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Evaluation of Different Conditions of Contact for Caprolactam Migration from Multilayer Polyamide Films into Food Simulants

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ABSTRACT

Caprolactam, the polyamide 6 (PA-6) monomer, can migrate during food processing. At cooking temperatures, migration is accelerated and plastic components could degrade, giving off low molecular mass compounds, which can migrate into food. In this work, caprolactam migration from multilayer films containing PA-6 for meat foodstuffs and cheese packaging was performed at contact conditions of 40°C/10 days and 100°C/30 min. The migration into water ranged from 0.89 to 1.22 mg/dm^2 and 0.92 to 1.21 mg/dm^2, into 3% acetic acid from 1.29 to 1.74 mg/dm^2 and 1.13 to 1.62 mg/dm^2 and into olive oil from 1.18 to 1.98 mg/dm^2 and 0.50 to 0.80 mg/dm^2 for films intended for meat foodstuffs for 10 days at 40°C and 30 min at 100°C, respectively. Among PA-6 films used for cheese, caprolactam migration into water ranged from 0.17 to 0.91 mg/dm^2 and 0.74 to 1.04 mg/dm^2, into 3% acetic acid from 1.15 to 1.26 mg/dm^2 and 1.11 to 1.37 mg/dm^2 and into olive oil from 0.23 to 0.83 mg/dm^2 and 0.37 to 0.56 mg/dm^2 for 10 days at 40°C and 30 min at 100°C, respectively. Caprolactam migration evaluation into water and 3% acetic acid at 100°C/30 min could replace the need to apply the test at 40°C/10 days, since similar results were obtained under both conditions. In the case of PA-6 for meat foodstuffs, caprolactam migration into olive oil was highly affected by different conditions of contact, showing values two to three times higher at 40°C/10 days than at 100°C/30 min. For cheese films, caprolactam migration into olive oil was higher at 40°C for 10 days. Copyright © 2013 John Wiley & Sons, Ltd.

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KEY WORDS: caprolactam; migration; multilayer polyamide films; food simulants; conditions of contact

INTRODUCTION

Polyamide-6 (PA-6) is widely used as food packaging. Typical applications of PA-6 are mono or multilayer films used for sausage and meat foodstuffs, for vacuum and modified atmosphere packaging for fresh and processed meat as beef and poultry and for cheeses. PA-6 is also used as cook-in, microwave and roasting bags (MRB) and boil-in-the-bag packaging for processed meat and foodstuffs that may be cooked inside the package. Caprolactam is the monomer used in the manufacture of PA-6. After polymerization, residual caprolactam can remain in the plastic. Low molecular mass oligomers, additives, degradation compounds, etc. can also be present. All of them have the potential to migrate into food in contact.[1–3]

Multilayer film based on PA-6 is usually submitted to heat treatment during food processing. High temperatures are applied during the processing of some meat foodstuffs and cheeses, and the packaging

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could be exposed to these conditions during filling. During cooking of meat or sausages, the PA film is exposed to hot water or steam on the package outside as well as to the fatty food on the inside.[3] PA is one of the few polymers that can store food directly for cooking because it is heat resistant and has the capacity to retain exudates.[4] To simulate the contact time and temperature between food and packaging during food processing, it is important to take into account the conditions of time/temperature during storage.

The conditions of time/temperature of contact between packaging material and food simulants are a factor that should be considered when the potential of compounds migration from packaging into food is evaluated. The conditions of temperature and time for contact between food and packaging applied during the migration tests are standardized according to legislation.[5,6] They simulate the actual use of packaging material and food.

Temperature influences the level and kind of substances that migrate because it affects the velocity of the diffusion process and the solubility of the compounds. The diffusion coefficient of the migrants in the polymer and into the food and the partition coefficients between them are also influenced by temperature.[7,8] Thus, migration could be affected by differences in cooking time and temperature, and composition of food. Oven and microwave cooking may accelerate migration to a considerable extent. It is expected that volatile compounds from the plastic evaporate and migrate into food at oven temperatures. In addition, components of the plastic could degrade at cooking temperatures giving off low molecular mass compounds.[9]

Some authors[1,3,4,7,8,10–13] have studied the thermal effect on specific migration of several substances under different temperature conditions. Regarding caprolactam migration evaluated at high temperatures, the extraction time and thickness of the film were described as the parameters that affected the migration of caprolactam and the cyclic oligomers from PA-6 films used as boil-in-the-bag into boiled water for 1 h.[11] The migrants released from PA-6 films corresponded to around 1% of the film weight, and after 1 h, the levels were found to decrease.[11] Begley et al.[12] and Soto-Valdez et al.[4] found comparable values of migration of caprolactam and oligomers into Miglyol 812™ and into olive oil from similar PA-6/66 oven roasting bags and MRBs studied at 175°C/1 h and at 176°C/30 min, respectively. PA-6/66 is made from condensation of caprolactam and diamines and diacids.[13] Bradley et al.[1] evaluated the effect of heating procedures on caprolactam migration into foods (spaghetti bolognese, sliced beef in gravy, haddock steaks and chicken) from PA pouches suitable for cooking/heating either by immersion in boiling water or by using a microwave oven and also from PA-6 roasting bags. The heat treatment increased the caprolactam migration in some cases. Stoffers et al.[3] exposed PA-6 and PA-12 films, used as sausage casings, to olive oil and water simultaneously for 2 h at 100°C. Migration of caprolactam into water was observed, and for laurolactam, the PA-12 monomer, a similar amount was released into both food simulants. Bustos et al.[13] analysed caprolactam migration from different PA-6 and PA-66 cooking utensils (spoon, ladle, turner, etc.) into 3% acetic acid food simulant at 100°C for 2 h. Caprolactam levels were lower than its specific migration limit (SML), 15 mg/kg,[6,14] in all samples.

Caprolactam migration at 40°C for 10 days was reported from mono and multilayer PA films, PA/PE laminates, PA granulates and PA casings into distilled water, 3% acetic acid, 95% ethanol and olive oil.[2,15–17] In a general way, caprolactam migration evaluated at 40°C for 10 days seems to show higher levels than those at higher temperatures. However, most papers reported caprolactam migration at high temperatures (100–200°C) using only olive oil food simulant or fatty foodstuffs. In addition, there are no studies comparing caprolactam migration using different food simulants at different conditions of contact. To confirm that caprolactam migration increases at a certain condition of contact used in the migration assays, it is necessary to analyse the same packaging material at different conditions of time and temperature, preferably using several food simulants.

The aim of this work was to compare caprolactam migration from 13 multilayer films containing PA-6, used as meat foodstuffs and cheese packaging, into food simulants at different conditions of contact, 10 days at 40°C and 30 min at 100°C.

MATERIAL AND METHODS

Chemicals and reagents

Caprolactam (purity >99%) was used as the analytical standard, and 2-azacyclononanone (purity>98%) was used as the internal standard, both purchased from Sigma Aldrich (Buchs, Switzerland). Methanol,

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n-heptane and ethanol, all HPLC grade, were purchased from Mallinckrodt-Baker (Phillipsburg, USA). Extra virgin olive oil (La Española), purchased at the Brazilian retail market, and distilled water were also used. Acetic acid (P.A. grade) was acquired from Merck (Darmstad, Germany). Distilled water, 3% acetic acid solution (w/v) and extra virgin olive oil were used as food simulants.

Samples

Commercial multilayer films containing PA-6 were supplied by Brazilian packaging materials companies. Virgin films from eight commercial brands used for meat foodstuffs and five brands for cheese, named brands 1–8 and 9–13 (Table 1), were studied. It should be noted that meat foodstuffs and cheese packed in these types of samples are usually processed already packaged at temperatures from 70 to 100°C and stored refrigerated or at room temperature.

GC-FID analysis

Chromatographic analyses were performed in a 17-A Shimadzu Gas Chromatograph (Shimadzu Corporation, Kyoto, Japan) equipped with a flame ionization detector. A DB-1701 (J&W Scientific, Folsom, USA) capillary column (30 m × 0.25 mm and 0.25 μm film thickness) was used at 130°C for 1 min, programmed at 10°C/min up to 170°C for 1 min, then heated to 200°C at 10°C/min and held for 2 min. Hydrogen was the carrier gas (1.0 ml/min) and nitrogen was the makeup gas. Injections (1 μl) were made at 240°C in split mode (1 : 20). Detector temperature was 250°C.

The GC-FID method used to determine caprolactam in water, 3% acetic acid and olive oil food simulants was previously developed and validated in our laboratory.[2,16] Validation parameters such as calibration and linearity, limit of detection (LOD), limit of quantification (LOQ), precision and accuracy were evaluated based on the protocol from the International Union of Pure and Applied Chemistry.[18]

Migration

The conditions of contact (time/temperature) used during the migration tests were in accordance to Brazilian legislation.[19] It should be noted that the work was performed when the current Brazilian legislation[11] was not yet valid. Pieces of films (2 × 3 cm^2) were individually placed in contact with

Table 1. Characteristics of the multilayer PA-6 films and initial concentration of caprolactam (mg/dm^2) in the packaging materials.

Brand	Composition	Thickness (μm)	Caprolactam level[d] (mg/dm^2)
1	PA homopolymer (67%)/PA copolymer (20%)[a]	55 ± 5	1.56 ± 0.07
2	PA homopolymer (67%)/PA copolymer (20%)[a]	55 ± 5	1.32 ± 0.03
3	PA homopolymer (77%)/PA copolymer (20%)[a]	55 ± 5	1.48 ± 0.04
4	PA homopolymer (67%)/PA copolymer (20%)[a]	65 ± 5	1.50 ± 0.01
5	PA homopolymer (77%)/PA copolymer (20%)[a]	55 ± 5	1.60 ± 0.02
6	PA homopolymer (77%)/PA copolymer (20%)[a]	55 ± 5	1.83 ± 0.03
7	PA homopolymer (80%)/PA copolymer (10%)[a]	55 ± 5	1.41 ± 0.03
8	PA homopolymer (80%)/PA copolymer (10%)[a]	50 ± 5	1.22 ± 0.001
9	PA/Adhesive/PA[b]/Adhesive/Sealant layer[c]	60 ± 5	1.16 ± 0.005
10	PA/Adhesive/PA[b]/Adhesive/Sealant layer[c]	55 ± 5	1.73 ± 0.03
11	PA/Adhesive/PA[b]/Adhesive/Sealant layer[c]	60 ± 5	1.47 ± 0.02
12	EVA/Adhesive/PA[b]/Adhesive/EVA	60 ± 5	<LOQ
13	EVA/Adhesive/EVOH/Adhesive/PE	65 ± 5	<LOQ

[a]Multilayer PA-6 films containing PA-6 (homopolymer) and PA-6/PA-66 (copolymer) layers and masterbatch of additives, all from different companies.
[b]Internal layer ranges from 30–50% of PA-6/PA-66 copolymer.
[c]PE or EVA structure from different companies.
[d]Data according to Araújo et al.[21] converted to mg/dm^2 using the average weight ($n = 12$) for each brand film (6 cm^2); LOQ: limit of quantification (32 μg/g).

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10 ml of water, 3% acetic acid solution (w/v) and olive oil food simulants inside glass vials, which were hermetically capped. These vials were stored in an SL 100/80 oven (Solab, SP, Brazil) thermostatically set at 40 ± 1°C for 10 days and at 100 ± 1°C for 30 min. Triplicate samples of each commercial brand of multilayer PA-6 films were analysed. A blank prepared only with simulant was used as reference and was exposed and analysed under the same conditions. After migration contact, the film samples were removed, the internal standard solution (2-azacyclononanone, 14 μg/ml) was added, and then migration into water and 3% acetic acid was analysed using GC-FID, based on the European Committee for Standardization (CEN) caprolactam method.[20] For the olive oil simulant, the internal standard solution (2-azacyclononanone, 9.4 μg/g) was added to an aliquot of simulant, and a liquid–liquid extraction using two parts of n-heptane and one part of ethanol/water (1 : 2, v/v) was carried out. After separation of the phases, the aqueous phase was collected, filtered (PTFE, 0.22 μm) and then injected (1 μl) in the GC-FID.[20] Two injections for each replicate of the migration test were made into the chromatographic system. All migration tests were carried out by total immersion. Caprolactam levels obtained were submitted to ANOVA, and a Tukey test was used to compare the differences among means at $p \leq 0.05$.

RESULTS AND DISCUSSION

Since the method had been validated, it was used to quantify caprolactam that migrated from multilayer PA-6 films into the food simulants. The validation parameters (Table 2) indicated that the method showed good precision and accuracy, and therefore, it can be reliably used to determine caprolactam migration.

The initial concentration of caprolactam in the multilayer films containing PA-6 here described has been shown previously[21] and ranged from 1.16 to 1.83 mg/dm^2 (Table 1).

Concerning caprolactam migration, the levels into water food simulant ranged from 0.89 to 1.22 and 0.79 to 1.21 mg/dm^2, into 3% acetic acid from 1.29 to 1.74 and 1.13 to 1.62 mg/dm^2 and into olive oil from 1.18 to 1.98 and 0.50 to 0.80 mg/dm^2 for films used as meat foodstuffs packaging for 10 days at 40°C and 30 min at 100°C, respectively. For water food simulant (10 days at 40°C), the highest level of caprolactam migrated from brand 3 (1.22 mg/dm^2), which did not differ ($p > 0.05$) from brands 4 and 6, while for 30 min at 100°C, the highest level migrated from brand 6 (1.21 mg/dm^2), which did not differ ($p > 0.05$) from brands 1, 3 and 4. For 3% acetic acid, the migration of caprolactam from multilayer PA-6 films, for 10 days at 40°C, showed that the highest level migrated from brand 4 (1.74 mg/dm^2), which showed no difference ($p > 0.05$) only from brand 6, while for contact of 30 min at 100°C, the highest level migrated from brand 6 (1.62 mg/dm^2), which differed ($p \leq 0.05$) from all the other brands. Migration results obtained from olive oil for contact for 10 days at 40°C showed that the highest level of caprolactam (1.98 mg/dm^2) migrated from brand 6, which did not differ

Table 2. Validation parameters obtained by using GC-FID for caprolactam in water, 3% acetic acid and olive oil food simulants.

	Food simulants		
Parameters	Water[a]	3% acetic acid[a]	Olive oil[a]
Working range (μg/ml)	0.96–642.82	1.60–640.00	1.06–1062.34
Correlation coefficient	0.9999	0.9999	0.9999
RSD (%)	4.9	6.4	7.2
LOD (μg/ml)	0.32	0.24	0.10[b]
LOQ (μg/ml)	0.96	1.60	1.06[b]
LOQ recovery (%)	99	132	73
Intraday precision (%)	0.6–1.1	2.9–3.9	0.6–2.4
Interday precision (%)	1.0–2.1	2.9–4.3	2.3–4.8
Recovery (%)	89–105	101–106	72–99

[a]Validation parameters previously evaluated.[2,16]
[b]Values expressed as μg/g.

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significantly ($p > 0.05$) only from brand 4. In addition, for the migration for 30 min at 100°C into olive oil, the highest level was from brand 6 (0.80 mg/dm^2), which did not differ ($p > 0.05$) from brands 1, 2 and 4 (Table 3). Chromatograms of caprolactam that migrated into each food simulant at both conditions of contact are shown in Figure 1.

Regarding the different conditions of contact (10 days/40°C and 30 min/100°C), caprolactam migration from brands 4 and 7 into water showed similar behaviour. All the other brands of multilayer PA-6 films intended for meat foodstuffs showed difference ($p \leq 0.05$) at different conditions. For 3% acetic acid, caprolactam migration did not differ ($p > 0.05$) from brands 5, 6, 7 and 8 at both conditions of contact and was reduced ($p \leq 0.05$) for brands 1, 2, 3 and 4 when 30 min at 100°C was used. For olive oil, caprolactam migration for 10 days at 40°C and 30 min at 100°C showed difference ($p \leq 0.05$) among all the brands, with levels approximately twice higher for 10 days of contact at 40°C (Table 3).

Among multilayer PA-6 films used for cheese, caprolactam migration levels into water ranged from 0.17 to 0.91 and 0.74 to 1.04 mg/dm^2, into 3% acetic acid from 1.15 to 1.26 and 1.11 to 1.37 mg/dm^2 and into olive oil from 0.23 to 0.83 and 0.37 to 0.56 mg/dm^2 for 10 days at 40°C and 30 min at 100°C, respectively. Brand 10 showed the highest level of caprolactam migration into water (0.91 and 1.04 mg/dm^2) for 10 days at 40°C and 30 min at 100°C, respectively, differing significantly ($p \leq 0.05$) from all the other brands. For 3% acetic acid, a similar migration behaviour from water was observed. The highest level of caprolactam migrated from brand 10 (1.26 and 1.37 mg/dm^2) into 3% acetic acid at both conditions of contact, although migration for 10 days at 40°C showed no significant difference ($p > 0.05$) from brand 11. For olive oil, it was found that the highest level of caprolactam migrated from brand 9 (0.83 mg/dm^2) for 10 days at 40°C, which also differed ($p \leq 0.05$) from all the other brands. In a general way, there was a reduction ($p \leq 0.05$) in caprolactam migration into olive oil from 10 days of contact at 40°C to 30 min at 100°C, which was not verified for the other simulants. In both conditions of contact, brands 9 and 10 showed the highest caprolactam migration into olive oil ($p > 0.05$). Caprolactam migrations from brand 12 into water and olive oil (30 min at 100°C) and 3% acetic acid (both conditions of contact) and from brand 13 into olive oil (30 min at 100°C) were below the LOQ of the method, i.e. 0.96 μg/ml, 1.60 μg/ml and 1.06 μg/g for water,[2] 3% acetic acid[16] and olive oil,[2] respectively, so it was not quantified. Caprolactam migration from brand 13 into water and 3% acetic acid at both conditions of contact and into olive oil for 10 days at 40°C was not detected (Table 3). LOD values for water, 3% acetic acid and olive oil were 0.32 μg/ml,[2] 0.24 μg/ml[16] and 0.10 μg/g,[2] respectively.

Comparing the conditions of contact, brand 11 showed no difference ($p > 0.05$) on caprolactam migration level into water between both conditions, while brands 9 and 10 differed ($p \leq 0.05$), showing the highest migration at 30 min of contact at 100°C. Caprolactam migration from brands 9 and 11 into 3% acetic acid showed no difference ($p > 0.05$) from the different conditions of contact, while brand 10 differed ($p \leq 0.05$), with the highest migration at 30 min of contact at 100°C. For olive oil, caprolactam migration for 10 days at 40°C and 30 min at 100°C showed difference ($p \leq 0.05$) among all the brands, with the highest levels at 10 days of contact at 40°C (Table 3).

When the initial concentration of caprolactam in the multilayer films containing PA-6 is taken into account, the percentage of migration ranged from 50 to 82% into water, 73 to 116% into 3% acetic acid and 25 to 128% into olive oil. In general, higher levels of caprolactam were observed for 3% acetic acid. This food simulant was reported as the worst scenario for caprolactam migration using polyamide materials because of its chemical nature and type of polymer.[13] The percentage of migration greater than 100% could be explained considering the recovery of the analytical method, since migration is an extraction itself. Thus, sample matrix, sample processing procedure and analyte concentration can affect recovery. When the analyte levels range from 1 to 10 ppm, recovery from 80 to 110% is acceptable.[22] It is also important to consider the analytical errors, the standard deviation values and the method of extraction of caprolactam from PA-6 films used.[21]

The most important factors affecting migration are initial concentration of the migrant in the packaging, thickness of the packaging material, kind of migrant, type of polymer and time/temperature of contact with food/simulant, among others.[23] Comparing brands 1 and 4, which have the same material specifications and similar initial concentration of caprolactam, higher migration was found for the highest thickness brand, as expected. In addition, Barkby and Lawson[11] suggested the extraction time and thickness of PA-6 film as the parameters that most affected migration when investigating caprolactam migration from 80 μm (1.8 mg/

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Table 3. Migration levels (mg/dm^2) of caprolactam from multilayer PA-6 films, used for meat foodstuffs and cheese, into water, 3% acetic acid and olive oil food simulants at different conditions of contact.

Brand	Water: 40°C/10 days	Water: 100°C/30 min	3% acetic acid: 40°C/10 days	3% acetic acid: 100°C/30 min	Olive oil[a]: 40°C/10 days	Olive oil[a]: 100°C/30 min
Packaging for meat foodstuffs						
1	1.02 ± 0.05 (65) bcB	1.10 ± 0.01 (70) aA	1.58 ± 0.06 (101) bcA	1.20 ± 0.02 (77) dB	1.33 ± 0.05 (85) dA	0.76 ± 0.05 (48) abB
2	0.93 ± 0.02 (71) cdA	0.79 ± 0.06 (60) dB	1.32 ± 0.04 (100) eA	1.13 ± 0.04 (85) dB	1.18 ± 0.03 (89) eA	0.75 ± 0.01 (56) abB
3	1.22 ± 0.06 (82) aA	1.09 ± 0.09 (74) abB	1.61 ± 0.07 (108) bA	1.40 ± 0.10 (94) bcB	1.62 ± 0.07 (109) cA	0.71 ± 0.02 (48) bB
4	1.19 ± 0.07 (79) aA	1.17 ± 0.06 (78) aA	1.74 ± 0.11 (116) aA	1.41 ± 0.07 (93) bcB	1.88 ± 0.11 (125) abA	0.75 ± 0.06 (50) abB
5	1.08 ± 0.06 (67) bA	0.96 ± 0.02 (60) bcB	1.48 ± 0.09 (93) cdA	1.42 ± 0.09 (89) bA	1.51 ± 0.10 (94) cA	0.63 ± 0.03 (39) cB
6	1.15 ± 0.06 (63) aB	1.21 ± 0.02 (67) aA	1.65 ± 0.08 (90) abA	1.62 ± 0.03 (89) aA	1.98 ± 0.13 (109) aA	0.80 ± 0.02 (44) aB
7	0.95 ± 0.06 (68) cdA	0.93 ± 0.16 (66) cA	1.43 ± 0.04 (101) deA	1.41 ± 0.03 (100) bcA	1.80 ± 0.04 (128) bA	0.71 ± 0.01 (51) bB
8	0.89 ± 0.01 (73) dB	0.92 ± 0.02 (76) cA	1.29 ± 0.09 (106) eA	1.32 ± 0.02 (108) cA	1.47 ± 0.09 (121) cdA	0.50 ± 0.01 (41) dB
Packaging for cheese						
9	0.79 ± 0.01 (68) bB	0.88 ± 0.01 (76) bA	1.15 ± 0.08 (99) bA	1.17 ± 0.06 (101) bA	0.83 ± 0.02 (71) aA	0.56 ± 0.01 (48) aB
10	0.91 ± 1.04 (52) aB	1.04 ± 0.07 (60) aA	1.26 ± 0.05 (73) aB	1.37 ± 0.06 (79) aA	0.68 ± 0.01 (39) bA	0.56 ± 0.02 (33) aB
11	0.80 ± 0.04 (54) bA	0.74 ± 0.05 (50) cA	1.17 ± 0.05 (79) abA	1.11 ± 0.06 (75) bA	0.48 ± 0.01 (33) cA	0.37 ± 0.03 (25) bB
12	0.17 ± 0.01 c	<LOQ	<LOQ	<LOQ	0.23 ± 0.01 d	<LOQ
13	ND	ND	ND	ND	ND	<LOQ

Mean of six replicates of the found value ± standard deviation (SD); migration percentage (%) inside parentheses.
Values within a vertical column followed by different letters are significantly different ($p \leq 0.05$).
Values within a horizontal line followed by different capital letters are significantly different ($p \leq 0.05$).
ND: not detected; LOQ: limit of quantification.
[a]Reduction factor was not used.

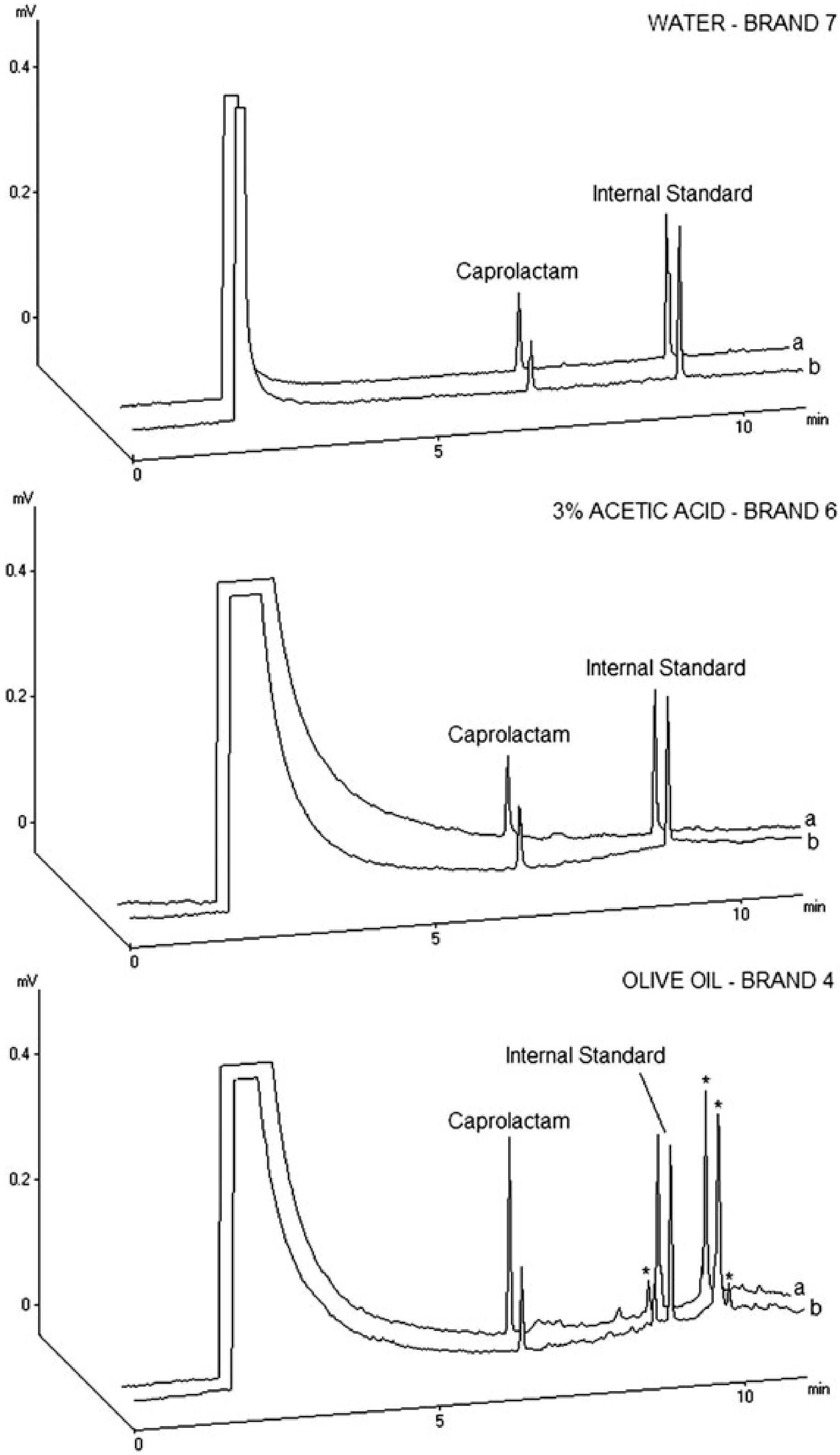

Figure 1. Typical chromatograms obtained for caprolactam migration from meat foodstuffs packaging into olive oil, 3% acetic acid and distilled water at (a) 40°C for 10 days and at (b) 100°C for 30 min (b). *Compounds not identified in olive oil.

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dm^2) and 15 μm (0.3 mg/dm^2) PA-6 film into boiling water after 1 h of contact. In the same way, for brands 5 and 6, with the same material specifications and thickness but different initial concentration, the higher the migration, the higher the initial concentration. This is due to the exhaustive migration character, i.e. almost the whole amount of caprolactam present in the film migrates.

Similar levels of caprolactam migration into water and 3% acetic acid simulants at both conditions of contact were obtained. It is possible to conclude that caprolactam diffusion in both aqueous simulants was strongly influenced by temperature, whereas with only 30 min of contact at 100°C, caprolactam reached levels close to those obtained after 10 days at 40°C. Caprolactam migration into water and 3% acetic acid at high temperature and short contact time (100°C/30 min) could be used as a quick test, a faster alternative test for rapid extraction of thin PA films with aqueous food simulants for compliance test purposes. Thus, it could replace the need to apply the migration tests at 40°C for 10 days, since similar results were obtained under both conditions due to the rapid extraction of caprolactam. Bradley et al.[1] also reported the temperature as a very influential factor to increase of caprolactam migration from PA pouches used for boiling, microwaving or roasting foodstuffs.

In the case of the packaging intended for meat foodstuffs, caprolactam migration into olive oil was highly affected by the different conditions of contact, showing values two to three times higher at 40°C for 10 days than 100°C for 30 min. These findings can be explained using the Arrhenius relationship reported in the EU Resolution 10/2011.[6] Applying the Arrhenius equation makes it possible to assume that the same migration value obtained for 10 days at 40°C for olive oil could be achieved at 100°C only after 1.7 h. Thus, in order to suggest a faster test for olive oil, it is necessary to extend the time of contact up to 2 h.

Stoffers et al.[3] investigated caprolactam migration from PA-6 and PA-6/PA-12 films simultaneously exposed to olive oil by one side and boiling water on the other. 99% of caprolactam migrated into water (0.3–2.5 mg/dm^2) while 1% migrated into olive oil (0.002–0.02 mg/dm^2). In addition, a mathematical model was used to compare the results. The authors reported that caprolactam initially migrated into olive oil (13 mg/kg) and then permeated back through the swollen film into the water phase in the two-sided migration test. Modelling the one-sided migration test, the concentration of caprolactam in the oil was about 9 mg/kg after 2 h at 100°C, meaning that migration on the one-sided test was higher than in the two-sided test.

Caprolactam migration from multilayer PA-6 films, the same films used in this work, into 95% ethanol at 40°C for 10 days (1.3–1.7 mg/dm^2) showed levels close to those obtained here for olive oil.[17] 95% ethanol is an alternative food simulant for vegetable oils.[17] Our findings confirm the availability of using 95% ethanol as a substitute simulant for olive oil. Additionally, caprolactam levels into water simulant, slightly higher than ours, were also reported (1.3–2.2 mg/dm^2), although solid phase microextraction has been used.[17]

Finally, it should be pointed out that all the samples studied in this work showed caprolactam migration levels below to the SML established for caprolactam (15 mg/kg or 2.5 mg/dm^2), and therefore, they are in accordance to legislation.[6,14]

CONCLUSIONS

Caprolactam migration into water food simulant ranged from 0.89 to 1.22 mg/dm^2 and 0.92 to 1.21 mg/dm^2, into 3% acetic acid from 1.29 to 1.74 mg/dm^2 and 1.13 to 1.62 mg/dm^2 and into olive oil from 1.18 to 1.98 mg/dm^2 and 0.50 to 0.80 mg/dm^2 for films used as meat foodstuffs packaging for 10 days at 40°C and 30 min at 100°C, respectively. Among multilayer PA-6 films used for cheese, caprolactam migration into water ranged from 0.17 to 0.91 mg/dm^2 and 0.74 to 1.04 mg/dm^2, into 3% acetic acid from 1.15 to 1.26 mg/dm^2 and 1.11 to 1.37 mg/dm^2 and into olive oil from 0.23 to 0.83 mg/dm^2 and 0.37 to 0.56 mg/dm^2 for 10 days at 40°C and 30 min at 100°C, respectively.

Caprolactam migration evaluation from multilayer PA-6 films, intended for meat foodstuffs and cheese packaging, into water and 3% acetic acid at high temperature and short contact time (100°C/30 min) could replace the application of the test for 10 days at 40°C. Initial concentration of caprolactam and packaging material thickness are important factors to consider. In the case of olive oil, caprolactam migration from multilayer PA-6 films for meat foodstuffs was highly affected by the conditions of contact, showing

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values two to three times higher at 40°C for 10 days than at 100°C for 30 min. For cheese films, caprolactam migration into olive oil was higher at 40°C for 10 days.

The present study shows a contribution to the migration caprolactam data in two different conditions of time and temperature of contact between packaging and food simulants. Migration tests with real food matrices could be performed in order to construct a complete approach of caprolactam migration from multilayers PA-6 films.

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