 200 µL saturated potassium iodide solution were subsequently added. After shaking for one minute, 12 mL distilled water were added, and the sample was titrated with a 0.1 N sodium thiosulfate solution. The POV was calculated as followed:

$$POVmeqO_2 \Big/ kgoil = \frac{V * N * 1000}{m}$$

V … volume titrated (mL).
N … normality of sodium thiosulfate.
m … weight of sample (g).

2.4.3. Solid phase microextraction followed by gas chromatography/mass spectrometry (SPME-GC/MS)

The analysis of the volatile components was done as described in a previous study (Guillén et al., 2005). For this purpose, 2.5 g oil was transferred to a 20 mL glass vial and a fiber coated with DVB/CAR/PDMS (divinylbenzene/carboxen/ polydimethylsiloxane (50/30 µm film thickness, 1 cm length)) was used to extract the volatile compounds. A pre-equilibrium of 5 min was set before the fiber was injected into the headspace of the vial at 50 °C for 55 min. It was then inserted into the injection port and remained there for 10 min for desorption of the extracted components. The injection mode was splitless with a 5 min purge time. The GC/MS (GC-QP2010 Ultra, of Shimadzu, Korneuburg, Austria) was equipped with a Zebron ZB-5 ms column (30 m x 0.25 mm × 0.25 µm Phenomenex, Aschaffenburg, Germany), and helium as a carrier gas with a constant pressure at 117 kPa. The temperatures of the injector and interface were set at 250 °C and 305 °C, respectively. The initial temperature of the oven was kept at 50 °C for 5 min, increased to 300 °C at a rate of 4 °C per minute and was kept there for another 30 min. Ion source and quadrupole mass analyzer temperatures were held at 230 °C and 150 °C respectively. An ionization energy of 70 eV was used. The compounds were identified by matching of their mass spectra with spectra from a commercial library by more than 85% (NIST, ver. 11.0 library). Semi-quantification was based on arbitrary units of the base peak ion area counts. The purpose of this study was not the determination of absolute but of relative concentrations that are valid for comparative purposes. All the determinations were carried out in quadruplicate in order to obtain a mean value with the corresponding standard deviation for each of the components studied.

2.4.4. p-anisidine value

p-anisidine value (*p*-aV) was measured according to the method of AOCS (Cd 18–90) with slight modifications. The *p*-anisidine reagent was prepared prior to the measurement, with 25 mg *p*-anisidine being added to 10 mL glacial acetic acid. A total of 1.5 g of sample were dissolved in 25 mL isooctane. To 5 mL of the sample solution 1 mL *p*-anisidine reagent was added and subsequently incubated in the dark for 10 min. The samples were transferred into a 96-well plate and measured at an absorbance of 350 nm with a Spark photometer (Tecan Group Ltd., Switzerland) before (Ab) and after *p*-anisidine was added (Aa). The value was calculated with the sample weight in grams (m) as followed:

$$p - aV = \frac{25 * (1.2Aa - Ab)}{m}$$

p-anisidine values of 0.2 and 1.8 were obtained as the limit of detection (LOD) and limit of quantification (LOQ), respectively.

2.4.5. Quantification of tocopherols by high performance liquid chromatography (HPLC)

The tocopherol content was determined according to Fruehwirth et al. (2020). Briefly, 50 mg oil were mixed with 1 mL 2-propanol and filtered through a 0.2 µm nylon syringe filter (Phenomenex, Phenex™-NY 15 mm, 0.2 u). A total of 1 µL rac-tocol (5 µg/mL) was added to the samples and used as an internal reference. The samples were analyzed by the LC-20 (Shimadzu, Korneuburg, Austria) equipped with a C18 column (Shim-pack VP-ODS 5 µm, 150 mm × 4.6 mm, Shimadzu, Korneuburg, Austria) and a photodiode array detector (SPD-M30A, Shimadzu, Korneuburg, Austria) at 10 °C. The flow rate was 0.5 mL/min. The mobile phase was water (solvent A) and methanol (solvent B). The gradient was 0–4 min 95% methanol, 4 – 36 min 100% methanol, 36 – 38 min 95% methanol. The tocopherols were measured at a wavelength of 294 nm and were quantified using a standard curve, with a linear concentration ranging from 19.5 to 625.0 mg/kg for both α-tocopherol and γ-tocopherol. A limit of quantification (LOQ) of 70.0 mg/kg and 26.5 mg/kg for α-tocopherol and γ-tocopherol, respectively, was determined by the signal to noise ratio of 10. The recovery of tocol in the samples was 90 ± 10%.

2.5. Analysis of migrated compounds from the bottle to the contained oil

2.5.1. Liquid chromatography/mass spectrometry (LC-MS)

As PLA is a novel and promising packaging material, this study determined whether migration products and potential PLA derived compounds can migrate into the sunflower oil under the specific storage conditions. For this purpose, these compounds were analyzed in both, the bottle material and in the oil on day 1 and 56. For the bottle material, the extraction of the compounds was made based on the method previously described by Baumjohann and Harms (2015), and the preparation was done according to Tsochatzis et al. (2022) with some modifications. A total of 40 mg of the bottle was cut out around the middle area, dissolved in 2 mL tetrahydrofuran (THF), and stored in a drying oven at 55 °C for 2 h. Subsequently, the solution was evaporated under a stream of nitrogen and the residue was reconstituted in 600 µL of acetonitrile. It was then filtered through a 0.45 µm PVDF syringe filter. Samples were separated on a C18 column (Atlantis T3 3 µm 2.1 mm × 150 mm, Waters) connected to a Dionex Ultimate 3000 (Thermo Fisher Scientific, Vienna, Austria) system at 25 °C. The analytes were detected by a microToF-QII (Bruker Corporation, Billerica, MA, USA). A mobile phase consisting of 0.1% formic acid in water (A) and 0.1% formic acid in acetonitrile (B) was selected, with the following gradient: 0–6 min 40% acetonitrile, 6–20 min 75% acetonitrile, 20–32 min 100% acetonitrile, 32–50 min 40% acetonitrile at a flow rate of 0.1 mL/min. MS^1 measurement took place in positive scan mode (ESI+) with a mass range of *m/z* 100 – 1000. The following ESI ion source settings were applied: capillary voltage: of 3.2 kV; nebulizer pressure of 1.2 bar (N_2), a dry gas flow of 8.0 L/min (N_2) and dry temperature of 180 °C. Data-dependent MS^2 analysis were performed using a collision energy of 35 V in product ion scan mode, with a mass range of *m/z* 100–1000. For measurement of PLA-derived migration compounds that might have transferred into the oil stored in the PLA bottles for 1

and 56 days, 100 μL oil were diluted in 600 μL acetonitrile, vortexed and then filtered using a 0.45 μm PVDF syringe filter. The measurement was done with the same chromatographic method and MS settings. Identification of the migration compounds was done by comparing the MS spectra obtained to those previously described by Ubeda et al. (2019).

2.5.2. Quantification of benzene by SPME-GC/MS

To confirm and quantify benzene in the samples stored in different plastic materials, a standard curve spiking benzene at different concentrations in sunflower oil was acquired through SPME-GC/MS, applying the same GC settings as described above (Section 2.4.3.). A linear concentration ranging from 0.003 to 0.595 μg/g was used for the quantification of benzene in all samples. A limit of detection (LOD) of 0.004×10^{-1} μg/g and a LOQ of 0.011×10^{-1} μg/g were calculated by a signal to noise ratio of 3.3 and 10, respectively.

2.6. Statistical analysis

Statistical analysis was performed with GraphPad Prism 9.4.1. A Shapiro-Wilk test was performed to confirm normal distribution followed by a one-way analysis of variance (ANOVA) for benzene and for the other compounds (Figs. 1–4) a two-way ANOVA followed by Tukey's post hoc test. Results were considered to be significant with a *p*-value lower than 0.05. For each experiment (plastic material) and for each day of sampling, four independent samples (different bottles) were measured.

3. Results and discussion

The purpose of the current study was to study the oxidative stability of sunflower oil stored in PET, r-PET, PE, Green-PE, and PLA bottles under retail and household conditions, and investigate whether the biodegradable and renewable plastics could be a good alternative to the conventional ones for storing edible oils.

3.1. Impact of plastic materials on the linoleic acyl groups during storage

As mentioned before, the sunflower oil used in this study mainly consists of linoleic acyl groups (55.5 ± 0.2%). ^{1}H NMR of sunflower oil samples stored in different bottles revealed that the concentration of linoleic acyl groups remained stable over the time with no significant differences between the packaging materials (Table 1). The overall extent of lipid oxidation in the current study seemed to be low as the determination of the molar percentage of linoleic groups did not reveal any significant changes over storage time and packaging material. In this sense, Ha et al. (2011) analyzed the change of fatty acid composition of corn oil by headspace GC-MS after conducting a 2-month storage study at room temperature. Corn oil has a similar composition to sunflower oil, with linoleic and oleic as the main acyl groups. These authors did not observe any change in the concentration of linoleic acyl groups, despite an increase in lipid oxidation measured by peroxide value and the content of hexanal.

3.2. Occurrence of primary oxidation compounds

In addition to the aforementioned linoleic acyl groups, other more sensitive oxidation markers are the hydroperoxides. They are the primary oxidation compounds derived directly from the oxidation of unsaturated acyl groups.

To evaluate the occurrence of primary oxidation compounds in differently packaged sunflower oil the peroxide value (POV) was determined (Fig. 1a). It is evident that the fresh sunflower oil at day 0 was slightly oxidized but was still below recommended threshold of 10 meq O_2/kg (Codex Alimentarius Commission, 1999). During the storage for 56 days, the POV increased significantly in all samples, although some differences were observed depending on the packaging material (10.6 ± 0.8, 9.0 ± 0.5, 10.4 ± 0.6, 16.0 ± 0.9 and 19.8 ± 0.4 meq O_2/kg for PLA, r-PET, PET, PE and Green-PE, respectively) (Fig. 1a). This could be related to the plastic bottle characteristics, wall thickness and color, leading to a higher oxidation the lower the thickness and the higher the transparency. However, looking at the bottles'

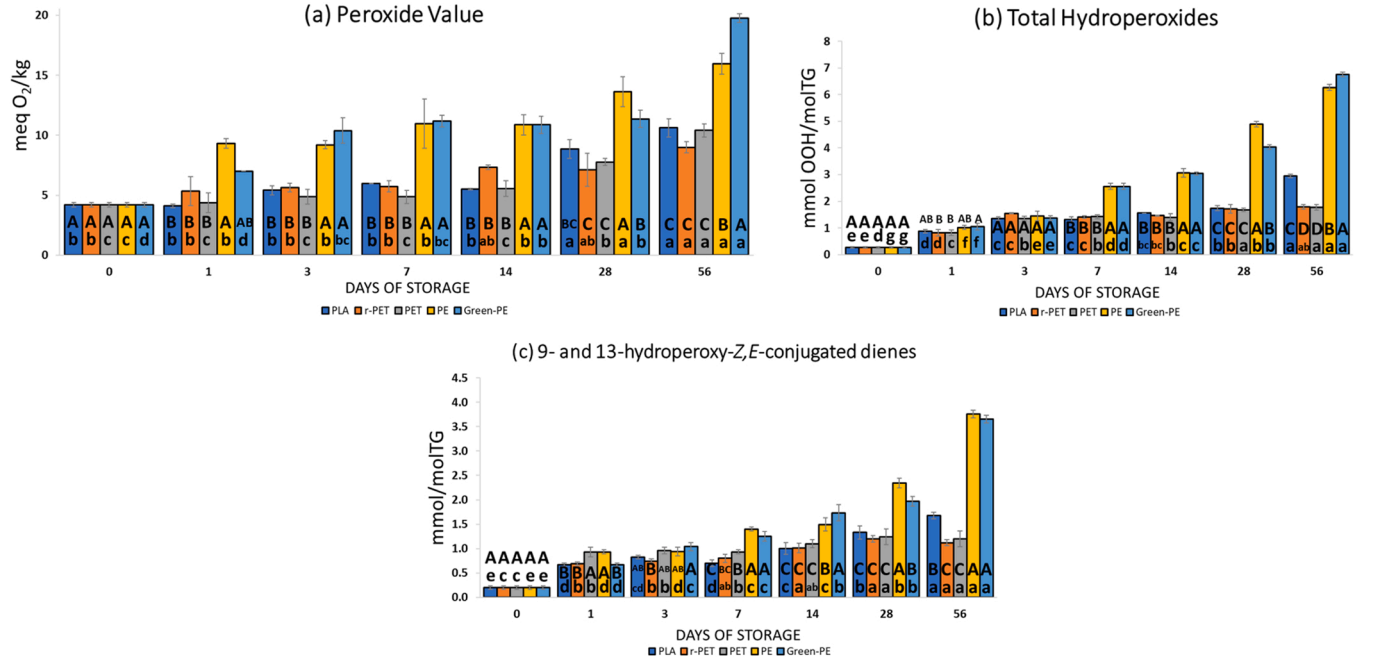

Fig. 1. Progress of lipid peroxidation during storage of sunflower oil in different packaging materials. Evolution of (**a**) peroxide value, expressed as meq O_2/kg, and the concentration, expressed as mmol/mol TG, of (**b**) total hydroperoxides and (**c**) 9 and 13-hydroperoxy-*Z,E*-conjugated dienes. Different capital letters show significant differences between the plastic material for each day. Different lowercase letters show significant differences for each material over the time of 56 days. Data are shown as mean ± SD.

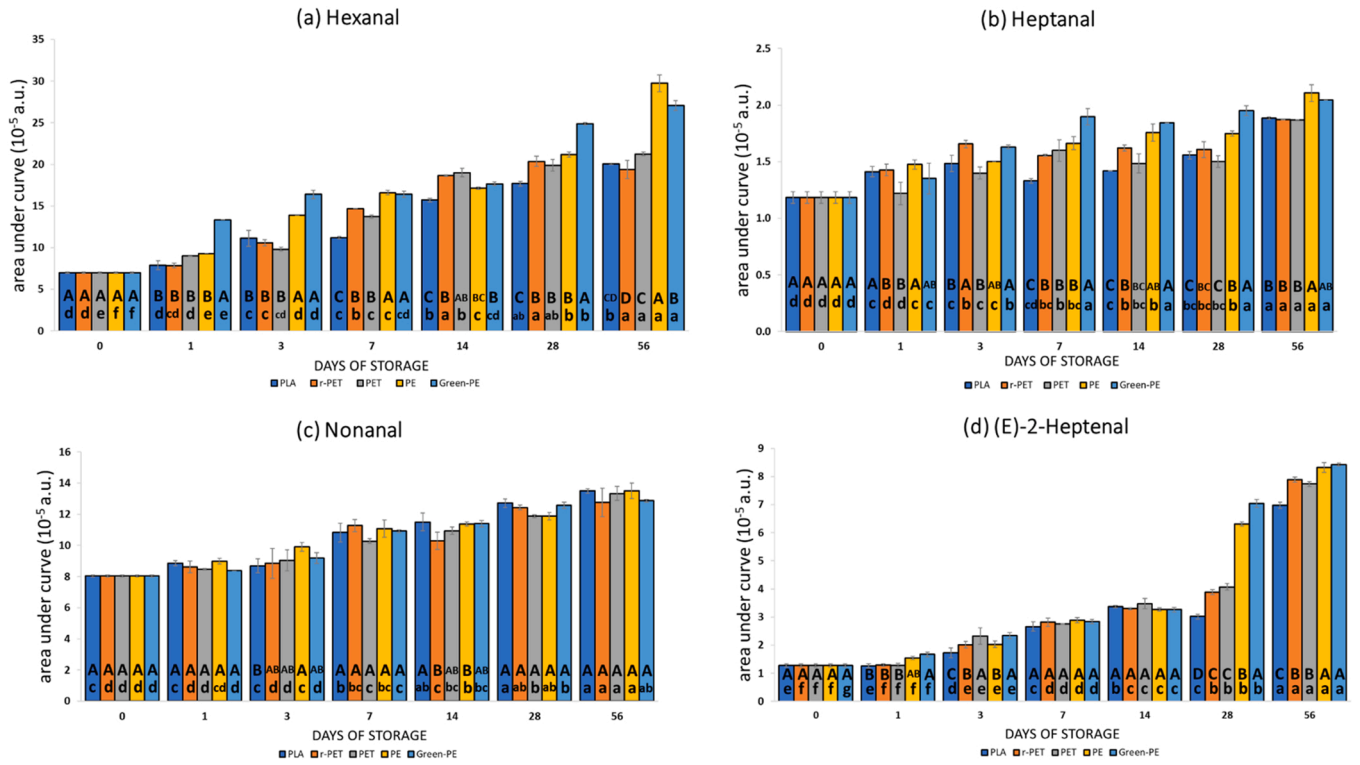

Fig. 2. Evolution of (**a**) hexanal, (**b**) heptanal, (**c**) nonanal and (**d**) (*E*)-2-heptenal in sunflower oil during storage in different packaging material expressed as area counts of their mass spectra base peak. Different capital letters show significant differences between the plastic material for each day. Different lowercase letters show significant differences for each material over the time of 56 days. Data are shown as mean ± SD.

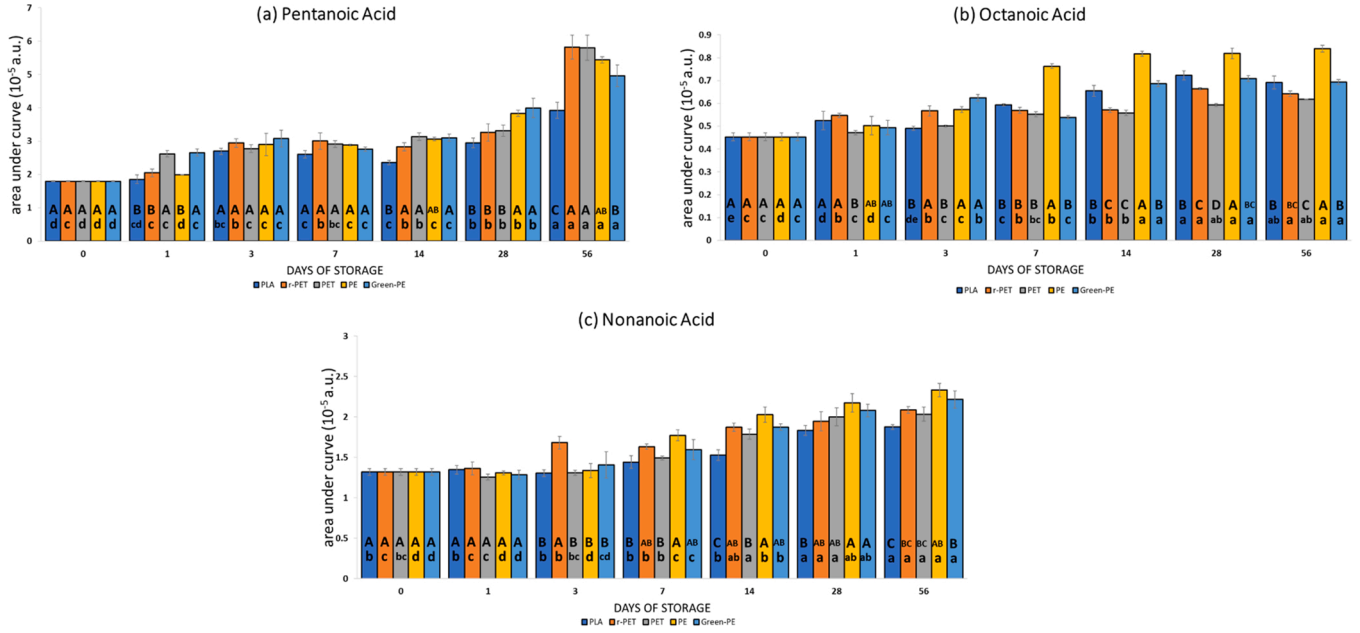

Fig. 3. Evolution of (**a**) pentanoic acid, (**b**) octanoic acid and (**c**) nonanoic acid in oil during storage in different packaging material expressed as area counts of their mass spectra base peak. Different capital letters show significant differences between the plastic material for each day. Different lowercase letters show significant differences for each material over the time of 56 days. Data are shown as mean ± SD.

characteristics mentioned above and the obtained results the opposite was observed. Therefore, it can be assumed that the lower oxidative stability of samples stored in PE bottles could be related to the oxygen permeability of the plastic material. The oxygen permeability of PLA lies between 6.2 and 17.3 cm^3 mm/(m^2 day bar) depending on the ratio between L-lactic acid and D-lactic acid, but it is still higher than for r-PET and PET at 1.2 – 2.8 cm^3 mm/(m^2 day bar), while the permeability of PE is estimated to be at 202.7 cm^3 mm/(m^2 day bar) (Lagaron et al., 2005; Bao et al., 2006; Guinault et al., 2010; Nisticò, 2020). However, the oxygen permeability of PLA was determined with PLA as a film material of μm scaling. Thus, the barrier properties as a bottle with thicker material should be better than the ones from the film. Although

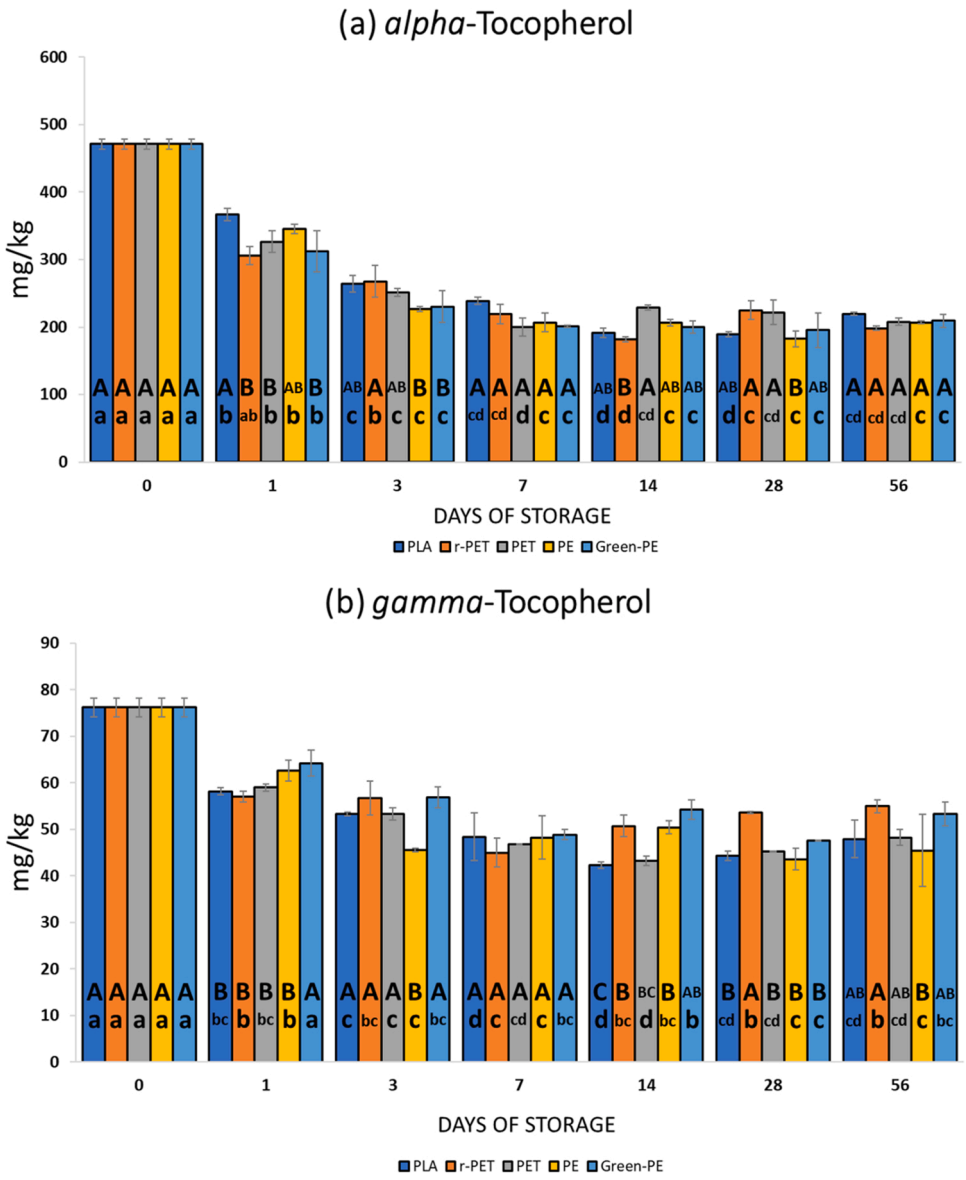

Fig. 4. Concentration (mg/kg) of (**a**) α-tocopherol and (**b**) γ-tocopherol in sunflower oil during storage in different packaging materials. Different capital letters show significant differences between the plastic materials for each day. Different lowercase letters show significant differences for each material over the time of 56 days. Data are shown as mean ± SD.

Table 1
Concentration of linoleic acyl groups, expressed as molar percentage, in sunflower oil during storage in different packaging materials. Different capital letters show significant differences between the plastic material for each day. Different lowercase letters show significant differences for each material over the time of 56 days. Data are shown as mean ± SD.

Samples	Storage time (days)						
	0	1	3	7	14	28	56
PLA	55.5 ± 0.2^{Aa}	55.6 ± 0.2^{Aa}	55.5 ± 0.2^{Aa}	55.5 ± 0.1^{Aa}	55.4 ± 0.2^{Aa}	55.1 ± 0.3^{Aa}	55.5 ± 0.2^{Aa}
r-PET	55.5 ± 0.2^{Aa}	55.5 ± 0.2^{Aa}	55.4 ± 0.2^{Aa}	55.5 ± 0.1^{Aa}	55.6 ± 0.2^{Aa}	55.2 ± 0.4^{Aa}	55.3 ± 0.5^{Aa}
PET	55.5 ± 0.2^{Aa}	55.5 ± 0.1^{Aa}	55.4 ± 0.2^{Aa}	55.5 ± 0.1^{Aa}	55.6 ± 0.2^{Aa}	55.6 ± 0.4^{Aa}	55.3 ± 0.9^{Aa}
PE	55.5 ± 0.2^{Aa}	55.2 ± 0.3^{Aa}	55.4 ± 0.2^{Aa}	55.4 ± 0.1^{Aa}	55.3 ± 0.2^{Aa}	55.4 ± 0.2^{Aa}	55.4 ± 0.3^{Aa}
Green-PE	55.5 ± 0.2^{Aa}	55.5 ± 0.1^{Aa}	55.6 ± 0.2^{Aa}	55.7 ± 0.4^{Aa}	55.5 ± 0.1^{Aa}	55.6 ± 0.2^{Aa}	55.4 ± 0.2^{Aa}

the oxygen permeability in PLA is slightly higher than in PET, there were no significant differences between the oil samples packaged in PLA and PET and r-PET during the storage until day 28. However, sunflower oil in PE and Green-PE bottles showed much higher values of peroxides in comparison with the oil stored in other bottles. During the first 14 days an approximately two-fold higher peroxide value was obtained in oils filled in PE and Green-PE bottles compared to the oil in the other bottles. This effect could be attributed to the higher oxygen permeability of PE and Green-PE compared to the other materials, offering a poor protection against lipid oxidation (Nisticò, 2020).

To confirm the results provided by the POV an ^{1}H NMR study of the samples was performed. As expected, the ^{1}H NMR results evidenced that

all samples contained hydroperoxides. In addition, in the spectra of all samples, ^{1}H NMR signals appeared corresponding to hydroperoxy-*Z,E*-conjugated dienes. From these signals it was possible to determinate separately the total concentration of hydroperoxides and the concentration of hydroperoxy-*Z,E*-conjugated dienes, expressed as millimol per mol of triglyceride (mmol/mol TG).

Fig. 1b and c show the concentration of total hydroperoxides and hydroperoxy-*Z,E*-conjugated dienes in the differently packaged oil during storage for 56 days, respectively. It should be noted that the total hydroperoxide concentration (Fig. 1b) was twice as high as the concentration of hydroperoxy-*Z,E*-conjugated dienes (Fig. 1c). Therefore, it can be assumed that the oils contained other hydroperoxides different from the hydroperoxy-*Z,E*-conjugated dienes. In fact, Lee and Min (2010) showed that non-conjugated hydroperoxides formed during photosensitized oxidation of linoleic acid with $^{1}O_2$. In addition, by means of GC-MS, (*E*)-2-heptenal could be identified in all samples of the current study (section 3.3.2.). This aldehyde is a secondary oxidation product mainly derived from the cleavage of the C11-C12 bond of non-conjugated hydroperoxides formed by photosensitized oxidation of linoleic acyl groups. Therefore (*E*)-2-heptenal can be used as a marker of photosensitized oxidation and could also indicate the formation of non-conjugated hydroperoxides. Moreover, the same observation was found in the study of Min et al. (2003), as they detected (*E*)-2-heptenal only in the presence of a photosensitizer and light. With the detection of (*E*)-2-heptenal in the current study the missing hydroperoxides may be related to non-conjugated dienes.

The concentration of total hydroperoxides increased significantly over the period of 56 days in all bottles. The concentration of total hydroperoxides was two-fold and three-fold higher in PE and Green-PE samples (6.2 ± 0.3 and 6.8 ± 0.7 mmol OOH/mol TG) than in PLA, r-PET, and PET ones (3.2 ± 0.4, 1.9 ± 0.2 and 1.8 ± 0.1 mmol OOH/mol TG respectively) after 56 days of storage (Fig. 1b). Regarding oil samples stored in PLA, similar concentrations of total hydroperoxides as for those stored in r-PET and PET bottles were observed until day 28 showing a significant increase of hydroperoxide concentration at the end of the storage. As expected, the concentration of hydroperoxy-*Z,E*-conjugated dienes showed a similar trend (see Fig. 1c).

Thus, according to these oxidation markers the oxidative stability of sunflower oil was higher when it was stored in PET and r-PET bottles, while Green-PE and PE showed the worst results. These results are in agreement with the POV. The variation of lipid oxidation between oils stored in r-PET, PET and PLA was low with a similar outcome after storage for 56 days at room temperature. Thus, the possibility for PLA to be used as an alternative packaging material for sunflower oil or other vegetable oils with similar composition should be considered.

3.3. Occurrence of secondary oxidation compounds

Further oxidative degradation of the oil causes the primary oxidation compounds to break into volatile and non-volatile compounds. These compounds are considered as secondary oxidation compounds and are the main reason for a change in aroma and off-flavor of the oil with advanced lipid oxidation (Grebenteuch et al., 2021). The secondary compounds comprise of aldehydes, ketones, alcohols, and acids and can be detected by methods such as the *p*-anisidine value or SPME-GC-MS (Frankel, 2005).

The *p*-anisidine value is a classic method to detect aldehydes in oxidized oils and is based on the reaction of their carbonyl groups with *p*-anisidine, to form a colored Schiff base which can be measured by UV spectroscopy (Skiera et al., 2012). It mainly reacts with 2-alkenals and 2, 4-alkadienals and is more sensitive to unsaturated aldehydes, which leads to a higher absorption in wavelength than that of saturated aldehydes (Yang & Boyle, 2016; Skiera et al., 2012). In the current study it is shown in Fig. S2 that the *p*-aV increased slightly, especially in PE and Green-PE after 56 days of storage; however, it remained stable with a value between 4 and 5. In a previous study from Guillén and Cabo (2002) it was shown that under accelerated oxidation conditions (70 °C), the *p*-aV in sunflower oil did not rise until a POV of almost 200 meq O_2/kg was reached. This could imply that the concentration of (*E*)-2-heptenal was not high enough in the samples to indicate a change in the *p*-aV over the storage time.

SPME-GC-MS provided information on the specific nature of volatile oxidation compounds generated as consequence of unsaturated acyl groups degradation during storage. Figs. 2 and 3 show the abundance of some of the volatile compounds detected in sunflower oil. Most volatile oxidation markers detected in this study were aldehydes, among which can be differentiated in saturated aldehydes such as hexanal, heptanal and nonanal and one unsaturated aldehyde, (*E*)− 2-heptenal (Fig. 2). Likewise, an increase of some acids, such as pentanoic, octanoic and nonanoic acid was observed (Fig. 3) since they represent further decomposition products of hydroperoxides and can be considered as markers as well (Schaich, 2005).

Nonanal and heptanal derive from the breakdown of oleic acid, whereby hexanal and (*E*)− 2-heptenal are generated by the oxidation from linoleic acid (Schaich, 2005, Grebenteuch et al., 2021). As above-commented, (*E*)− 2-heptenal can be considered as a marker for photosensitized oxidation occurring in oils rich in linoleic acyl groups. Photosensitized oxidation may lead to the formation of non-conjugated hydroperoxides which may decompose to (*E*)− 2-heptenal (Min et al., 2003; Lee & Min, 2010). With sunflower oil's main acyl groups being oleic and linoleic acyl groups, the observed aldehydes correspond to the findings in the literature. In the current study hexanal showed a three- to four-fold significant increase in the samples stored in PE and Green-PE after 56 days (Fig. 2a). In addition, (*E*)− 2-heptenal showed a remarkable rise during the storage as well, while less pronounced increase was observed for heptanal and nonanal (Fig. 2b-d). On the other hand, PLA, r-PET and PET led to the lowest formation of hexanal, heptanal and (*E*)− 2-heptenal in stored oil whereby the abundance of the latter was significantly less in PLA stored oil than in the oils stored in the other packaging materials after 28 and 56 days. The results provided by GC-MS showed that mostly saturated aldehydes were formed by the breakdown of hydroperoxides. Since *p*-aV is more sensitive to unsaturated aldehydes, this observation may explain the non-significant change of *p*-aV in the sunflower oil over the storage time.

Acids occur as secondary products in lipid oxidation from their respective aldehydes (Schaich, 2005). In the current study pentanoic acid, octanoic acid and nonanoic acid could be detected (Fig. 3). Although nonanoic acid can derive from both oleic acid and linoleic acid, octanoic acid is a marker for the breakdown of a hydroperoxide derived from oleic acid. Pentanoic acid is mainly formed from linoleic acid hydroperoxides (Schaich, 2005). In the current study, the overall abundance of acids observed in oil stored in PE and Green-PE was higher than in the oil packaged in the other plastic materials. While the results between PLA- r-PET and PET stored oil was similar, the abundance of pentanoic acid (Fig. 3a) in PLA packaged sunflower oil, however, was much lower than in the other bottles. Compared to r-PET, approximately 30% less pentanoic acid could be detected in sunflower oil stored after 56 days in PLA bottles, thereby corroborating the results for (*E*)− 2-heptenal also showing the lowest abundance in oils stored in PLA bottles and indicating that PLA may be a good alternative as a packaging material for edible oils.

3.4. Stability of tocopherols in sunflower oil

Tocopherols naturally present in sunflower oil have antioxidative capability (Tena et al., 2019). The fresh sunflower oil had a concentration of 471.4 ± 7.5 mg/kg α-tocopherol and 76.2 ± 2.0 mg/kg γ-tocopherol (Fig. 4), being these values aligned with those reported in the literature (Grilo et al., 2014). Over the time α-tocopherol decreased by 53.4 – 57.9% in the current study, reading 219.8 ± 2.4, 198.2 ± 3.2, 207.9 ± 5.4, 206.8 ± 2.2 and 209.3 ± 9.3 mg/kg ($p < 0.0001$) for PLA, r-PET, PET, PE, and Green-PE respectively. Meanwhile, γ-tocopherol

decreased by 27.9 – 40.3% to a concentration of 47.9 ± 4.1, 54.9 ± 1.4, 48.2 ± 1.7, 45.6 ± 7.7 and 53.3 ± 2.6 mg/kg for PLA, r-PET, PET, PE, and Green-PE, respectively. This could be due to that the tocopherols act as natural antioxidants inhibiting the progress of oxidative degradation. Like α-tocopherol, γ-tocopherol stabilized after day 7 or in case of further degradation, this was not that high to be detected. Overall, tocopherols presented the same pattern of oxidation in all the samples. Therefore, it can be said that as no differences regarding the tocopherols content in sunflower oil could be detected between PLA, r-PET and PET bottles, PLA might be a renewable and non-fossil alternative to the conventional plastic bottles.

3.5. Migration of non-intentionally added substances from the bottle material

Packaging or food contact materials (FCMs) protect food from external contamination and preserve the nutritional value as well as the physical and sensory quality of food. According to Regulation (EC) No. 1935/2004 on materials and articles intended to come into contact with food, FCMs should neither release substances into foodstuffs in any amount that is suitable to induce a possible health risk, have an unreasonable change in their composition nor any alteration of their organoleptic properties. However, with the degradation of the material over time it is still possible for non-intentionally added substances (NIAS) to migrate from the packaging material into the oil. One of such NIAS is benzene. A maximum limit for benzene migrating into water intended for human consumption (tap water) was set to 1 μg/L (European Union, 2020), but to our knowledge no limit for vegetable oils has been established. The exact origin of benzene is still unclear; however, it is a product which derives from pyrolysis of PET resin, with higher amounts in r-PET due to contaminants and impurities forming during the recycling process (Thoden van Velzen et al., 2020). Giuffrida et al. (1999) investigated the occurrence of benzene in different vegetable oils packaged in aluminum boxes or PET boxes. Despite there being traces of benzene in a few samples stored in aluminum boxes, in all PET packaged oil samples the concentration of benzene was much higher. A study from Maalouly et al. (2013) was also able to detect benzene in sunflower oil samples stored in PET; however, under accelerated aging conditions, such as higher storage temperatures of 40 °C. In the current study, it was possible to detect and quantify benzene with SPME-GC/MS in sunflower oil stored in r-PET and PET after 28 and 56 days (Table 2). It should be noted that benzene concentration in oils stored in PLA, PE, or Green-PE was below the LOD. These results were expected since there has been only evidence of the release of benzene in PET materials so far, although this is the first time where this formation was investigated in PE, Green-PE and PLA to the best of our knowledge. After 56 days the concentration of benzene in oils packaged in PET and r-PET bottles was 0.153 ± 0.027 μg/g and 0.187 ± 0.024 μg/g, respectively. Even though the amount of oil consumed per day is much lower than the daily consumption of tap water and therefore a limit for benzene in sunflower oil cannot be claimed, consumers might prefer products free of NIAS. Thus, PLA may be an interesting option in this respect.

As commented above, PLA seems to be a good alternative to the conventional plastic bottles in order to store edible oils. Therefore, with the aim to investigate whether migration compounds from PLA could be detected in the oil, samples were analyzed by LC-MS in the current study. Several, migration tests with PLA were conducted in the previous years; however, most of them were investigated as plastic films and/or under accelerated conditions of 60 °C with food simulants, such as ethanol as a fat simulant (Conn et al., 1995; Mutsuga et al., 2008; Ubeda et al., 2019; Aznar et al., 2019). PLA is a polymer consisting of cyclic and linear oligomers of lactic acid molecules. Most migration products from the PLA material were linear PLA oligomers which were already present in the material. It was concluded that cyclic oligomers did not migrate into the simulants because they reacted with the simulant and formed linear oligomers which then would migrate (Ubeda et al., 2019). The current study investigated whether these oligomers would migrate into the sunflower oil during storage. Thus, both PLA bottle material and oil samples were analyzed by LC-MS. The MS spectra were compared to those previously described in Ubeda et al. (2019). Two linear oligomers and four cyclic oligomers ranging from cyclic$[LA]_8$ to cyclic$[LA]_{13}$ were observed in the bottle material (Table S1). However, none of them or other oligomers were detected in the oil samples throughout the storage process, suggesting that the migration of these oligomers is inexistent or under the limit of detection. This provides, once again, evidence to consider PLA as a safe alternative sunflower oil packaging material under these specific storage conditions (short storage at room temperature), due to the absence of NIAS or any other unexpected FCM-derived substance along the 56 days of this study. Nonetheless, further longer storage studies should be performed to assess the safety of PLA for vegetable oils over time.

4. Conclusions

After storing the sunflower oil for up to 56 days at room temperature and under cold fluorescence light, it has been demonstrated that lipid oxidation was not prevented in the oils packaged in PE or Green-PE bottles to the same extent compared with the oils stored in PLA, PET and r-PET bottles. Likewise, sunflower oil packaged in PLA bottles showed similar results for primary oxidation compounds, such as peroxide value, total hydroperoxide and hydroperoxy *Z,E*-conjugated dienes as the oils stored in r-PET and PET bottles. Nevertheless, the formation of secondary lipid oxidation products, (*E*)− 2-heptenal and pentanoic acid, was even shown to be less pronounced in sunflower oil stored in PLA than in r-PET or PET bottles. Therefore, PLA could be used as a renewable and non-fossil packaging material for edible oils, as it could prevent lipid oxidation of sunflower oil to a similar extent as r-PET and PET bottles. Moreover, benzene was not found in hazardous concentrations in any of the oil samples, being undetected for the ones stored in PLA bottles. All of this evidence suggests that using PLA bottles to store edible oils might be an alternative to r-PET or PET, providing oils free of NIAS which could have a better acceptance by the consumers. This study confirms the use of PLA as a plausible alternative to conventional plastic packaging such as PET for vegetables oils. Nevertheless, more research needs to be done on longer storage conditions, evaluating the light intensity and light transmission of the different packaging materials, their oxygen permeability as well as their color and thickness, to assess their impact on compound migration and oxidative stability.

CRediT authorship contribution statement

Martina Holler: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft. **Jon Alberdi-Cedeño**: Conceptualization, Methodology, Formal analysis, Investigation, Data curation, Writing – original draft & editing, Visualization. **Arturo Auñon-Lopez**:

Table 2
Concentration of benzene in sunflower oil packaged in r-PET and PET after 28 and 56 days expressed as μg/g. Data are shown as mean ± SD.

	PLA		r-PET		PET		PE		Green-PE	
Days of storage	28	56	28	56	28	56	28	56	28	56
Benzene (μg/g)	< LOD	< LOD	0.057 ± 0.009	0.187 ± 0.024	0.069 ± 0.004	0.153 ± 0.027	< LOD	< LOD	< LOD	< LOD

LOD = Limit of detection, LOQ = Limit of quantification.

Methodology, Formal analysis, Data curation, Writing – review & editing. **Tobias Pointner**: Methodology, Formal analysis, Writing – review & editing. **Andrea Martínez-Yusta**: Writing – review & editing. **Jürgen König**: Writing – review & editing. **Marc Pignitter**: Conceptualization, Resources, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare no conflicts of interest.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fpsl.2023.101051.

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