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Food-packaging interaction during ultrasound processing: migration of monomers from multilayer polyamide packages to different food simulants

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Abstract:

This study evaluated the migration of monomers from two multilayer packages for three food simulants due to ultrasound processing. A three (PE/PA/PE) and a five (PE/PA/PE/PA/PE) layers packages, based on polyethylene (PE) and polyamide (PA6/6.6), were studied. The packages were filled with aqueous, acid and fatty food simulants and processed in an ultrasound bath (25 kHz, volumetric power of 9.74 W/L, 25 °C) up to 60 min, simulating possible food processes. The migration of ϵ -caprolactam was influenced by packaging material, food simulant and ultrasound processing time, being higher in the three-layers package. The ultrasound processing did not influence the overall migration nor those of hexamethylenediamine, in any packages, food simulant nor process conditions. Although all results met the migration limits established by both Brazilian and European Union legislations, this study highlights the importance of packaging design and evaluation in the development of emerging technologies of food processing.

Keywords: Food contact materials; Food safety; Flexible packaging; Emerging technologies; Specific migration; Food-package interaction

1. Introduction

Packaging plays a key role in the production, processing, storage, transport, preparation and consumption of food [1]. The most common food contact materials are metal, glass, paper and plastics. Plastics are widely used for their low price, light weight, durability and excellent properties [2]. However, these materials contain different substances that can migrate to food [3], which can interfere with the sensory quality and toxicological aspects of packaged products [4]. The main substances present in food contact materials that migrate to food include antioxidants, plasticizers, monomers, metals, among others [5,6].

Among plastic materials, polyamide (PA) is used in multilayer films as a gas barrier layer for packaging for various products, such as vegetables, meat and cheese [2,7]. In addition to a good barrier to gases, PA has excellent mechanical properties and high thermal stability [8]. The different types of PA depend on their repeating units, PA6 and PA6.6 are widely used in packaging market [9,10]. PA6 is the result of the polymerization of ϵ -caprolactam, this polyamide is a linear polymer, with a sequence of amide groups in the chain [8,11]. PA6.6 is a linear polymer with diamine and diacid groups obtained by polymerization between adipic acid (AA) and hexamethylenediamine (HMDA) [11,12]. It is very common to find materials that use a combination of PA6 and PA6.6, called PA6/6.6. Such combinations aim to improve some property not attainable with a single polyamide. In this regard, a suitable copolymer can be made from a combination of monomers such as ϵ -caprolactam, AA and HMDA [11].

The different high molecular weight polyamides (PA6 and PA6.6) are obtained from the polymerization of low molecular weight compounds (such as ϵ -caprolactam and HMDA) [13]. However, the monomer conversion is less than 100% and the residual monomer remains in the resin and consequently can migrate from the packaging that contains PA in its composition to the food [13,14]. The migration of these monomers (ϵ -caprolactam and HMDA) from packaging to food is defined by several factors, such as the characteristics of the food and eventual processes to which the food-packaging system is subjected - for example, conventional thermal processes (pasteurization and sterilization) and new food processing technologies (microwave-assisted thermal sterilization; high-pressure processing, ultrasound, among others).

The specific limits of monomer migration are regulated by government bodies such as the National Health Surveillance Agency of Brazil (Anvisa), through Resolutions, for example, Resolution of the RDC n° 56/2012 [15], and Directive n° 10/2011 of the European Union [16]. These regulations have a maximum migration limit for hexamethylenediamine of 2,4 mg kg⁻¹ of food simulant and for ϵ -caprolactam of 15 mg kg⁻¹ of food simulant. In addition to specific migration, Anvisa Resolution n° 589/21 [17] and EU Regulation n° 10/2011 [16] determine the overall migration limit of food contact materials, with the maximum overall migration limit being 10 mg dm⁻².

In many applications, food is processed inside the package, as in the case of traditional pasteurization and sterilization, or using emerging technologies such as microwaves, irradiation, high pressure processing and ultrasound. In this sense, it is important to investigate whether these processing technologies can change the behavior of the migration of compounds from plastic materials to food and/or food simulant. In the literature, data collected showed that the migration of ϵ -caprolactam from PA6 packages to food simulants was influenced by cooking time and temperature [18]. Migration experiments with a film of PA6 and PA6.6 were carried out under contact conditions of 2 h/100 °C (simulating the heat treatment of the food in the package). Migration of PA6 and PA6.6 monomers and oligomers has been detected in aqueous and fatty food simulants [19]. The effect of gamma irradiation on ϵ -caprolactam migration from PA6 films in contact with aqueous and fatty food simulant was investigated. Irradiation caused almost no change in migration to the aqueous simulant, but increased migration to the fatty simulant [20]. Furthermore, as irradiation doses increased, the migration of ϵ -caprolactam from PA6 multilayer films was greater [14]. The migration behavior of ϵ -caprolactam was investigated under a combination of heat and ultraviolet exposure. Monomer migration did not show a different behavior compared to standard migration conditions [21]. The effect of high-pressure processing and pasteurization on the migration of ϵ -caprolactam from PA packages was evaluated for different food simulants. The migration of monomer was higher for pasteurized samples compared to samples processed by high pressure [22]. Recently, research was published [23] evaluating the ultrasound processing of LLDPE and PPAcPVDC films in contact with ethanol 10% (v/v) and acetic acid 3% (w/v). The films were subjected to an ultrasound for 30 min at 60 °C (± 2 °C) and with an amplitude of 100% followed by storage for 10 days at 40 °C. Analyzes showed an impact of ultrasound treatment on overall migration for all food simulants used.

It is important to highlight that research is being developed to evaluate the effectiveness of ultrasound processing on the quality of packaged products (although the effect on packaging properties still needs to be understood). For instance, meat products receive notable attention from the scientific community, as for example the microbiological decontamination of packaged chicken by ultrasound [24], the influence of ultrasound on color maintenance of vacuum-packed beef during storage [25] and post-packaging ultrasound pasteurization of vacuum-packed sausages [26].

In this context, as meat products often use multilayer packaging materials based on different polyamides, these materials deserve attention when it comes to ultrasound processing. In a previous study, the effect of ultrasound processing on PA multilayer packaging structure and performance properties was addressed [27]. Ultrasound had little or no influence on the crystallinity, melting temperature, chemical groups, and tensile strength of the films. On the other hand, there was a loss of water vapor barrier and a reduction in heat seal tensile strength after ultrasonic processing. Based on this study, it is observed that ultrasound technology can have some influence on packaging materials. However, to date, no studies have been found evaluating the effect of ultrasonic treatment on the migration of PA monomers, although the interest of this technology in food processing is increasing.

Therefore, the aim of this study was to evaluate the effect of ultrasonic processing on the overall and specific migration of hexamethylenediamine and ϵ -caprolactam monomers from multilayer food packages with PA6 and PA6.6. As each processing technology has a different behavior in each material and compound migration, it is essential to study ultrasonic processing in other packaging and food systems. Therefore, this work expanded the first study by evaluating three food simulants, aqueous, acid and fatty, in contact with packaging. To the best of our knowledge, this is the first time that specific migration of monomers has been investigated considering ultrasound treatment.

2. Materials and methods

2.1. Standards, Reagents and Solutions

The standards used for the analysis were: hexamethylenediamine (>99.9% purity, Sigma Aldrich, USA) and ϵ -caprolactam (99.3% purity, Red Analytical, UK), 2-aza-cyclo-nonanone (99.8 % purity, TCI, Japan). The reagents used for the tests were: glacial acetic acid ($\geq 98.0\%$, Merck, Germany), ethanol (99.9%, PanReac AppliChem, Spanish), methanol ($\geq 99.9\%$, Merck,

Germany), ammonia solution 25% (w/w) (26.1% purity, Merck, Germany), sodium hydroxide (99.6% purity, Merck, Germany), ethyl chloroformate (99.8% purity, Sigma Aldrich, USA), toluene ($\geq 99.9\%$, Merck, Germany). The solutions were prepared with deionized water (Millipore Milli-Q Direct). The Nitrogen 5.0 (White Martins) was used to dryness.

For the ammonia solution (NH_3) of 3% (w/w) of, 190 mL was added to 30 mL of 25% (w/w) NH_3 solution in a volumetric flask of 250 mL, being mixed thoroughly. The flask volume was filled up to the mark with deionized water.

For the solution of 5 M sodium hydroxide (NaOH), 50.0 g \pm 0.1 g of NaOH was added in a volumetric flask of 250 mL and filled with deionized water, being mixed thoroughly. The flask volume was filled up to the mark with deionized water. This solution is exothermic and one ice-bath was required.

The solution of 3% (w/w) of NH_3 and 5 M sodium hydroxide (NaOH) was used to determine by derivatization of free diamine (hexamethylenediamine), using ethyl chloroformate as derivatization agent followed by analysis of the resulting diurethane.

2.2. Packaging Material and Food Simulants

Two multilayer films containing polyamide were evaluated (Figure 1). The two films, PE/PA/PE (120 μm) and PE/PA/PE/PA/PE (105 μm) are generally used for packaging meat, cheese and vegetables products. For the two films, the layers of polyethylene (PE) comprise a blend of linear low-density polyethylene (LLDPE) and low-density polyethylene (LDPE) and the layers of polyamide (PA) are a blend composed of PA6/6.6. The packages were analyzed using the proportion of 2 dm² of plastic material for 100 mL of simulant.

Three food simulants were used, as described by Brazilian legislation [28]: (i) aqueous: deionized water (non-acidic aqueous food simulant, representing foods with $\text{pH} > 4.5$), (ii) acid: 3 % (w/v) acetic acid solution in distilled water (acidic aqueous food simulant, representing foods with $\text{pH} \leq 4.5$) and (iii) fatty: 95% ethanol solution (v/v) in deionized water (fatty food simulant, representing foods rich in lipids). The simulants represent the main food products usually packaged in the materials studied here, such as vegetables, meats and cheeses.

2.3. Ultrasound processing

The ultrasound processing conditions were those defined in a previous study [27], in order to reproduce normal or predictable conditions applied to food.

The packages with food simulants i, ii and iii were processed in an ultrasound bath (Q 13/25 A CR, Ultronique, Indaiatuba, Brazil) with a frequency of 25 kHz and volumetric power of 9.74 W/L. The volumetric potency was determined by the calorimetric method, as described by [29]. The water was used as a wave propagation medium for the packages. The processing temperature was 25 °C, being maintained using a heat exchanger. Samples were processed for 30 and 60 min. The 30 min conditions are similar to the conditions applied for chicken breast [30,31], bologna with low sodium content [32] and meat emulsions with low phosphate and sodium content [33]. Furthermore, the 60 min treatment considers a prolonged condition of exposure to ultrasonic processing, which can be used in some cases, such as the acidification of vegetables [34] or juice processing [35]. The ultrasound processes were performed in duplicate.

2.4. Overall migration

The packages were evaluated for overall migration soon after the different processing conditions by ultrasound. In addition, considering that the food would be submitted to ultrasound processing in the same package that will be marketed, more critical contact conditions were employed, with contact time of 10 days to 40 °C (BD400, Binder, Germany). The overall migration tests were performed according to the standards [36,37] in accordance with RDC n° 51/10 [28].

After the processing and conditioning periods, the total migration was determined by gravimetry [28]. The food simulants were evaporated in the heating plate (TE038, Tecnal). An analytical balance with accuracy of 0.00001 g (MSA225P-1CE-DA, Sartorius) was used. The tests were performed with four replications.

2.5. Specific migration

After different ultrasound processing conditions, samples were evaluated for specific migration of hexamethylenediamine and ϵ -caprolactam. In addition, the control sample and the processed samples were conditioned in an oven (BD400, Binder, Tuttlingen, Germany) at 40

°C/10 days, simulating the most critical condition of food storage determined by Legislation RDC n° 51/2010 of ANVISA [28].

2.5.1. Migration of hexamethylenediamine

2.5.1.1. Preparation of limit of quantification

Two standard stocks solutions were made of 25.41 mg and 26.45 mg hexamethylenediamine in 50 mL of distilled water ($0.5082 \text{ mg mL}^{-1}$ for aqueous and fatty food simulants and $0.5290 \text{ mg mL}^{-1}$ for acid food simulant for dilutions) and reserved. After, 1 mL of the simulants (water, 3 % (w/v) acetic acid solution in distilled water and 95 % (v/v) ethanol solution in distilled water) were added in vials of 10 mL, separately for each simulant. The stock solution ($0.5082 \text{ mg mL}^{-1}$) was added to vial 2.4 mL in water simulant and 2.2 mL (95 % (v/v) ethanol solution in distilled water) and the stock solution ($0.5290 \text{ mg mL}^{-1}$) was add to vial 2.1 mL (3 % (w/v) acetic acid solution in distilled water). Every vial was closed with a rubber septum.

Prior to gas chromatography, the limit of quantification for each simulant was subjected to a derivatization reaction, thus transforming free diamine into corresponding diurethane. Subsequently, the vial was opened and 1 mL 3% w/w NH_3 solution, 3 mL of 5 M NaOH, 2 mL of toluene and 100 μL of ethyl chloroformate were added. The vial was closed using a Teflon septum and aluminum cap, mixed and shake in an orbital table for 15 minutes. After the separation phase, 1 mL of aliquot was transferred from the upper toluene layer into 2 mL sample vial and evaporated to dryness using a gentle stream of nitrogen. Afterwards, it was re-dissolved in 0.5 mL of toluene and analyzed by gas chromatography.

The final concentration obtained for limit of quantification was 1.2 mg kg^{-1} of hexamethylenediamine for aqueous food simulant, 1.1 mg kg^{-1} of hexamethylenediamine (hexamethylenediurethane) for acid food simulant and 1.1 mg kg^{-1} of hexamethylenediamine (hexamethylenediurethane) for fatty food simulant.

2.5.1.2. Preparation of simulants

After the contact time of the samples with the simulants, 1 mL of the food simulants (aqueous, acid and fatty) were added in 10 mL vials and closed with a rubber septum. For derivatization, the samples vials were opened and 1 mL of 3% w/w NH_3 solution, 3 mL of 5 M

NaOH, 2 mL of toluene and 100 μL of ethyl chloroformate were added. The vial was closed using a Teflon septum and aluminum cap, mixed and shook in an orbital table for 15 minutes. After the separation phase, 1 mL of aliquot from the upper toluene layer was transferred into 2 mL sample vial and evaporated to dryness using a gentle stream of nitrogen. Then, it was re-dissolved in 0.5 mL of toluene and analyzed by gas chromatography. The process was repeated for each of the analyzed packaging specimens and for the simulant blank.

2.5.1.3. *Migration of hexamethylenediamine by gas chromatography (GC)*

The migration of hexamethylenediamine was carried out without internal standard, using aqueous, acid and fatty food simulants by gas chromatography (GC), according to the method [38] of the European Standardization Committee. Tests were performed in a gas chromatograph with flame ionization detection (HP 6890 N, Agilent Technologies, China) and a liquid injector (G4513A, Agilent Technologies, China), operating with a capillary column (HP-1, Agilent J&W Capillary GC Columns, USA) ($60\text{ m} \times 0.25\text{ mm} \times 1.0\text{ }\mu\text{m}$). The initial column temperature was set at $100\text{ }^\circ\text{C min}^{-1}$ for 3 minutes, with a ratio of $25\text{ }^\circ\text{C min}^{-1}$ to $270\text{ }^\circ\text{C}$, remaining at $270\text{ }^\circ\text{C}$ for 15 min. The running time was 24.8 min. Each specimen of the sample and the analytical curve was injected in duplicate. Injector and detector temperatures were $280\text{ }^\circ\text{C}$ and $300\text{ }^\circ\text{C}$, respectively. The gas (helium) was maintained with a constant column flow rate of 1.2 mL min^{-1} at a pressure of 27.67 psi. Flow rates of hydrogen and oxygen through the detector were 40.0 and 80.0 mL min^{-1} , respectively. The volume of $1.0\text{ }\mu\text{L}$ was injected in the gas chromatograph, with split in the 15:1 proportion. For control of hexamethylenediamine, the concentration of quantification limit was used. The test was carried out in four repetitions for samples and one blank simulant.

2.5.2. *Migration of ϵ -caprolactam*

2.5.2.1. *Preparation of simulants and analytical curve*

A standard stock solution was made of 52.79 mg ϵ -caprolactam in 100 mL of methanol (0.5279 mg mL^{-1}), and the internal standard stock solution was made of 35.13 mg 2-aza-cyclo-nonanone in 100 mL of methanol (0.3513 mg mL^{-1}). For intermediate standard stock solution, a series of 25 mL volumetric flasks were added 0, 1, 2, 4, 6 and 8 mL of the standard stock solution of ϵ -caprolactam and for each of the flasks 5 mL of the internal standard stock solution of 2-aza-cyclo-nonanone and the volume was completed with methanol. The intermediate

standard stock solution concentrations obtained were 0; 21.1; 42.2; 84.5; 126.7 and 168.9 $\mu\text{g mL}^{-1}$ of ϵ -caprolactam and 70.3 $\mu\text{g mL}^{-1}$ 2-aza-cyclo-nonanone in methanol.

For analytical curve, 4 mL of the simulants were added in a series of test tube, and 1 mL of an intermediate standard stock solution. The final concentrations obtained for the analytical curve in the simulants were 0; 4.22; 8.45; 16.89; 25.34; and 33.79 mg kg^{-1} of ϵ -caprolactam with 14.1 mg kg^{-1} of internal standard (2-aza-cyclo-nonanone).

After the simulant had been in contact with the samples, 4 mL of the simulants were added, placed in test tubes with the aid of a micropipette and 1 mL of 70.3 $\mu\text{g mL}^{-1}$ of intermediate standard solution of 2-aza-cyclononanone was added and mixed. The final concentration of the internal standard in the samples was 14.1 mg kg^{-1} of 2-aza-cyclo-nonanone. A small amount of this solution was transferred to a 2.0 mL glass vial for injection in the gas chromatograph. The process was repeated for each of the analyzed specimens and for the simulant blank.

2.5.2.2. *Migration of ϵ -caprolactam by gas chromatography (GC)*

Specific migration of ϵ -caprolactam was evaluated by gas chromatography (GC) according to the [39] method of the European Standardization Committee, using the aqueous, acid and fatty simulants. The assays were performed in a gas chromatograph with flame ionization detection (HP 6890 N, Agilent Technologies, China) and a liquid injector (G4513A, Agilent Technologies, China), operating with a capillary column (DB-17, Agilent J&W Capillary GC Columns, USA) (30 m \times 0.53 mm \times 1.5 μm). The initial column temperature was set at 180 $^{\circ}\text{C min}^{-1}$, with a ratio of 10 $^{\circ}\text{C min}^{-1}$ to 200 $^{\circ}\text{C}$, remaining at 200 $^{\circ}\text{C}$ for another 7 min (aqueous, acid and fatty simulants). The running time was 10 min for the aqueous, acid and fatty simulants. Each specimen of the sample and the analytical curve was injected in duplicate. Injector and detector temperatures were 240 $^{\circ}\text{C}$ and 270 $^{\circ}\text{C}$, respectively. The gas (helium) was maintained with a constant column flow rate of 3.0 mL min^{-1} at a pressure of 3.98 psi. Flow rates of hydrogen and oxygen for the detector were 40.0 and 80.0 mL min^{-1} , respectively. The volume of 1.0 μL was injected in the gas chromatograph with split in the 14:1 proportion. For the quantification of ϵ -caprolactam, an analytical curve with internal standardization of 2-aza-cyclo-nonanone was used. The test was carried out in four repetitions and one blank simulant.

2.6. *Statistical analysis*

The results obtained were reported as mean of four repetitions and standard deviation. In addition, results were statistically evaluated by analysis of variance (ANOVA) and mean values were evaluated by Tukey's test.

3. Results and discussion

3.1. Overall migration

Table 1 shows the results of overall migration of PE/PA/PE and PE/PA/PE/PA/PE films in contact with the aqueous, acid and fatty food simulants evaluated soon after ultrasound processing and after processing and conditioning at 40 °C/10 days.

None of the process conditions evaluated resulted in overall migration of compounds from the packaging to the studied simulants, presenting results below the quantification limit (LOQ) of the method used ($\leq 2.33 \text{ mg dm}^{-2}$) – with the exception of the sample of PE/PA/PE/PA/PE in contact with a fatty food simulant, processed by ultrasound at 25 °C for 30 min followed by conditioning at 40 °C/10 days, which showed an overall migration value of $2.35 \pm 0.05 \text{ mg dm}^{-2}$ (statistically equal to the limit of quantification).

On the other hand, in a recent article, LLDPE and PPAcPVDC films filled with aqueous food simulants (ethanol 10% (v/v)) and acid (acetic acid 3% (w/v)) and processed by ultrasound for 30 min to 60 °C followed by storage at 40 °C/10 days showed an increase in overall migration compared to films not processed by ultrasound [23]. However, it is not possible to evaluate whether in fact the increase in overall migration is a consequence of ultrasound or high process temperature, because the results were not compared with an ultrasound processing at room temperature. Even so, it is worth mentioning that the study of [23] was made with packaging material different from the present work.

Therefore, all samples studied comply with both ANVISA Resolution n° 589/21 [17] and EU Regulation n° 10/2011 [16], as the values were below the established limit of 10 mg dm^{-2} . Thus, in the ultrasonic processing and conditioning conditions employed, the evaluated packaging materials can be approved for contact with aqueous, acid and fatty foods in relation to overall migration. However, to ensure that ultrasound can be used in the processing of low and high acidity and fatty aqueous foods packed with the materials studied here, it is also necessary to evaluate the migration of specific compounds, notably the monomers hexamethylenediamine and ϵ -caprolactam, as described below.

3.2. Specific migration of hexamethylenediamine and ϵ -caprolactam

Tables 2 and 3 shows the results of specific migration of hexamethylenediamine and ϵ -caprolactam of flexible packaging of PE/PA/PE and PE/PA/PA/PE in contact with different food simulants (aqueous, acid and fatty) which were evaluated shortly after the different exposure times to ultrasound processing (30 and 60 min) and after processing and conditioning at 40 °C/10 days.

For the samples evaluated after the different ultrasound processing conditions, all specific migration results of hexamethylenediamine and ϵ -caprolactam in aqueous, acid and fatty food simulants were below the quantification limit of the method used which, in turn, is below the value established by Brazilian legislation [15]. Such results indicate that the processing time, imposed conditions and/or modifications in the packaging materials during processing were not sufficient for the diffusion of monomers to the food simulants or release in quantities higher than the limit of legislation [15,16].

In this sense, in addition to evaluating the specific migration of hexamethylenediamine and ϵ -caprolactam right after the ultrasound processing, the samples were conditioned at 40 °C/10 days, simulating the most critical predictable conditions of use. In addition, for comparison purposes, control samples, that is, without exposure to ultrasound processing, were also conditioned at 40 °C/10 days, according to the results presented in Tables 2 and 3.

The results of specific migration of hexamethylenediamine were also below the limit of quantification, for the same two samples and for the aqueous, acid and fatty simulants processed by ultrasound for 30 and 60 minutes, followed by the contact condition of 40 °C/ 10 days (simulation of storage). The same behavior was observed for the control film conditioned at 40 °C/ 10 days, that is, film not processed by ultrasound, according to Table 2. It was observed that the different times of exposure to ultrasound processing, followed by the condition of 40 °C/ 10 days were also not enough for the diffusion of hexamethylenediamine monomer as already mentioned earlier for the different food simulants.

On the other hand, the results of migration of ϵ -caprolactam from the PE/PA/PE film to the aqueous simulant processed by ultrasound and conditioned at 40°C/10 days were between 4.76 ± 0.32 and 5.06 ± 0.35 mg kg⁻¹ and for the acid simulant between 4.37 ± 0.42 e 4.77 ± 0.24 mg kg⁻¹. Regarding the fat simulant, the results were between 6.11 ± 0.30 and 6.44 ± 0.28 mg kg⁻¹ (Table 3). It was observed that the different exposure times to ultrasound processing did not significantly influence the migration of residual ϵ -caprolactam monomer in the same food

simulant when compared to the control sample. In other words, ultrasound processing did not alter the structure of packaging materials to the point of releasing and/or facilitating the diffusion of this compound to food simulants. However, the migration values of ϵ -caprolactam were significantly higher for the fatty simulant when compared to the aqueous and acid simulants.

Monomers of ϵ -caprolactam exhibit molecular weight <1000 Da, and generally migrate from PA6 films to aqueous/acid/ethanolic simulants [19]. The ϵ -caprolactam has a hydrophilic characteristic and this favors its migration to the food simulants used in this study. In addition, it is known that aqueous solutions can penetrate PA6 films, leading to swelling and increasing diffusion of migrants [5,19]. Therefore, although the inner layer of the multilayer film is a moisture barrier, after ultrasound processing followed by storage at $40\text{ }^{\circ}\text{C}$ the interactions between the packaging and the food simulant can be favored. Finally, in the presence of organic compounds, such as the fatty simulant - 95% ethanol, the diffusion of ϵ -caprolactam tends to increase [40]. In addition, the layer directly in contact with the simulant was the PE, that is, there is the question of the affinity of the simulant with this first layer influencing the migration speed of the monomer that is coming from the intermediate layer of PA (without direct contact with the simulant). Considering that ultrasound technology influences several mass-transfer processes [41], it could be expected that such processing would increase the migration of compounds in the present study - unlike what was observed. Also, it is important to note that migration in the actual condition of use, that is, direct to the food, may be lower compared to the migration test with food simulant. Thus, certainly the use of food simulants is considered as a worst-case scenario [40,42].

The PE/PA/PE/PA/PE film showed specific migration values of ϵ -caprolactam between 1.98 ± 0.07 and $2.19 \pm 0.17\text{ mg kg}^{-1}$ for the aqueous simulant, between 2.12 ± 0.08 and $2.52 \pm 0.19\text{ mg kg}^{-1}$ for the acid simulant and between 2.52 ± 0.19 and $2.98 \pm 0.25\text{ mg kg}^{-1}$ for the fatty simulant (Table 3). The different ultrasound processing conditions did not significantly influence the specific migration of ϵ -caprolactam monomer when in contact with the aqueous and acid simulants, compared to the control. On the other hand, for the fatty simulant there was a slight increase in the migration of ϵ -caprolactam from samples exposed to ultrasound processing for 60 min compared to the control and samples processed for 30 min. In this case, the ultrasound processing for a long period of exposure (60 min) potentiated the migration of the ϵ -caprolactam monomer.

This behavior can be related with both chemical and physical aspects. From the chemical perspective, due to the polar nature of the ϵ -caprolactam molecule, a large interaction with the fatty simulant (95% ethanol in water) is expected. Moreover, each simulant has specific physical properties (vapor pressure, viscosity, surface tension), thus resulting in different patterns of ultrasound wave propagation and cavitation – a phenomenon related to the creation and implosion of vapor bubbles due to the pressure oscillation during ultrasound wave travelling, resulting in high shear stresses able to affect the exposed materials [43]. In other words, the energy released during bubbles implosion bursts the surface of the film [23,44], which can alter the structure of the material, potentially favoring a greater interaction between the packaging and the food simulant.

When comparing the results of the different packaging materials, the PE/PA/PE film showed significantly higher values of ϵ -caprolactam migration values than the PE/PA/PE/PA/PE film. These results may have been influenced by the thickness of the PA layer of the PE/PA/PE film, which is greater than the thickness of the second PA layer (the layer closest to the food simulant in contact with the film) of the PE/PA/PE/PA/PE film, and which may consequently have a higher amount of residual ϵ -caprolactam monomers. Also, the thicker layer ensures higher mechanical resistance to the material, also affecting the incident ultrasound waves reflection and its propagation. Similar behavior was reported in a previous study on the effect of high-pressure processing on the specific migration of ϵ -caprolactam from different PA-containing packaging materials [22].

Finally, it is noteworthy that the values obtained from the migration of hexamethylenediamine and ϵ -caprolactam both for the control samples and for the samples processed by ultrasound, followed or not by conditioning at 40° C/10 days of the two packaging materials in contact with aqueous, acid and fatty food simulants are less than 2.4 and 15 mg kg⁻¹ of simulant, respectively. Therefore, these results meet the maximum migration limits tolerated by legislation [15,16].

4. Conclusions

After the different ultrasound processing conditions used in this study, the results of global migration, specific migration of hexamethylenediamide and ϵ -caprolactam of the two packaging materials studied were below the quantification limit of the methods used. The samples processed by ultrasound and followed by conditioning at 40 °C/10 days showed values

of overall migration and specific migration of hexamethylenediamide below or very close to the quantification limit of the methods used, indicating that the ultrasound processing did not change the structure of the materials to the point of resulting in the release and/or facilitating the diffusion of the compounds studied. The specific migration of ϵ -caprolactam monomer from samples processed by ultrasound, followed by conditioning at 40 °C/10 days was influenced by packaging material, food simulant and exposure time to ultrasound processing. For both materials, the migration in fatty simulant was superior compared to the aqueous acid simulant. Ultrasonic processing of the PE/PA/PE/PA/PE package for 60 min followed by conditioning increased the migration of ϵ -caprolactam in the fatty simulant. However, all results met the limits of total migration and specific migration of hexamethylenediamide and ϵ -caprolactam established in Brazilian and European Union legislations. The results here presented highlight the need of conducting connected studies in food-package-processing relationships for emerging technologies, considering not only the food and processes characterization, properties and development, but also their interaction with different materials for packaging.

Code availability

Not applicable.

Declaration of interest

The authors report there are no competing interests to declare.

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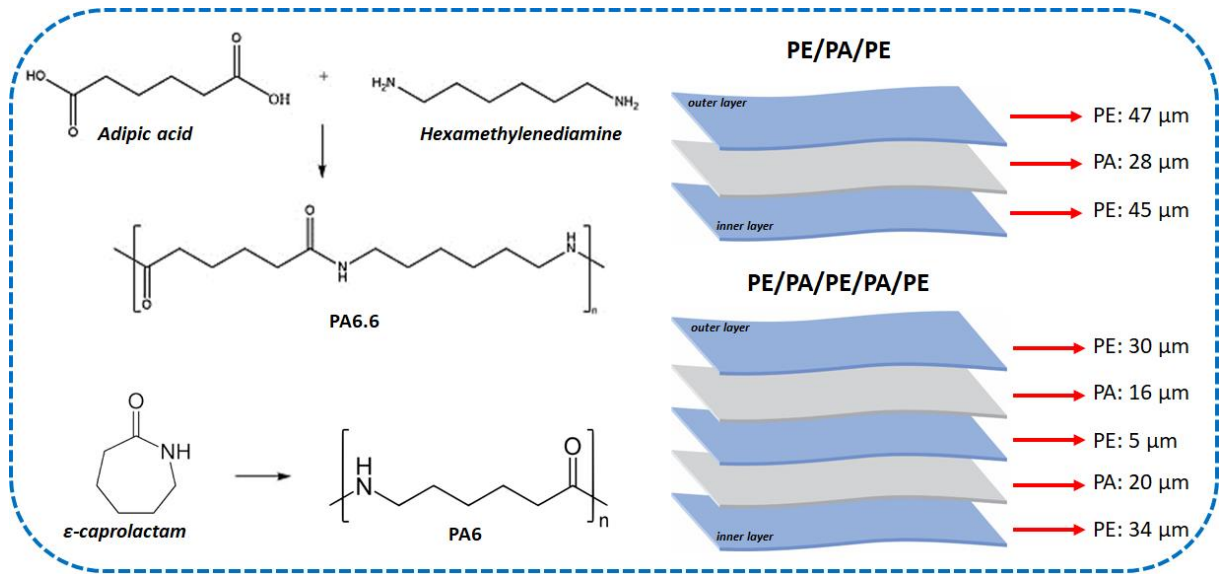


Figure 1. Chemical structure of polyamide 6, polyamide 6.6, their monomers, composition of multilayer PE and PA films and their respective thicknesses.

Table 1. Overall migration in food simulant after different ultrasound processing conditions and conditioning at 40 °C/10 days.

Packaging material	Ultrasound processing time (25 °C)	Food Simulants	Overall migration (mg dm ⁻²)	
			After ultrasound processing	After ultrasound processing and conditioned at 40 °C/10 days
PE/PA/PE	Unprocessed (control)	Aqueous	-	≤ 2.33*
	30 min		≤ 2.33*	≤ 2.33*
	60 min		≤ 2.33*	≤ 2.33*
	Unprocessed (control)	Acid	-	≤ 2.33*
	30 min		≤ 2.33*	≤ 2.33*
	60 min		≤ 2.33*	≤ 2.33*
	Unprocessed (control)	Fatty	-	≤ 2.33*
	30 min		≤ 2.33*	≤ 2.33*
	60 min		≤ 2.33*	≤ 2.33*
PE/PA/PE/PA/PE	Unprocessed (control)	Aqueous	-	≤ 2.33*
	30 min		≤ 2.33*	≤ 2.33*
	60 min		≤ 2.33*	≤ 2.33*
	Unprocessed (control)	Acid	-	≤ 2.33*
	30 min		≤ 2.33*	≤ 2.33*
	60 min		≤ 2.33*	≤ 2.33*
	Unprocessed (control)	Fatty	-	≤ 2.33*
	30 min		≤ 2.33*	2.35 ± 0.05
	60 min		≤ 2.33*	≤ 2.33*

Reported results are expressed as mean of four replicates ± standard deviation.

* Limit of quantification (LOQ) of the method under the analytical conditions used.

The LOQ was calculated as the resolution of the balance (0.00001 g) multiplied by a factor of 100 and divided by an area of 0.43 dm².

Table 2. Migration of hexamethylenediamine in food simulant after different ultrasound processing conditions and conditioning at 40 °C/10 days.

Packaging material	Ultrasound processing time (25 °C)	Food Simulants	Migration of hexamethylenediamine (mg kg ⁻¹)	
			After ultrasound processing	After ultrasound processing and conditioned at 40 °C/10 days
PE/PA/PE	Unprocessed (control)	Aqueous	-	≤ 1.2 [*]
	30 min		≤ 1.2 [*]	≤ 1.2 [*]
	60 min		≤ 1.2 [*]	≤ 1.2 [*]
	Unprocessed (control)	Acid	-	≤ 1.1 ^{**}
	30 min		≤ 1.1 ^{**}	≤ 1.1 ^{**}
	60 min		≤ 1.1 ^{**}	≤ 1.1 ^{**}
	Unprocessed (control)	Fatty	-	≤ 1.1 ^{***}
	30 min		≤ 1.1 ^{***}	≤ 1.1 ^{***}
	60 min		≤ 1.1 ^{***}	≤ 1.1 ^{***}
PE/PA/PE/PA/PE	Unprocessed (control)	Aqueous	-	≤ 1.2 [*]
	30 min		≤ 1.2 [*]	≤ 1.2 [*]
	60 min		≤ 1.2 [*]	≤ 1.2 [*]
	Unprocessed (control)	Acid	-	≤ 1.1 ^{**}
	30 min		≤ 1.1 ^{**}	≤ 1.1 ^{**}
	60 min		≤ 1.1 ^{**}	≤ 1.1 ^{**}
	Unprocessed (control)	Fatty	-	≤ 1.1 ^{***}
	30 min		≤ 1.1 ^{***}	≤ 1.1 ^{***}
	60 min		≤ 1.1 ^{***}	≤ 1.1 ^{***}

Reported results are expressed as mean of four replicates ± standard deviation.

^{a,b,c} Averages followed by the same letters in the column to the same film do not differ at the 95% confidence level ($p < 0.05$).

Limit of quantification of hexamethylenediamine of the method under the analytical conditions used for the food simulants (^{*}) aqueous (≤1.2), (^{**}) acid (≤1.1), and (^{***}) fatty (≤1.1).

Table 3. Migration of ϵ -caprolactam in food simulant after different ultrasound processing conditions and conditioning at 40 °C/10 days.

Packaging material	Ultrasound processing time (25 °C)	Food Simulants	Migration of ϵ -caprolactam (mg kg ⁻¹)	
			After ultrasound processing	After ultrasound processing and conditioned at 40 °C/10 days
PE/PA/PE	Unprocessed (control)	Aqueous	-	4.97 ± 0.22 ^a
	30 min		≤ 0.35 [*]	5.06 ± 0.35 ^a
	60 min		≤ 0.35 [*]	4.76 ± 0.32 ^a
	Unprocessed (control)	Acid	-	4.74 ± 0.42 ^{ac}
	30 min		≤ 0.84 ^{**}	4.77 ± 0.24 ^{ac}
	60 min		≤ 0.84 ^{**}	4.37 ± 0.42 ^c
	Unprocessed (control)	Fatty	-	6.44 ± 0.28 ^b
	30 min		≤ 0.80 ^{***}	6.11 ± 0.30 ^b
	60 min		≤ 0.80 ^{***}	6.35 ± 0.81 ^b
PE/PA/PE/PA/PE	Unprocessed (control)	Aqueous	-	2.07 ± 0.13 ^{de}
	30 min		≤ 0.35 [*]	2.19 ± 0.17 ^{de}
	60 min		≤ 0.35 [*]	1.98 ± 0.07 ^d
	Unprocessed (control)	Acid	-	2.30 ± 0.06 ^{de}
	30 min		≤ 0.84 ^{**}	2.18 ± 0.23 ^{de}
	60 min		≤ 0.84 ^{**}	2.12 ± 0.08 ^{de}
	Unprocessed (control)	Fatty	-	2.52 ± 0.19 ^{de}
	30 min		≤ 0.80 ^{***}	2.60 ± 0.19 ^e
	60 min		≤ 0.80 ^{***}	2.98 ± 0.25 ^f

Reported results are expressed as mean of four replicates ± standard deviation.

^{a,b,c} Averages followed by the same letters in the column to the same film do not differ at the 95% confidence level ($p < 0.05$).

Limit of quantification of ϵ -caprolactam of the method under the analytical conditions used for the food simulants (^{*}) aqueous (≤0.35), (^{**}) acid (≤0.84), and (^{***}) fatty (≤0.80).