



Safety profile of ZnO active packaging PBAT based biomaterial for food packaging. First tier evaluation

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A B S T R A C T

Materials produced with polybutylene adipate terephthalate (PBAT) and starch are raising great interest for packaging and food contact applications, including as support for active antimicrobial agents such as zinc oxide nanoparticles (ZnO). Studies focusing on the safety of these materials as evaluated with the current reference rules for food contact materials, are lacking. A commercially available PBAT/starch-based material was incorporated with ZnO and the overall and specific migration of the films were studied at different conditions of simulants and temperature. The overall migration (OM) limit is exceeded due to the release of starch as confirmed by infrared spectroscopy. The impact of temperature on the OM was higher for the ethanol 10%. The incorporation of ZnO particles reduced the OM, for both temperatures tested for ethanol 10%. The impact of incorporating ZnO in the migration into acetic acid was relevant at 20 °C only. Beside starch, most relevant migrants were PBAT oligomers made of butanediol and two different kinds of diacids, terephthalic acid or adipic acid. The cyclic diester of 1,4-butanediol and adipic acid, butenyl butanediol adipate in either cyclic and linear form and oligomers terephthalic acid, but-3-enyl hexadecyl ester were detected in an untargeted screening with GC-MS. A second TPA oligomer was not fully identified. The specific migration was in several cases, depending on the simulant and on the temperature, higher than 50 µgkg⁻¹ (semi-quantification), the threshold value for requiring additional toxicity test (genotoxicity tests applied to oligomers below 1000 Da). This indicates the need for more detailed studies with more precise quantification to verify the need for toxicity tests.

1. Introduction

Bioplastics are rising interest for food packaging and being developed as an alternative to fuel-based plastics. These results from environmental concerns about the production and disposal of conventional plastic materials, reflected in the legislation: the European packaging and packaging waste directive recognises that bio-based, compostable and biodegradable for limited packaging applications can result in environmental benefits (European Commission, 2022). Furthermore, bio-based materials, and in particular biodegradable, are generally perceived by the consumer as a solution for more sustainable packaging, although the difference between both concepts is not generally understood (Poças & Selbourne, 2023). The term bioplastics is applied to either bio-based, biodegradable or both (European Bioplastics, 2022).

The main current applications of biodegradable plastics in (food) packaging are food service ware and shopping bags, therefore relatively low demanding applications, where short contact time or no-direct contact with the food is observed. Great efforts are under development

to improve the performance of these materials rendering them suitable for a wider and more demanding range of applications, including the improvement of the functional properties of the materials with active and smart systems. Examples include the incorporation of essential oils and phenolic compounds of different plants (Laorenza and Harnkarnsujarit, 2021), approved preservatives such as nisin and sorbate or benzoate (Leelaphiwat et al., 2021; Wangprasertkul et al., 2020), combinations with lignin (Olonisakin et al., 2023), hemp micronized fibres (Lamsaf, et al., 2023) and antimicrobial agents as zinc oxide in nanoform (Soares Silva et al., 2023). However, little information is available regarding composition and safety of many biopolymers in the market. A previously published report on the analyses of bio-based and/or biodegradable food contact articles made of nine material types showed baseline toxicity for almost 67% of the materials, 42% resulted in induced oxidative stress, 23% in induced antiandrogenic effects and one sample in induced estrogenicity (Zimmermann et al., 2020). High values of migration were also reported by other authors while testing biopolymers (Canellas et al., 2015; Osorio et al., 2020; Ubeda et al., 2019).

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Therefore, it cannot be assumed that bioplastics and plant-based materials are necessarily safer than fossil-based plastics and the safety profile evaluation of these new materials must be further studied.

The basic principle underlying European law for food packages and other contact materials including active and intelligent materials and articles indicates that materials shall be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents to food in quantities which could: a) endanger human health; b) bring about an unacceptable change in the composition of the food; c) bring about a deterioration in the organoleptic characteristics thereof (Regulation (EC) No 1935/2004). This principle should be met by all materials including plastics, paper and board, biomaterials whether biodegradable and/or bio-based and sets its ground on both safety and inertness requirements. These requirements are laid down in specific legislation measures, which for plastics is the Regulation (EU) No October 2011 and amendments.

Definitions of plastic and polymer indicate that biomaterials are included in the scope the Regulation (EU) No October 2011 if they are produced by a conventional polymerisation process (polyaddition or polycondensation), by microbial fermentation or by chemical modification of natural or synthetic macromolecules. Therefore, biomaterials should be evaluated in terms of the overall migration, as a measure of the material inertness, and migration of specific substances according to the composition of the material, like the fossil-based and non-biodegradable plastics: monomers and starting substances, additives, and migration of non-intentionally added substances (NIAS) formed during the manufacture or storage of the packaging material.

Oligomers are present in the materials as NIAS although they may be expected, and their structure can be anticipated after the typical formulation of the base material. Additionally, in case of bio-based material migration of source contaminants present in the natural material, like persistent organic pollutants, residues, heavy metals, and trace elements, may be of interest in safety evaluations (Bonwick et al., 2019; Bradley, 2010). Presence of NIAS is already been explored in the case of conventional plastics such as (PET) polyethylene terephthalate (Nerin et al., 2013). However, despite the interest in developing biomaterials for food packaging, most of the work do not focus on the safety aspects of the materials (Kato and Conte-Junior, 2021; Riboni et al., 2023).

The global production capacity of bioplastics in 2022 was: polylactic acid (PLA) 21%, polybutylene adipate terephthalate (PBAT) 5%, polyhydroxyalkanoates (PHA) 4%, PBS 1% and regenerated cellulose films 4% (European Bioplastics, 2022). Blends with thermoplastic starch are the second most popular materials accounting 18% of the global capacity of production. PBAT is a biodegradable polyester synthesised using fossil-based monomers. This plastic is used often in blends with biobased plastics, namely PLA, to improve its properties. It may be anticipated that PBAT will be made from biobased resources in near future, as there is potential for the building blocks (butanediol and adipic acid) used in its production to be derived from biobased sources valorising organic waste streams (Maaskant et al., 2023).

Starch-based bioplastics are typically produced from blends of biodegradable petroleum-based polymers as the continuous phase, namely PBAT, with gelatinised starch, bio-based polymers (e.g. PHAs and PLA), compatibility agents and conventional additives, for mechanical, thermal and barrier properties improvement (Encalada et al., 2018). Those components should be authorised, listed in the Regulation, and comply with any restrictions applied.

Starch has been targeted in an enormous body of research on biomaterials using both native and modified starch (Bangar et al., 2021). As it is naturally present in the human diet, it is generally considered safe when used in materials for food contact. However, because it is often chemically modified and additives are incorporated, safety should be evaluated, and the compositional and migration tests should be performed. Furthermore, often the full composition of the material where

starch was incorporated and combined with is not known due to industry confidentially issues. Therefore, it is important to identify and quantify possible compounds and/or NIAS that could migrate into food from biomaterials.

Several studies have been published focusing on the use of these materials combined with active agents to increase the shelf-life of different foods (Bumbudsanpharoke et al., 2022; Kim et al., 2022). However, studies focusing on the safety of these materials as evaluated with the current reference rules for food contact materials, are lacking (Markkinen, 2022). The objective of this work was to perform a first-tier evaluation of the safety of a biomaterial produced with a commercial resin based on starch and PBAT, as assessed by the chemical criteria applied to plastics. This is an initial evaluation in a process which can be multi-step depending on the results in each tier. A schematic flowchart of this study is presented in Fig. 1. A screening of the potential migrants was performed by untargeted analyses of the migration solutions and of the materials after contact with simulants. The overall and specific migration of selected substances and the impact of incorporation of an active substance (zinc oxide) were determined.

2. Materials and methods

2.1. Films preparation

The films with a thickness of ca 15 μm were obtained by industrial blown extrusion (Inventive Materials, Portugal) with the processing temperature at different zones set at 125–144 $^{\circ}\text{C}$ and a screw speed of 295 rpm. The polymer with the ZnO were mixed in a co-rotating twin-screw extruder at a constant speed of 80 rpm, feeding at 10 kg/h and a temperature profile ranging from 60 to 180 $^{\circ}\text{C}$ (different zones of the extruder). An image of the extruded film is presented in Fig. 2

2.2. Overall migration

The samples were tested with aqueous food simulants ethanol 10% (v/v) and acetic acid 3% (v/v) and at two conditions: 40 $^{\circ}\text{C}$ and 20 $^{\circ}\text{C}$ for 10 days (conditions OM1 and OM2 of Regulation 10/2011), according to the standard EN 1186-3. Migration into olive oil simulant, was tested for 10 days at 40 $^{\circ}\text{C}$ (condition OM2 of Regulation 10/2011), according to the standard EN 1186-2. All samples were tested by total immersion of 1 dm² into 100 mL of food simulant.

2.3. Infrared analysis of the materials

The films were analysed by infrared spectroscopy before and after migration to highlight components that migrated (PerkinElmer Spectrum BX FTIR System with a DTGS detector, USA). Spectra were acquired in diffuse reflectance mode through a PIKE Technologies Gladi attenuated total reflectance (ATR) accessory within the wavenumber interval of 4000 to 600 cm^{-1} , with a resolution of 4 cm^{-1} . Each spectrum resulted from 32 scan co-additions. Films were twice folded (due to its reduced thickness), further placed in the ATR crystal and a constant pressure was applied. The ATR crystal was cleaned, and a background was acquired between each sample. Five spectra per sample were acquired, each in a different sample spot.

2.4. Thermal properties

The material was characterized based on the glass transition temperature (T_g), melting point (T_m) and crystallization temperature, by differential scanning calorimetry (DSC 204 F1 Phoenix by Netzsch, Germany). These parameters were determined according to the ASTM standard D3418, with the following conditions: initial temperature -50 $^{\circ}\text{C}$, heating rate 10 mL min^{-1} , final temperature 250 $^{\circ}\text{C}$. Determinations were made in the second heating cycle.

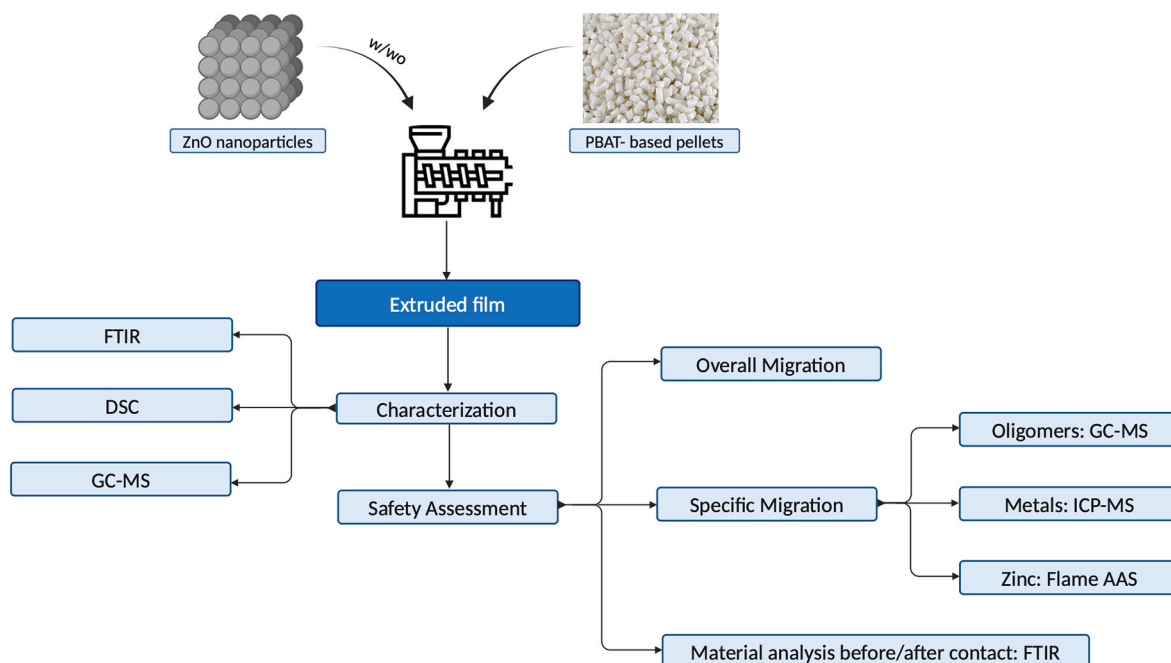


Fig. 1. A schematic flowchart of the work.

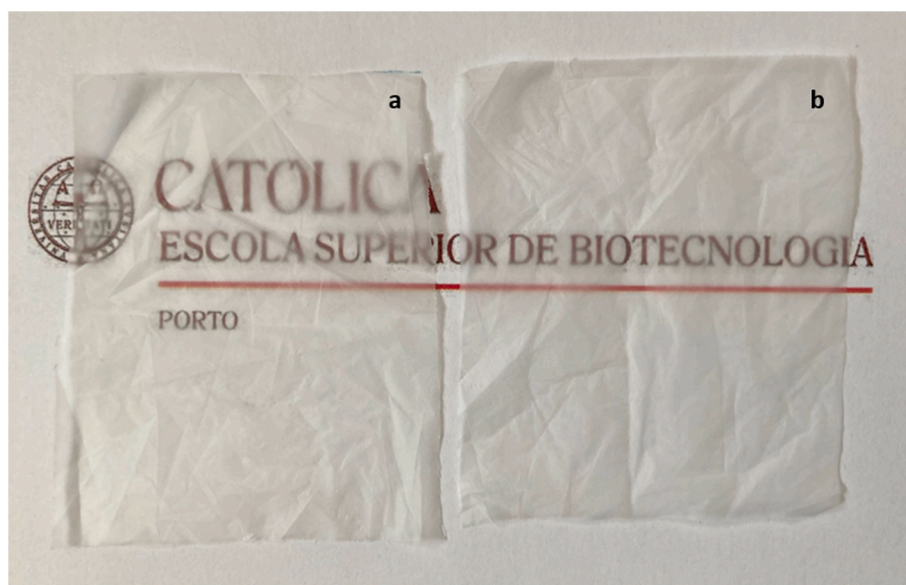


Fig. 2. Films extruded a) without ZnO b) with ZnO incorporated.

2.5. Screening of potential migrants in the material

Samples were analysed after extraction with solvents in the following conditions: sample (0.1 g) was extracted with 5 mL of solvent - dichloromethane (Merck, Germany), acetone (Merck, Germany), ethanol (Valente & Ribeiro, Portugal), and hexane (VWR chemical, Poland) by sonication for 20 min followed by 24 h at 60 °C. After filtration with 0.45 µm PTFE filters extracts were analysed by GC-MS operated in EI at 70eV, scan mode from 33 to 700 m/z. Identification of substances was performed by comparison of spectra (NIST library 2.3. 2017) and calculated of the Retention Index.

2.6. Migration of selected compounds

Samples (0.6 dm²) were in contact with 100 mL of ethanol 10% (v/v), acetic acid 3% (v/v) and oil for 10 days at 40 °C and 20 °C. The migration into food simulants of three detected oligomers was semi-quantified as equivalent to terephthalic acid, bis(2-ethylhexyl)ester DEHT (CAS 6422-86-2) standard solution with a concentration 0.0105 mgL⁻¹ for ethanol 10% (v/v) and acetic acid 3% (v/v), and a concentration of 1.05 mgL⁻¹ for semi-quantification of the oligomers in olive oil. Migration solutions were extracted 1 min by vortex with hexane (aqueous simulants) or acetonitrile (olive oil) in 1:1 proportion. After centrifugation for 5 min at 2500 rpm an aliquot of the organic phase was collected for injection into GC-MS operated in SIM mode at 70 + 112+149 + 167+261 + 279 m/z (DEHT), 55 + 111+129 + 201 m/z for

butenyl adipate, 55 + 104+149 + 221 m/z for terephthalic acid ester derivative 1 and 54 + 104+132 + 149+369 for terephthalic acid ester derivative 2.

2.7. Gas-chromatography analysis

GC-MS analyses (GC-MS SCION TQ, Bremen, Germany) were conducted with the following chromatographic conditions: column 30 m × 0.25 mm with 0.25 μm BR5ms phase, the injector temperature was 280 °C, the temperature program used was 50 °C for 3 min raised at 10 °Cmin⁻¹ to 320 °C for 15 min. Injected volume of 1 μL (splitless mode). Helium was the carrier gas (1.2 mLmin⁻¹).

2.8. Metals migration

Migration of metals according to the Regulation October 2011 (Al, Cu, Co, Zn, Fe, Ni, Li, As, Sb, Cd, Cr, Pb, Hg, Mn and Ba) was performed for 10 days at 40 °C with immersion of 0.6 dm² into 100 mL of food simulant acetic acid 3% (worst case). The concentration of each element was determined by Inductively coupled plasma optical emission spectrometry (ICP-OES) (Avio™ 220 Max, France).

Kinetics of the migration of Zn, into food simulant acetic acid 3% (v/v) at 20 °C and 40 °C and into simulant ethanol 10% (v/v) at 20 °C was performed by immersion of 0.6 dm² of the material into 100 mL of the simulants. Measurements of the Zn concentration on each migration solution at 1, 3, 5 and 10 days of contact was done by Flame Atomic Absorption Spectrometry (AAnalyst 400, PerkinElmer, Germany).

2.9. Toxicity assessment of specific migrants

The software “Toxtree v3.1.0.1851 (Ideaconconsult Ltd.) was used to estimate the toxic potential of the specific migrants. The migrants were classified in one of the three “Cramer Classes” (I, II, III) based on their structure using the decision tree following the Cramer rules with and without extensions (EFSA CEF Panel, 2016; Tsochatzis, Lopes, Kappenstein, Tietz, & Hoekstra, 2022) and the Kroes Threshold of toxicological concern (TTC) decision in relation to alerts for potential safety concern (Kroes et al., 2004).

2.10. Statistics and data analysis

The SPSS 27.0 statistical program Windows (SPSS Inc., Chicago, IL, USA) was used for data analysis. Differences between means were evaluated by pair-sample T tests, *p < 0.05; n.s. (not significant).

Infrared spectra were modelled through a principal component analysis (PCA) (Jolliffe, 2002). Prior modelling spectra were pre-processed with standard normal variate (SNV) (Næs et al., 2002) and the Savitzky-Golay filter (15 smoothing points, 2nd order polynomial and 2nd derivative) (Savitzky and Golay, 1964) and further mean centred. Spectral pre-processing and modelling were performed in MATLAB R2023a (MathWorks, Natick, MA) and PLS Toolbox 9.2.1 (Eigenvector Research, Manson, WA).

3. Results and discussion

3.1. Overall migration

Overall migration test is relevant on assessing safety of new substances to be authorised for plastics in contact with food when larger amounts of oligomers are suspected (EFSA CEF Panel, 2008). Migration results largely exceed the limit of overall migration set by the European Commission for the aqueous simulants at both temperatures (Fig. 3a). The limit is 10 mg dm⁻² ± 30%. For simulant ethanol 10%, the migration value ranges between 15 and 25 mg dm⁻² and for acetic acid 3% ranges from 19 to 21 mg dm⁻², for the two temperatures tested (20 °C and 40 °C). The impact of temperature seems to be higher for the

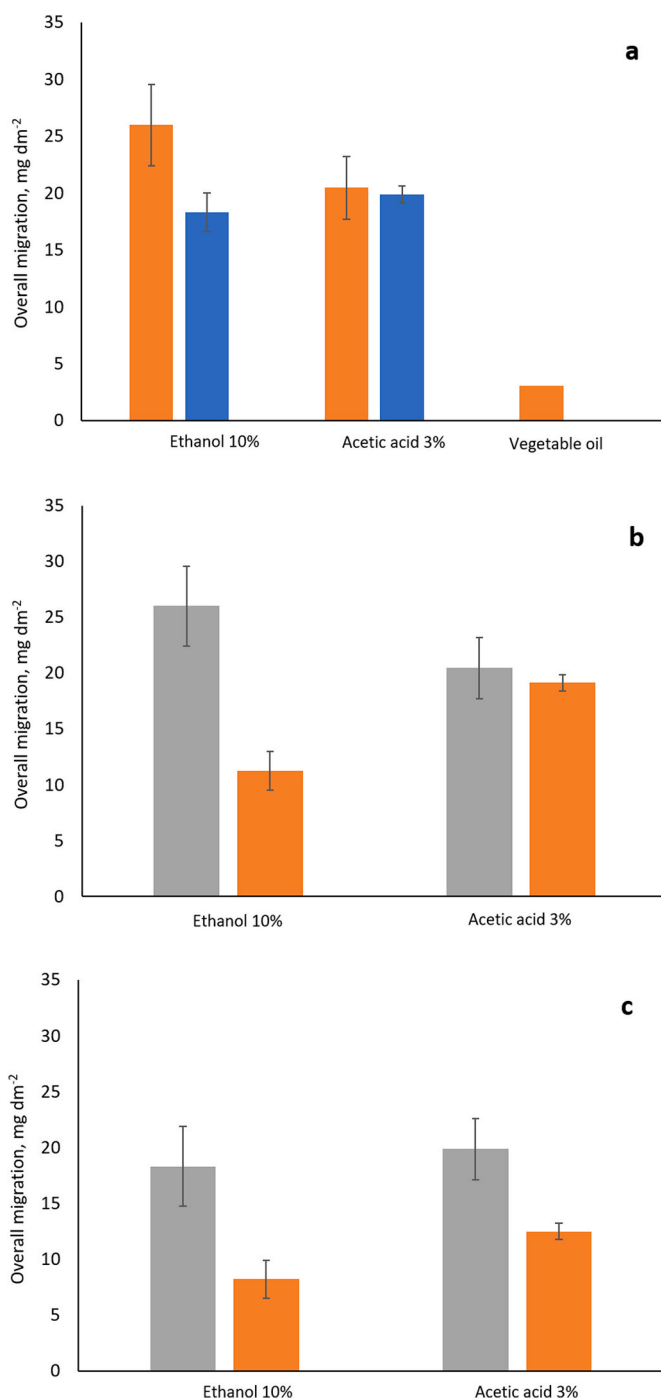


Fig. 3. Overall migration of PBAT based material a) effect of simulants at 40 °C (orange) and 20 °C (blue); b) effect of ZnO incorporation at 40 °C and at c) 20 °C (grey - no zinc; orange - with zinc).

ethanol 10% and no significant difference is observed between the results for acetic acid 3% at both temperatures. These values are higher than those reported in the literature for migration from PBAT blends into aqueous simulants (Apicella et al., 2023; Huang et al., 2023). The reported high values of overall migration may be due to the release of starch-based species and high molecular weight oligomers as already previously reported (Chongcharoenyanon and Sane, 2021), and/or leaching out of fillers like cellulose, silica, talc and/or calcium carbonate, which are main additives used in bio-based polymers (Falco et al., 2023). This is because these additives are not tightly bound to the polymeric matrix and therefore are liable to be transferred to the

simulants in contact.

The overall migration into olive oil was much lower than that into aqueous simulants, in the range of the limit of quantification, 3 mg dm^{-2} , probably due to the polarity of the migrants and hydrophobic nature of oil.

The impact of incorporation of ZnO particles, to render antimicrobial activity to the films, in the overall migration is shown in Fig. 3 b) and c). Results indicate that the incorporation of the inorganic particle reduces the overall migration. This is observed at both temperatures tested for the ethanolic simulant. For the acetic acid 3% simulant the impact is significant only for the lower temperature. The impact of ZnO incorporation at 40°C and simulant acetic acid 3% is not significant, possibly because of the synergic effect of the acidity and temperature in the Zn solubility. Similar observation was reported before (Phothisarattana and Harnkarnsujarit, 2022).

To elucidate the main migrants responsible for the high values in the overall migration, the films were analysed by FTIR before and after contact with the food simulant 10% ethanol.

3.2. FTIR spectroscopy

The infrared spectra of the PBAT based films before and after contacting the simulant (10% ethanol solution) were compared. Fig. 4(A-C) shows the infrared spectra of the films. Globally, infrared spectra present several absorption bands compatible with the PBAT polymer structure, one of the main film components. Namely, the broad band between 3200 and 3600 cm^{-1} , due to the O–H stretching, the ones between 3000 and 2800 cm^{-1} due to the symmetric stretching of –CH groups of saturated hydrocarbons, the very intense band at 1720 cm^{-1} due to the C=O vibration, the band at 1270 cm^{-1} , characteristic of the C–O vibration of the ester linkage and the sharp band nearly 725 cm^{-1} due to the existence of four or more adjacent methylene groups. Acquired spectra also present several absorption bands in the region between 1200 and 900 cm^{-1} , characteristic of carbohydrates bonds vibrations. Those bands corroborate the presence of starch in the films for which the most intense absorption broad band is between 950 and 1060 cm^{-1} (Ruggero et al., 2020). The comparison between the spectra of films before and after contact (Fig. 4A) clearly points to a lower starch content in the film after migration (lower infrared absorption bands in the carbohydrates vibration regions) suggesting a starch release from the film to the migration solution. This is in agreement with the observations during the overall migration tests where a yellowing of the drying residue was observed.

The analysis was performed also for the films containing ZnO nanoparticles incorporated (Fig. 4B). Also in this case, the film after contact with the simulant seems to present a lower amount of starch (lower intensity bands).

A detailed comparison of all the acquired spectra was performed (Fig. 4C). Regarding the films without (black lines) and with ZnO nanoparticles (blue lines) before migration, no naked-eye differences were observed in the analysed spectral region (spectra were totally superimposable). Regarding the film samples after contact, both seems to have lost some starch amount (lower absorption bands in the region of the carbohydrates vibrations). However, the sample with the ZnO nanoparticles appears to have lost a lower starch amount when compared to the samples without ZnO nanoparticles (the former shows higher intense carbohydrates absorption band). Therefore, results suggest that ZnO nanoparticles could act as a barrier for the starch release. A principal component analysis (PCA) was performed with the IR spectra obtained for all the samples to evaluate samples clusterization and additionally to depict the spectral regions that mostly contributed for it. The PCA was performed using the spectral region from 1500 to 800 cm^{-1} . The scores map of the PCA model is presented in Fig. 5A. The first two principal components encompass together 95.62% of the spectral variability. Three well defined clusters were observed in the PCA scores map. Samples of the film (with and without ZnO nanoparticles) were

placed in the positive part of the first principal component (PC1) while samples of the films after migration (with and without ZnO nanoparticles) appear in the negative part of PC1. The film samples before migration (with and without ZnO nanoparticles) appear in a single cluster due to the range of spectral region not including the range of ca 500 cm^{-1} characteristic of ZnO. The samples of the film after migration appear in two different clusters. Fig. 5A shows that PC1 is the responsible for the discrimination between the two samples (before and after migration) independently of the presence/absence of ZnO nanoparticles. The corresponding model loadings allow to infer about the spectral region(s) mainly responsible for the discrimination (Fig. 5B) and it was shown that the wavelength region between 1200 and 950 cm^{-1} (higher loading values) mainly contributes for the discrimination observed among PC1. This range corresponds were to where starch have the stronger vibrations, therefore, corroborating the hypothesis of starch release from the film to the migration solution. Furthermore, the spectra of the film samples without ZnO nanoparticles (red points) are further away from the film samples spectra before migration (black and blue points) than the ones with ZnO nanoparticles (green points). This relative position is consonant with the higher overall migration values (higher starch release) of the films without the incorporation of ZnO nanoparticles. The linkage of ZnO with the –OH group of starch and the cohesive structure of ZnO increases the barrier of the film, therefore, decreasing the leaching out of starch (Ma et al., 2016; Ni et al., 2018).

3.3. Thermal properties

The thermal transitions of the films were determined by DSC. The incorporation of ZnO did not show a major impact on the transition temperatures of the film. The film without ZnO had melting, crystallization and glass transition temperatures, respectively 120.9°C , 70.4°C and -31.2°C and the film with ZnO showed respectively 121.3°C , 70.8°C and -30.9°C , values according to those reported in the literature (Deng et al., 2018; Jiang et al., 2006; Wei et al., 2019).

3.4. Screening of potential migrants from the matrix

Fig. 6 presents the chromatogram of the ethanol extract of the material obtained by GC-MS. The extractions with other solvents do not show additional relevant substances. The prominent peaks are listed in Table 1 together with information on identification, retention index, extraction solvents and the possible origin of the substance.

Polyesters are produced by combining polyol(s) with aliphatic and/or aromatic dicarboxylic acids. A typical formulation of starch-based biodegradable polyester includes the starch (up to 50%) and the aliphatic-aromatic copolyester PBAT (20–70%) which is based on 1,4-butanediol, adipic or sebacic acid and terephthalic acid or terephthalic acid derivative (e.g. dimethyl terephthalate DMT). It may also include PHA (10–50%), PLA (3–25%) and for some applications an epoxy group-containing polymer, based in styrene, methyl (meth) acrylate and glycidyl (meth) acrylate. Additionally conventional additives and processing aids such as plasticizers, stabilizers, anti-flaking and antiblocking agents, nucleating agents, and fillers (cellulose, silica, talc and/or calcium carbonate) are included (EP2984138A1). The specific composition of the material analysed was not disclosed which brings obvious limitation to the identification of the potential migrants detected.

The more intense peaks correspond to different PBAT oligomers made of butanediol [BD] and two different kinds of diacids, terephthalic acid [TPA] or adipic acid [AA]: the cyclic diester of 1,4-butanediol and adipic acid (peak 2) which is reported as PBAT marker (Falco et al., 2023), butenyl butanediol adipate, in either cyclic and linear form (peak 5) and oligomers terephthalic acid, but-3-enyl hexadecyl ester (Osorio et al., 2022) and a second TPA oligomer that was not fully identified. It is recognised the difficulty in identifying material oligomers without chemical standards. The chemical form (cyclic or linear) present and its detection limit also depend on the sample treatment and analytical

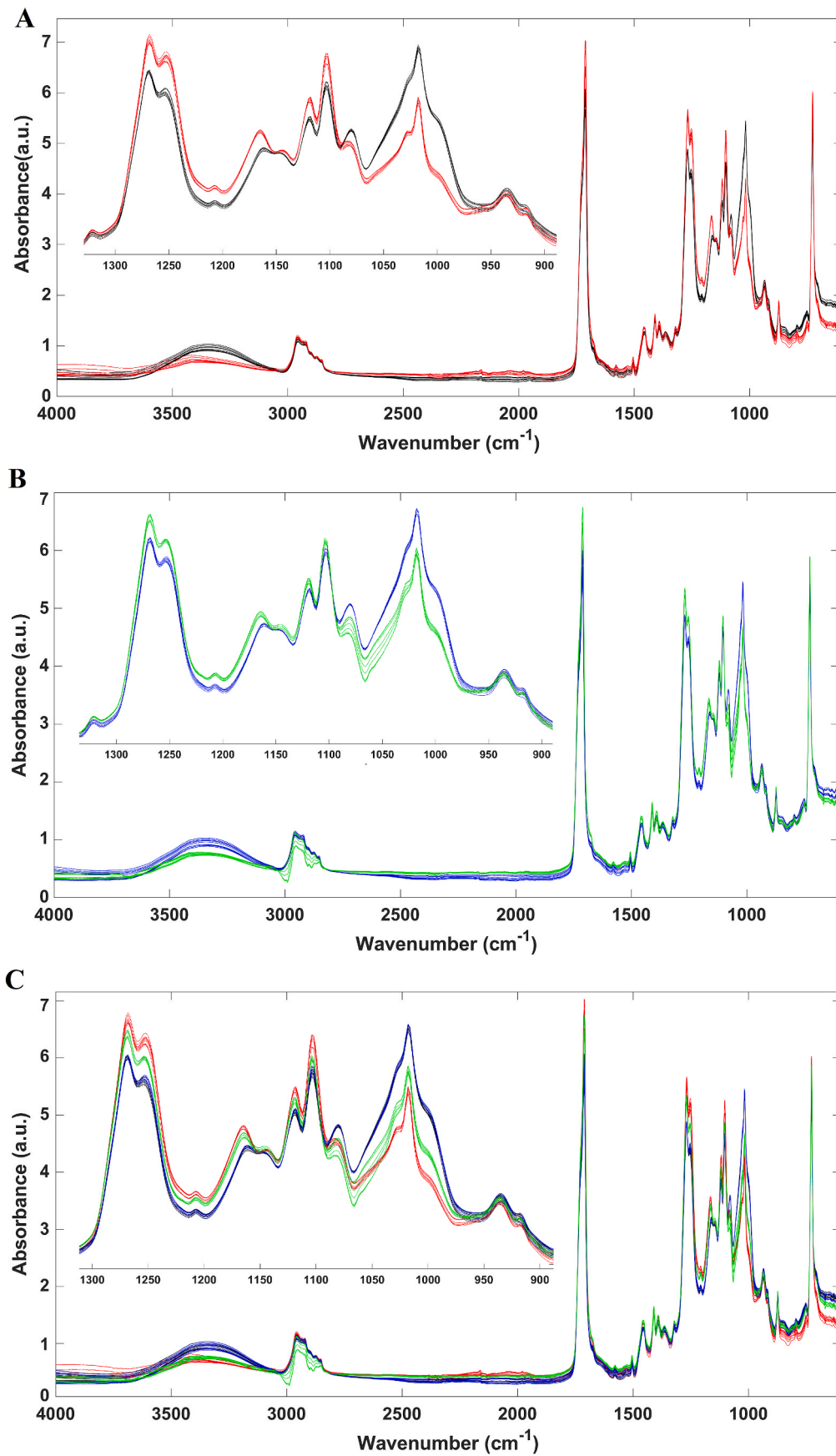


Fig. 4. Infrared spectra of the studied samples: A) film before migration (black) and film after migration (red); B) film with ZnO before migration (blue) and film with ZnO after migration (green); C) panel A and B superimposed for comparison purposes.

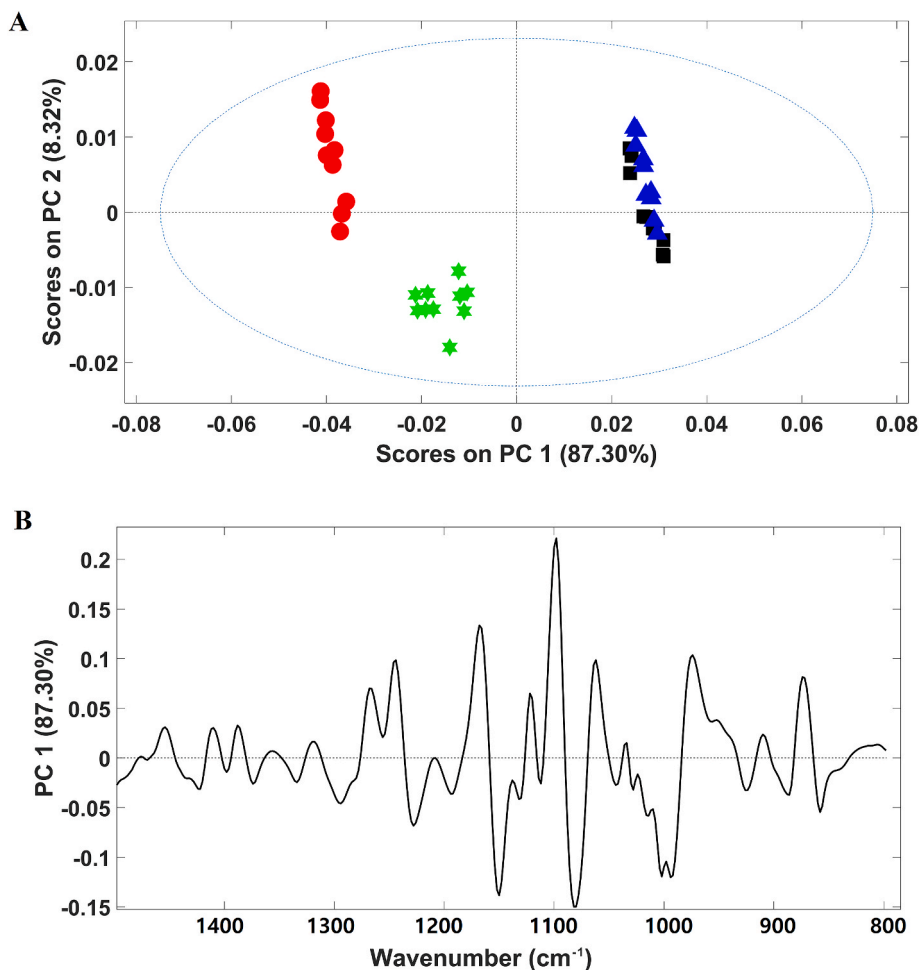


Fig. 5. A) Scores map of the PCA model developed with the infrared spectra of all samples in the spectral region $1500\text{--}800\text{ cm}^{-1}$. Legend: ■ film before migration; ● film after migration; ▲ film with ZnO before migration; ★ film with ZnO after migration; B) Loadings plot of the PCA model.

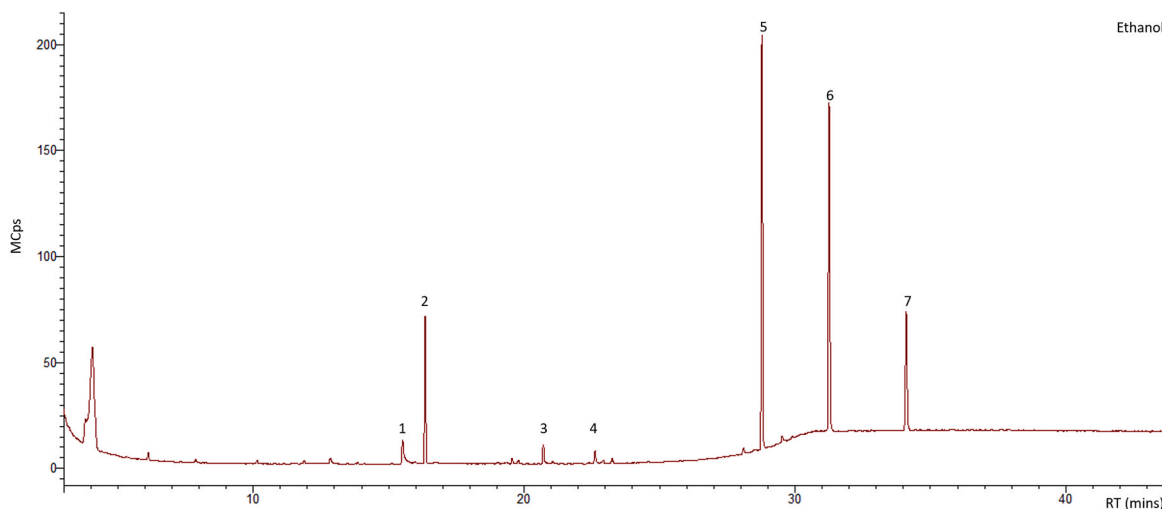


Fig. 6. GC-MS chromatogram of ethanol extract of the neat PBAT based film.

technique used.

In previous work twenty-four oligomers were detected in PBAT, 18 linear and 6 cyclic, with 3–5 repeating units each composed of different combinations of [BD], [TPA] and [AA], using liquid chromatography-

Electrospray Ionization Process (LC-ESI MS) (Song et al., 2011; Zhang et al., 2022; Zhang et al., 2023). The oligomers [TPA-BD]-2[AA-BD] (cyclic), 2[TPA-BD]-[AA-BD] (cyclic), 3[AA-BD] (cyclic), [TPA-BD]-3 [AA-BD] (cyclic) and 2[AA-BD] (cyclic) were detected at the highest

Table 1
Substances detected in the extracts of the films by GC-MS.

Peak	CAS	NAME	RI library	KI Calculated	Solvent	Observation	Cramer Class
	37112-31-5	Levoglucosenone	1107	1125	E,A	Thermal decomposition of cellulose	3
	67-47-0	5-Hydroxymethylfurfural	1233	1237	E,A	Thermal decomposition of cellulose	3
	652-67-5	Isosorbide	1300/-	1305	E,A	Plasticiser of thermoplastic starch	3
	822-06-0	Hexane, 1,6-diisocyanate-	na	1380	E	PBAT additive (chain extender)	3
	141-28-6	Diethyl adipate	1385	1398	E	Plasticiser of thermoplastic starch	1
1	498-07-7	Levoglucosan	1487	1509	E,A	Thermal decomposition of cellulose or starch	3
2	777-95-7	1,6-Dioxacyclododecane-7,12-dione	na	1579	E,A,H,D	PBAT cyclic oligomer	1
	na	Benzoic acid ester	na	1893	E,A		
3	57-10-3	n-Hexadecanoic acid	1968	1986	E,A	Additive	1
	628-97-7	Hexadecanoic acid, ethyl ester	1993	2022	E		1
4	57-11-4	Octadecanoic acid	2172	2194	E,A	Additive	1
	111-61-5	Octadecanoic acid, ethyl ester	2195	2229	E	Related to sebacic acid	1
	na	Unknown	na	2267	E,A		
	na	Unknown	na	2910	E,A		
5	na	Butenyl Butanediol Adipate	na	3012	E,A,D	PBAT oligomer	3
6	na	Terephthalic acid, but-3-enyl hexadecyl ester	na	3391	E,A,H,D	PBAT oligomer	1
7	na	Terephthalic acid ester ??	na	3691	E,A,H,D		-

Note: E-ethanol, A-ketone, H-hexane, D-dichloromethane.

intensity in starch/PBAT material by ultra-high performance liquid chromatography-mass spectroscopy (Quadrupole Time-of-Flight) abbreviated as UPLC-MS (QTOF) analysis (Osorio et al., 2022). The present results are aligned with previous work because as only GC-MS was used, the lower molecular weight and more volatile compounds could be expected to be detected in the present case. Similar results and detection of detect [AA-BD], [(AA)2-(BD)2], and [TPA-AA-(BD)2] were previously reported using GC-MS with electron ionization with a single quadrupole mass analyser (Osorio et al., 2019).

Several low intensity peaks identified as the fatty acids n-hexadecanoic and octadecanoic acids, as well as the corresponding ethyl esters were also detected. These substances are expected given the nature of the base material and maybe used as lubricants, processing aids, heat stabilisers, emulsifiers or result from some of the starting substances used as reported previously (Osorio et al., 2019). These are listed in Regulation 10/2011, without restriction.

Additionally, to the oligomers and fatty acids and esters, two additives used as plasticizers of thermoplastic starch were detected (isosorbide and diethyl adipate) and the hexane, 1,6-diisocyanate reported as chain extender, cross linker and/or compatibiliser in PBAT/starch materials (Falco et al., 2023). Isosorbide is listed in Regulation October 2011 with a SML of 5 mgkg⁻¹ and restriction to be used only as: (a) a co-monomer in poly (ethylene-co-isosorbide terephthalate); (b) a co-monomer in combination with ethylene glycol and/or 1,4-bis (hydroxymethyl)cyclohexane, to produce polyesters, and some restrictions regarding contact with containing more than 15% alcohol. Dioctoate of isosorbide is mentioned as a “green plasticiser” used in the production of PLA (Yang et al., 2016). Diethyl adipate is not listed in the plastics regulation. Hexane, 1,6-diisocyanate is listed in the Regulation October 2011 with a SML of non-detectable plus the restriction of maximum 1 mgkg⁻¹ in the final material expressed as isocyanate moiety.

Substances produced from thermal decomposition of cellulose (levoglucosenone and 5-hydroxymethylfurfural) were also detected in trace amounts as well as from starch (levoglucosan) (Stanfield et al., 2023).

Table 2
Migration of oligomers in mg/kg food.

	Acetic acid 3%			Ethanol 10%			Vegetable oil		
	40 °C		20 °C	40 °C		20 °C	40 °C		20 °C
Butenyl Butanediol Adipate	ND		0.161 ±0.002	0.966 ±0.078	0.511 ±0.048	7.235 ±0.328	6.876 ±0.874		
Terephthalic acid ester	0.017 ±0.003	0.005 ±0.001	0.077 ±0.003	0.005 ±0.002	2.446 ±0.325	2.408 ±0.234			
Terephthalic acid, 3-butenyl alkyl ester	0.056 ±0.001	0.051 ±0.001	0.444 ±0.028	0.093 ±0.012	4.876 ±0.634	4.346 ±0.692			

3.5. Migration of selected compounds

As indicated above some of the detected substances in the ethanol extract are authorised for use in food contact plastics with the single restriction on the overall migration limit. Therefore, the most intense peaks detected in the ethanol extract, corresponding to oligomers, were studied regarding the migration behaviour for liquid simulants (acetic acid 3%, ethanol 10% and olive oil). The effect of temperature on the migration of these substances was also studied.

Results are shown in Table 2. The migration level is highest for butenyl butanediol adipate, following terephthalic acid, 3-butenyl alkyl ester and lower for the unidentified terephthalic acid ester, for all simulants, according to the substance retention time in the GC-MS analysis and molecular weight. However, butenyl butanediol adipate was not detected in the simulant acetic acid 3% tested at 40 °C. Possibly the compound got hydrolysed at these conditions. At 20 °C, the migration of butenyl butanediol adipate was 0.16 mgkg⁻¹ to acetic acid, 0.51 mgkg⁻¹ to ethanol and 6.8 mgkg⁻¹ to olive oil. These values are indicative only as they refer to a semi-quantification based on DEHT and not on the specific substances. No reported values for migration into olive oil were found in the literature. Previous works used simulant D2 (ethanol 95%) as non-aqueous simulant, to study the migration of oligomers from PBAT based polyesters, instead of using olive oil. However, no quantification was done and just the intensity of peaks was given (Aznar et al., 2019; Osorio et al., 2022; Ubeda et al., 2019, 2021). Alternative the solid simulant Tenax® was also reported (Canellas et al., 2015). Therefore, comparison is not possible.

Contrary to the overall migration, the specific migration of the studied oligomers is much higher to olive oil than to the aqueous simulants, being the lowest to acetic acid 3% simulant. This agrees with the solubility in olive oil of such compounds as compared to aqueous simulants, as reported elsewhere (Conchione et al., 2020). Migration of higher molecular weight oligomers depends largely on the fat content of the simulant. However, those heavy compounds cannot be detected by the applied technique GC-MS. The overall migration in ethanol and acetic acid is heavily influenced by starch and other additives (as concluded by the FTIR analysis) with higher affinity to those media than

to olive oil.

The effect of temperature on the migration can be tentatively observed also from Table 2. Migration was tested at two temperatures only (20 and 40 °C, corresponding to the recommended migration testing conditions for room and refrigerated temperatures applications). It is well known that the relationship between temperature and the migration is not linear and often follows a pattern that can be described by the Arrhenius equation (Poças, 2018), presenting an exponential effect with the inverse of temperature. Therefore, the data at more than just two temperatures would be required to full assess the impact of temperature on migration. Nevertheless, data reported can be useful. Results indicate that butenyl butanediol adipate, and terephthalic acid, 3-butenyl alkyl ester register an increase in migration into olive oil and into ethanol 10% with temperature in the range tested (20–40 °C) of ca 20 $\mu\text{gkg}^{-1}\text{°C}^{-1}$, while the heavier unidentified terephthalic acid ester sees an increase of only ca 3 $\mu\text{gkg}^{-1}\text{°C}^{-1}$, in the same simulants. The impact of temperature on the migration into acetic acid 3% is much lower. It could not be calculated for the butenyl butanediol adipate because this compound was not detected, but for the other oligomers the increase with temperature was lower than 0.6 $\mu\text{gkg}^{-1}\text{°C}^{-1}$.

The results observed are, in several cases, depending on the simulant and on the temperature, higher than 50 μgkg^{-1} , the threshold value for requiring additional toxicity tests. In particular, genotoxicity tests applied to oligomers below 1000 Da would be required (EFSA CEF Panel, 2008). Different approaches have been followed for the evaluation of oligomers present in authorised plastics, according to specific characteristics of the system and data available. It is recognised that oligomers mixtures are largely dependent not only on the initial composition but also on the polymerisation and manufacturing processes. Therefore, the evaluation of these oligomers and reaction products should be conducted case by case (Castle and Barthélémy, 2016).

The safety evaluation of these so-called non-intentionally added substances (NIAS) is complex, and where the structure is known, the use of the TTC has been suggested as a possible approach (EFSA CEF Panel, 2016). In some cases, the toxicity of the oligomers is inferred through reading across from monomers. If the starting monomers are non-genotoxic, and as the oligomers are expected to be less reactive than their monomers, then no concern on genotoxicity for the oligomeric species is identified (EFSA CEF Panel, 2014).

3.6. Migration on Zn and other metals

The kinetics of Zn migration for the material with ZnO incorporated is shown in Fig. 7. After 1 day of migration the limit of 5 mgkg^{-1} food is exceeded at both 20 °C and 40 °C for the simulant acetic acid. However, after 2 days of contact, a continuous decrease of Zn in the simulant is observed suggesting that there is a reabsorption of Zn by the material.

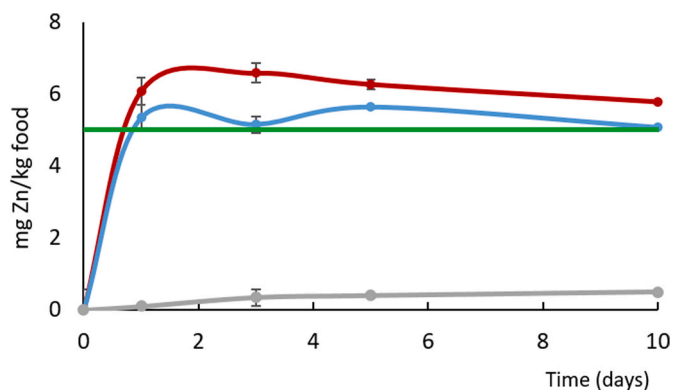


Fig. 7. Kinetics of Zn migration into aqueous simulants and different temperatures. Legend: —●— Acetic acid 3%, 40 °C; —●— Acetic acid 3%, 20 °C; —●— Ethanol 10%, 20 °C; —●— Limit.

This effect of apparent reabsorption of migrants has already been reported for migration from cellulose-based materials (Poças et al., 2011; Soares Silva et al., 2023). This can be associated to the starch fraction on the material, and possibly to interaction of the hydroxyl groups present in the matrix. The migration of ZnO into the simulant ethanol remains lower than 0.5 mgdm^{-2} at 10 days of contact, similar to the results previously reported (Phothisarattana and Harnkarnsujarit, 2022).

For the metals As, Ba, Co, Cu, Li, Mn, Ni and Sb values were lower than the correspondent limit of quantification i.e., between 0.001 and 0.005 mgkg^{-1} of food. Migration of heavy metals (Cd, Cr, Hg and Pb) is lower than the LOQ for all metals. Quantifiable values are reported for Al ($0.031 \pm 0.006 \text{ mgkg}^{-1}$ food) and for Fe ($0.015 \pm 0.004 \text{ mgkg}^{-1}$ food), without no differences between the material with or without ZnO incorporation.

4. Conclusions

Current analytical methods for establishing migration from fossil-based plastics to food are typically used on materials that contain bio-based components, such as starch, as well as risk assessment protocols. Starch/PBAT based materials are becoming very popular for low demanding food contact application but increasingly as a matrix for advanced active systems through incorporation of organic and inorganic substances that provide antimicrobial or antioxidant activity to the material. The safety of these materials needs to be better characterised. The overall migration was higher than the limit established of 10 mgdm^{-2} and the analytical results indicate that starch release is responsible for the high values. The incorporation of ZnO as active substance decreased the overall migration, especially for the simulant ethanol 10% and to a less extend for the acetic acid simulant. The effect of temperature on the overall migration under acidic conditions is more significant for the films with ZnO incorporated films as compared to films with no ZnO. The effect of temperature is more relevant in the case of migration into ethanol 10%. GC-MS extracts in ethanol provided more information on the potential migrants than other extracts tested. Specific migration of the polymer oligomers corresponding to the most intense peaks was determined. Results were higher than 50 μgkg^{-1} when tested with simulant 10% ethanol and with olive oil. This indicates the need for more detailed studies with more precise quantification to verify the need for toxicity tests.

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Srishti Singh: Writing – original draft, Investigation, Formal analysis. **Joel Pereira:** Writing – original draft, Methodology, Investigation. **Patricia Guerreiro:** Investigation, Formal analysis. **Céu Selbourne:** Methodology, Investigation, Formal analysis. **Cidália Paula:** Resources, Methodology. **António Cunha:** Resources, Methodology. **Clara Sousa:** Writing – review & editing, Validation, Supervision, Methodology, Investigation. **Fátima Poças:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial

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Data availability

Data will be made available on request.

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