J. Food Sci. Gastron. (July - December 2023) 1(2): 1-6
https://doi.org/10.5281/zenodo.13994642
ISSN: 3073-1283

JFSG
JOURNAL OF FOOD SCIENCE AND GASTRONOMY

ORIGINAL ARTICLE

Global migration of non-volatile substances and specific migration of €-caprolactam in polyamide 6 casings with Ag^{+}-Zn^{++} ions

Migración global de sustancias no volátiles y migración específica de €-caprolactama fundas de poliamida 6 con iones Ag^{+}-Zn^{++}

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Received: 06 February 2023 / Accepted: 17 May 2023 / Published online: 15 July 2023

Abstract Food packaging plays a key role in preserving the quality and safety of meat products. In this context, packaging materials, such as polyamide casings, must comply with migration regulations that ensure food safety. This study evaluated the total migration of non-volatile substances and the specific migration of the monomer ε-caprolactam in polyamide 6 casings used for meat products, with and without the addition of silver (Ag^{+}) and zinc (Zn^{++}) ions. Food simulants were used to represent real processing and storage conditions of sausages, applying total immersion, pouch, and cell. The results indicated that the global migration of the casings, both under control conditions and with additives, complied with international regulations (limits of 50-60 mg/kg). Furthermore, the specific migration of ε-caprolactam was below the regulatory limit (15 mg/kg), with no significant differences between casings with and without additives. The highest values were obtained with the ethanol (95%) simulant.

Keywords polyamide 6, global migration, ε-caprolactam, active packaging, food safety, food simulants.

Resumen El envasado de alimentos desempeña un rol clave en la preservación de la calidad y seguridad de los productos cárnicos. En este contexto, los materiales de empaque, como las fundas de poliamida, deben cumplir con normativas de migración que garantizan la inocuidad alimentaria. Este estudio evaluó la migración total de sustancias no volátiles y la migración específica del monómero ε-caprolactama en fundas de poliamida 6 utilizadas para embutidos cárnicos, con y sin la adición de iones plata (Ag^{+}) y zinc (Zn^{++}). Se utilizaron simulantes de alimentos para representar condiciones reales de procesamiento y almacenamiento de embutidos, aplicando métodos como inmersión total, bolsa y celda. Los resultados indicaron que la migración global de las fundas, tanto en las condiciones control como con aditivos, cumplió con las normativas internacionales (límites de 50-60 mg/kg). Además, la migración específica de ε-caprolactama fue menor al límite reglamentario (15 mg/kg), sin diferencias significativas entre las fundas con y sin aditivos. Los valores más altos se obtuvieron con el simulante etanol (95 %).

Palabras clave poliamida 6, migración global, ε-caprolactama, envases activos, seguridad alimentaria, simulantes de alimentos.

How to cite
Patiño, J. P, Henríquez, L. E., & Lantero, M. I. (2023) Global migration of non-volatile substances and specific migration of €-caprolactam in polyamide 6 casings with Ag^{+}-Zn^{++} ions. *Journal of Food Science and Gastronomy*, *1*(2), 1-6. https://doi.org/10.5281/zenodo.13994642

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PUBLIS EDITORIAL

Introduction

Packaging plays a fundamental role in the food chain. Among its many functions, the most important is maintaining or enhancing the quality and safety of food. Since the end of the last century, new technologies have been developed that improve the properties of packaging materials and systems, increasing the positive interactions between food and packaging (Pocas et al., 2011; Zigoura & Pascal, 2011; Brody, 2012).

The areas of packaging evolution have been primarily focused on the development of new packaging techniques (López-Rubio et al., 2006; Catalá & Gavara, 2011); the use of gases or materials mainly centered on analyzing possible interactions between food and packaging materials; adaptation to new preservation techniques (irradiation, non-thermal treatments such as high pressure, light pulses, etc.); innovation in packaging design, due to the diversity of products on the market, such as "reusable" packaging (Lagaron, 2006; Gavara et al., 2011); and studies on recycling and the environmental impact of different types of packaging (Ariosti et al., 2010).

Traditional packaging materials are derived from petroleum and pose health risks associated with migrating hazardous compounds. Thus, it is desirable to develop packaging capable of integrating shelf life, safety, and the retention of bioactive substances without causing major alterations in the migration rate of compounds in the packaging food system (AIMPLAS, 2008). The migration of substances from packaging to food is a fundamental aspect of food safety. This process involves the transfer of compounds such as monomers, plasticizers, and antioxidants from the packaging to the food under storage or processing conditions, affecting product quality and consumer health (Sablani et al., 2020). Migration is influenced by both the properties of the food and the characteristics of the packaging, making it a technical and regulatory challenge (Ariosti, 2011).

There are two types of migration: global and specific. Global migration refers to the total amount of substances transferred from the packaging to the food under normal use conditions or laboratory simulation, without considering the chemical nature of the migrated compounds (Helmroth et al., 2002). In contrast, specific migration refers to the amount of a particular substance of toxicological interest that migrates into the food. This type of migration is key to regulating potentially hazardous compounds, such as plasticizers, whose limits are established in regulations (Alamri et al., 2021).

International regulations, such as the European Union's Directive 2002/72/EC, set clear limits for global and specific migration to protect consumer health. These legislations define positive lists of substances permitted in packaging manufacturing and stipulate the necessary analytical methods to ensure compliance with migration limits, both quantitatively and qualitatively.

In recent years, there have been significant advances in the development of active packaging, which not only prevents the undesirable migration of compounds but also provides additional functionalities, such as antimicrobial capabilities. Examples include packaging that incorporates silver (Ag^{+}) and zinc (Zn^{++}) ions, which have demonstrated antimicrobial properties that extend the shelf life of food without compromising food safety (Patiño et al., 2014; Patiño et al., 2022).

This regulatory and scientific framework regarding the migration of substances from plastic materials into food highlights the need to continue developing robust analytical methods and innovative packaging that not only comply with safety limits but also offer additional benefits in terms of food preservation and quality. Therefore, the objective of this work was to determine the sanitary suitability of polyamide 6 film with and without the addition of Ag^{+}-Zn^{++} ions, through global migration of non-volatile substances and specific migration of ε-caprolactam.

Materials and methods

The films were obtained at the ALICO S.A. film plant (Medellín, Colombia) using proprietary technology, through a tubular blown film extrusion process, which consists of a blowing system with a circular die and a flat lip. Its stages involve the plasticization of the raw material, which is presented in the form of granules or powder, the introduction of the plasticized product into a mold that shapes it into the desired form (cylinder), solidification, and winding into rolls or cutting into units. The extrusion conditions are temperature of 130 °C, pressure of 14,000 kPa, a draw speed of 2.5, and a time of 3 minutes. The films have a layer distribution of PA/adhesive/PE-pigment/adhesive/PA from outside to inside (Aliflex, ALICO S.A.).

The films containing Ag^{+} and Zn^{++} ions (TA) were obtained by modifying the previous technology, by adding 3% (m/m) of the antimicrobial product (IRGAGUARD® B7000, CIBA) to the inner layer, which was added with the plasticizer (Ultramid®, BASF Corporation) to ensure homogeneous dispersion. The films made according to conventional technology (without the addition of Ag^{+} and Zn^{++} ions) were identified as control film (TP).

The global migration of non-volatile substances from the packaging to food simulants (A: distilled water; B: 3% (m/v) glacial acetic acid in aqueous solution; D: absolute ethanol 95% (v/v) in aqueous solution) was determined according to the criteria and guidelines outlined in Resolutions 683 and 4143 (MSPS-Colombia, 2012), Directives 85/572, 82/711, and 97/48 (EU Regulation No. 10, 2011), FDA (1995), FDA (2000), and FSA (2010).

Reference methods applied included total immersion contact; pouch and cell, where 1 dm² of the sample was exposed to 100 mL of each simulant, followed by conditioning for 2.5 hours at 60 °C, and then 10 days at 40 °C, simulatin g the conditions that the meat product would experience during production, processing, and prolonged storage. After conditioning, the residues obtained were evaporated in a porcelain capsule at a controlled temperature until a constant weight was achieved.

In determining the specific migration of ε-caprolactam, the same conditions of time, temperature, and simulants used for determining global migration were applied. After conditioning (2.5 hours at 60 °C, followed by 10 days at 40 °C), methylation and extraction were performed using methanol/sulfuric acid and immersion in hexane; a second extraction with 20 mL of hexane for 20 minutes, followed by dilution with 10 mL of ACN (v/v) with centrifugation, and finally, an aliquot was taken for analysis by GC-FID-Capillary of the specific compound ε-caprolactam.

The values of the evaluated indicators were analyzed using analysis of variance (ANOVA) with Statistics software (version 7, 2004, StatSoft Inc., Tulsa, USA). To identify statistically significant differences between samples, Duncan's multiple range test was applied with a significance level of $p \leq 0.05$.

Results and discussion

Table 6 shows the mean values and standard deviations obtained from the global migration test, understood as a measure of the inertia to transfer non-volatile substances from the films (TP) and (TA) to the simulants A, B, and D (Catalá, 2012; Sendón, 2005).

The addition of Ag^+ and Zn^{++} ions did not significantly increase ($p \leq 0.05$) the values of global migration compared to the control in the three evaluated methods. The global migration values were higher for simulant D (absolute ethanol 95%), followed by B (3% glacial acetic acid), and to a lesser extent A, due to their extractive power characteristics.

The ease with which these migrating components pass through the polymer molecules largely depends on properties of these substances, such as initial concentration, compatibility, size, and molecular structure (Rardniyom, 2008), as well as the thermodynamic properties of the polymer, including its polarity, solubility, density, crystallinity, degree of crosslinking, and branching, among others, all of which play a fundamental role in the interaction between the different parts of this system (Catalá, 2012). These migration processes are accelerated by the effect of temperature involved in simulating the actual conditions of use of the packaging, increasing the flexibility of the polymer molecules (Zigoura & Pascal, 2007).

Table 1. Global migration from films TP and TA in simulants A, B, and D

Simulant	Casing	Method	Global migration (mg/kg)
A	TP	Total immersion	2,7 (0,7) b
		Pouch	2,3 (1,1) b
		Cell	3,1 (1,8) a
	TA	Total immersion	3,9 (1,0) a
		Pouch	4,0 (2,3) a
		Cell	3,4 (1,2) a
B	TP	Total immersion	4,4 (0,6) a
		Pouch	4,1 (0,9) a
		Cell	4,0 (1,7) a
	TA	Total immersion	4,4 (1,0) a
		Pouch	4,3 (0,9) a
		Cell	4,3 (1,4) a
D	TP	Total immersion	6,6 (0,4) a
		Pouch	6,2 (1,7) a
		Cell	7,1 (2,4) a
	TA	Total immersion	7,2 (1,3) a
		Pouch	6,0 (0,7) a
		Cell	7,3 (1,5) a

Mean (standard deviation); n = 3.

TP: control films; TA: films with the addition of Ag^+ and Zn^{++} ions.

Simulants A: distilled water; B: 3% (m/v) glacial acetic acid in aqueous solution; D: absolute ethanol 95% (v/v) in aqueous solution.

The global migration values for both films in the tested simulants and in the three methods ranged from 2.7 to 7.3 mg/kg, complying with the global migration limits established by various regulations: Colombian legislation (50 mg/kg - Resolution 834/13); Mercosur (50 mg/kg - GMC Resolution No. 12/10); FDA (50 mg/kg - Section 177.1520); and the Regulation by the European Commission (60 mg/kg - Regulation 10/11) (Grob et al., 2007).

Figure 1 presents the migration of the monomer ε-caprolactam, a compound of toxicological interest and high molecular weight resulting from the polymerization of polyamides (PA-6) (Osváth et al., 2020) over 30 days.

The partition and diffusion coefficients for TP and TA in simulants A and D are presented in Table 2.

For both simulants, A and D, and types of film (TP and TA), the results obtained remained within a similar range due to the solubility of the monomer ε-caprolactam in water and 95% ethanol under the test conditions (Stoffers et al., 2005).

The highest migration value of ε-caprolactam at 30 days was reached in simulant D (95% ethanol), resulting in 6.20 mg/kg for the film with the addition of Ag^{+} and Zn^{++} ions, with no significant difference compared to the film without ion addition under the same conditions. The results do not exceed the migration limits established by current legislation (15 mg/kg - Resolution No. 105, 1999) and the European Commission Directive 2002/72/EEC.

Song et al. (2018) produced PA 6 sheets using a twin-screw extruder to evaluate their safety. Migration concentrations of caprolactam from the PA 6 sheets to food simulants were assessed according to the standard migration testing conditions of the Korean Food Standards Code (KFSC). The concentrations were investigated in various food simulants (distilled water, 4% acetic acid, 20 and 50% ethanol, and heptane) and under storage conditions (25, 60, and 95 °C). The migration concentrations of caprolactam in the food simulants were determined as follows: 4% acetic acid (0.982 mg/L), distilled

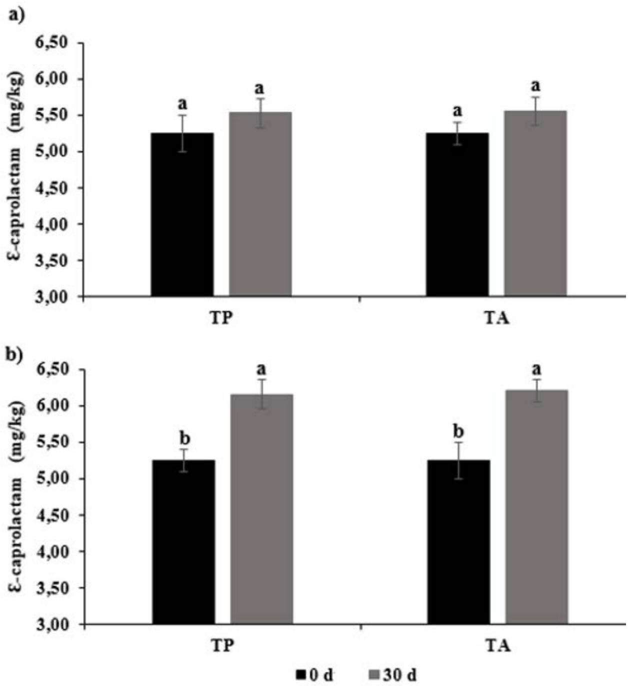

Figure 1. Migration of ε-caprolactam from control films (TP) and films with the addition of Ag^{+} and Zn^{++} ions (TA) in simulants A (a) and D (b).

Table 2. Diffusion and partition coefficients of the migration of ε-caprolactam in simulants A and D

Simulant	Film	Diffusion coefficient	Partition coefficient
A	TP	0.0768	0.0008
	TA	0.0856	0.0014
D	TP	0.0688	0.0200
	TA	0.0819	0.0196

Simulant A: water; simulant D: absolute ethanol 95% (v/v) in aqueous solution.

water (0.851 mg/L), 50% ethanol (0.624 mg/L), 20% ethanol (0.328 mg/L), and n-heptane (not detected). The migrations were below the regulatory concentration (15 mg/L) according to the KFSC testing conditions. Together, these results confirmed that the KFSC standard migration testing conditions are reliable for assessing the safety of PA 6.

Conclusions

Adding Ag^{+} and Zn^{++} ions did not significantly increase global migration or the specific migration of ε-caprolactam compared to films without additives. The results obtained comply with the limits established by international regulations, demonstrating that the use of these films is safe for contact with processed meat products. However, the ethanol simulant (95%) showed a greater extractive capacity, highlighting the importance of appropriately selecting simulants when evaluating migration in different types of food.

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Conflicts of interest

The authors declare that they have no conflicts of interest.

Author contributions

Jairo H. Patiño, Luis E. Henríquez and María I. Lantero: Conceptualization, data curation, formal analysis, investigation, methodology, supervision, validation, visualization, drafting the original manuscript and writing, review, and editing.

Data availability statement

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Statement on the use of AI

The authors acknowledge the use of generative AI and AI-assisted technologies to improve the readability and clarity of the article.

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