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Food-Package-Processing relationships in emerging technologies: Ultrasound effects on polyamide multilayer packaging in contact with different food simulants

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ABSTRACT

In this study, the effect of ultrasound processing on the properties of two packages widely used in food products was evaluated: polyamide (PA) and polyethylene (PE) multilayer packaging. Packages composed of PE/PA/PE (Film A) and PE/PA/PE/PA/PE (Film B) were filled with aqueous and fatty food simulants and treated in an ultrasound water bath (frequency 25 kHz, volumetric power of 9.74 W/L, temperature of 25 °C, and time of 30 and 60 min). Materials were evaluated in term of structure and performance properties. Ultrasound did not or induced small changes in chemical groups, crystallinity, melting temperature, and tensile strength of the films. Film A showed a reduction in heat sealing tensile strength of 25% in the machine direction and 22% in the transverse direction. Film B showed a 20% increase of water vapor transmission rate after ultrasound processing. Although ultrasound had little impact on the properties of the evaluated materials, these modifications do not compromise the use of these packages for applications in ultrasound-processed foods. Therefore, the results indicate that ultrasound can be used as a food processing technology in multilayer PA and PE packaging.

1. Introduction

Packaging is an essential component for the development of the food industry, as it is able to protect food from physical, chemical, and biological contamination, aiming to increase the shelf life of products (Alias et al., 2022; Kan & Miller, 2022). Plastic materials are widely used in food packaging applications due to their excellent properties, especially when combined in multilayer packaging composed of different materials. The final properties of multilayer packaging are affected by a combination properties of each material, which allows to improve their performance (Ibarra et al., 2019). The most commonly used polymers in this application include polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), ethylene–vinyl alcohol copolymer (EVOH), polyvinylidene chloride (PVDC), ethylene–vinyl acetate copolymer (EVA), and polyamide (PA) (Marangoni Júnior, Cristianini, et al., 2020; Marangoni et al., 2020).

Polyamides are linear polymers with a sequence of amide groups in the chain in different ways, which depend on their monomer. There are different types of polyamides, which include PA6, PA6.6, PA11, PA12, and PA46; among these, the first two are widelyused (Krishna et al., 2021). PAs are widely used in flexible multilayer packaging, often combined with polyolefins. The main characteristics of PA are good mechanical performance, thermal resistance, and oxygen barrier (Marangoni Júnior, Oliveira, et al., 2020; Tyuftin & Kerry, 2020). Films

Abbreviations: Ac, acrylic; ATR, attenuated total reflectance; BOPP, biaxially oriented polypropylene; coex, coextruded; DSC, differential scanning calorimetry; EVA, ethylene-vinyl acetate copolymer; EVOH, ethylene-vinyl alcohol copolymer; FT-IR, fourier-transform infrared; LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; MD, machine direction; OTR, oxygen transmission rate; PA, polyamide; PE, polyethylene; PET, polyethylene terephthalate; PP, polypropylene; PVDC, polyvinylidene chloride; TD, the transverse direction; WVTR, water vapor transmission rate; XRD, X-ray diffraction.

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containing PA are particularly used for the packaging of meat and cheese products such as vacuum packaging, thermoformed tray lids, modified atmosphere packaging, among others (Tyuftin & Kerry, 2020). In addition, PA packaging is used for in-package food processing, such as conventional thermal processing (pasteurization and sterilization) of meats and vegetables. The advantage of applying processing to in-packaged foods is associated with reducing the risk of post-processing contamination and avoiding expensive aseptic packaging lines.

Although conventional thermal processing techniques are consolidated in the food processing industries, there is a growing search for processing methods with minimal effects on food quality, environmental impact, processing efficiency, and other improvement characteristics (Kubo et al., 2021). Ultrasound technology is an emerging alternative for food processing.

High-power (>1 W/cm^2) and low-frequency (20–100 kHz) ultrasound supports many food processing operations such as extraction, freezing, drying, thermal processes, emulsification, enzyme and pathogenic bacteria inactivation in food contact surfaces (Awad et al., 2012; Ozuna et al., 2015). In an ultrasound system, electrical energy is converted into vibrational mechanical energy, which will be transmitted through a medium (for instance, food). When crossing the medium, the high and low acoustic pressure zones promote movement (micro and macro) and induce the phenomenon of cavitation, which in turn produces chemical, physical, or biological effects. Acoustic cavitation in liquid medium involves physical forces that are considered the main mechanism responsible for changes in food materials exposed to ultrasound (Alarcon-Rojo et al., 2019).

In the literature, several studies have applied ultrasound to packaged foods. Application of ultrasound at 16 and 28 W/cm^2, at 5 °C for 40 min, followed by simulated retail exposure (3 °C, 12 h light) for 6 days was evaluated on vacuum-packed beef steaks. Ultrasound increased the redness of vacuum-packed beef during storage, and can be considered as a strategy to improve the color of vacuum-packed beef without adversely affecting pH and water holding capacity (Garcia-galicia et al., 2019). Vacuum-packed sausages were processed in an ultrasound water bath (25 kHz, 200 W for 10.5 min at 74 °C), followed by storage for 60 days at 15 °C. The treatment inhibited the growth of psychrotrophic lactic bacteria, reduced lipid oxidation, and caused few changes in pH and texture during storage (Cichoski et al., 2015). Furthermore, the literature presents studies of processes that could be carried out in packaged foods such as the hydration or acidification of vegetables (Miano et al., 2017, 2018).

The aforementioned studies have shown the potential that ultrasound processing has for food processing. However, most of these studies did not specify the characteristics of the packaging material used and neither assessed whether the ultrasound processing resulted in changes in the properties of the packaging material. Therefore, the literature is scarce in information about the effect of ultrasound processing on the properties of packaging materials, mainly considering the availability of different materials, which often have multilayers to meet the protection requirements of the packaged product.

The few results found in the literature show that ultrasound can change the properties of packaging materials. Biaxially oriented polypropylene (BOPP) coated with acrylic/polyvinylidene chloride (BOPPAc/PVDC) and biaxially oriented coextruded polypropylene (BOPPcoex) films were processed by different ultrasound conditions (600 W, 20 kHz, 2, 4 and 6 min) (Ščetar et al., 2017, 2019). The results indicated that ultrasound processing can change the oxygen permeability and structure of packages. Linear low-density polyethylene (LLDPE) and polypropylene coated with acrylic/polyvinylidene chloride (PPAc/PVDC) films in contact with different food simulants showed significant reduction in barrier properties and increase in total migration after ultrasound processing (640 W, 35 kHz, 5, 10, and 15 min) (Ščetar et al., 2022).

In addition, as new food processing methods (such as ultrasound) reach commercial importance, it is necessary to study the impact of this technology on the structure and physicochemical properties of packaging materials (Marangoni Júnior et al., 2022). As far as we know, few packaging materials have been investigated, making it urgent to develop studies with this purpose. Therefore, the objective of this study was to evaluate the effect of different ultrasound processing conditions and foods of different characteristics (represented by two food simulants) on the mechanical and barrier properties of multilayer packaging materials. Two multilayer flexible packaging containing a layer of polyamide and polyethylene were selected. Accordingly, the materials were evaluated as for crystallinity, chemical structure, and thermal properties to understand the possible changes that ultrasound can cause in packaging.

2. Materials and methods

2.1. Materials

Two polyamide-containing multilayer packaging materials were evaluated (Fig. 1): Film A: PE/PA/PE and Film B: PE/PA/PE/PA/PE (Parnaplast, Paraná, Brazil). The selection of two materials with different layer arrangements was due to their potential different mechanical and barrier performance. In addition, both films are commonly used as vacuum packaging for meat products and cheese, representing real applications. For both films, the inner and outer layers of polyethylene (PE) comprise a blend of low-density polyethylene (LDPE) with linear low-density polyethylene (LLDPE); and the polyamide layer (PA) is a blend composed of PA6 and PA6.6.

2.2. Food simulants and packaging sample preparation

As mentioned, the packaging materials selected for this study are mainly applied to meat products and cheese. Therefore, food simulants (model foods) representing the nature of those products were considered, that is, nonacidic and fatty simulants: simulant A (nonacidic aqueous food simulant [pH > 4.5]: distilled water) and simulant D (fatty food simulant: 95 % (v/v) ethanol solution in distilled water), as described in the Brazilian legislation RDC n° 51, of November 26, 2010 of the National Health Surveillance Agency (ANVISA) (Brazil, 2010). For the preparation of the fatty food simulant, ethanol (≥99.9 %, Merck, Germany) was used. Solutions were prepared with deionized water (Millipore Milli-Q Direct).

First, packages with dimensions of 100 mm × 100 mm were prepared using a sealer (Haramura – A380, São Paulo, Brazil). The sealing with a

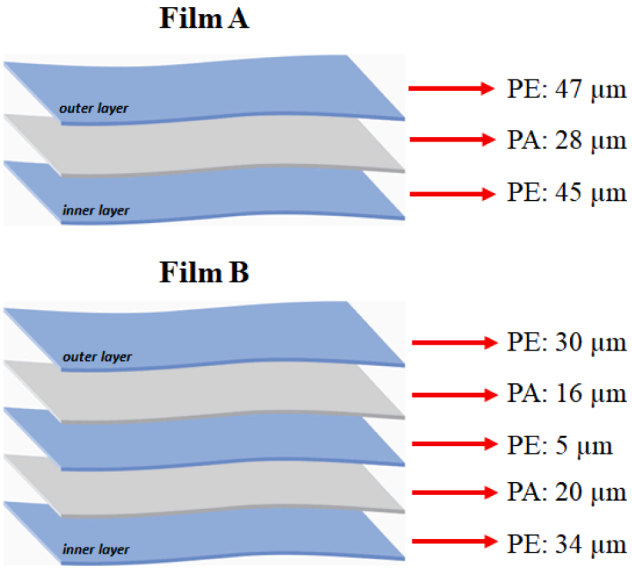

Fig. 1. Composition of PE and PA multilayer films and their respective thicknesses.

width of 3 mm was carried out with a time of 1.5 s, followed by cooling for 2.0 s. Subsequently, the packages were filled with 100 mL of different food simulants and heat sealed.

2.3. Ultrasound processing

The packages were processed using an ultrasound water bath (Q 13/25 A CR, Ultronique, Indaiatuba, Brazil) with a frequency of 25 kHz and a volumetric power of 9.74 W/L [determined by the calorimetric method (Margulis & Margulis, 2003)]. Water was used as a wave propagation medium for the packages, which was maintained at 25 °C through a heat exchanger. Initially, the processing time was selected as 30 min, similar to the conditions applied to meat emulsions with low phosphate and sodium content (Pinton et al., 2020), low-sodium bologna (Leães et al., 2021), and chicken breast (Chen et al., 2015; Leal-Ramos et al., 2011). In addition, the samples were also processed for 60 min, seeking to evaluate a prolonged condition of exposure to ultrasound processing. Therefore, possible applications were covered by the chosen process conditions. The ultrasound processes were performed in duplicate.

The treatments performed were described as follows: control (unprocessed samples), aqueous/30 min (aqueous food simulant processed by ultrasound for 30 min), fatty/30 min (fatty food simulant processed by ultrasound for 30 min), aqueous/60 min (aqueous food simulant processed by ultrasound for 60 min), fatty/60 min (fatty food simulant processed by ultrasound for 60 min). The packaging materials were evaluated by, optical microscopy, Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), differential scanning calorimetry (DSC), tensile strength, heat sealing tensile strength, water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) as described next.

2.4. Characterization of packaging materials

2.4.1. Optical microscopy

In order to identify possible defects on the surfaces of materials resulting from ultrasound processing, an evaluation was carried out on the surface of the internal and external layers of the materials using a stereomicroscope (M165C, Leica, Germany) with a magnification capacity of up to 120 ×, connected to the LAS EZ software.

2.4.2. Fourier-transform infrared (FT-IR) spectroscopy

FT-IR analyses were recorded using a Spectrum 100 spectrometer (PerkinElmer, Waltham, MA, USA). For all samples, the inner and outer layers were analyzed using the attenuated total reflectance (ATR) mode (zinc selenide crystal), using the Perkin Elmer Spectrum software version 10.4.00, at 4000–650 cm^{-1}, with resolution of 4 cm^{-1}, scan: 4 (ASTM-E1252-98, 2021; ASTM-E573-01, 2021). Three spectra were recorded at different locations on the film for each sample and for each layer (inner and outer) to estimate the average of the film inhomogeneous potential and measurement variability.

2.4.3. X-ray diffraction (XRD) analysis

X-ray diffraction patterns were obtained from a Philips X'Pert-MPD (Almelo, Netherlands). The operating conditions of the equipment were: Cu Kα (λ = 1.54056 Å) at a scanning rate of 0.033333°/s (step = 0.04° and time per step = 1.2 s), with the accelerating voltage of 40 kV and the applied current of 40 mA. The diffraction intensity was recorded as a function of the increase in the scattering angle ranging from 10 to 30° (2θ). The percentage of total crystallinity of the films was estimated by the ratio between the area under the peaks (crystalline regions) and the total area (crystalline and amorphous regions). To this end, the deconvolution of peaks was carried out with the aid of Fityk free software. The areas of the curves were determined by numerical integration.

2.4.4. Differential scanning calorimetry (DSC)

The thermal properties of the films were measured by DSC using a calorimeter (TA Instruments – DSC 250, New Castle, USA), at a heating rate of 10 °C/min in the range of 40 °C − 300 °C. The sample weight was approximately 5 mg and the determinations were carried out under a dry nitrogen purge. The melting temperature (T_m) and the enthalpy of melting (ΔH) were estimated based on the DSC thermograms (ASTM-D3418-21, 2021). The results were the average of three replicates.

2.4.5. Mechanical properties

Samples 25.4-mm wide were used, cut with high precision equipment to avoid burrs (JDC Twing Albert). The tensile strength and heat sealing tensile strength tests were performed at 23 ± 2 °C and 50 ± 5 % RH after conditioning the samples for a period of at least 48 h under the same conditions. All tests were performed with five repetitions.

2.4.5.1. Tensile strength. Tensile properties were determined on a universal testing machine (Instron, 5966-E2, Norwood, USA) operating with a 1 kN load cell. The test speed was 500 mm min^{-1} and the distance between the specimen clamps was 50 mm. The test was performed in the machine direction (MD) and in the transverse direction (TD) of the material. (ASTM-D882, 2018).

2.4.5.2. Heat sealing tensile strength. The heat sealing tensile strength until failure was determined on a universal testing machine (Instron, 5966-E2, Norwood, USA), operating with a 100 N load cell at a speed of 300 mm min^{-1}. The distance between the specimen clamps was 10 mm (ASTM-F88/F88M, 2021).

2.4.6. Water vapor transmission rate (WVTR)

The water vapor transmission rate was determined using an infrared sensor device, PERMATRAN (3/34 G, MOCON, Minneapolis, USA). The effective permeation area of each specimen was 50 cm^2. The test was performed at 38 °C and 90 % RH in three repetitions (ASTM-F1249, 2020).

2.4.7. Oxygen transmission rate (OTR)

The oxygen transmission rate was determined in an OXTRAN equipment (2/20H, MOCON, Minneapolis, USA). The external side of the sample was placed in contact with the permeating gas (100 % O_2) and the permeation area was 50 cm^2. The reading was corrected for a permeating gas partial pressure gradient of 1 atm. The test was performed at 23 °C under drying condition in three repetitions (ASTM-D3985, 2017).

2.5. Statistical analysis

Results were expressed as mean ± standard deviation and statistically evaluated by analysis of variance (ANOVA). Comparisons between mean values were determined by Tukey's tests ($p < 0.05$).

3. Results and discussion

3.1. Optical microscopy

In order to assess whether the ultrasound processing caused any defects on the surface of the inner and outer layers of the materials, an optical microscopy evaluation was performed on the packages before and after the ultrasound processing. The two packaging materials studied (Film A and Film B) in contact with the different food simulants (aqueous and fatty) did not present visual nor microscopic defects after different times of exposure to ultrasound processing (Fig. 2). As no defect was detected, it was decided to present only the images obtained in the outer layer and in the control sample and aqueous/60 min. Therefore, we proceeded with all samples for the other

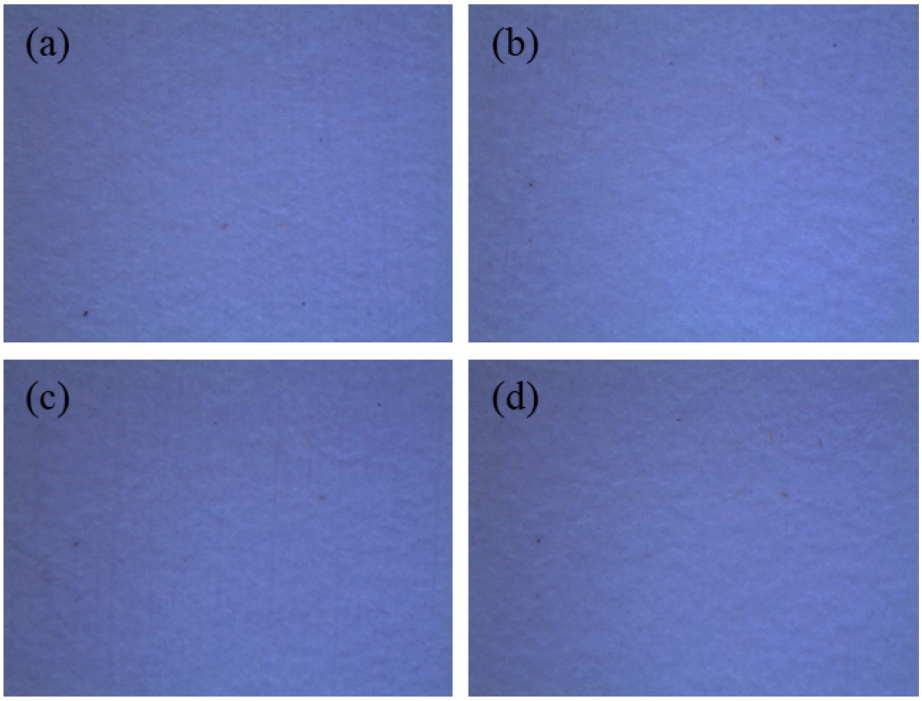

Fig. 2. Outer layers surface of samples analyzed under a stereomicroscope with 10× magnification. (a,c) control, (b,d) aqueous food simulant processed by ultrasound for 60 min, (a,b) Film A and (c,d) Film B.

characterizations.

3.2. FT-IR analysis

FT-IR was used to identify the functional groups of the outer and inner layers of Film A and Film B, as well as to assess whether food simulants in contact with packaging and exposure to ultrasound processing for different times exert an influence on these groups. As the results were similar for the inner and outer layers, considering that the layers are composed of the same materials, only the results of the inner layer (i.e., the one that came in contact with the model food) are shown and discussed in this article.

Fig. 3(a,b) show the FT-IR spectra of the inner layer of Films A and B. Both materials are composed of a blend of LDPE and LLDPE. The characteristic polyethylene peaks are observed in Films A and B, corresponding to asymmetric C—H and symmetrical C—H stretching vibrations in CH_2 at the absorption peaks of 2915 cm^{-1} and 2849 cm^{-1}, respectively. Peaks at 1471–1472 cm^{-1} can be attributed to C—H deformation vibrations at CH_2, peaks at 1372–1378 cm^{-1} are attributed to bending at CH_3, and the peak at 717 cm^{-1} is due to C—C balance vibrations in CH_2 (De Geyter et al., 2008; Kochetov et al., 2017). The results are similar to those found for PE films by (Ahmed et al., 2018; Mulla et al., 2017).

No significant changes were observed in the surface spectra of the films, regardless of the food simulant in contact with the material and the time of exposure to ultrasound processing. This behavior shows that the chemical nature of the polyethylene layers of the evaluated films was not modified and/or destroyed by the ultrasound treatment, even under long-term exposure conditions. Similar behavior was found for BOPPAc/PVDC and BOPPcoex films processed by ultrasound (20 kHz) with 600 W of power processed up to 6 min, in which no significant changes were observed in the FT-IR spectra of the PP layers of the films processed by ultrasound in relation to unprocessed films (Ščetar et al., 2019).

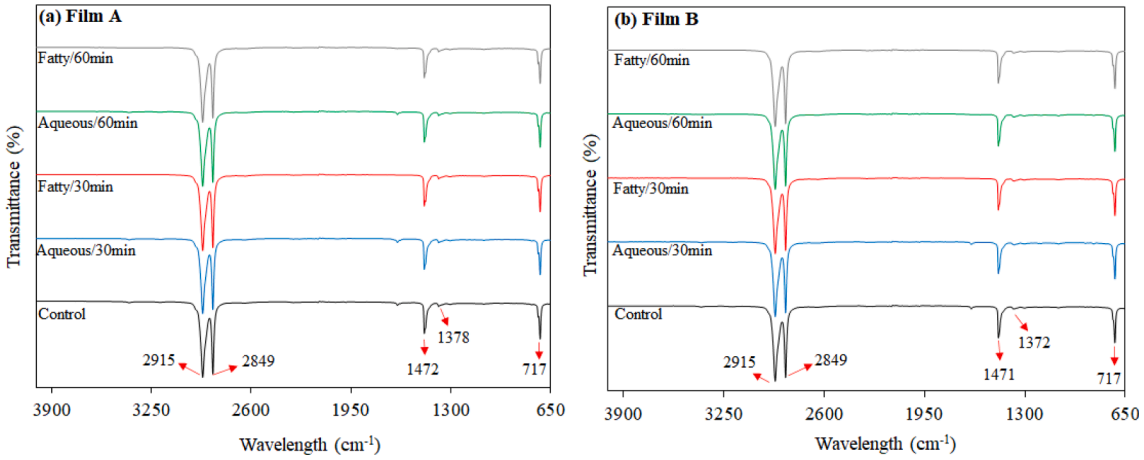

Fig. 3. FT-IR spectra of inner layer of different packaging materials processed by ultrasound. (a) Film A: PE/PA/PE and (b) Film B: PE/PA/PE/PA/PE.

3.3. XRD analysis

X-ray diffraction patterns for Film A and Film B before and after treatments are shown in Fig. 4. The peaks of the two materials are similar, as both are composed of the same polymers. The peaks observed at approximately 2θ = 21.6° and 23.8° corresponded to PE and PA, respectively. These values are similar to those found in the literature for films with PE and PA (Bhunia et al., 2016). For Film A, the different ultrasound processing conditions, as well as the different food simulants, hardly changed, or had a slight reduction in the PE and PA peak areas in relation to the peaks of the control sample. However, an exception was the sample processed by ultrasound for 60 min in contact with the fatty simulant (Fatty/60 min), where a slight increase in peaks was observed in relation to the control (Fig. 4(a)). Similar behavior was observed for Film B (Fig. 4(b)). The slight change or the small reductions in the peak intensities resulted in very close overall crystallinity values: between 24.5% and 25.4% for Film A; and between 21.7% and 22.6% for Film B. Nevertheless, for Fatty/60 min samples, there was a slight increase in overall crystallinity to 28.9% (Film A) and 23.2% (Film B), suggesting possible processing-induced partial crystallization.

The increase in the overall crystallinity of the Fatty/60 min samples may be associated with the formation of large crystal clusters, as suggested for BOPPAc/PVDC films (Ščetar et al., 2019). This behavior may be due to the stress of acoustic cavitation on the surface of the material, i.e., due to the high energy release of the bubbles (Price et al., 1995; Ščetar et al., 2019), leading to possible changes in the crystalline regions resulting from chain breaks followed by secondary recrystallization (Miraftab et al., 2002; Roy et al., 2006; Ščetar et al., 2019). Lastly, this behavior may have been intensified by a possible absorption of organic compounds from the fatty simulant (ethanol) in the PA layer (Tsochatzis et al., 2020) and, consequently, structural changes of the material (Heimrich et al., 2015; Stoffers* et al., 2005).

3.4. Thermal properties

The thermal characteristics of Films A and B after ultrasound processing were evaluated by DSC. The thermal profile of the different samples is shown in Fig. 5, and the melting temperature (T_m) of each structure material and the total enthalpy of melting (ΔH) of the entire structure for both films before and after processing are shown in Table 1.

The DSC curves of the different films showed four melting peaks, corresponding to LDPE (1st peak), LLDPE (2nd peak), PA6/6.6 (3rd and 4th peaks). For Film A, the results of the different peaks and the total enthalpy of melting showed no significant difference after the different conditions of ultrasound processing, in which the T_m of the 1st and 2nd peaks was between 106.5 °C – 107.5 °C and 122.4 °C – 122.8 °C, respectively. These ranges are similar to those found in the literature for LDPE and LLDPE (Benítez et al., 2013). Regarding the 3rd and 4th peaks, the T_m was between 177.7 °C – 180.1 °C and 189.9 °C – 190.4 °C, respectively. These values were also previously found for the PA layer in PE/PA/PE multilayer film (Marangoni Júnior, Oliveira, et al., 2020) and for PA6/6.6 copolymers (Men & Rieger, 2004). Overall, the T_m of PA6 and PA6.6 are ~ 230 °C and ~ 225 °C, respectively (Marchildon, 2011). The observed decrease in the T_m of PA6/6.6 blends is typical of the copolymerization process, in which only a single copolymer constituent is forming the crystals, resulting in the reduction of T_m (Harvey & Hybart, 1970). Lastly, the total enthalpy of melting of Film A was between 71.4 and 72.9 J/g.

Regarding Film B, the results of the 1st, 3rd, and 4th peaks were between 98.9 °C – 101.7 °C, 180.0 °C – 180.9 °C, and 188.5 °C – 190.3 °C, respectively. These results did not show any significant changes induced by ultrasound processing and/or food simulant. Conversely, the 2nd peak showed a slight increase in T_m after ultrasound processing for 60 min in contact with aqueous simulant compared with the control. In addition, there was a slight reduction in ΔH after processing for 60 min in contact with the fatty simulant. This behavior can be attributed to mechanochemical degradation in the solid state of the polymer, caused by the long exposure time to ultrasound processing. This phenomenon can result in a decrease in the molecular weight and intrinsic viscosity of polyethylene (Li et al., 2005) and, consequently, it may lead to changes in the thermal properties of the polymer. In addition, the different T_m values of the same polymer, but in a different sample, can be attributed to different degrees of resins, different proportions of polymers (LDPE + LLDPE), additives and process conditions used in the manufacture of films.

3.5. Tensile strength

The tensile strength results of Film A in the machine direction (MD) ranged between 39.4 ± 3.6 MPa and 41.9 ± 3.3 MPa; and in the transverse direction (TD), between 36.5 ± 3.2 MPa and 40.8 ± 0.9 MPa, as shown in Fig. 6(a). Film B showed tensile strength in MD between 47.1 ± 3.5 MPa and 51.0 ± 1.3 MPa; and in TD, between 44.0 ± 5.2 MPa and 48.6 ± 1.8 MPa (Fig. 6(c)). The different ultrasound processing conditions applied to the two materials did not result in a significant difference in the tensile strength results when compared with the control. Regarding the elongation at break, the applied ultrasound conditions did not significantly influence the results of Film A and Film B when compared with the control films (Fig. 6(b) and 5(d)). Film A results ranged from 547.1 ± 35.6% to 598.1 ± 24.0% in MD and 572.5 ± 31.8% and 611.5 ± 11.7% in TD; and for Film B, the results were between 538.5 ± 17.6% and 556.8 ± 24.7% in MD and between 561.3 ± 23.2% and 593.5 ± 30.6% in TD. These findings show that the applied ultrasound conditions do not compromise the mechanical performance

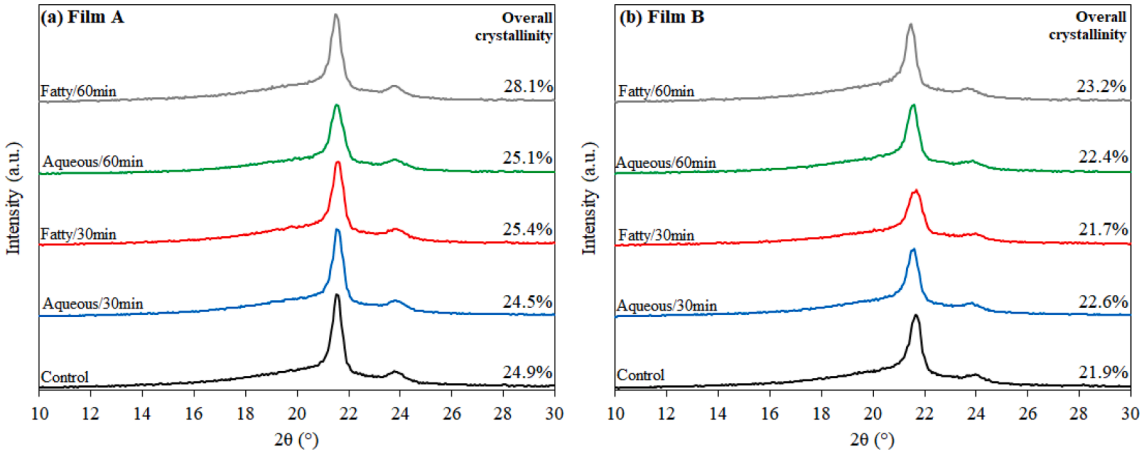

Fig. 4. X-ray diffraction patterns of different packaging materials processed by ultrasound. (a) Film A: PE/PA/PE and (b) Film B: PE/PA/PE/PA/PE.

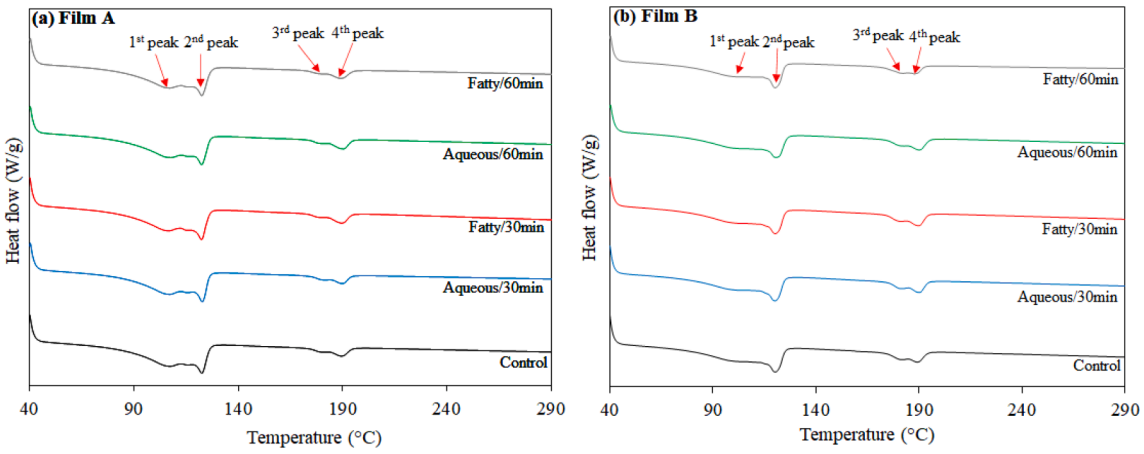

Fig. 5. Differential Scanning Calorimetry of different packaging materials processed by ultrasound. (a) Film A: PE/PA/PE and (b) Film B: PE/PA/PE/PA/PE.

Table 1
DSC results of different packaging materials processed by ultrasound.

Film A	PE		PA		ΔH* (J/g)
	T_m (C°) 1st peak	T_m (C°) 2nd peak	T_m (C°) 3rd peak	T_m (C°) 4th peak	
Control	107.4 ± 0.6[a]	122.6 ± 0.2[a]	179.8 ± 1.7[a]	189.9 ± 0.7[a]	71.5 ± 1.9[a]
Aqueous/30 min	107.1 ± 0.5[a]	122.8 ± 0.1[a]	180.1 ± 1.9[a]	190.2 ± 0.3[a]	72.1 ± 4.1[a]
Fatty/30 min	106.5 ± 0.5[a]	122.4 ± 0.3[a]	177.7 ± 0.5[a]	190.0 ± 0.7[a]	71.4 ± 1.3[a]
Aqueous/60 min	107.5 ± 0.3[a]	122.5 ± 0.3[a]	178.7 ± 0.2[a]	190.4 ± 0.3[a]	72.9 ± 1.1[a]
Fatty/60 min	106.9 ± 0.8[a]	122.6 ± 0.2[a]	178.0 ± 1.3[a]	189.9 ± 1.3[a]	71.5 ± 0.7[a]
Film B	**PE**		**PA**		**ΔH* (J/g)**
	T_m (C°) 1st peak	T_m (C°) 2nd peak	T_m (C°) 3rd peak	T_m (C°) 4th peak	
Control	100.0 ± 0.5[a]	120.1 ± 0.1[b]	180.8 ± 0.9[a]	189.9 ± 0.9[a]	61.7 ± 2.1[b]
Aqueous/30 min	98.8 ± 0.9[a]	120.0 ± 0.3[b]	180.9 ± 0.9[a]	190.2 ± 0.1[a]	60.9 ± 2.7[b]
Fatty/30 min	98.9 ± 1.4[a]	120.1 ± 0.4[b]	180.0 ± 0.8[a]	189.9 ± 0.3[a]	63.4 ± 3.4[b]
Aqueous/60 min	100.0 ± 1.7[a]	121.4 ± 0.8[a]	180.8 ± 1.0[a]	190.3 ± 0.6[a]	62.0 ± 0.7[b]
Fatty/60 min	101.7 ± 1.2[a]	120.3 ± 0.4[ab]	180.8 ± 2.2[a]	188.5 ± 1.1[a]	58.1 ± 1.8[a]

Film A: PE/PA/PE, Film B: PE/PA/PE/PA/PE, PE: polyethylene, PA: polyamide, T_m: melting temperature, ΔH*: total enthalpy of melting ($\Delta H^* = \Delta H_{PE} + \Delta H_{PA}$). Values referring to the mean of three repetitions ± standard deviation.
[a,b,c] means followed by the same letter in the column do not differ at the 95 % confidence level ($p < 0.05$).

of the tested packaging materials.

3.6. Heat sealing tensile strength

Heat sealing tensile strength is a critical feature of flexible packaging in food processing, as it ensures the integrity of the seal. When poorly sized, it can allow product leakage or contaminants to enter. The heat sealing tensile strength results of Film A and Film B are shown in Fig. 7 (a) and 7(b), respectively.

For Film A, there was a significant reduction of 25% of the seal strength in the machine direction (MD) after the ultrasound processing (aqueous/60 min) in relation to the control. The other processing conditions did not significantly affect the results. Regarding the transverse direction (TD), the aqueous/30 min, fatty/30 min, aqueous/60 min and fatty/60 min samples had their seal strengths reduced by 22%, 13%, 24%, and 17% in relation to the control sample. This heat sealing strength reducing behavior can be based on the hypothesis that the aqueous food simulant can be absorbed by the packaging material, mainly because the multilayer structure presents a polar polymer, which consequently causes impacts on the sealant layer. Also, these results may be due to the effects of acoustic cavitation on the sealing region of the material, that is, probably the physical forces in this region led to a fragility of the connections between the interfaces of the layers. However, it is noteworthy that the packages did not show signs of leakage of simulants after the ultrasound processing and, therefore, the integrity was not compromised. Moreover, the reductions observed in heat sealing tensile strength are within the acceptable range for the industry, which is up to 25% (Lambert et al., 2000; Marangoni Júnior, Oliveira, et al., 2020). Still, strategies to improve the sealing process can be studied, minimizing the impact of this change after processing, such as increasing the width of the sealing region, applying double sealing, replacing the sealing layer polymer by polymers with special sealing characteristics, among others. Concerning Film B, no significant difference in heat sealing tensile strength was observed in MD and TD after different ultrasound processing conditions.

3.7. WVTR and OTR

The results of water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of Films A and B, before and after ultrasound processing, are presented in Table 2. The control Film A showed a WVTR of 3.53 ± 0.15 g water.m^{-2}.day^{-1}, a result similar to that found in the literature for PE/PA/PE film (Marangoni Júnior, Alves, et al., 2020). In relation to the control Film B, the WVTR was 5.65 ± 0.21 g water.m^{-2}.day^{-1}. The higher water vapor permeability value of Film B in relation to Film A is related to the thickness of the material, as Film A has a greater total thickness (Film A: 120 μm and Film B: 105 μm), the diffusion of water molecules tends to be smaller. Furthermore, the water vapor barrier material that composes the two films are the polyethylene layers. In this sense, the thickness of the polyethylene layers of Film A is 25% greater than that of Film B. In addition, Film A has greater crystallinity in relation to Film B, as shown in Fig. 4.

The different ultrasound processing conditions, as well as the different food simulants, did not significantly influence the WVTR results of Film A. On the other hand, the WVTR of Film B, after ultrasound processing for 30 min and 60 min in contact with the aqueous simulant, significantly increased in relation to the control and did not significantly differ from samples processed in contact with the fatty simulant. In general, there was an increase in the average permeability values of the samples after treatment in relation to the control sample and an increase

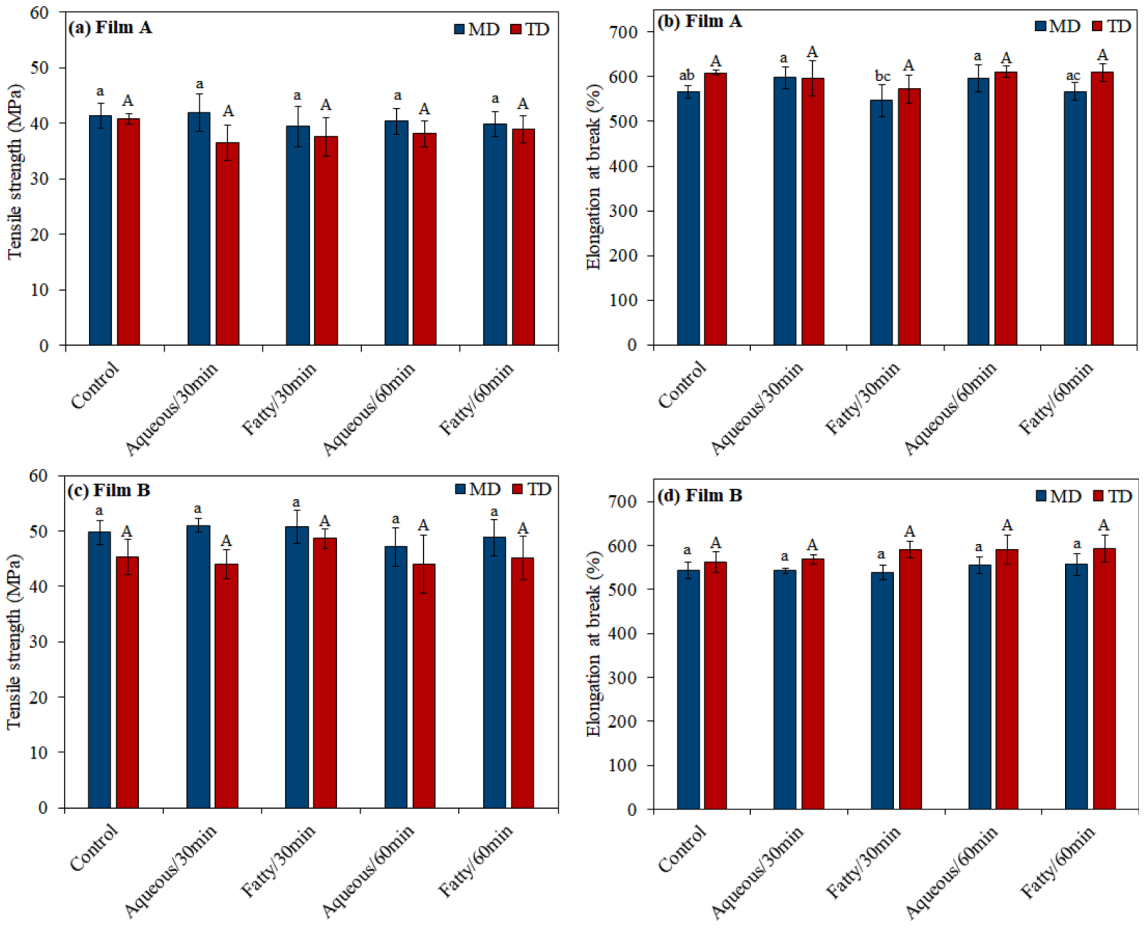

Fig. 6. Tensile strength (MPa) (a) and (c) and elongation at break (%) (b) and (d) of different packaging materials processed by ultrasound. (a) and (b) Film A: PE/PA/PE, (c) and (d) Film B: PE/PA/PE/PA/PE, MD: machine direction and TD: transverse direction.

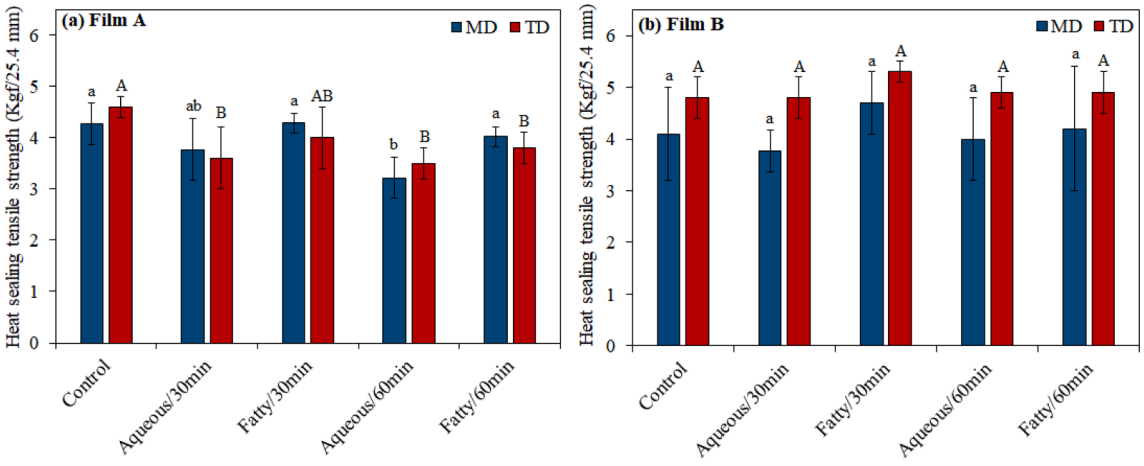

Fig. 7. Heat sealing tensile strength of different packaging materials processed by ultrasound. (a) Film A: PE/PA/PE, (b) Film B: PE/PA/PE/PA/PE, MD: machine direction and TD: transverse direction.

in the permeability of both films was observed. A significant increase in the water vapor permeability of ultrasound-processed LLDPE film for 5 min was also found in the literature, which was attributed to ultrasound-induced structural changes of the material (Ščetar et al., 2022). Nonetheless, a hypothesis that can justify this behavior is based on the possible movement of the crystalline and amorphous regions of the material (mainly of the polyethylene layers, which is the water vapor barrier material) induced by ultrasound, which, although it did not affect the crystallinity of the material, may have resulted in a rearrangement of the polymer molecules, which consequently may increase the void spaces, allowing an increase in water vapor permeation.

In relation to OTR, Film A presented values of 36.26 ± 0.22 (mL (STP).m^{-2}.day^{-1}) and Film B, 34.39 ± 2.48 (mL(STP).m^{-2}.day^{-1}). The lower OTR value of Film A in relation to Film B is associated with the greater thickness of the polyamide layers, which is the oxygen barrier material. The different ultrasonic processing conditions and the different

Table 2
Water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) of films before and after ultrasound processes.

Treatment	WVTR (g water.m^{-2}.day^{-1}) 38 °C/90% RH		OTR (mL(STP).m^{-2}.day^{-1}) 23 °C	
	Film A	Film B	Film A	Film B
Control	3.53 ± 0.15[a]	5.65 ± 0.21[b]	36.26 ± 0.22[a]	34.39 ± 2.48[a]
Aqueous/30 min	3.96 ± 0.25[a]	6.73 ± 0.51[a]	34.27 ± 0.61[a]	35.55 ± 1.85[a]
Fatty/30 min	3.87 ± 0.10[a]	6.55 ± 0.18[ab]	37.27 ± 2.40[a]	38.63 ± 1.71[a]
Aqueous/60 min	3.76 ± 0.29[a]	6.84 ± 0.50[a]	36.34 ± 0.59[a]	34.08 ± 3.11[a]
Fatty/60 min	3.65 ± 0.11[a]	6.18 ± 0.26[ab]	38.18 ± 2.00[a]	32.71 ± 1.86[a]

Film A: PE/PA/PE, Film B: PE/PA/PE/PA/PE, PE: polyethylene and PA: polyamide.
Values referring to the mean of three repetitions ± standard deviation.
[a,b,c] means followed by the same letter in the column do not differ at the 95 % confidence level ($p < 0.05$).

food simulants in contact with the packaging did not significantly influence the OTR results. This behavior indicates that the processing did not induce penetration of water from the food simulants and/or the ultrasound water bath into the packaging material until reaching the O_2 barrier layer (PA). That is because, when PA absorbs moisture, part of the hydrogen bonds are broken and new hydrogen bonds are formed with the water molecules. This phenomenon results in the plasticization of the material and consequently in the modification of the mobility of the chains, causing an impact on the properties (Marangoni Júnior, Oliveira, et al., 2020; Miri et al., 2009). Therefore, in terms of barrier, the evaluated materials can be used to package ultrasound-processed foods, as the oxygen barrier was not affected and the loss of water vapor barrier was minimal.

4. Conclusions

The two multilayer packaging materials composed of polyamide and polyethylene [PE/PA/PE (Film A) and PE/PA/PE/PA/PE (Film B)] were processed by ultrasound at 25 °C for different exposure times (30 and 60 min), compatible with food processing methods described in the literature. The samples showed no surface defects after the different ultrasound processing. In addition, they were shown to be stable in terms of their chemical structure, crystallinity, thermal properties, tensile strength, and oxygen transmission rate. Conversely, ultrasound processing induced small reductions in the heat sealing tensile strength and an increase in the water vapor transmission rate. However, these small modifications did not compromise the functionality of the evaluated materials. Hence, the results obtained in this study indicate that the packaging materials evaluated can be used to package foods that will be treated by ultrasound. Future studies are suggested covering other ultrasound processing conditions, food products, packaging materials and evaluations, including migration of compounds, to expand the knowledge about food-package-processing relationships for emerging technologies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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