Talanta 172 (2017) 68–77

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Identification of non-intentionally added substances in food packaging nano films by gas and liquid chromatography coupled to orbitrap mass spectrometry

M.J. Martínez-Bueno[a,*], M.D. Hernando[b], S. Uclés[a], L. Rajski[a], S. Cimmino[c], A.R. Fernández-Alba[a]

[a] University of Almeria, Department of Physics and Chemistry, Agrifood Campus of International Excellence (ceiA3), Ctra. Sacramento s/n, La Cañada de San Urbano, 04120 Almería, Spain

[b] National Institute for Agricultural and Food Research and Technology, INIA, 28040 Madrid, Spain

[c] Institute for Polymers, Composites and Biomaterials (IPCB), Consiglio Nazionale delle Ricerche (CNR), Via Campi Flegrei 34 Olivetti, 80078 Pozzuoli, Italy

ARTICLE INFO

Keywords:
Food contact materials
NIAS
migration studies
HRAMS
non-target analysis
Polylactic acid

ABSTRACT

The control of chemical migration from new functionalized food contact materials (FCMs) is a challenge for meeting food safety requirements. The non-intentionally added substances (NIAS) constitute a group of chemicals that are not applied, but may be introduced or formed during the production process of FCMs. This study describes a multi-analytical approach for the evaluation of unknown substances that migrate from FCMs. A case study is presented using a developed polymer consisting of a monolayer film with polylactic acid (PLA), polylimonene (PL) and zinc oxide nanoparticles (ZnO NPs). This approach incorporates the platforms of ICP-MS (inductively coupled plasma mass spectrometry), to determine whether there is transference of ZnO NPs used as antimicrobial agent and, the systems GC-MS and LC-MS (gas / liquid chromatography coupled to a quadrupole orbitrap mass spectrometer) for the characterization of the chemical structure of NIAS using the molecular mass and specific features of mass fragmentation. The screening of unknown compounds comprised retrospective analysis and data processing using both, a mass spectral library and databases, for GC and LC data, respectively. This approach has provided the tentative identification and quantification of seven NIAS, 3 by GC (Tripropylene glycol diacrylate, 10-Heneicosene and α-Tocopherol acetate) and 4 by LC (N,N-Diethyldodecanamide, N-[(9Z)-9-Octadecen-1-yl]acetamide, 1-Palmitoylglycerol and Glycerol stearate). This migration study was carried out according to the standard protocols established by EU regulation for FCMs.

1. Introduction

The production and use of food contact materials (FCMs) have been increased in the last years [1,2]. Modern FCMs are designed to fulfil multiple purposes including the protection of food products from external sources of contamination as well as the prevention of its deterioration by controlling or inhibiting pathogen growth, thus extending shelf-life, safeguarding quality and safety. The packaging industry is making an effort to meet food safety requirements, appearance improvement for consumer appeal, low environmental impact and cost savings. Some of the most used packaging materials are made of synthetic polymers such as polyvinyl chloride (PVC), polyvinyl acetate (PVA), polyethylene (PE), polypropylene (PP) or polylactic acid (PLA). PLA is the most common bio-based plastic obtained by chemical synthesis, in place of the usual fossil-based monomers [3]. PLA can also be blended with other polymers to further extend the applications, depending on enhance impact strength, flexibility and/or viscosity [4].

Only substances included in the list of authorized additives may be intentionally used in the manufacture of FCMs. The list contains more than 150 compounds including among others, monomers or other starting substances, additives (excluding colorants), polymer production aids (excluding solvents) and macromolecules obtained from microbial fermentation [5]. Some functional additives such as antimicrobial agents, antioxidants, stabilizers or plasticizers have a major effect in the processing and shelf-life of plastics, being responsible for specific features of the FCMs. The antimicrobial activity of certain metal ions such as silver (Ag) or zinc oxide (ZnO) have been shown to be effective, both at the micro and nano scales [6,7]. In the nano form, they are being used in a wide range of FCMs due to their effectiveness

* Corresponding author.
E-mail address: mjbueno@ual.es (M.J. Martínez-Bueno).

http://dx.doi.org/10.1016/j.talanta.2017.05.023
Received 16 March 2017; Received in revised form 8 May 2017; Accepted 10 May 2017
Available online 11 May 2017
0039-9140/

against a broad spectrum of bacterial, but also against fungal, algal strains, and some viruses [1]. A polymer, is an inert structure with low potential risk for human health since compounds with a molecular weight greater than 1000 Da cannot absorbed. However, plastic additives or organic colorants with a lower molecular weight may migrate from plastics into foods, and it is needed a control for ensuring food safety [8,9]. Moreover, it is possible to detect migration of monomers that have not reacted during the polymerization, non-intentionally added substances (NIAS), or other impurities [2].

For the analysis of substances that migrate from FCMs, there are standardized tests, established by the EU regulation [5] and, applicable to all materials which come in direct contact with food. For this purpose, some food simulants are used to determine whether there is migration of non-desirable contaminants from a FCM. A release of NIAS may be the result of the interactions between different ingredients in the formulation, of degradation processes due to impurities present in raw materials or derived from additives used in the manufacture [10]. The chemical identification of NIAS is complex, in part because of the incomplete information about the ingredients used to manufacture the FCMs.

The majority of studies have focused on the development of methods using gas (GC) and liquid (LC) chromatography coupled to mass spectrometry (MS) as the suitable choice for the identification of migrant compounds [11]. GC-MS is the choice for volatile and semi-volatile compounds, whilst LC-MS for thermally unstable and non-volatile organic chemicals. Although, these studies have focused on the identification of NIAS using commercial or in house libraries; they also present a limitation, the degree of confidence when identification is based on unit mass resolution. High resolution mass spectrometry (HR-MS) provides accurate mass measurement in both operation modes, full scan and fragmentation. Other studies have reported the advantages of using high resolution accurate mass spectrometry techniques (HRAMS) for the screening of unknown substances [12]. This approach allows to detect a wide range of chemicals by means full-scan acquisition mode, with a high sensitivity, a high-resolving capacity (> 50,000 FWHM) and with an accurate mass measurement (with a deviation of approx. 1–5 ppm) [13–15]. Applications include the detection of known compounds, target screening without the use of reference standards, and the screening of unknown chemicals by retrospective analysis [1,11,16]. To our knowledge, HRAMS has been used in the target study of certain chemicals such as primary aromatic amines in different plastic materials; few studies have been described using this technique in non-targeted analysis of migrants from FCMs [8–10,16,17].

In this study, we seek to take the advantage of GC and LC systems coupled to quadrupole orbitrap mass spectrometers (Q-Orbitrap-MS) for the identification of NIAS released from two FCMs. This work aims to evaluate two antimicrobial nanocomposites prepared with PLA, polylimonene (PL) and ZnO nanoparticles (ZnO NPs). Potential migration of ZnO NPs added as antimicrobial agent, is also evaluated by using inductively coupled plasma mass spectrometry (ICP-MS).

2. Experimental section

2.1. Reagents

The standards 1-Palmitoylglycerol (CAS 542-44-9), Glycerol stearate (CAS 123-94-4) and α-Tocopherol acetate (CAS 7695-91-2) were purchased from Sigma-Aldrich Quimica S.A (Madrid, Spain). All were of analytical quality. Individual stock standard solutions were prepared at about 1 mg/mL in acetonitrile, and stored at −20 °C. Individual standard solutions of lindane-d6 and dimethoate-d6 prepared in ethyl acetate and methanol were used as injection internal standards for the GC and LC analysis, respectively.

Water used for LC-MS analysis and for the preparation of food simulants was obtained from a Milli-Q water purification system (Direct-Q™ 5 Ultrapure Water System Millipore, Bedford, MA, USA), which provided a specific resistance of 18.2 MΩ cm. Formic acid (98% purity) was purchased from Fluka (Buchs, Germany). Methanol (MeOH) and acetonitrile (AcN) HPLC-MS grade were supplied from Merck (Darmstadt, Germany). Glacial acetic acid and ethanol were purchased from Fluka (Buchs, Germany). Polylimonene (Piccolite C115) was kindly supplied by PINOVA Inc. (Brunswick, GA, USA). Piccolite C115 is produced from d-limonene, a natural terpene of citrus origin. ZnO NPs were synthesized using a pyrolysis method; this procedure was described in a previous publication [18]. Polylactic acid (PLA 4032D), was supplied by NatureWorks LLC (Minnetonka, Minnesota, U.S).

2.2. Active food contact materials

Two nanocomposites prepared with PLA/PL and ZnO NPs, designed as antimicrobial FCMs for the preservation of aqueous and acidic foods [6,7], were tested to determine potential migration of NIAS into food simulants. PLA is an aliphatic polyester produced by the polymerization of lactic acid (2-hydroxypropionic acid). It is a common bio-based polymer obtained by chemical synthesis [8]. In this investigation it was used a PLA, in pellets form, acquired from Nature Works LLC, code PLA 4032D. Some characteristics are the following: d=1.24 g/cm^3; Mw=2.1×105 (g/mol), Mn=1.3×105(g/mol), polydispersity=1.6 Mw/Mn (measured by GPC-150C Waters at IPCB-CNR); glass transition temperature (Tg) and melting temperature (Tm) determined at IPCB-CNR by Mettler DSC 822e with a HR of 20 °C/min, were: Tg=58 °C and Tm=160 °C. The polylimonene (PL) was used as additive for the reduction of oxygen permeability and as antimicrobial agent. The PL used was Piccolite C115, kindly supplied by PINOVA Inc. PL is produced from d-limonene, a natural terpene of citrus origin; the resin is characterized by light colour, resistance to aging, high thermal stability. It has Mn=625, Mw=1150; Mz=2050, Tg=65 °C, Softening Point (Ring & Ball)=112–118 °C. ZnO was synthesized by using a preindustrial spray scale pyrolysis platform, and kindly supplied by Pylote SAS in Dremil-Lafage, France.

The films consisted of (i) PLA 95% wt / ZnONPs 5% wt, hereinafter referred to as PLA/ZnONPs and (ii) PLA 85% wt / PL 10% wt / ZnONPs 5% wt, hereinafter referred to as PLA/PL/ZnONPs. PLA pellets were first dried in an oven at 65 °C for 12 h; the pellets with ZnONPs and PL added to PLA in the due concentration in order to have the films with the desired composition, were processed by single screw extruder (Collin Teach-Line Extruder E20T/SCR15, Dr. Collin GMBH, Ebersberg, Germany) and again pelletized; finally these last pellets (containing PLA mixed with ZnONPs or PL/ZnONPs) were converted to films by a Collin Teach-Line Chill Roll CR72T (Dr. Collin GMBH, Ebersberg, Germany). The nanocomposites' preparation conditions have been previously described [18].

2.3. Migration test

Testing was carried out according to standard operating protocols, as laid down by EU legislation [5] to assess whether there was any transference of constituents coming into contact with foodstuffs. Two aqueous solutions, at 10% ethanol (simulant A, v/v) and at 3% acetic acid (simulant B, v/v), were used to mimic potential transference in two different food types, hydrophilic foods at pH > 4.5 and pH < 4.5, respectively. With regard to the selected time-temperature conditions, different approaches are recommended depending on the intended use of the FCMs. For refrigerated food applications, a test temperature of 20 °C over 10 days is recommended, covering the maximum shelf life of a packed food. The films were exposed to food simulants using conditions equivalent to the worst foreseeable use. The films were cut into small pieces (10×10 cm). A weight (~ 0.5 g) of each film was transferred into polytetrafluoroethylene (PTFE) tubes (Waldorf Corporation, St. Paul, MN, USA). PTFE is a common material that