

Critical moisture, glass transition, and color properties of hard confections enriched with eucalyptus essential oil and *Hibiscus sabdariffa* L. tincture.

Humedad crítica, transición vítrea, y propiedades cromáticas de confites duros enriquecidos con aceite esencial de eucalipto y tintura de *Hibiscus sabdariffa* L.

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Abstract The aim of this work was focused on the development of colored hard candies using crystallized sucrose, glucose, and citric acid, adding strawberry, cherry and grape flavors that were incorporated at three different levels. Extracts of *Hibiscus sabdariffa* L. (Malvaceae: Hybiscus) were used as natural colorants and essential oil of *Eucalyptus* sp (Myrtaceae: Eucalyptus), keeping the moisture content at 13,6 g/100 g and the sugars at 41,5 g/100 g with a citric acid level of 0,80 g/100 g. Flavorings were incorporated at three different levels (0,1; 0,2 and 0,3) and natural coloring of *H. sabdariffa* (0,8; 1,6 and 2,5) g/100 g and eucalyptus essential oil at 300 mg/kg. In the evaluation of the resulting formulations, the parameters of moisture and sorption isotherm at 15, 25 and 35 °C were considered, which in turn were projected through the Gordon and Taylor model, which in the end was shown to be a linear relationship. The relationships between critical moisture, glass transition temperature and water activity and the chromaticity parameters (CIELab) as a function of the added components are evaluated in general.

Keywords: candies, isotherms, chromaticity, glass transition.

Summary El objetivo de este trabajo se centró en el desarrollo de caramelos duros coloreados con sacarosa cristalizada, glucosa y ácido cítrico, adicionando aromas de fresa, cereza y uva. Se usó como colorante natural el extracto de *Hibiscus sabdariffa* L. (Malvaceae: Hybiscus) y aceite esencial de eucalipto, manteniendo el contenido de humedad en 13,6 g/100 g y los azúcares en 41,5 g/100 g, con un nivel de ácido cítrico de 0,80 g/100 g. Los aromas fueron incorporados a tres niveles distintos (0,1; 0,2 y 0,3), el colorante natural de *H. sabdariffa* (0,8; 1,6 y 2,5) g/100 g, y el aceite esencial de eucalipto en 300 mg/kg. En la evaluación de las formulaciones resultantes se consideraron los parámetros de humedad, humedad en el equilibrio e isoterma de sorción a 15, 25 y 35 °C que fueron a su vez proyectados a través del modelo de Gordon y Taylor, que a la postre se evidenció como una relación lineal. Se evalúan de forma general las relaciones entre humedad crítica, temperatura de transición vítrea y actividad de agua y los parámetros de cromaticidad (CIELab) en función de los componentes adicionados.

Palabras clave: caramelos, isotermas, cromaticidad, transición vítrea

Introduction

Candies have always been part of the human diet, and today they are part of popular gastronomy, they are confectionery products made from the crystallization of sugars and are classified into crystalline and soft. The production of sugar today and the increases in its trade and consumption, in relation to quality standards and technological development, have allowed the evaluation of confectionery products (Archaina et al., 2018; Edwards, 2003). In developed countries, sugar consumption is close to 7 kg person/year.

Hard candies have an amorphous structure, where the molecules remain in the matrix in random conditions. Products with amorphous structure have different formation; one of them is the decrease of temperature below the melting point, and another from the evaporation of the water they contain. The preparation of confectionery products is based on the preparation of concentrated sugar syrups, which undergo a cooking operation until the mixture is concentrated (Campo et al., 2018; Lesme, 2013; Hartel et al., 2010; Ergun and Hartel, 2009).

There are many factors that affect quality in confectionery production. Formulation, temperature, processing time, and moisture content of the final product are the most important factors. The use of sugar solutions in the production of hard candies makes them solid, shiny, oversaturated, supercooled, and glassy in consistency (Cardoso and Abreu, 2004; Chung et al., 1999).

Sucrose, glucose, fructose, sorbitol, and maltose may be included in the formulation of hard sugars. Organic acids such as citric, malic, and lactic acid are added to provide inversion towards the end of the cooking stage in open kettles or vacuum. Preferably, flavor is added; the product is obtained by kneading, folding, shaping, and cooling (Sanchez-Orozco et al., 2022).

The moisture content of hard candies is usually 2%. The mixtures used in the preparation are subjected to high temperatures for concentration and elimination of water. Once the mixture is concentrated, colorants, flavorings and acids are added, and finally the product is stamped, cooled, and wrapped. While soft candies are basically made of sugar, glucose, condensed milk, and fat. These candies are known as fruity, toffees and fudge whose main characteristic is to be crystallized, and do not need refrigeration during storage (Ergun et al., 2010).

Color is a quality parameter in food processing and presentation (Zellner et al., 2018). Regarding the use of natural pigments, anthocyanins are preferred in relation to other colorants from plant sources, because they present greater stability to thermal and pH changes, due to the acylation of these anthocyanins. The consumption of nutraceutical foods, such as hibiscus calyx extracts (*H. sabdariffa* L.), improve health, and prevent various diseases, this attributed in part to the activity of their anthocyanins. As an important source of anthocyanins are the calyxes of the hibiscus flower (*H. sabdariffa* L.), which are mainly consumed as refreshing drinks.

In hard candy stability studies, the inflection point of the sorption curve is used in the determination of the critical relative moisture that induces the glass transition, considered as a reversible change of a material from a glassy solid state to a rubbery liquid state by changing its temperature or moisture content (Ergun and Hartel, 2009). The glass transition temperature (T_g) of low molecular weight carbohydrates such as glucose, fructose, and sucrose has been studied as a critical factor in predicting the stability of confections and candies (Saavedra-Leos et al., 2012).

In confectionery products with low moisture content, sugars show glassy and amorphous structure, which ensure the conditions of (T_g) to have a transparent and clear appearance (Tan and Kerr, 2017).

Hard candies stored below (T_g), generally, show stability for a long-time during storage. However, when the storage temperature is higher than (T_g), the glassy structure is lost, adopting sticky characters, which negatively affect its physicochemical and sensory quality (Carpenter et al., 2012). The (T_g) is a unique property of the amorphous portion of the solid. Amorphous structures whose (T_g) is low are in a stable state, above this condition, they are in a rubbery state.

If the product is above the (T_g), the water mobility properties will be increased, the viscosity will be reduced, and with it, uncharacteristic stickiness will develop. When changes occur from the glassy to the rubbery state, there is a phase transition that causes changes in the physicochemical properties of the material. The factors that must be controlled in formulation and confectionery manufacturing processes are process temperature, hardness of the water used, and percentage of solids (Khaddour et al., 2010; Hartel et al., 2010).

Hard candies can also exhibit high or low hygroscopic properties, depending on the formulation, can rapidly gain moisture from the medium, and change the glass transition properties of the sugars. For the production of confectionery products, it is important to consider the equilibrium relative humidity parameter (X_{eq}), which allows predicting product behavior and stability. When the (X_{eq}) of the candy is higher than that of the environment, the product will give up its moisture and finally crystallize. On the contrary, if the (X_{eq}) is lower than the relative humidity of the air, then, the tendency is to hydration (Ergun et al., 2010). Hard candies are generally stable products because they have a low water content.

A specific condition of (T_g) allows to evaluate the product shelf life, avoiding stickiness of the finished candies. This parameter can be determined by using different methods such as differential scanning calorimetry (DSC), dynamic thermo-mechanical analysis (DMTA) and thermal expansion techniques (TGA). The

theoretical method for the determination of (T_g) proceeds by applying the Gordon Taylor equation, which takes into account the weights of the sugar fraction and their corresponding glass transition temperatures (Ergun et al., 2010).

Moisture content is a critical parameter in the manufacture of hard and amorphous confectionery; its availability and physical state influence physical properties, chemical stability, sensory characteristics of foods, and is linked to water activity (a_w) (Salamanca, 2012; Ouiazzane et al., 2008). The molecular mobility in the glassy state is low, due to the high viscosity of the matrix, so diffusional reactions are not expected. The (T_g) can be taken as a reference parameter to characterize properties, quality, stability, and safety of food systems. In virtue of the above, the objective of this work has been oriented to the generation of hard candies, enriched with eucalyptus essential oil (EEO), and hibiscus flower tincture extract, evaluating the effect of the composition in the parameters of critical relative moisture, sorption isotherms, glass transition, and chromatic properties.

Materials and methods

Raw Materials

High quality purified and crystallized sucrose (density 1,588 g/cm³, pH 6,95 ± 0,15 and melting point 160 - 186 °C), glucose (Globe 43 °Be), and food grade citric acid were used in the elaboration of hard candies enriched with (AEE). The extraction of (AEE) was obtained by microwave-assisted hydro distillation operations with steam drag (MWHD), in a modified clewenger equipment with capacity for 500 g, operating the system for 45 min. with 3 pulses of 15 min. at 600 - 700 and 800 Watts, on a mass of 100 g of fresh leaves. The (AEE) was stored in amber vials at 4 °C.

As for the color, a concentrate of 80 % of the natural dye of Jamaica flower (*H. saldariffa*) obtained by hydro distillation in a soxhlet system and incorporated in three concentrations (8 - 16 - 25 %) to the process mixture was used. The final determinations were made by evaluating

spectral readings at 520 and 700 nm, in a UV-Visible spectrophotometer Genesys 180 Thermo Scientific. The monomeric anthocyanin content was estimated as cyanidin-3-glucoside using the ratios given in Equation 1.

Equation 1

$$A = (A_{520} - A_{700})_{pH\ 1.0} - (A_{520} - A_{700})_{pH\ 4.5}$$
$$AT(mg/kg) = \frac{A * PM * FD * 1000}{\epsilon * l}$$

Where:

A is the change in absorbance, AT corresponds to the anthocyanin content (mg/L), for cyanidin-3-glucoside (PM molecular mass of 449,2 g/mol), and ϵ molar extinction coefficient for (26900 l/mol.cm) in 10 mm cell, with dilution factor (DF).

Formulations

In the formulation of the hard confectionery, the water content was kept constant, 13,6 % g/100 g of mixture and the fraction of 41,5 g/100 g for each of the sugar's glucose and sucrose. While citric acid was kept at 0,8 g/100 g. The concentrations of strawberry (CF), cherry (CC), and grape (CU) flavors were incorporated at three different levels for each of the component's level one (0,1), second level (0,2), and third at (0,3) g/100 g. The natural colorant of *H. sabdariffa* L. flower was added at 0,8, 1,6 and 2,5 g/100 g, and the essential oil of *Eucalyptus sp* leaves at 300 mg/kg.

Process

The candies were elaborated in the processing laboratory of the National School of Confectionery of the National Learning Service (SENA), in the Agricultural Center of Buga. The fraction of carbohydrates in each of the formulations was dissolved in water and subjected to slow cooking until reaching 130 °C and a moisture percentage of 2 to 3 %. The resulting mixture was immediately placed on a cooling table at 90 °C, and citric acid was added, which allows the initiation of the glass transition of the product.

The natural colorants were added with the AEE, the microencapsulation is propitiated in the dough that was processed in a battering machine

at 65 °C, and the formation of caramel threads is facilitated through the legalizer, in the direction of the die-cutter and the drying tunnel at 35 °C, where the glass transition of the confectionery was completed.

Physicochemical parameters

Moisture content. A 30 g sample fraction of each of the candy formulations was subjected to desiccation allowing estimation of moisture content, by weight loss in a vacuum oven at 60 °C and 30 millibars, for 24 h following the AOAC 934.01 method (AOAC, 2006). Moisture content was determined in triplicate for each sample and corresponds to the amount of water lost by evaporation. The determinations allowed estimating the initial moisture content of the samples, which were then evaluated in the determination of sorption isotherms.

Color. The color evaluations of the processed confectionery were carried out on the Color Flex EZ M - 45/0 unit in relation to the CIELab system (1976) parameters of red/green (a^*), yellow/blue (b^*), chroma (C) and hue angle (h) chromaticity.

Sorption isotherm. The critical moisture of each of the formulations was evaluated from the sorption isotherms at 15, 25 and 35 °C with the use of hermetic desiccation systems; The formulations were prepared with saturated salts of lithium chloride (LiCl), potassium acetate (AcK), potassium carbonate (K_2CO_3), magnesium chloride ($MgCl_2$), sodium chloride (NaCl), potassium nitrate (KNO_3), and potassium sulfate (K_2SO_4). The salts used were reagent grade (Merck). Five units of dry caramel were placed inside the drying units, estimating the weight of water retained (P_0), (Wolf, 1985). The sorption isotherms relate the equilibrium moisture content reached in relation to the thermodynamic activity of water in the product at constant temperature in the interval (aw) from 0,700 to 0,906.

Critical relative humidity (CRH). This parameter was determined by mathematical operations of extrapolation through linear relationships and intersection of the

extrapolated linear portions, before and after the critical point. Taking into account the glass transition temperature which is considered as the transition between adsorption on the surface and absorption in the matrix for the marginal moisture content, which consequently allows dividing the isotherm into two portions: before and after the critical point.

Isosteric heat. The net isosteric heat of sorption (q_{st}) was estimated from the heat of vaporization of water as a function of the total heat of sorption (Q_{st}), with the experimental data of aw and temperature using Clausius-Clayperon Equation 2, assuming that the net isosteric heat of sorption (q_{st}) is independent of temperature (Equation 2).

Equation 2

$$\ln(a_w) = -\frac{q_{st}}{R} \left[\frac{1}{T} \right] + K$$

Here $q_{st} = Q_{st} - (\lambda w)$, (a_w) is the activity of water. Latent heat of vaporization of pure water (kJ/kg), T the absolute temperature, K is a constant and R constant of gases (0,4618 kJ/kg). The heat of vaporization of pure water (λ) was estimated from the relation = [6887 - 5,31 T], (Silva et al., 2002).

Glass transition (T_g): The model proposed by Gordon and Taylor (GT) linear form allows to estimate the glass transition temperature assuming a dissolution approach between sugars and water fraction in candies enriched with eucalyptus essential oil. In the glass transition temperature of water (T_{gw}) and glucose (T_g) components in °Kson (138) and 311,8 °K, respectively, and 315,5 °K for sucrose (Yilmaz and Gökmen, 2019). X_w represents to wet fraction in the samples. In the variation of (T_g) with moisture, the estimated values using the model, (GT), correspond to 5.0886 for k and 49.375 (T_{gs}) of anhydrous solids (Tan and Kerr, 2017; Hartel et al., 2010).

Equation 3

$$T_g = \frac{((1-X_w)T_{gs})+(kX_w-T_{gw})}{(1-X_w)+(kX_w)}$$

The moisture at equilibrium (X_{eq}) after the weight gain measurements at the end of the sorption isotherm evaluations was estimated from the

relationship given in Equation 4, where P_o and W_o , represent the initial weight and moisture fraction of the confection and is the weight gain at the end of the sorption isotherm evaluation.

Equation 4

$$X_{eq} = \frac{P_o W_o + \Delta P}{P_o (1 - W_o)}$$

Statistical analysis

Statistical evaluation of the data was carried out using SPSS software (SPSS Inc., Chicago, IL, USA). In the data obtained, the effect of the parameters on the results was determined by analysis of variance and the differences between means ($p < 0,05$) were determined by Duncan's multiple comparison test.

Results and discussion

Equilibrium isotherms in syrups or syrups used in the production of hard candies allow to evaluate the effect of water on the matrix containing it. The composition of hard candies and the water retention have a crucial effect on the adsorption properties and diffusion rate of the added components. The amount of ingredients in the starting material of hard candies has an important influence on the hygroscopicity of the product. The equilibrium moisture and water content of the hard candies, after being exposed to the environment (temperature and relative humidity), present significantly different values in the evaluated isotherms (0,041 to 0,314 at 15 °C), (0,037 to 0,321 at 25 °C) and (0,032 to 0,341 at 35 °C), which at the end are consolidated as values equivalent to the critical relative humidity, represent the effect of the syrups used in the glucose and sucrose formulations evaluated, and present inflection points in the sorption isotherms in relative humidity environments (54,9 % ; 52,7 a 50,7 %).

The shape of the sorption curve is indicative of how the water remains bound or adhered. In the isotherms of hard candies, monolayer water (zone I) is present, with high stability, and can be considered as a constituent

part of the food since it is not freezable at any temperature. The water in zone II remains weakly bound, acting as a plasticizing agent that promotes the swelling of the solid matrix; and in zone III it is present as free water contained in the micropores, available for metabolic reactions and microbial growth. Sucrose in crystalline state exhibits a type III isotherm, while in the amorphous state it has a type II behavior. On the other hand, glucose syrup has plasticizing effects that allow water retention, in addition to its slight anti-crystallization effect.

The relationships are far from linear and are presented exponentially (Table 1, Figure 1). The moisture at equilibrium (X_{eq}) in relation to the water activity (a_w) as a transition boundary

between zones I and II at 15 °C; is presented at 0,130 g water/g dry solids and 0,6069 (a_w), at 25 and 35 °C, with slightly lower values (0,100 g water/g dry solids and 0,5456 (a_w); 0,07950 g water/g dry solids and 0,5456 (a_w), respectively) as evidenced in (Table 2, Figure 2).

Generally, jams are presented as amorphous structures where sugars, initially present as viscous solutions, dehydrate until they reach the glass transition temperature (T_g). The natural colorants, which were added with the essential oil of eucalyptus, favor the microencapsulation in the mass, also, they exert a plasticizing effect. The content of *H. sabdariffa* as cyanidin-3-glucoside is around 1250 ± 25 mg/kg.

Table 1

Generalized relationships for sorption isotherms of hard candies enriched with eucalyptus essential oil and H. sabdariffa dye

| Temperature °C | Expressions | R ₂ |
|----------------|---|----------------|
| 15 | $X_{eq} = 10,392(a_w)^6 - 28,114(a_w)^5 + 29,5(a_w)^4 - 14,48(a_w)^3 + 3,36(a_w)^2 - 0,193(a_w) + 0,043$ | 0,999 |
| 25 | $X_{eq} = -4,360(a_w)^6 + 12,2(a_w)^5 - 13,3(a_w)^4 + 8,091(a_w)^3 - 2,749(a_w)^2 + 0,5651(a_w) + 0,0085$ | 0,999 |
| 35 | $X_{eq} = 4.915(a_w)^6 - 16,0(a_w)^5 + 19,7(a_w)^4 - 10,35(a_w)^3 + 2,276a_w^2 - 0,0460(a_w) + 0,028$ | 0,998 |

Note. X_{eq} : moisture at equilibrium; a_w : water activity. Own elaboration.

Table 2

Water and moisture activity in the equilibrium of oil-enriched hard candies enriched with eucalyptus essential oil and H. sabdariffa colouring agent.

| | Sales | | Temperature | | | |
|--------------------------------------|-------|----------|-------------|----------|-------|----------|
| | 15°C | | 25°C | | 35°C | |
| | a_w | X_{eq} | a_w | X_{eq} | a_w | X_{eq} |
| LiCl | 0,071 | 0,041 | 0,070 | 0,037 | 0,067 | 0,032 |
| CH ₃ CO ₂ K | 0,115 | 0,049 | 0,113 | 0,047 | 0,112 | 0,041 |
| MgCl ₂ *6H ₂ O | 0,244 | 0,065 | 0,224 | 0,061 | 0,208 | 0,055 |
| K ₂ CO ₃ | 0,332 | 0,081 | 0,322 | 0,069 | 0,321 | 0,062 |
| NaBr | 0,445 | 0,092 | 0,441 | 0,087 | 0,433 | 0,082 |
| CoCl ₂ | 0,549 | 0,112 | 0,527 | 0,098 | 0,507 | 0,084 |
| NaCl | 0,655 | 0,152 | 0,634 | 0,139 | 0,614 | 0,122 |
| KCl | 0,753 | 0,187 | 0,758 | 0,202 | 0,752 | 0,213 |
| KNO ₃ | 0,852 | 0,257 | 0,835 | 0,264 | 0,821 | 0,262 |
| K ₂ SO ₄ | 0,906 | 0,314 | 0,901 | 0,321 | 0,894 | 0,341 |

Note. a_w : Water activity. X_{eq} : Equilibrium moisture. Own elaboration.

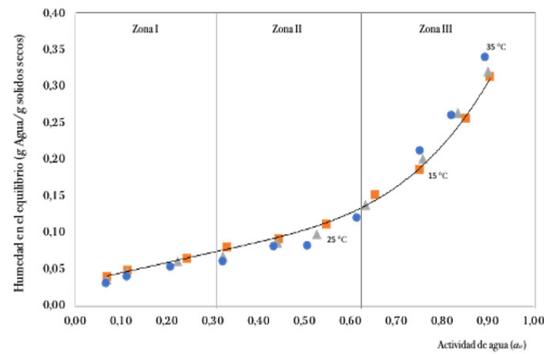


Figure 1

Sorption isotherms of hard candy at 15, 25 and 35 °C

Note. Own elaboration.

Sugar syrups are saturated solutions that increase in concentration during the candy making process as the boiling point of the solution increases. The thermal effect results in thickening, reduction of bubble size, and modification of rheological properties; where viscosity becomes consistency, then texture, and the sugars added are a function of moisture content. The addition of fructose and sucrose provide sweetness sensations and a stabilizing effect. The estimated values for (T_g) are of the order of 23 and 30 °C at temperatures of 15, 25 and 35 °C, which are consistent with (a_w) of 0.40, and (X_{eq}) of 0,08 and 0,10.

adsorbed water; therefore, it is a measure of the physicochemical stability of the food matrices, indicating the binding strength between the water molecules and the surface of the candies. For the case of hard candies, the (Q_{st}) decreases with increasing equilibrium moisture. As the moisture fraction increases, the value of the parameter decreases, because water occupies fewer active sites (Figure 3). The equilibrium moisture is maintained up to 21 days of storage. The estimated value for (Q_{st}) is of the order of 4915 kJ/kg, the net isosteric heat of sorption (q_{st}) from 76 to 327 kJ/kg, and the relationships between $\ln(a_w)$ and $1/T$ are linear (r^2 0.995). The relationships between (X_{eq}), (a_w) and (T_g) for each of the temperatures evaluated in this work for the candies enriched with essential oil and natural dye are shown in Figure 4.

The evaluation of the isosteric heat of sorption (Q_{st}), as a property of the system, is an indication of the magnitude and state of the

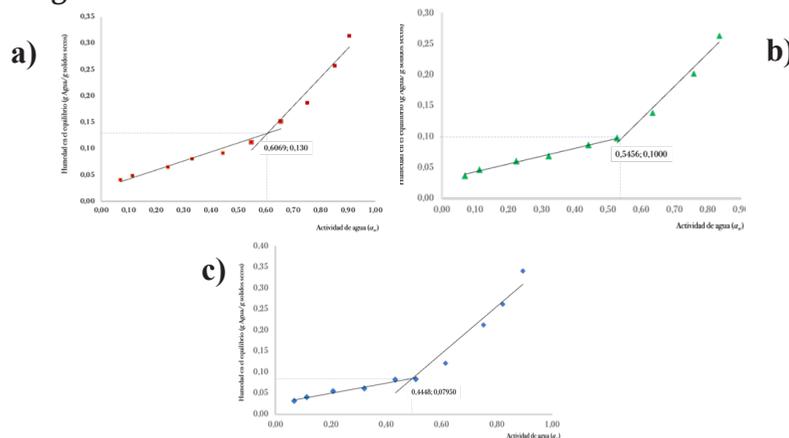


Figure 2

Sorption isotherm and critical moisture profile of hard candies enriched with eucalyptus essential oil and H. sabdariffa dye at three temperatures.

Note. a) 15 °C; b) 25 °C; c) 35 °C. Own elaboration.

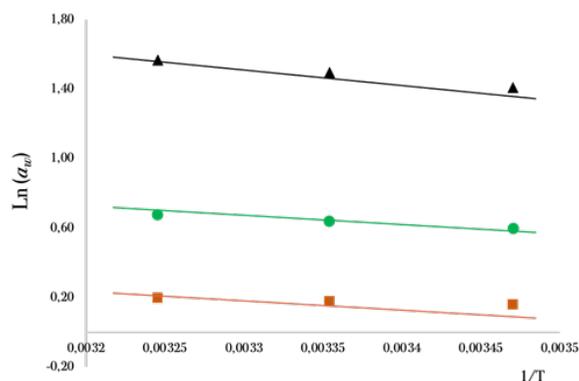


Figure 3

Linear representation of $\ln(a_w)$ versus $1/T$ of the Clausius-Clayperon equation for the estimation of esoteric heat of sorption.

Note. Own elaboration.

The effect of (X_{eq}) on (T_g) , considering the Gordon and Taylor model, is presented as a

linear relationship of the form $T_g = [-145,98(a_w) + 64.8]$ with $r^2 (0,987)$.

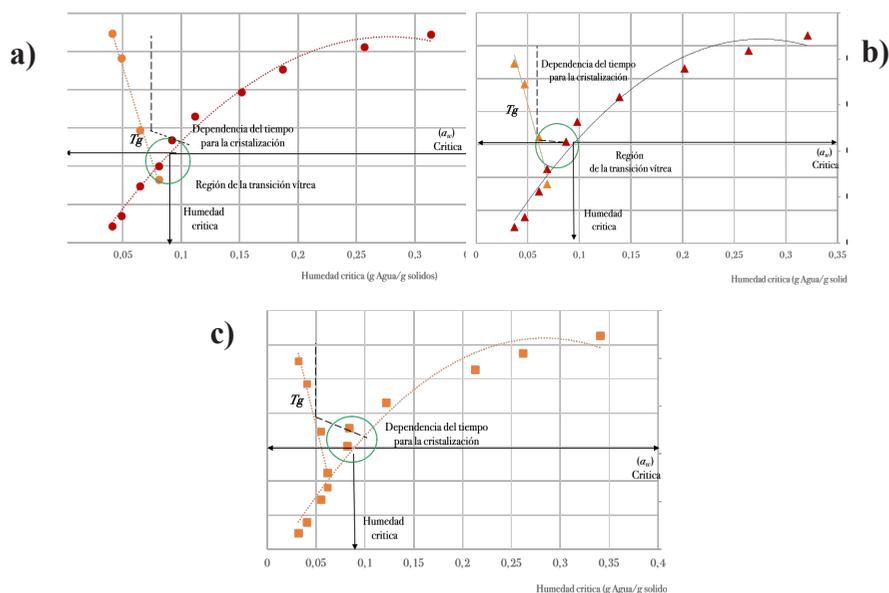


Figure 4

Effect of water-moisture activity on the equilibrium and glass transition temperature of hard candies enriched with eucalyptus essential oil

Note. Own elaboration.

The glass transition temperature (T_g) is defined by the solids content and the moisture retained at the end of the preparation process and is consolidated as a determining parameter for storage stability, as it is related to phase transitions. In a system of components (water/solids) a phase transition occurs when the temperature of the environment is reduced. The freezing point of the mixture is delayed

relative to the pure solvent. Water is the main plasticizer of amorphous carbohydrates and other biological systems; at low concentration it significantly decreases the (T_g) values. Also, it interacts with the hydrophilic groups in the matrix and its plasticizing effect translates into increased free volume and molecular motion, so the more water present, the (T_g) values of the system approach the (T_{gw}) value of water.

In the thermal descent, a solid phase is generated whose melting point depends on the proportion and type of components immersed in the matrix. When the total fraction of solutes is in the majority, and water is the second component, the reduction of the freezing point is generated. The curves for (T_g) in a state diagram are a function of the solid mass fraction of the moisture content, which mainly delimits the two possible physical states that an amorphous material with low moisture content can have. Above (T_g) it will be in a rubbery state and below this, in a glassy state. The curves for (T_g) acquire low values when the matrix has a high-water content, which represents the vitrification of a solution, due to the effect of the instantaneous decrease in temperature below the glass transition temperature of pure water (T_{gw} at -135 °K) (Salamanca, 2012).

In relation to the chromaticity parameters and taking into account the components added as strawberry (C_F), cherry (C_C) and grape (C_U) flavoring, which were incorporated at three levels (0,1, 0,2

and 0,3) g/100 g, together with eucalyptus oil and natural *Hibiscus* flower coloring, are shown in Table 3. The formulation designed with strawberry flavor C_{1F1} at 0,1 g/100 g presented higher values for the luminance parameter (L), followed by the cherry formulation (C_{1C2}) at 0,2 g/100 g and grape (C_{1U3}) with 0,3 g/100 g. In the other formulations the values of (L) were distributed between $21,7 \pm 0,20$ and $28,5 \pm 3,20$. The red/green chromaticity values (a^*) were lower in the formulations with higher (L) values and higher in the remaining formulations.

The profile of the ratio (a^* , b^*) allows to discriminate the values of chromaticity of the processed candies according to the added coloring agent between groups: Candies with strawberry (C_{1F1}) added at 0.1 g/100 g, cherry (C_{1C2}) at 0.20 and grape (C_{1U3}) 0.30 (Figure 5). The second for formulation candies (C_{3F}), (C_{3C}) and (C_{2F}), with a third heterogeneous group (C_{2F}), (C_{2c}) and (C_{2U}), these differences can be explained taking into account the additions to 0.8; 1.6 and 2.5 g of *Hibiscus*.

Table 3

Chromaticity parameters of hard candies enriched with eucalyptus essential oil and hibiscus flower natural coloring

| Formulation | Chromaticity parameters | | | | | |
|-------------|-------------------------|-------------------|-------------------|-----------------|-----------------|-----------------|
| | S | L | a^* | b^* | C_{ab} | h_{ab} |
| C_{1F1} | | $42,3 \pm 3,40^a$ | $3,60 \pm 0,30^a$ | $8,55 \pm 0,90$ | $9,30 \pm 1,00$ | $67,3 \pm 0,1$ |
| C_{1C2} | | $31,7 \pm 4,00^b$ | $3,50 \pm 0,20^a$ | $8,40 \pm 0,90$ | $9,06 \pm 0,80$ | $67,2 \pm 3,3$ |
| C_{1U3} | | $30,7 \pm 3,30^b$ | $3,65 \pm 0,20^a$ | $8,34 \pm 0,60$ | $9,10 \pm 0,60$ | $66,3 \pm 0,60$ |
| C_{2F} | | $26,7 \pm 4,40^b$ | $6,34 \pm 2,20^b$ | $8,00 \pm 2,20$ | $10,2 \pm 3,10$ | $52,3 \pm 2,90$ |
| C_{2c} | | $25,7 \pm 1,70^b$ | $7,25 \pm 0,90^b$ | $8,98 \pm 0,40$ | $11,6 \pm 0,91$ | $51,2 \pm 3,10$ |
| C_{2U} | | $28,5 \pm 3,20^b$ | $7,60 \pm 0,70^b$ | $9,80 \pm 0,30$ | $12,4 \pm 0,10$ | $52,2 \pm 3,60$ |
| C_{3F} | | $21,7 \pm 0,20^d$ | $8,10 \pm 1,30^b$ | $6,60 \pm 1,10$ | $10,4 \pm 1,71$ | $38,9 \pm 0,80$ |

| Formulation | Chromaticity parameters | | | | | |
|------------------|-------------------------|-----------------------|--------------------------|-------------|-----------------|-----------------|
| | S | L | a* | b* | C _{ab} | h _{ab} |
| C _{3C} | | 24,3±1, ^b | 8,18 ± 0,41 ^b | 6,85 ± 0,70 | 10,7 ± 0,70 | 39,8 ± 1,40 |
| C _{3EU} | | 26,2±0,3 ^b | 8,85 ± 0,10 ^a | 6,90 ± 0,10 | 9,78 ± 2,60 | 37,9 ± 0,50 |

Note. a, b, c, d: significance levels. L: luminance; a*: red/green chromaticity; b*: yellow/blue chromaticity. Own elaboration.

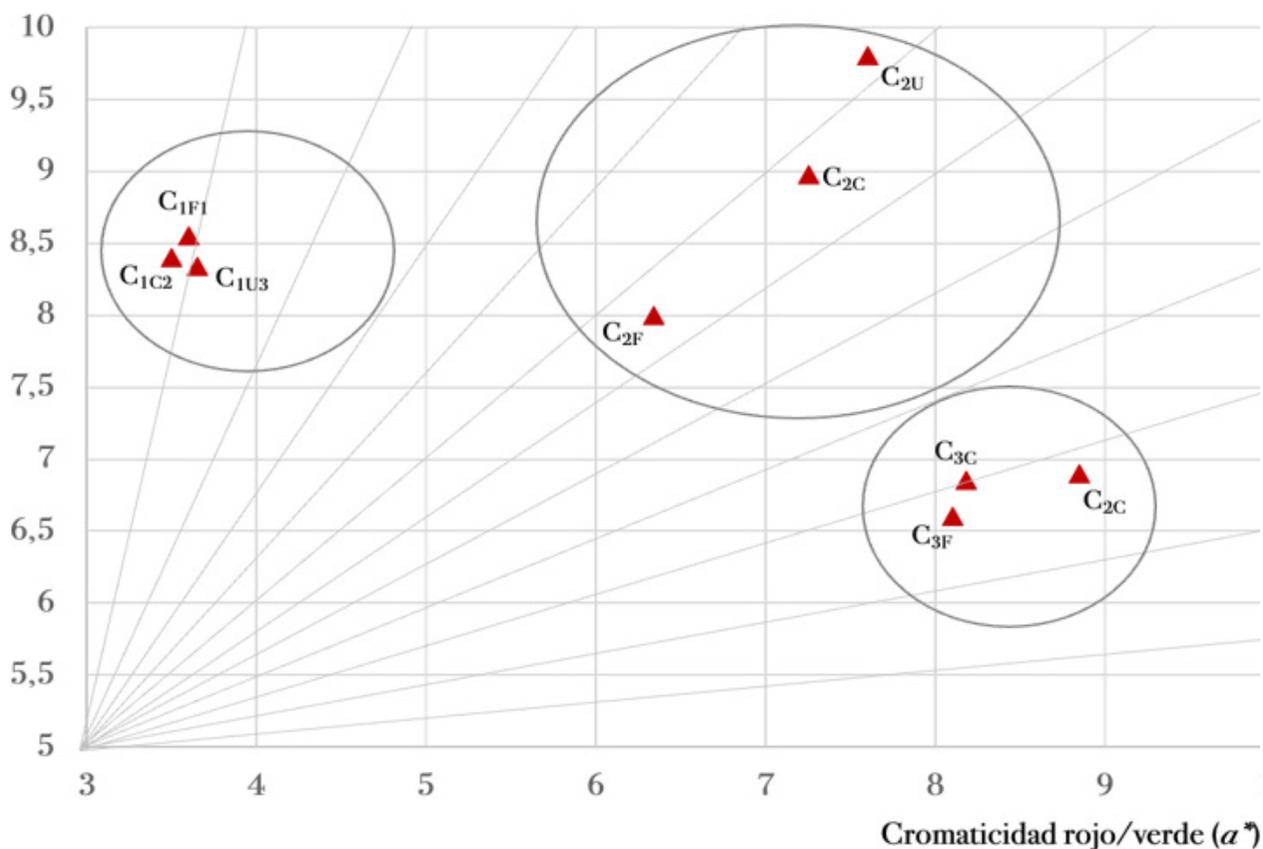


Figure 5

Distribution of the chromaticity values of hard candy enriched with eucalyptus essential oil, natural coloring and added flavorings

Note. Own elaboration.

Conclusions

The related work allowed to elaborate hard candies based on sucrose, glucose, and citric acid, adding a natural colorant of *H. sabdariffa* and aromas of strawberry, cherry, and grape, evaluating and projecting the generalized relations between the critical humidity and the water activity through

sorption isotherms and that were estimated as polynomial functionals.

The use of natural dyes and essential oils in the confectionery sector allows the incorporation of secondary metabolites that also present a consumption trend as functional foods. The candies with higher dye concentration showed a higher intensity

in red color, and those elaborated with lower concentration showed higher values in brightness and tonality.

In the sorption isotherms, the effect of bound and free water present in the functionalized candies was evaluated, by virtue of the water content and the plasticizing effect together with the aromas and colorant added, identifying three defined zones.

Additionally, estimates were made for the net isosteric heat of sorption and total heat of sorption considering water activity parameters and temperature through the Clausius-Clayperon equation.

The dependence between critical moisture content, water activity, and glass transition temperature, estimated from the linear relationship of the Gordon and Taylor model for hard candies enriched with eucalyptus essential oil, was evaluated in an approximation that is valid as a diagnostic tool for estimating glass transition temperatures when other techniques for measuring this stability parameter are not available.

Literature data on sorption isotherms and glass transitions of different products are presented as a gap that shows how the two molecular processes perceive stability at the molecular level. An inverse relationship between the glass transition temperature and the retained humidity is perceived, the higher the humidity the lower the values of the transition.

The study of the glass transition temperature defines stability regions of hard candies, elaborated from the water-

carbohydrate components that are of great interest to optimize the processing and storage to maintain textural characteristics accepted by the consumer.

The chromaticity parameters by virtue of the components added as flavorings together with the natural coloring present significantly different values in relation to all the evaluated groups and the values of red/green chromaticity were lower in the formulations with higher luminance.

Conflict of interest

The authors declare that they have no conflict of interest with respect to the work performed. Financial support for the research was appropriately acknowledged.

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