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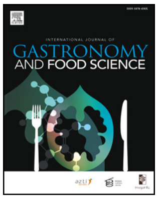

Exploring innovation in a traditional sweet pastry: Pastel de Nata

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ABSTRACT

Pastel de Nata (Portuguese custard tart) is a traditional Portuguese pastry product, consumed in several parts of the world. Its popularity has led to the emergence of new products with similar characteristics as well as new versions of *Pastel de Nata*.

The aim of this work was to develop an innovative food product inspired by *Pastel de Nata*. The product developed has a spherical shape and comprises a crispy coating of puff pastry, a filling of *Pastel de Nata* custard and, in the center, a cassia cinnamon-flavored reverse spherification. The development of the layers was made possible by the application of hydrocolloids (alginate, xanthan gum, locust bean gum and κ-carrageenan). The product developed was designated *Pastel de Nata Bonbon* (PNB).

The different layers of the *Pastel de Nata Bonbon* were optimized according to their texture and rheological behavior. The mechanical strength of the reverse spherification was tested by uniaxial compression. The texture and rheological properties of PNB custard were crucial to achieve a product with a global perception similar to the traditional product. The crispy coating of the PNB was analyzed by simple penetration. The texture profile analysis and rheological parameters were compared to the same tests performed on a traditional *Pastel de Nata*, established as reference (RPN). Analysis of the volatile compounds was performed by Headspace Solid-Phase Microextraction in Gas Chromatography – Mass Spectrometry equipment. The acceptability of the PNB was ascertained through sensory analysis by a group of untrained tasters. The acceptability of the PNB was satisfactory (52% of the tasters rated it as pleasant and 36% as very pleasant), and its flavor was associated to the traditional *Pastel de Nata* by most of the tasters (65%).

1. Introduction

Pastel de Nata is a popular traditional Portuguese sweet, nowadays consumed in different parts of the world. Its popularity has led to the emergence of new products with similar characteristics, as well as new versions of *Pastel de Nata*. The historical origin of *Pastel de Nata* dates back to the time when feminine religious orders prospered and kept secret recipes of conventual sweets (Vilhena, 2000). These remained secret until the extinction of religious orders, but with its decline, convents were forced to hire external workers and confidentiality was broken (Almeida, 1922). The historical origin of the recipe of *Pastel de Nata* is still unknown due to the existence of many recipes found in different convents, that share similar methods of manufacture and ingredients, but have different designations (Braga, 2016). This shows that the origin of the present *Pastel de Nata* is not related to a specific sweet, created in a certain convent, but it rather derives from a set of recipes with common characteristics, shared between the nuns of the various convents, despite the regulated secrecy (Algranti, 2001).

Product development is a dynamic activity in the food industry. Innovations are in part forced by general trends. Novelty and variety represent a group of drivers that continuously shape food products (Moskowitz and Hartmann, 2008; Nielsen, 2015). Each year, new products flood the marketplaces, existing over 20,000 new product launches on a global scale per year. However, the food industry displays low research and development (R&D) investments when compared to industries in other sectors and is quite conservative in the type of innovations it introduces to the market (Moskowitz and Hartmann, 2008). Disruptive or breakthrough innovations are often associated with high risk, explaining why "me too" innovations are frequently common to find. Despite the risk, innovation can drive profitability and growth (Nielsen, 2015).

Food consumption is intimately linked to cultural aspects, habits,

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Abbreviations: PNB, (Pastel de Nata Bonbon); RPN, (Reference Pastel de Nata); TPA, (Texture Profile Analysis); HS-SPME, (Headspace Solid-Phase Microextraction); GC-MS, (Gas Chromatography – Mass Spectrometry)

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lifestyles and individual neophilia/neophobia (Pliner and Salvy, 2010). Consequently, not only the slow-moving nature of the food industry can be associated to low investment in R&D, but also to the conservatism in food habits and to the tendency to dislike new foods (Guerrero et al., 2016, 2009; Vanhonacker et al., 2013). Generally speaking, unfamiliar food products or profound changes in familiar products make consumers more critical, which in turn can lead to aversion. As a result, familiarity with food can be pointed out as one of the main determinants of acceptance and is, therefore, one of the most important obstacles when introducing new food products on the market (Guerrero et al., 2016). Recently, there has been an increasingly consumers' interest in traditional food products, that are perceived as gastronomic heritage (Guerrero et al., 2009; Jordana, 2000). Food with connections to history or tradition provide an element of trustworthiness that align with consumers' desires (Zegler, 2017). This way, the trust in the familiar allows for tradition to be a source of inspiration for new products. A recent trend that has stood out in the food sector is the use of unexpected texture inputs to provide new multisensory food experiences (Zegler, 2018). Convenient and on-the-go type of products (snacks) represent another major food trend. Premium convenience food has become essential to consumers who seek sophisticated snacks (Zegler, 2019). The present work sought to incorporate the mentioned food trends into the product developed.

Hydrocolloids are a diverse group of long-chain polymers that are readily dispersive, fully or partially soluble, and prone to swell in water (Williams and Phillips, 2009). Presence of many hydroxyl groups conspicuously increases their affinity for binding water rendering them hydrophilic. In addition, hydrocolloids produce a dispersion, which is intermediate between a true solution and a suspension and exhibit the properties of a colloid. Consequently, they are termed as 'hydrocolloids' (Saha and Bhattacharya, 2010). Hydrocolloids have a wide diversity of functional properties in the food industry, such as enhancing viscosity (e.g. pie fillings), creation of gel (e.g. puddings) and foam-structures (e.g. mousses), formation of films (e.g. sausage casings), control of crystallization (e.g. ice custards), inhibition of syneresis (e.g. yogurts), texture improvement and stabilization (e.g. emulsifiers in salad dressings), among others (Nussinovitch and Hirashima, 2013).

Hydrocolloids provide functional solutions for reformulated (e.g. low-fat mayonnaise), innovative (e.g. frozen dinners), and creative products (e.g. extruded products). Although some of the hydrocolloids have been around for many years (e.g. starch, gelatin), only recently chefs are able to explore wider opportunities for creating innovative food: food preparations entrapped in gels, transparent films, crispy, crunchy, and crackly textures, spherifications, etc. (Moskowitz et al., 2009). Spherification is a technique that has been applied to produce alginate gels in the food industry, for many years. In 2003, chef Ferran Adrià brought the reverse spherification technique to the avant-garde and modernist cuisine to produce liquid core products (Fu et al., 2014; Lee and Rogers, 2013). This technique was applied in this work.

The aim of the present work was to develop a new food product inspired by *Pastel de Nata*, aligned with the new main trends for the food industry. The product developed is composed by different layers stabilized by hydrocolloids, such as alginate, xanthan gum, locust bean gum and κ-carrageenan. Each layer offers a specific texture and flavor, related to the traditional product. The product developed was designated *Pastel de Nata Bonbon* (PNB).

2. Material and methods

The PNB has a spherical shape and comprises a crisp coating of puff pastry, a filling of *Pastel de Nata* custard and, in the inner center, a cassia flavored reverse spherification.

The development of the PNB was made by layers, which were assembled in the final phase of development.

Different types of analytical tests were performed in order to characterize the product developed and its different types of textures. Additionally, a traditional *Pastel de Nata* was selected as a reference (RPN) for comparison. The selected *Pastel de Nata* won the gastronomic national contest "Best *Pastel de Nata*", 2016 edition.

2.1. Materials

Ingredients used in the preparation of PNB such as sugar, cassia, eggs, corn starch, flour, milk, lemons and puff pastry were purchased from local supermarkets. Cocoa butter in powder (Mycryo™) was purchased from Callebaut®. Calcium gluconolactate (Sosa Gluconolactato®), isomalt (Sosa Isomalt Refinado®) and hydrocolloids were bought from Sosa®: xanthan gum (Sosa Goma Xantana Clear®), alginate (Sosa Alginat®) and Sosa Elastic®, a mix of κ-carrageenan and locust bean gum.

2.2. Developing steps of Pastel de Nata Bonbon

2.2.1. Explosive core

The center of the PNB consists of a cassia infusion in a weak sugar syrup, encapsulated in a microsphere, by application of the reverse spherification technique. The reason for opting for the cassia spherification is directly related with the traditional way of eating *Pastel de Nata*: powder cinnamon/cassia is sprinkled over the *Pastel de Nata*. The explosive cassia spherification was designed to add a new and unexpected texture.

The weak sugar syrup was prepared using a water-sugar ratio of 1:1. After reaching 101 °C, cassia sticks were removed from the sugar syrup and 0.3% (w/w) of xanthan gum and 2.5% (w/w) of calcium gluconolactate were added, at room temperature, and dispersed with agitation. The gelling bath was prepared by dissolving 0.5% (w/w) alginate in mineral water. For the reverse spherification procedure, the cassia infused syrup was placed into a 1 mL measuring spoon, and the content poured into the alginate bath. Microspheres were left in the bath for 1 min to enhance the crosslinking between the sodium alginate and calcium gluconolactate (Tsai et al., 2017).

2.2.2. Custard

The layer of the PNB covering its core is an adaptation of the *Pastel de Nata* custard's traditional recipe. For the custard confection, a weak sugar syrup (49% w/w) (water-sugar ratio of 1:2) infused with cassia sticks and lemon peel was prepared. Wheat flour (4.3% w/w), corn starch (0.7% w/w) and milk (6.5% w/w) were mixed together. Milk (26.2% w/w) was boiled and added to the previous mixture. Egg yolks (9.2% w/w) and whole egg (3.3% w/w) were mixed and added to the mixture previously prepared. The final mixture was heated to 85 °C. When the custard was ready and cooled down to 40 °C, 0.3% (w/w) of xanthan gum and 0.5% (w/w) of Sosa Elastic® were added and dispersed with agitation, creating a malleable but thick mixture, as reported by Casas and García-Ochoa (1999). Although at 40 °C κ-carrageenan does not form a typical gel structure, the custard showed, since the beginning of work, a pleasant texture. When a group of trained tasters were asked to compare the texture of custards prepared with hydrocolloids added at 40 and 85 °C, the tasters chose the custard with added hydrocolloids at 40 °C. Following this preference, the PNB's preparation was carried out with the selected method for custard confection.

2.2.3. Crispy coating

For the crispy layer, puff pastry was placed in a paper-lined tray and baked in an oven at 180 °C, for 15 min. Once cooked, it was allowed to cool to room temperature and was then crushed in a food processor. After crushed was then mixed with 6.5% (w/w) of isomalt and baked again at 180 °C, for 10 min. The objective was to cover puff pastry pieces with melted isomalt to keep the puff pastry crispy.

2.2.4. Assembly of the Pastel de Nata Bonbon

For the PNB to acquire a spherical shape the assembly of its layers was performed using a silicone mold suitable for culinary use. In the first stage of assembly, each semispherical concavity of the mold base was filled with custard, using a pastry bag. A cassia reverse spherification was placed on top of the custard, in each concavity of the mold. The remaining volume of the spheres was then filled with PNB custard. The mold was kept in the freezer (−18 ± 2 °C), for 3 h, to allow the spheres to be unmolded and handled while maintaining their shape. The frozen spheres were then dipped in melted cocoa butter. While the cocoa butter was still warm, the spheres were immediately coated with the crushed mixture of puff pastry and isomalt. Finally, the spheres rested for a few minutes to promote the crystallization of the cocoa butter. At the end of the process, bonbons were kept in the fridge, inside a paper box.

2.3. Characterization of the Pastel de Nata Bonbon

2.3.1. Mechanical properties

The characterization of the texture properties was performed with a texturometer, (TA.XTplus, Stable Micro Systems, UK), with a load cell of 5 kg, in a room with controlled temperature (20 ± 1 °C). Three types of tests were performed: i) Uniaxial compression test, applied to the spheres of cinnamon syrup; ii) Simple penetration test, applied to the finished PNB, and iii) TPA (Texture Profile Analysis) applied to the custards of the PNB and RPN. In all the cases at least ten replicates were performed.

All measurements applied on the characterization of the PNB and the RPN texture and rheological behavior were performed on samples with controlled temperature, set to 20 °C. Before all measurements, the samples were placed in a controlled-temperature room at 20 °C for 30 min, to equilibrate.

Uniaxial compression tests: Tests were performed on the reverse spherification prepared in 2.1.1. The test aimed to evaluate the impact of time of the gelling bath (1, 5, 10, 15 and 20 min), in their texture. Tests were performed with a 75 mm diameter (P/75) aluminum flat probe, at 0.5 mm/s.

Simple penetration tests: Firmness of the PNB was evaluated through a simple penetration test. A 4 mm diameter metal cylindrical probe (P/4) was used to puncture the PNB 20 mm deep, at a speed of 1 mm/s. The tests were performed at different time periods, with an initial test (day 1) and a final test (day 5), targeted to evaluate the influence of time on the texture of the crispy coating and on the custard of the PNB. A maximum force peak was registered as firmness (rupture of crispy coating by probe) and remaining area under the curve was calculated, representing work done by the probe as it punctured through PNB custard.

Texture profile analysis (TPA): PNB and RPN custards were placed in 20 mm × 35 mm (diameter × height) glass jars. TPA was carried out using a 10 mm diameter acrylic cylindrical probe (P/10) to puncture 6 mm into the custards, at 1 mm/s. The time interval between the first and second compression cycles was 5 s. A force vs. time graph was generated and textural parameters, such as firmness (N), cohesiveness (dimensionless) and adhesiveness (N.s) were calculated from the obtained profiles using the equipment software. The characterization assessment of the rheological properties of the custards of the PNB and the RPN was conducted using a controlled stress rheometer (MARS III Thermo Scientific, Haake, Germany), equipped with serrated parallel plates geometry (35 mm diameter, 1 mm gap) and a Peltier system for temperature control. All measurements were carried out in triplicate at 20 ± 0.5 °C.

Frequency sweep tests: In order to study the linear viscoelastic behavior of the custards, dynamic tests were carried out in a range of 0.01–100 Hz, within the linear viscoelastic region (LVR), previously determined for each sample. To estimate the complexity of the entanglement network developed by the macromolecules, Plateau modulus (G_N^0) was calculated according to:

$$G_N^0 = G'(\omega)_{\tan\delta \to min} \tag{1}$$

where the value of G_N^0 is the value of G' obtained for the minimum value of $\tan\delta = G''/G'$ ratio (Wu, 1989).

Shear rate flow tests: To determine the apparent viscosity (η_a) of the samples, shear rate flow tests were conducted using a continuous ramp from 0.01 to 1000 s^{-1}. The slope of the curve (viscosity (η) in function of shear rate ($\dot{\gamma}$)), was fitted with the power law fluid model (Ostwald de Waele) according to Ahmed et al. (2017):

$$\eta_a = K \times \dot{\gamma}^{n-1} \tag{2}$$

where η_a is the viscosity at any specific shear rate (Pa.s), $\dot{\gamma}$ is the shear rate (s^{-1}), K the flow consistency index (Pa.s^n) and n the flow behavior index (power law index) (dimensionless). The flow behavior index n provides information about the extent of the shear-thinning behavior of the samples: $n < 1$ indicating shear-thinning behavior; $n = 1$ is a Newtonian flow behavior; $n > 1$ indicating shear-thickening behavior. The values for the flow behavior index n, and the consistency index K were obtained from plots of log viscosity versus log shear rate, according to:

$$log\eta_a = logK + (n-1) \times log\dot{\gamma} \tag{3}$$

2.3.2. Water activity and brix measurements

Water activity (a_w) measurements were performed on the reverse spherification, on the custards of the PNB and the RPN. Water activity was measured using a hygrometer (HygroPalm HP23-AW, Rotronic). Ten replicates were performed for each set of samples, at 20 ± 1 °C.

Measurement of Total Soluble Solids (TSS) – Brix Refractometry (°Brix) was performed on the sugar cassia infused syrup (before being encapsulated) and on the custards of the PNB and the RPN. TSS was measured using a portable refractometer (PAL-1, USA). Ten replicates were performed for each set of samples, at 20 ± 1 °C.

2.3.3. Gas chromatography

The volatile compounds of the PNB and the RPN were extracted by combination of headspace solid-phase microextraction (HS-SPME) and gas chromatography–mass spectrometry (GC–MS), with a GC equipment (Model 6850, Agilent Technologies, USA) coupled to a mass spectrometer (5975C VL MSD).

For the sample's preparation PNB and RPN were frozen in liquid nitrogen and crushed into powder. For each sample, 8 g were weighted into 10 mL glass vials. NaCl 30% (w/w) was added to each sample to reduce the solubility of organic compounds and increase the volatile's extraction. Prior to the volatile's extraction, the vials with the samples were conditioned in an ultrasound device and subjected to 37 kHz, for 10 min at 60 °C. For extraction, PDMS-DVB (65 µm) fiber (Sigma-Aldrich® Supelco SPME Fiber Assembly Polydimethylsiloxane/Divinylbenzene), previously conditioned according to the manufacturer's instructions, was exposed to the vial's headspace with extraction time of 45 min, at 60 ± 2 °C. Four replicates of each test were performed.

The identified compounds were assigned according to their mass spectrum and retention indices (RI). Their mass spectra were compared to those present in the reference database (NIST Mass Spectral Data 14), being considered for the present work only the ones with good adjustment (Match > 850). RI were obtained from the NIST software. To determine the key volatile compounds, the percentage ratio of the peak area of the compound to the total area of the chromatogram and its Odor Threshold Value (OTV) were taken in consideration (Brevard et al., 2011; Van Gemert, 2011).

2.3.4. Sensory analysis

Sensory analysis tests (acceptance tests) were performed on the PNB by a group of 33 untrained tasters. The evaluated PNB's attributes were:

texture, flavor, color, aroma, appearance, global appreciation, as well as purchase intention, using a 5-point hedonic scale. The tasters, being unaware of the type of product and its ingredients were asked to identify (if found) any flavor associations between the PNB and other traditional Portuguese desserts.

2.4. Statistical analysis

Analysis of variance was applied to the experimental data. ANOVA was applied on statistical analysis of the effect of gelling time of the reverse spherifications on the firmness of the alginate gel. T-test was applied in all the comparisons between PNB and RPN. Tuckey post hoc test was used to reveal means significantly different. Results were considered significant when $p < 0.05$. The statistical analysis was performed using Minitab 18.1 software (Penn State University, Pennsylvania, PA, USA).

3. Results and discussion

As stated before, the multilayered PNB was designed to give a sensory experience similar to the one provided by the traditional *Pastel de Nata*. A schematic representation of PNB layers and the *Pastel de Nata* components correspondence is shown in Fig. 1.

3.1. Explosive core

3.1.1. Texture (uniaxial compression)

Prolonged contact time with the alginate solution to produce the reverse spherifications resulted in an increase of the firmness of the outer gel membrane (Fig. 2.). The increase of the mechanical resistance is a consequence of the diffusion of calcium ions into the outer periphery of the spherification. The diffusion of calcium ions through the gel network continues until it reaches a point when the amount of calcium ions inside the core of the spherification is depleted, thus being necessary to optimize the gelling time to avoid an unpleasant and firmer membrane. Kurozawa and Hubinger (2017) and Leick et al. (2010) also reported, for similar spheres, an increase of membrane firmness with the time of exposure to the gelling agents.

After 1 min, the spherifications presented a thin outer membrane which did not cause an unpleasant sensory sensation. After 5 min in the gelling bath, and despite the absence of significant differences in firmness relatively to that corresponding to a gelling time of 1 min ($\rho > 0.05$), reverse spherifications presented a firmer outer membrane that could be felt in the mouth after being burst by the teeth. For this reason, gelling bath time was set to 1 min.

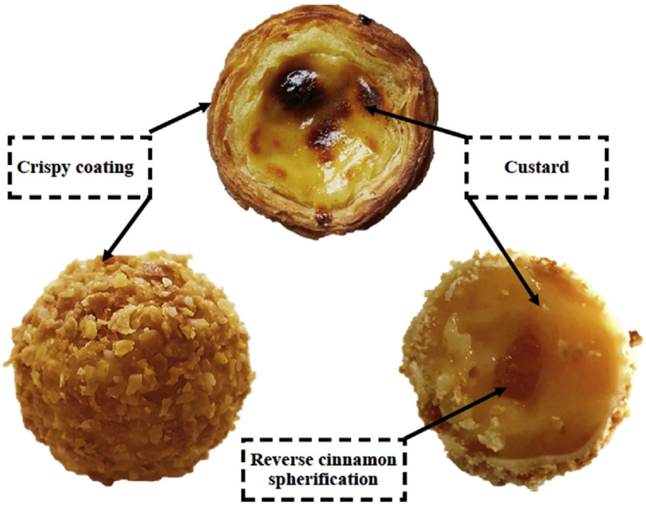

Fig. 1. Correspondence of the Pastel de Nata Bonbon layers and the components of the traditional Pastel de Nata.

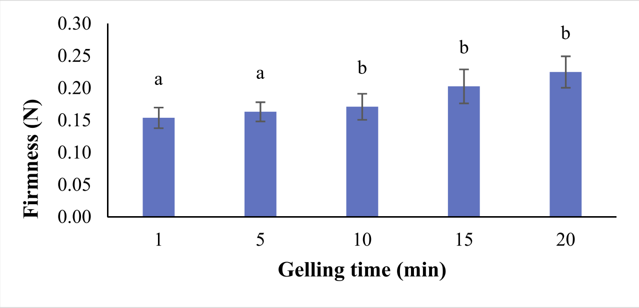

Fig. 2. Effect of gelling time of the cinnamon spherifications in the firmness of the alginate gel. Bars with different letters are significantly different at $\rho < 0.05$ (ANOVA).

Table 1
Water activity and °Brix measurements for the cassia reverse spherification and PNB custard (mean data ± SD). Means within the same line with different letters are significantly different at $\rho < 0.05$ (*t*-test).

	Cinnamon spherification	PNB custard
Water activity	0.808 ± 0.003^{a}	0.977 ± 0.744^{b}
°Brix	59.0 ± 0.321^{a}	53.7 ± 0.032^{b}

3.1.2. Water activity and TSS measurements

Water activity (a_w) and °Brix values of the cassia reverse spherification and the PNB custard are shown in Table 1. The PNB custard presented a higher a_w and a lower °Brix. Despite the significant differences, no changes were observed on the integrity of the layers when cutting the PNB after 5 days of manufacture. In the first attempts of producing PNB with reverse spherifications covered by the custard, the spherifications wrinkled due to water exit (osmosis). To prevent shrinkage of spherifications, °Brix of cinnamon syrup was increased so that water would not come out and, thereby, spherifications would not lose their bursting texture. Although different a_w of the two layers of the PNB could lead to moisture migration, the presence of high molecular weight soluble ingredients used in the PNB custard, such as proteins and hydrocolloids, created a three-dimensional network and bounded water (Barbosa-Cánovas et al., 2017).

3.2. Custard

3.2.1. Texture profile analysis

Significant differences ($\rho < 0.05$) were found in the firmness of custards from the developed PNB and from the RPN. As for adhesiveness and cohesiveness, no significant differences were found. (Table 2). The RPN custard is significantly ($p < 0.05$) firmer than the PNB. The analysis of the ingredients responsible for the formation of the three-dimensional gel network, as well as the cooking method, can allow a better understanding of the texture properties. Eggs consist of about 70% egg white (globular proteins) and 30% egg yolk (various types of low-density lipoproteins). Heat-induced gelation of eggs in the custards

Table 2
Texture properties (firmness, adhesiveness and cohesiveness) of PNB and RPN custards (mean data ± SD). Means within the same line with different letters are significantly different at $\rho < 0.05$ (*t*-test).

Texture properties	PNB	RPN
Firmness (N)	0.076 ± 0.001^{a}	0.109 ± 0.010^{b}
Adhesiveness (-N.s)	0.165 ± 0.007^{a}	0.163 ± 0.021^{a}
Cohesiveness	0.685 ± 0.014^{a}	0.682 ± 0.032^{a}

is consistent with the model of globular proteins heat gelation. As custards are cooked, proteins denature exposing their hydrophobic internal structure, and interact to form high molecular weight aggregates that can further interact with each other to result in a three-dimensional gel (Nys et al., 2011). As for starch, this ingredient is not always used in traditional *Pastel de Nata*. In the PNB custard, starch reinforced the gel by binding water. Protein-starch interactions lead to the formation of a protein-starch matrix, where hydrogen bonding take place (Alloncle and Doublier, 1991). Swollen granules increased the viscosity of the PNB custard however, by being sheared into a fluid gel its physical/mechanical/textural properties were affected, which might help explaining PNB's custard lower firmness (Kasapis et al., 2009). As for sugar, it causes an increase in the thermal transition temperature of egg proteins and subsequently raises the temperature at which they form a gel (Raikos et al., 2007). RPN custard that is cooked at higher temperatures (> 250 °C) might beneficiate from a more intense protein gel formation.

As for the method of confection of the custards, it also provides different conditions for the gel formation. The RPN was prepared according to a traditional procedure, involving the preparation of a syrup-based custard and puff pastry. In the traditional recipe, the puff pastry, previously rolled up, is cut in discs which are pressed in to muffin tins. The tins are filled with custard and pastries are baked in the oven. The PNB custard was cooked on the stovetop, under direct heat, with continuous stirring. This difference in the cooking method influences the texture properties. By stirring the PNB custard regularly, the gel is broken up, thus resulting in a weaker gel (Wolf et al., 2001). Lower firmness of the PNB custard can be explained by the stirring procedure, worsen by the dispersion of hydrocolloids with added shear.

3.2.2. Rheological measurements

Small oscillatory shear measurements (SAOS) performed for both custards can be compared from Fig. 3. For the whole frequency range, the values of the elastic modulus (G') were higher than the ones observed for the viscous modulus ($G' > G''$). Tan δ values were less than one ($\delta < 0°$) reflecting a predominance of elastic from the viscous behavior. Both custards showed increasing tan δ values with frequency, presenting a higher contribution of the viscous component at higher frequencies. The noted slight dependence of the moduli with frequency and the relative magnitude of G', being less than 10 times higher of G″, indicate that both samples behave as weak gels. In this type of gels, junction zones can be easily destroyed in a wide range of frequencies, with a frequency dependence (Williams and Phillips, 2009). In previous studies, addition of xanthan and locust bean gum to starch gels have also revealed typical weak type gels (Alloncle and Doublier, 1991).

Although the RPN custard is manufactured under quiescent conditions, resulting from a polysaccharide-protein mixed gel, the PNB custard was produced by submitting the similar structure to mechanical energy, under shear. This process results in a fluid gel that presents rheological structure of a highly concentrated suspension of gel particles of irregular shape in a continuous phase (Frith et al., 2002). The processing of the mixtures using multiple conditions (various temperature profiles and mixing shear rates) can affect the formation of the gel characteristics (Zapata Noreña et al., 2015). Addition of hydrocolloids to the PNB custard improved both its texture and stability. Given the shear force applied to the mixture, the addition of hydrocolloids can increase the shear forces applied on the granules of starch, as xanthan gum is concentrated around the swollen granules, forming with the already leached amylose, a film around their surface (Mandala and Bayas, 2004). This results in a custard that, despite being sheared, can show a similar gel structure to the RPN custard. Synergy of hydrocolloids also played a major role in the PNB custard's structure. At low temperature (between 25 and 40 °C) xanthan gum shows an ordered structure. When it interacts with locust bean gum, a high viscosity gel is formed at low total polysaccharide concentration, caused by association of xanthan double helicoidal structure with sequences of unsubstituted mannosyl residues in the galactomannan (Casas and García-Ochoa, 1999). In more detail, the likely mechanism for the synergistic behavior of xanthan gum and locust bean gum is believed to occur via the formation of mixed heterotypic junction zones, where xanthan is present as a dispersion of weakly associated microgels and locust bean may interpenetrate the microgels and cross-link them (Morris, 2007). Nonetheless, the precise nature of which is still an object of strong debate (Copetti et al., 1997; Rao, 2007). The role of κ-carrageenan is quite different. Despite the necessity of higher temperature (> 70 °C) for gelling of κ-carrageenan, in moderate concentrations and in the absence of ions, carrageenan can form weak gels, characterized by $G' > G''$ and both moduli depend on frequency (Tecante and Santiago, 2012).

The plateau modulus (G_N^0) values for the PNB custard was lower (925.8 Pa) than the value of the RPN custard (2280.0 Pa). The lower values of the PNB custard suggest that RPN custard has a stronger polymer entanglement stablished by the heat-induced protein gel, reflecting into a greater degree of structuring. Cross-linked polymers have a wide and predominant plateau region, where entanglements act like a kind of constraint to the motion of the polymer contour, thus leading to the plateau region (Sunthar, 2010). Thus, the higher plateau modulus obtained for the RPN can be associated to its ingredients' molecular interactions and its superior ability to resist flow. The RPN custard consists of a heat-induced protein gel – egg proteins represent the gelling system – and for the PNB custard the gelling system is formed by a polysaccharide-protein mixed gel, i.e., a similar heat-induced protein gel that contains a small amount of swollen starch granules as filler, as well as hydrocolloids (Morris, 2007; Rao, 1998).

The flow behavior of the custards should be strongly related with its sensory perception (De Wijk et al., 2006). From Fig. 4, it can be seen a very similar behavior of the two custards, under shearing, exhibiting a clear shear-thinning behavior, with a pronounced reduction of apparent

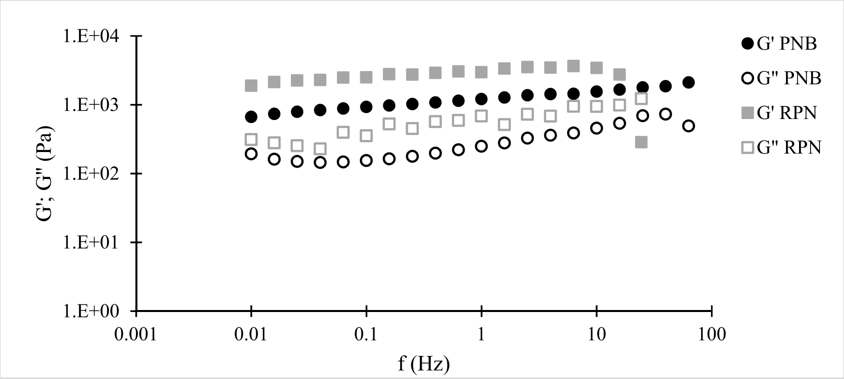

Fig. 3. Frequency sweeps of the PNB custard (PNB) and RPN custard (RPN).

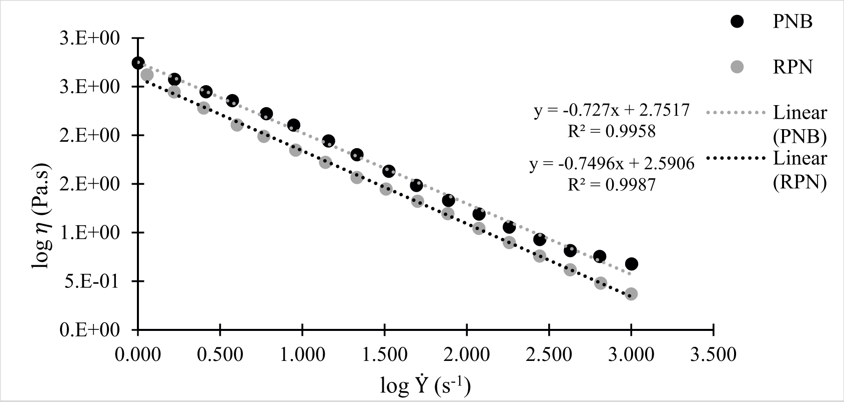

Fig. 4. Flow curves of the PNB custard (PNB) and the RPN custard (RPN).

viscosity as the shear rate increase. This is a typical behavior of many food systems, namely when the use of hydrocolloids is promoted (Alloncle and Doublier, 1991; Loisel et al., 2010). In these cases, upon shearing the chains begin to de-entangle and align along the flow (Wolf et al., 2001). The formation of polysaccharide-protein complexes occurs with protein-protein interaction (hydrophobic or electrostatic predominantly), while the polysaccharides, being naturally hydrophilic, remain in the in aqueous phase (Ghosh and Bandyopadhyay, 2012). The added hydrocolloids result in a modification of the continuous phase where polysaccharides remain located. As gelatinization begins, starch granules swell, giving rise to a concentration of the hydrocolloid within the continuous phase, resulting in a rise in its viscosity, thus explaining higher values for viscosity of the PNB custard (Alloncle and Doublier, 1991). Synergistic interactions between xanthan-locust bean gum can also help explaining the higher values of viscosity of the PNB custard (Casas and García-Ochoa, 1999).

Table 3 shows the flow parameters obtained from the power-law fitting for both custards. The PNB custard presented a higher value for K (564.5 Pa. s^n) and a higher value for n (0.273). It has been reported that an increase in the solid content enhances the consistency index and conversely reduces the flow index (Morris, 2007; Rao, 2007). In accordance with the literature, °Brix measurement of the PNB custard was found to be higher (44.7°Brix) then the RPN custard (40.4°Brix).

3.3. Crispy coating

The firmness and the work for rupture of the crispy coating was obtained by performance of the simple penetration test to the complete PNB, over a period of 5 days (Table 4.).

The force applied to the crispy coating during the simple penetration test significantly increased ($p < 0.05$) almost 5 times, between day 1 (4.255 N) and day 5 (20.509 N). This increase of firmness can be related with the interconversion of polymorphic forms of cocoa butter. Cocoa butter consists of a mixture of predominantly monounsaturated triacylglycerols. The triacylglycerols present polymorphism, being able to show different states of crystallization. Polymorphic transformation is an irreversible process that goes from the less stable to the more stable form, depending on the temperature and time involved in the process (Ribeiro et al., 2015). Modifications of the crystals, except for the form β^{VI}, can be obtained directly from the liquid state, under suitable cooling conditions. The transition $\beta^{V} \rightarrow \beta^{VI}$ is mediated only by the solid-solid transformation during storage. Thus, it can be hypothesized that the storage time of the PNB had an influence on the stability of the crystals (transition from the polymorphs β^{V} to β^{VI}), providing the increase in the firmness of the crispy coating.

Table 3
Flow parameters of the custards (K (Pa.s^n) and n) given by application of Power law model.

Sample code	Sample	K (Pa.s^n)	n	R^2
PNB	PNB custard	564.5	0.273	0.996
RPN	RPN custard	389.6	0.250	0.999

Table 4
Texture parameters (firmness (N) and work (N.s)) of the complete PNB (mean data ± SD). Means within the same line with different letters are significantly different at $\rho < 0.05$ (*t*-test).

	Day 1	Day 5
Firmness (N)	4.255 ± 0.833 ^{a}	20.509 ± 3.430 ^{b}
Work (N.s)	1.196 ± 0.178 ^{a}	3.000 ± 0.639 ^{b}

3.4. Complete Pastel de Nata Bonbon

3.4.1. Aroma profiling

The data obtained from GC-MS (Fig. 5.) allowed to identify 14 organic compounds in the PNB and 8 in the RPN. The identified key volatile compounds for the PNB were: 3-Methylbutanal, 2-Methylbutanal, D-Limonene, β-Myrcene and Eucalyptol; and for the RPN were: 3-Methylbutanal, 2,4-Decadienal, Nonanal, 2-Methylbutanal and Decanal. The samples share 5 volatile compounds: 2-Methylpropanal, 3-Methylbutanal, 2-Methylbutanal, D-Limonene and Nonanal.

In the literature, 2,4-Decadienal has been found in a set of foods with associated lipids, in many cases unsaturated aldehydes: oils (Boskou et al., 2006; Molina-Garcia et al., 2017; Vermeulen et al., 2007; Warner et al., 2001), margarines and shortenings (Gassenmeier and Schieberle, 1994; Wickramarachchi et al., 2015), puff pastry (Cavillot et al., 2009; Silow et al., 2016) and bread (Vermeulen et al., 2007). Industrial puff pastries contain special margarines and/or shortenings that present fat blends of palm fats and liquid oils (Aini and Miskandar, 2007). 2,4-Decadienal is formed by peroxidation of unsaturated fatty acids and it has also been detected in cooking fumes resulting from heating edible oils such as rapeseed oil (Boskou et al., 2006). The puff pastry used on the crispy coating of the PNB (bought in a local supermarket) presents palm oil and rapeseed oil listed as ingredients on the label. However, 2,4-Decadienal was not found on the PNB. A possible explanation for its detection only on the RPN might be related to the higher quantity of puff pastry in RPN (PNB presents a smaller portion of puff pastry per product unit than RPN). However, other factors might also interfere in the compound formation. Higher baking temperature (> 250 °C) of traditional *Pastel de Nata* may favor linoleic acid autoxidation (Maarse, 1991), and fat used on the RPN's puff pastry might have a higher quantity of unsaturated fatty acids.

D-Limonene was identified in both the PNB and the RPN however, it does not constitute a key volatile compound of RPN. Allegrone et al.

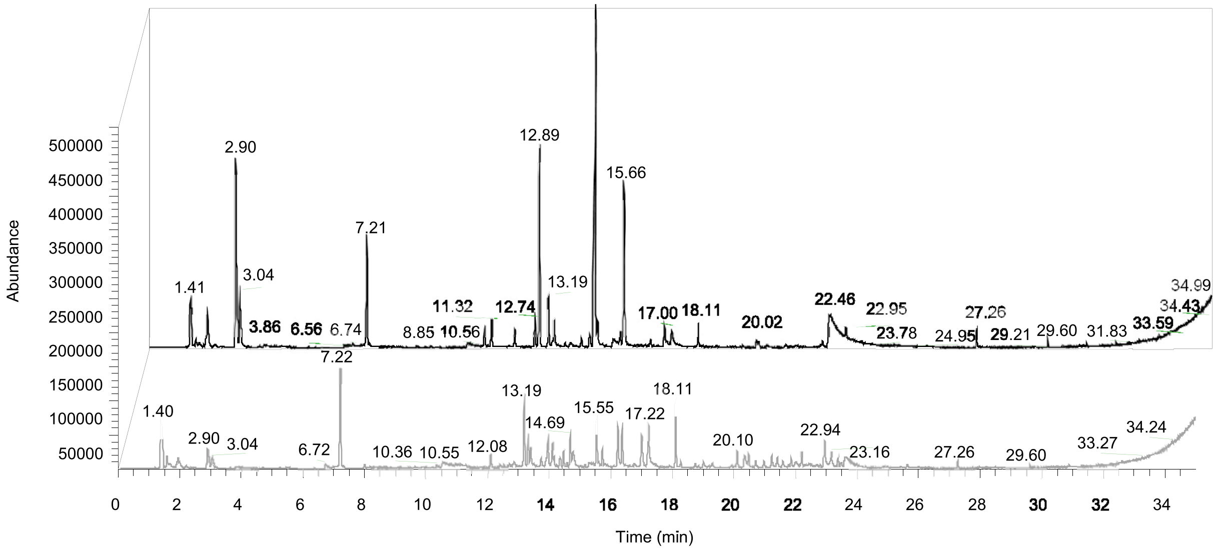

Fig. 5. Volatile compounds profile of PNB (on top) and RPN (on bottom) by HS-SPME-GC-MS.

(2006) identified D-Limonene and other monoterpenes (such as β-Pinene, β-Myrcene, α-Pinene and γ-Terpinene) in lemons. Among the monoterpenes found, D-Limonene was the most abundant. Zhong et al. (2014) identified the monoterpenes as the main components of the lemon flavor, with D-Limonene being the most abundant volatile compound (Zhong et al., 2014). All the monoterpenes mentioned above were found in the PNB. The presence of these volatile compounds, as well as D-Limonene in the PNB, can be associated to lemon which was used on the PNB (lemon peels were used in the preparation of the custard and the reverse spherification). The mentioned monoterpenes were not found in the RPN however, the presence of D-Limonene might be explained by a more moderate use of lemon peels in the flavoring of RPN's custard.

Cinnamaldehyde was only found on the PNB. In the literature, Cinnamaldehyde has been identified in cassia essential oils and barks (Maarse, 1991). In the confection of the PNB, the cassia was applied in the preparation of the custard and the on the reverse spherification syrup. Its absence on the RPN (the application of cinnamon or cassia is normally opted by the consumer, at the time of consumption) confirms a correct association of Cinnamaldehyde to cassia. Eucalyptol, also referred as 1-8-Cineole, is a volatile compound also found in cassia essential oils and barks (Maarse, 1991). Like Cinnamaldehyde, Eucalyptol was only found in the PNB and its absence in the RPN can also be accounted for the application of cinnamon or cassia being optional at the time of consumption of *Pastel de Nata*.

3-Methylbutanal, 2-Methylbutanal and 2-Methylpropanal compounds are branched-chain aldehydes identified as key volatile compounds in many foods (Smit et al., 2009). They are formed through the non-enzymatic degradation of Strecker that is temperature induced and occurs between amino acids and carbonyl compounds (Smit et al., 2009). Degradation of Strecker mainly produces a series of lower aliphatic aldehydes after the decomposition of Amadori intermediates in the Maillard reaction (Whitfield and Mottram, 2009). These aliphatic aldehydes, 3-Methylbutanal, 2-Methylbutanal and 2-Methylpropanal, have been found in milk which is the main ingredient of PNB and, most likely, RPN as well (Toso et al., 2002; Yue et al., 2015).

Saturated aliphatic aldehydes have particularly low threshold values. Nonanal and Decanal have a strong, fatty odor, developing a citrus note on dilution. Nonanal was found in both PNB and RPN, being one of the key volatile compounds of the latter. Nonanal has been found in lemon (de Rocca Serra et al., 2002; Zhong et al., 2014), in milk (Yue et al., 2015), and in products with fat, namely puff pastry (Gassenmeier and Schieberle, 1994). Unlike branched chain aldehydes that are formed via Strecker degradation, linear aldehydes like Nonanal and Decanal, come mainly from oxidative degradation of unsaturated fatty acids. Decanal was only found in the RPN. Like Nonanal, Decanal has been found in lemon (de Rocca Serra et al., 2002; Zhong et al., 2014) and in fats (Maarse, 1991).

3.4.2. *Sensory analysis*

Fig. 6a) shows the results of the mean values of the sensory attributes of the PNB and of its purchase intention. The highest mean value was reported for flavor (4.3), being on average classified as "Pleasant". The lowest mean value corresponds to the purchase intention (3.9) that designates "Probably would buy". Fig. 6b) presents the results for the association that tasters established between the PNB (tasters were not aware of the characteristics of the product under sensory review) and other Portuguese traditional desserts. The selection of traditional desserts was based on their common ingredients and methods of confection, which make their taste closely similar. *Pastel de Nata* flavor was associated to the PNB by 65% of the tasters.

4. Conclusion

Tests performed on the PNB allowed the characterization of its layers' textural, rheological, aromatic and sensory parameters. Tests performed on the custards revealed some differences in texture (significant differences for firmness of custards) and similarities in its rheological parameters (both custards showed a weak gel structure and shear-thinning behavior). Application of hydrocolloids allowed to obtain a final product with improved textural properties: xanthan gum allowed for freeze-thaw stability during the PNB's preparation and, together with κ-carrageenan and locust bean gum, promoted an improvement in the texture even with the gel network breaking; alginate allowed for a new texture, i.e. an explosive sphere of cinnamon. HS-SPME with GC-MS analysis showed that the PNB and RPN present key volatile compounds in common. The results of the sensory analysis allowed to conclude that the product developed was positively accepted by the tasters. The association of the PNB's flavor to the traditional *Pastel de Nata* by most of the tasters (65%) revealed a satisfactory result. Key volatile compounds found in both the PNB and the RPN might help account for the positive association of flavor.

Conflicts of interest

The authors declare no conflict of interest.

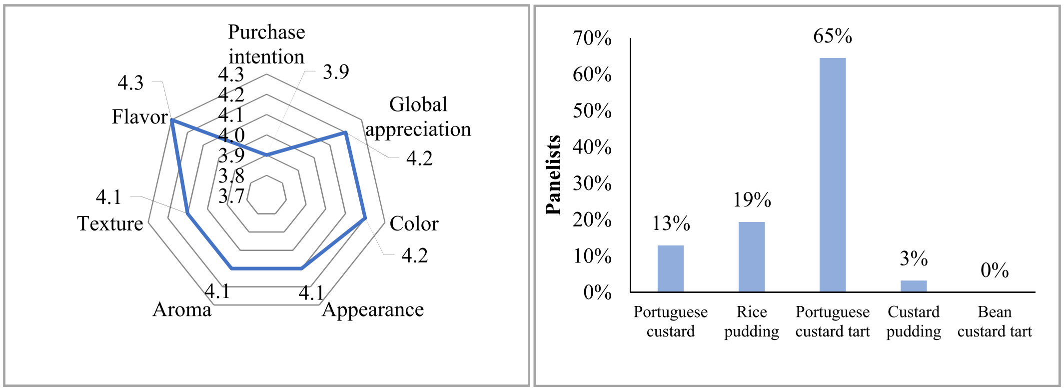

Fig. 6. a) Sensory attributes and intention of purchase of the bonbon. Scores for attributes and global appreciation: 5 - Very pleasant, 4 - Pleasant, 3 - Indifferent, 2 - Unpleasant, 1 - Very unpleasant. Scores for purchase intention: 5 - I would certainly buy, 4 - I would probably buy, 3 - I am in doubt if I would buy, 2 - I would probably not buy, 1 - I would certainly not buy. b) Association between the bonbon and traditional Portuguese desserts: Leite-creme (Portuguese custard), Arroz-doce (rice pudding), Pastel de Nata (Portuguese custard tart), Tigelada (custard pudding), Pastel de feijão (bean custard tart).

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