Effect of hydrocolloids on low-fat chocolate fillings

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Abstract The increase of diseases arising from nutritional misbehaviors in industrialized countries has caused a larger awareness for nutritional balanced products by the consumer and, consequently, by food industry. One of the challenges of industry is the quest for achieving low caloric products and keeping the same sensory properties. The aim of this work was to study the effect of different hydrocolloids in the filling of low caloric pralines, replacing creams by skimmed milk and lowering the chocolate content. Thirty-nine batches of low caloric fillings were prepared using six different hydrocolloids (carboxymethyl cellulose, xanthan gum, high methyl-esterified pectin, low methyl-esterified pectin, sodium alginate and iota-carrageenan), two different concentrations (0.5 and 1.0 % w/w) and three different chocolates (white, milk and dark). The rheological characterization concluded that all the low-fat fillings presented a shear-thickening behavior and both flow behavior and consistency index were correlated with hydrocolloid concentration and with the type of chocolate. The most thickening capacity for the low-fat filling was observed using alginate and iota-carrageenan. The effect of hydrocolloid on the digital image analysis presented different results, depending on the type of chocolate used in the matrix.

Keywords Chocolate · Pralines · Hydrocolloid · Rheology

Introduction

During the second half of the twentieth century, an increase of obesity in industrialized countries was observed, along with a larger incidence of diabetes and cardiovascular diseases. Although these diseases have a genetic component, there is a cause and effect relationship between energy intake and storage of excess energy as body fat (Beckett 2009). Nowadays, consumers are more health conscious and respond to the call for a diet that contains low fat, low sugar and low salt (Cheng et al. 2008), challenging industry to present nutritionally balanced products but maintaining the same sensory properties. The factors that contribute to a larger energetic density of foods and make them more leaning to obesity are fat, sugar, alcohol, protein content but also its daily intake. Due to the larger energetic density of fats (9 kcal/g), food products with larger content of fats are more responsible for obesity increase than food products rich in carbohydrates (4 kcal/g), proteins (4 kcal/g) or even alcohol (7 kcal/g) (Beckett 2009). Considering sensory properties, the effect of cocoa butter over viscosity affects directly the texture of chocolate, including smoothness and creaminess but also the release of flavors, which means that the same chocolate with the same cocoa content and even the same flavor profile...
can cause different sensory perceptions, accordingly to its texture (Afoakwa 2010). The process of sensory flavor perception of food is a dynamic process, starting in the moment when it is placed in the mouth and depending even on the tongue movements increasing shear rate and decreasing apparent viscosity due to the shear-thinning behavior of chocolate, making the release of flavors easier (Engelen et al. 2003).

In handmade chocolates, the most common type of filling is “ganache”, a mixture of chocolate and cream, where other products can be added to improve flavor or shelf life. The “ganache” is a multiphase system and consists in an emulsion of two immiscible liquids, the water present in cream and the fat present in cream and chocolate. Depending on the composition of the filling, it is possible to obtain a hydrophilic or a hydrophobic continuous phase (Wybauw 2010). For a larger stability, the emulsion must present yield stress and the forces applied by the disperse phase over the continuous phase (e.g., gravity and buoyant force) must be lower than the value of the yield stress (Rao 2007). The use of cocoa butter, and other fats, in handmade chocolates is crucial to obtain a smooth and pleasant texture to the consumer but it also contributes to a larger shelf life, due to the lower moisture content. An option to decrease fat content of emulsions is using hydrocolloids, long chain polymers, characterised by their properties of forming viscous dispersions and/or gels when dispersed in water (Saha and Bhattacharya 2010). Among the polymers, many options can be found like carbohydrates (e.g., dextrin, maltodextrin, pectin, alginic acid, etc.) but also proteins, like some vegetable proteins used for the stabilization of o/w emulsions (Franco et al. 1998; Raymundo et al. 2002). In some aspects it is possible to mimic the effect of cocoa butter. However, the use of hydrocolloids presents some limitations, like a lower aroma and a lower taste perception (Malone et al. 2003). Furthermore, a decrease of fat content will affect the dynamic profile of flavors (Druaux and Voilley 1997; Graf and De Roos 1996).

Materials and methods

Materials

Filled chocolates with low-fat filling were produced in a local confectionery (Sugar Bloom, Beja, Portugal), using tempered dark chocolate 51 % cocoa for couverture (CHD-R515-565, Sicao) at 29.5 °C. Thirty-nine batches of low-fat filling were produced using white chocolate (CDW-U2630-557, Sicao), milk chocolate (CHM-P38-565, Sicao), dark chocolate (CHD-R515-565, Sicao), commercial grade sucrose, glucose syrup (Icopa), skimmed milk (0.3 % fat) and inverted sugar (Trimoline 81 % dry extract, DGF). Six different hydrocolloids were tested, at 0.5 and 1.0 % w/w concentration, including carboxymethyl cellulose (Cekol 4000, CPKelco), xanthan gum (Keltrol, CPKelco), high methyl-esterified pectin (Unipectine RS150 Citrus, Cargell), low methyl-esterified pectin (Genu pectin type LM -101AS, CPKelco), sodium alginate (Algin, Sosa) and iota-carrageenan (Genu lacta carrageenan type LP-60, CPKelco). Additionally, a blank was prepared for each type of chocolate (white, milk and dark), with no added hydrocolloid, as the reference.

Methods

Technological methods

The preparation of low-fat fillings included the mixture of skimmed milk, hydrocolloid, inverted sugar and sucrose, followed by heating up to 90 °C, using a heating plate provided with a magnetic stirrer and according to the percentages presented in Table 1. The hydrocolloid was previously blended in sugar to avoid lumps. After reaching the temperature of 90 °C, the chocolate was included in the mixture, using a two blades hand blender to homogenize (Braun Multiquick 5MR500).

The mixture was allowed to cool down to 30 °C at room temperature. Then, about 6 g of low-fat filling were piped manually into the previously prepared dark chocolate cavities (30 mm 0x26 mm height) using a piping bag. After demoulding, the filled chocolates were kept at 25 °C for 24 h to totally crystallize the cocoa butter.

Physical tests

The rheological measurements were carried out with aVT 550 rotational viscometer (ThermoHaake, Germany) using cone- and-plate geometry at 20 °C. The measuring devices were PK1 1° (10 mm 0) and PK5 1° (50 mm 0). Shear stress ranged from 10¹ to 10³ s⁻¹. Water was pumped to the jacketed vessel of the viscometer (Grant LTD6G) to control the temperature of the samples at 20±1 °C.
during measurement. In this study the obtained flow curves were evaluated according to the rheological model of Ostwald, referred also as the Power law model, used in previous studies on chocolate (Glicerina et al. 2013). This model is represented in the following equation:

\[ \sigma' = K \gamma^n \]

where \( \sigma' \) is the shear stress (Pa), \( K \) is consistency index (Pa.s\(^n\)), \( \gamma \) is the shear rate (s\(^{-1}\)) and \( n \) is the dimensionless flow behaviour index. The evaluation of \( n \) index allows and important classification of the rheological structure of the food products in three main groups (Fischer et al. 2009): shear-thinning (\( n<1 \)), shear-thickening (\( n>1 \)) or Newtonian (\( n=1 \)).

Image analysis procedure of the produced chocolates was based on literature (Briones and Aguilera 2005; Briones et al. 2006; Nopens et al. 2008; Stoops 2011). An image analysis set up was built, using a digital camera Sony DSC-H50 (aperture \( f/7.1 \), exposure 1/13 s, ISO-400, no zoom, no flash, 3456x2592 pixel, JPEG format 24-bit sRGB) and two CIE D65 lamps (Phillips TL-D 18 W/965, Netherlands). The sample was placed on a blank sheet of paper, the camera was placed vertically 10 cm above the sample and both lamps were placed at 42 cm from the sample with an angle 45°, to avoid shades.
on sample (Fig. 1). Image was standardized with a white ceramic plate Minolta (Y = 92.7, x = 0.3159, y = 0.3324). All collected images were analyzed using the software IMAQ Vision Builder (National instruments, USA).

The first step was the extraction of the Region Of Interest (ROI) of each image, corresponding to the cross section of the filling (Fig. 2) and the surface of chocolate couverture (Fig. 3).

Second step was the adjustment of brightness and contrast, using standardized white plate Minolta. Finally, the third step was the RGB analysis of the ROI, using software IMAQ Vision Builder. The value of luminance was calculated using RGB values, according to Recommendation ITU-R BT.601-7 (ITU 2011):

\[ Y = \text{int}(0.299R + 0.587G + 0.114B) \]

Chemical analysis

The pH was evaluated at 20 ± 1 °C using a Metrohm 691 pH Meter (Switzerland). The moisture was determined using the gravimetric method 931.04 of the Official Methods of Analysis (AOAC 1990).

Microbiological analysis

Samples of filled chocolate (12 g) were diluted (1 in 10) in Ringer solution BR0052G (Oxoid, UK) and homogenised for 1 min in a Stomacher 400 Circulator (Seward, UK). A 1.0 ml aliquot of the homogenate was serially 10-fold diluted and 0.1 ml aliquots of appropriate dilutions were spread onto duplicate plates. The media for total aerobic mesophiles viable organisms was Plate Count Agar CM0325 (Oxoid, UK), incubated at 30 °C for 72 h. The media for moulds and yeasts was Rose-Bengal Chloramphenicol Agar Base CM 0549 (Oxoid, UK), incubated at 25 °C for 5 days.
Statistical analysis

All physical-chemical measurements were made in quintuplicates. The microbiological analyses were made in duplicates. The average, standard deviation and 0.95 confidence interval values were determined. Experimental data were subjected to one-way ANOVA (pairwise comparison of means with Scheffe test) in order to find differences in samples of the same type of chocolate but with different types (and amounts) of hydrocolloids. Data was analyzed using Statistica 6.0 (Statsoft, Tulsa, USA) (Alvarenga et al. 2008).

Results and discussion

Chemical properties

The use of hydrocolloids presented different results on the chemical properties of low-fat fillings depending on the chocolate used in the matrix, type and concentration of hydrocolloid. The results are presented in Table 2. The values of pH ranged between 5.55 and 6.40 and, generally, the higher values were observed in the fillings using alginate and the lower values were observed in the filling using HM pectin. The observed values of pH, as expected, were higher compared with those reported by previous studies in handmade chocolates with fruit or marshmallow filling (Pires 2007), due to the nature of the fillings composition.

The moisture of the low-fat fillings ranged from 40.1 to 45.3 %. The dark chocolate matrix presented the lowest results of moisture content, followed by milk chocolate and, finally, white chocolate. These differences can be explained by the milk content of the different type of chocolate, making more difficult the diffusion of water vapor during the gravimetric determination of moisture. The available literature presented a wide range of values for moisture, depending on the matrix used in the filling, starting from 6 % (fat based fillings) to 48 % (fruit based filling). The fillings based on emulsions, like the ganaches, present a moisture content around 1625 % (Wybauw 2010), but the values obtained in this study are higher, as a consequence of the substitution of cream by skimmed milk and also due to the lower chocolate content used in the ganache.
Physical properties

The study of rheological behavior of the fillings started with the representation of shear stress (\(\sigma\) versus shear rate \(\dot{\gamma}\)) (Fig. 4). The results show that all the low-fat formulations (white, milk and dark chocolates) presented shear-thinning behavior, as in previous studies made with reduced fat (Do et al. 2011) and full fat chocolates (Fernandes et al. 2013; Servais et al. 2003). On the other hand, the blank samples (with no added hydrocolloid) presented a rheological behavior close to a Newtonian fluid (\(n>0.87\)), similar to milk beverages (Brejnholt 2010; Yanes et al. 2002b). The Power Law model was used to determine the consistence and flow indexes, \(K\) and \(n\), respectively. The results are shown in Table 2 and significant correlations (\(P<0.05\)) with the concentration of hydrocolloid were observed in all fillings. Moreover, all hydrocolloids presented a negative correlation between concentration and \(n\) (\(P<0.05\)), on the other hand, all hydrocolloids presented a positive correlation between concentration and \(K\) (\(P<0.05\)). According to Scheffe comparison, HM pectin presented the lowest effect on the rheological parameters \(n\) and \(K\) of the fillings, especially for white and milk chocolate, probably due to the pH value of the fillings, higher than the ideal conditions (Brejnholt 2010). On the other hand, both iota-carrageenan and alginate showed the largest effect on the rheological properties, presenting the highest values of \(K\) and at the same time, the lowest values of \(n\). This effect can be due to the presence of \(Ca^{2+}\), resulting from the skimmed milk used in the preparation, which contributed to interactions with the alginate matrix known as “egg-box model” and to stronger gels when using iota-carrageenan (Helgerud et al. 2010; Blakemore and Harpell 2010), due to the interaction between iota-carrageenan and casein micelles (Yanes et al. 2002a), responsible for electrostatic bridges between molecules (Nunes et al. 2003b). The results obtained with LM pectin presented a more visible effect over rheological structure of the filling than HM pectin, because of the presence of \(Ca^{2+}\) and also the higher pH. In fact, the use of LM pectin in chocolate fillings has been studied recently in fillings with Porto wine (Almeida et al. 2005; Nunes et al. 2003a).

As expected, the results of flow index behavior presented a negative correlation with consistency, as reported in previous studies in chocolate beverages (Dogan et al. 2011; Yanes et al. 2002a) and low-fat dairy desserts (Gonzalez-Tomas et al. 2008), concluding that hydrocolloid concentration plays an essential role in the reinforcement of the matrix of the filling.

The digital image analysis of the chocolates included the analysis of the luminance of the filling (\(Y_{\text{filling}}\)) and also the luminance of couverture chocolate (\(Y_{\text{chocolate}}\)). Table 2 presents the results and Scheffe comparison test. Naturally, the fillings with white chocolate presented the highest \(Y_{\text{filling}}\) values, between 177 and 206, consequence of the light color of white chocolate. According to Scheffe comparisons, the results of the fillings using white chocolate presented no significant differences and no effect was observed on the type or concentration of hydrocolloid. The luminance of the fillings with milk chocolate ranged between 49 and 77 and presented a significant difference with alginate and xanthan gum at 1 %. The fillings with dark chocolate presented the lowest values of luminance, between 32 and 48 and presented significant difference with CMC, LM pectin and iota-carrageenan, especially in the concentration 1.0 %.

The correlation between the concentration of hydrocolloid and luminance can result of the larger water retention due to the presence of hydrocolloids, affecting the composition of the filling and the morphology of the surface. As a consequence, reflected radiation will increase and the surface will present a higher gloss and lightness (Briones et al. 2006). The results of luminance of chocolate couverture (\(Y_{\text{chocolate}}\)) are presented in Table 2. The values of luminance ranged between 63 and 81 and it was not observed an influence of the type of chocolate or hydrocolloid concentration on the luminance of chocolate couverture. Although some authors refer the influence of the filling on the appearance of chocolate couverture (Slettengren 2010), the short time period between production and image analysis (around 24 h) is not enough for measurable changes.
Table 2  Effect of type and concentration of hydrocolloid on mean values (standard deviation) of physical and chemical properties of low-fat fillings

| Hydrocolloid | %   | PH | Moisture (%) | Flow index N | Consistency K (Pa.sn) | Luminance Yfiling | Luminance Ychocolate |
|--------------|-----|----|--------------|--------------|-----------------------|-------------------|---------------------|
|              |     |    | White        | Milk         | Dark                  | White             | Milk                | Dark                | White               | Milk                | Dark                |
| Blank        | 0.0 | 6.00 (0.03) | 5.91 (0.02) | 61.5 (0.01) | 41.5 (0.02) | 42.3 (0.03) | 40.3 (0.03) | 0.88 (0.04) | 0.97 (0.05) | 0.87 (0.06) | 1.34 (0.07) | 0.88 (0.08) | 1.01 (0.09) | 177 (0.10) | 62 (0.11) | 32 (0.12) | 75 (0.13) | 75 (0.14) |
| CMC         | 0.5 | 5.89 (0.02) | 5.91 (0.02) | 61.2 (0.02) | 42.8 (0.02) | 43.1 (0.02) | 41.2 (0.02) | 0.46 (0.02) | 0.50 (0.02) | 0.56 (0.02) | 58.38 (0.02) | 41.00 (0.02) | 32.83 (0.02) | 54.9 (0.02) | 194 (0.03) | 54 (0.04) | 46 (0.05) | 81 (0.06) | 76 (0.07) | 75 (0.08) | 78 (0.09) |
| HM pectin   | 0.5 | 5.88 (0.02) | 5.73 (0.02) | 61.5 (0.02) | 42.8 (0.02) | 43.1 (0.02) | 41.2 (0.02) | 0.46 (0.02) | 0.50 (0.02) | 0.56 (0.02) | 58.38 (0.02) | 41.00 (0.02) | 32.83 (0.02) | 54.9 (0.02) | 194 (0.03) | 54 (0.04) | 46 (0.05) | 81 (0.06) | 76 (0.07) | 75 (0.08) | 78 (0.09) |
| Alginate    | 0.5 | 6.10 (0.02) | 6.33 (0.02) | 61.5 (0.02) | 42.8 (0.02) | 43.1 (0.02) | 41.2 (0.02) | 0.46 (0.02) | 0.50 (0.02) | 0.56 (0.02) | 58.38 (0.02) | 41.00 (0.02) | 32.83 (0.02) | 54.9 (0.02) | 194 (0.03) | 54 (0.04) | 46 (0.05) | 81 (0.06) | 76 (0.07) | 75 (0.08) | 78 (0.09) |
| Iota-carrageenan | 0.5 | 6.04 (0.02) | 5.90 (0.02) | 61.5 (0.02) | 42.8 (0.02) | 43.1 (0.02) | 41.2 (0.02) | 0.46 (0.02) | 0.50 (0.02) | 0.56 (0.02) | 58.38 (0.02) | 41.00 (0.02) | 32.83 (0.02) | 54.9 (0.02) | 194 (0.03) | 54 (0.04) | 46 (0.05) | 81 (0.06) | 76 (0.07) | 75 (0.08) | 78 (0.09) |
| LM pectin   | 0.5 | 6.24 (0.02) | 5.89 (0.02) | 61.5 (0.02) | 42.8 (0.02) | 43.1 (0.02) | 41.2 (0.02) | 0.46 (0.02) | 0.50 (0.02) | 0.56 (0.02) | 58.38 (0.02) | 41.00 (0.02) | 32.83 (0.02) | 54.9 (0.02) | 194 (0.03) | 54 (0.04) | 46 (0.05) | 81 (0.06) | 76 (0.07) | 75 (0.08) | 78 (0.09) |
| Xanthan gum | 0.5 | 5.83 (0.02) | 5.93 (0.02) | 61.5 (0.02) | 42.8 (0.02) | 43.1 (0.02) | 41.2 (0.02) | 0.46 (0.02) | 0.50 (0.02) | 0.56 (0.02) | 58.38 (0.02) | 41.00 (0.02) | 32.83 (0.02) | 54.9 (0.02) | 194 (0.03) | 54 (0.04) | 46 (0.05) | 81 (0.06) | 76 (0.07) | 75 (0.08) | 78 (0.09) |

*a,b,c* Means in the same column marked with different letters are significantly different (P<0.05, w=5, Scheffe test)
Fig 4 Low-fat filling flow curve using 0.5 and 1.0 % w/w concentration Legend: white chocolate (▲), milk chocolate (●) and dark chocolate (■)
Legend: white chocolate (A), milk chocolate (●) and dark chocolate (■)
The microbiological analysis included both groups moulds and yeasts (cfu/g) and total mesophiles (cfu/g). The short time period between the production of the pralines and the microbiological analysis (less than 24 h) was not enough to observe a significant and conclusive influence of both type and concentration of the hydrocolloid in the microbiological stability of the filling (data not shown).

Conclusions

Thirty-nine batches of low-fat filling chocolates were produced using white chocolate, milk chocolate and dark chocolate, comparing (1) six different types of hydrocolloids and (2) two different concentration of hydrocolloid. The characterization of the different fillings included physical-chemical parameters, rheological parameters and digital image analysis. The use of hydrocolloids in low-fat fillings did not present a major change in pH value and the only exception was the HM pectin. The moisture content of the filling was sensitive to the type of chocolate used in the matrix, but it was not correlated with the hydrocolloid concentration. The rheological characterization concluded that all the low-fat fillings presented a shear-thinning behavior (n < 1). Furthermore, the rheological parameters n-flow behavior and K-consistency index were correlated with hydrocolloid concentration and with the type of chocolate. The highest thickening capacity for the low-fat filling was observed using alginates and iota-carrageenan. The effect of hydrocolloid on the digital image analysis presented different conclusions, depending on the chocolate used in the matrix. The low-fat fillings using white chocolate, presented no correlation between luminance and concentration/type of hydrocolloid, as expected. In the case of milk chocolate, a positive correlation between luminance and concentration was observed for alginate and xanthan gum. In the fillings with dark chocolate, a positive correlation was observed for CMC and LM pectin. The results of the digital image analysis of chocolate couverture for luminance ranged from 63 to 81 and no influence of the filling on the visual properties of the chocolate couverture was detected.

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