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# Influence of the microstructure and composition on the thermal–physical properties of hard candy and cooling process

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ABSTRACT

In this paper, glass transition temperature ($T_g$) and microstructure of hard candy honey flavored have been investigated using differential scanning calorimetry (DSC) data and scanning electron microscopy images (SEM) respectively. Precisely, the glass transition temperature can be used as reference temperature to determine the operating mode of processing stages. In fact, the temperature at which hard candies may leave the cooling stage has to be equal or lower than 34 °C in order to ensure the glassy state and therefore improve product shelf life; due to the fact that the experimental results indicated a temperature range of glass transition of 35.36 ± 1.48–36.37 ± 1.63 °C. As regards to the microstructure, SEM images reveal overlapping of layers at samples edges which could be attributed to the water absorption from the environment leading to storage problems, like crystallization. In addition, micrographics also reveal the presence of air bubbles which may negatively affect the temperature profile inside the candy and consequently may change the operating mode of the cooling equipment. The influence of the air bubbles on the thermal conductivity of the candy is also investigated.

## 1. Introduction

The cooling of a liquid to well below its equilibrium melting temperature without crystallization retains the molecular disorder which is characteristic of an amorphous state. This property may allow the supercooling and freezing of the molecules to their random positions and formation of a solid-like but disordered, non-crystalline glass [1]. The solid liquid transformation of the amorphous material is known as glass transition. Glass transition is one of the most important physico-chemical characteristics of non-crystalline, amorphous solids, like hard candies. An amorphous material vitrifies to a solid-like, brittle and transparent structure typical of the glassy state when it is cooled below the glass transition temperature [2]. This is exactly what is observed after the cooling stage during hard candies processing.

The importance of the glass transition to processing and stability control of foods and pharmaceuticals is well-known in the development of dehydration and freezing technologies [3–6]. However, in general, there is no application of glass transition and microstructure analysis in hard candies manufacturing processes for modeling purposes in order to optimize and supervise the cooling stage. This work is part of a more complex research project, which consists on the model-based optimization of a full-scale facility to manufacture hard candies. Results here presented could be further used to develop realistic mathematical models describing the unsteady cooling of hard candies.

During last years the applications of microstructure visualization as well as the polymer science for the physico-chemical characterization of food systems and other chemical products have received much attention [3–9].

Noirez and Baroni [7] analyzed the behavior of Glycerol at ambient temperature. They revealed the solid–liquid nature of Glycerol to a temperature domain far away from the glass transition and above the melting point. The experiments consisted in measuring the linear dynamic response and the stress relaxation under a weak constant shear stress, exhibiting that the Glycerol presented a non-vanishing shear elasticity indicating a macroscopic solid-like character above its melting point.

Kasapis and collaborators [8] reported data on the macrostructural changes (visco-elasticity) in dehydrated apple tissue in relation to apparent porosity. The authors emphasized the importance of considering the glass phenomenon as a rather recent concept for quality control of a number of high-solid systems. The experiments combined calorimetry, rheology, and microscopy data with the adoption of a fundamental approach for the mechanical glass transition temperature. By rheological investigations, the authors found that the storage modulus derivative was the appropriate parameter for probing the manifestation of the mechanical $T_g$. The plot of the first derivative of shear storage modulus as a

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function of sample temperature vs the sample temperature for biomaterials exhibits the classic rubber-to-glass transformation due to the fact that is the indicator of molecular mobility. The minimum of the storage modulus trace clearly demarcates the mechanical glass transition temperature. Discrepancies in the glass transition temperature ($T_g$) – porosity relationship obtained from calorimetry and mechanical analysis were found. This fact was attributed to the different extent to which the two techniques respond to degrees of molecular mobility. But, the use of the micrographs evidenced that prolonged processing and the creation of high levels of intercellular spaces lead to the disintegration of the apple matrix and the destruction of its continuity. The magnitude of the structural weakening is probed in the mechanical profile as a reduction in the values of the macromolecular glass transition temperature. Thus, the lower the volume fraction of total pores is, the more intact the cell walls and the greater the extent to which the mechanical $T_g$ differs from the measurements of calorimetry.

Mazzobre and collaborators [9] presented a comparison of microscopic and macroscopic techniques to evaluate sugar crystallization kinetics using amorphous lactose and lactose–trehalose mixtures. Polarized light video microscopy (PLV) and differential scanning calorimetry (DSC) were applied to measure crystallization kinetics, induction times and time for complete sugar crystallization at different storage temperatures (60–95 °C). DSC was also employed to measure the glass transition temperature ($T_g$) of the systems. Microscopy was instrumental to distinguish sugars crystals from the supercooled material. This studied case was one of the several examples in which microscopy helped for understanding of many phenomena that depend on the microstructure rather than on bulk conditions. The works of Cardoso and Abreu [10] and Johari and collaborators [11] also described $T_g$ values and composition for sugar glasses but with no application in manufacturing processes.

The aim of this work is to analyze hard candy structure and its influence on the cooling stage during the production process. Studies of the hard candy microstructure are useful to understand their behavior during cooling and to determine the relationship between the composition and the operating conditions, which is crucial from the product quality point of view and operational mode of equipment as well. The probability of the presence of air bubbles in the structure and its influence on the cooling process will be also investigated by using microscopic analysis.

### 1.1. Hard candy: product and cooling process description

For the fabrication of candy is necessary to mix simple ingredients such as corn syrup, sucrose and water, and the subsequent addition of essence, artificial colors and, in some cases, acids to modify the flavor properties. Regardless of its simplicity, the resulting product has a complex structure.

Hard candies are a classic example of a product in the glassy state. Apparently, they are solids, but actually, in fact they are supercooled liquids in a non-crystalline state [10]. Hard candy could be considered like a liquid with high viscosity. This property interferes in the process of formation of crystals. Crystallization is an undesirable process during the fabrication and storage of hard candy, which begins if a nuclei crystal (crystal seed) is present [12].

Slade and Levine [13] reported how the glass transition affects various food properties. The key processes requiring understanding

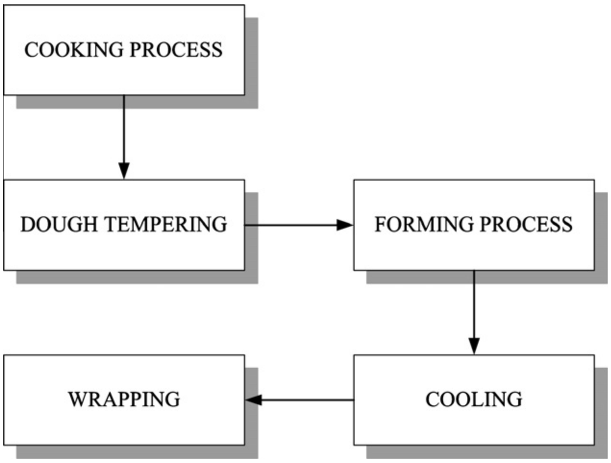

**Fig. 1.** Candies basic production flow sheet.

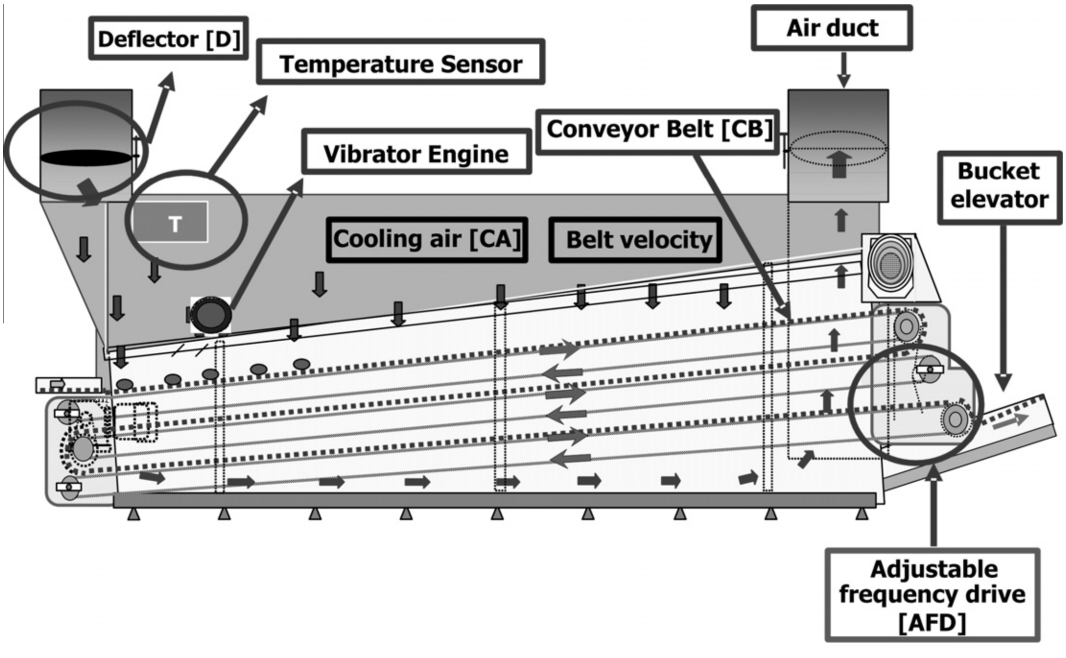

**Fig. 2.** Cross section cooling tunnel.

of the amorphous state and glass transitions of food systems are those occurring at limited water contents [14]. Hence, the process of vitrification, which consists of the solidification to a glassy substance during the cooling of a liquid-like material, has relevant importance in confectionary manufacturing plants, especially during hard candy processing, due to the fact that these processes occur at low water contents. For instance, the water content range of hard candies is approximately from 1.5% to 5% (w/w). So, in this context, $T_g$ value is one of the most important variables for designing and/or monitoring industrial processes of low water content foodstuffs.

Fig. 1 schematically shows the unit operations necessary for the production process of hard candy. Fig. 2 illustrates the cooling tunnel, where the temperature required for the wrapping and the glassy structure is reached removing only the energy contained inside the formed hard candies. The tunnel has two air ducts (entrance and exit). The incoming air flow is regulated by a deflector [D]. As is shown in Fig. 2, the tunnel is composed of three conveyor belts [CB] which are mechanically driven by an engine connected to an adjustable frequency drive [AFD] to vary the residence time of candies.

### 1.2. Importance of the composition

In any fabrication process, it is very important to control the parameters responsible of the product final quality. In thermal food processes, where the heat is transferred by conduction, solid and water contents play an important role and are considered to be two of the most important parameters influencing the product quality.

It is well known that full work capacity is beneficial for industries because it increases their performances. A food product with increased water content compared with the similar with lower water content has less thermal resistance and therefore better process performance related with the production costs. Then, from industrial point of view, the product water contents must be as high as possible. However, this may exhibit disadvantages in the quality aspect of the product. Certainly, higher water content may induce stickiness not only in cooling but also in the wrapping stage and storage [15]. There are no general rules about advantages and disadvantages of lower/higher product humidity contents because they strongly depend on the type of product to be processed. Besides, legislation establishes the water content limits for each food product.

Finally, it is possible to find air bubbles within the candy matrix structure.

## 2. Materials and methods

### 2.1. Hard candies

The samples used in this work were commercially available hard candies honey flavored with a water content of 2.5% (w/w). The sugar mixtures used in the candy formulation are sucrose (can sugar), glucose (corn syrup) and fructose.

The proximate hard candy composition given by the confectionery company (not mentioned in order to preserve the identity) was: water 2.5%, carbohydrates 97.13% and ash 0.18% (w/w).

### 2.2. DSC measurements

DSC measurements were performed on Mettler-Toledo DSC 821 instrument (Mettler-Toledo, Greifensee, Switzerland). Samples of about 20–25 mg were preventively sealed in an aluminum pan. Then, they were heated at constant rate of 2.0 °C/min in the 30–51 °C range. Three runs were taken to ensure reproducibility of the results, and the average of traces was considered. The expected experimental errors were ±0.1 °C in the temperature.

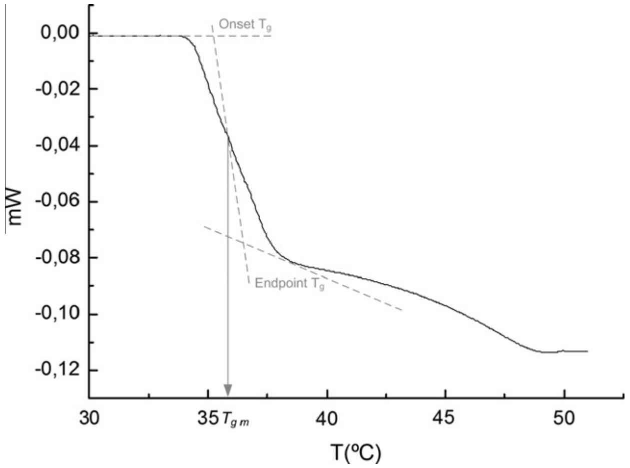

**Fig. 3.** Differential scanning calorimetry runs on hard candy honey flavored samples. Heating rate is 2 °C/min.

### 2.3. Scanning electron microscopy

The microstructure of hard candy was observed using SEM. In this case, the samples are of low moisture content; hence the preparation steps of fixing and dehydration were not necessary. Strips of approximately 10 × 5 × 3 mm were cut and used to study the microstructure. The samples were mounted on SEM stubs with silver conducting paint, and dried and coated with gold in argon atmosphere using a laboratory evaporator Veeco VE-300 (Veeco Instruments Inc., Long Island, NY, USA). The specimens were examined in a JEOL JSM-35C scanning electron microscope (JEOL Ltd., Tokyo, Japan) operated at an accelerating voltage of 20 kV. Images were obtained at (four) different magnifications (×).

## 3. Results and discussion

### 3.1. Glass transition

The glass transition takes place over a range of temperature. Currently, there is no agreement on the definition of $T_g$ point on a DSC curve among the various points that may be chosen (onset, midpoint, end-point), since none of them has a clear physical meaning. However, it is widely accepted that the glass transition should be reported with at least two parameters indicating its onset or midpoint and the width of the transition.

Fig. 3 shows the temperature profile obtained from the DSC experiments. The heat flow curve begins at the top (endothermic down), and the sigmoidal change is construed as evidence of vitrification phenomena. The midpoint of this thermal event is readily detectable and is considered as the glass transition obtained from DSC thermogram.

As is shown in Fig. 3, the experimental values of the glass transition temperatures (mean value ± standard deviation) graphically calculated as it was described in the work of Shamblin and Zografi [16] as well as Liu and collaborators [17] are:

$T_g$ onset = 35.36 ± 1.48 °C,
$T_g$ midpoint = 35.85 ± 1.51 °C,
$T_g$ endpoint = 36.37 ± 1.63 °C.

The experimental values of hard candy $T_g$ are above room temperature, just as was described by Liu and collaborators [17]. Also, in agreement with McFetridge and collaborators [18], $T_g$ were in the temperature range between the $T_g$ values of the individual sugar components.

The knowledge of the hard candy glass transition is important not only to ensure the quality during the storage [19] but also to control the temperature range during the cooling stage in order to reach the glassy structure.

In organic glasses, the increase of moisture content and storage temperature plays an important role on the rate of deteriorative reactions. The most important change affecting the behavior of amorphous carbohydrates is the plasticization which occurs at a quite narrow temperature range above $T_g$. This phenomenon leads to a dramatic decrease in viscosity, and therefore an increase in molecular mobility [20] which cause different time-dependent structural transformations during storage (stickiness, cold flow and crystallization) [21].

In the case that the storage temperature of an amorphous product is lower than its corresponding $T_g$, the product exists in a highly viscous glassy state and the diffusion-limited processes, like crystallization, become extremely slow [13]. Nevertheless, the moisture sorption in amorphous products during storage can dramatically lower the $T_g$. When this temperature is lower than the storage temperature, the amorphous state becomes less viscous and consequently the crystallization may exist [13]. The addition of glucose syrup and fructose enhances the physical stability interfering with crystallization [20].

With these results, it is easy to conclude that the lower the storage temperature that below its glass transition temperature, the bigger the prevention effect of undesired changes.

On the other hand, the glass temperature ($T_g$) is also important to determine the cooling operating conditions in order to obtain adequate temperature leaving the cooling tunnel. The maximum admissible final temperature is 34 °C to reach the glassy structure. In addition, because of hard candy composition, its thermal conductivity is very low (approximately 0.28 W/m °C), therefore a radial temperature transient is expected within a hard candy item. Thus, temperatures lower than 34 °C must be reached at the center of each hard candy article. Taking into account these considerations, it is then useful to develop a mathematical model to determine the optimal operating conditions (air cooling temperature and velocity as well as residence time). Moreover, the model will allow contemplating explicit constraints associated with quality aspects, for example, to impose the minimum value of the radial temperature difference.

It is generally known that $T_g$ of food products depends on its composition, especially with the water content. For example, some studies were conducted to demonstrate that $T_g$ is directly related to the water entrapped in the matrix by Cardoso and Abreu [10] as well as Johari and collaborators [11] for sugar-related glasses. So, it is expected that $T_g$ values for different candy samples with similar sugar formulation but different moisture contents will take a similar behavior that the last cited work [11]. From our experimental results (not shown), it can be concluded that $T_g$ decreases as the water content increases due to the low glass transition temperature of water (−135 °C) as is mentioned above.

According to this, the determination of $T_g$ for each candy formulation is required in order to assure a high product quality during the cooling stage and storage.

### 3.2. Microstructure and critical design parameters relationship

In the confectionary industry, several process operating parameters are critical to produce high quality products. For this reason, such parameters should be controlled. Also, the behavior of the ingredients plays an important role on the product quality and therefore should be considered.

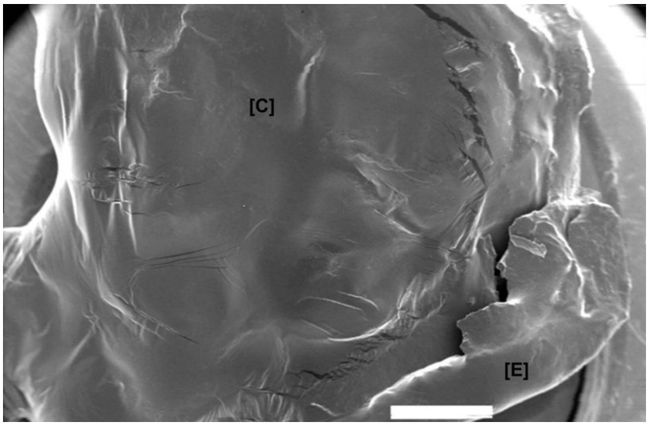

**Fig. 4.** Scanning electron micrograph at 20× magnification of control, cross section of honey hard candy. White scale bar represents 1000 µm. [C] = center of the hard candy sample, [E] = edge of the hard candy sample.

#### 3.2.1. Hygroscopic behavior

Specifically in hard candies manufacturing, hygroscopic properties are closed related with the wrapping stage during processing and the product storage. Also, the presence of air bubbles in hard candy matrix could affect the performance of the cooling stage. The problems mentioned above are analyzed in this section using SEM as a tool to reveal the strength in the relationship between the structure and properties.

SEM micrographs showing the microstructure of hard candy honey flavored are presented from Figs. 4 to 9. In these figures, it can be clearly observed the presence of supercooled material and the glass-like structure.

The non-equilibrium state of amorphous materials has no characteristic order of molecular arrangement, which has caused difficulties in understanding their properties [1].

In supersaturated solutions, molecules or molecular groupings tend to be in contact by short range forces. Once contact has been established, they are attracted in one direction only, being free to glide in any direction on the surface. When molecules move along a projection, they form a layer front that continues until meeting an angle. When this action is being repeated by the constant bombardment, migration and attachment of fresh molecules from the solution, the cumulative effect is visible by the advance of the layer fronts [22], as can be seen in Figs. 4–6.

Fig. 4 illustrates a portion of the edge [E] and the center [C] of a hard candy. Figs. 5 and 6 clearly show the overlapping of layers [OL] at samples edges. This overlap between the edge and the center may be attributed to the ageing of the hard candy, which is caused by the water absorption from the environment, related with the storage problems. The quality problem of ageing is due to hard handy exhibits hygroscopic properties. Consequently for sucrose composition less than 55% (in this case, sucrose composition is 39%), sucrose dissolution and candy melting occurs due to moisture uptake causing quality problems related to stickiness during storage [12]. In the microstructural aspects, this phenomenon is observed as the formation of a film with lower viscosity than the original at the hard candy periphery, as is shown in Figs. 5 and 6.

#### 3.2.2. Trapped air influence on cooling process

Concerning with the cooling stage, the shaped hard candies are cooled through a cooling tunnel, where the candies moisture does not change. It is well known that the presence of air bubbles in hard candies increases the resistance to heat transfer (internal thermal resistance) due to the low value of air thermal conductivity and consequently the cooling process is not efficient. Certainly,

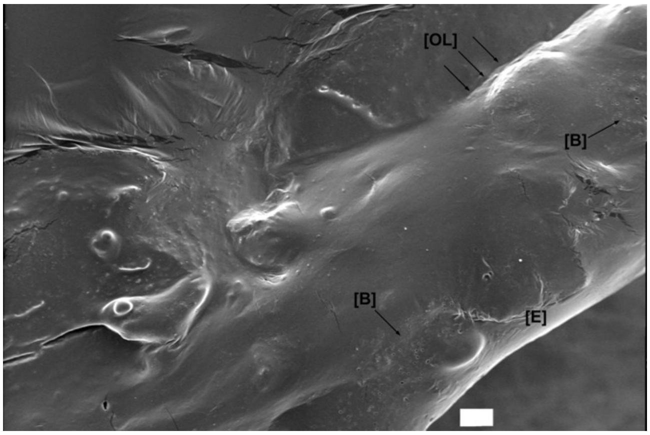

**Fig. 5.** Scanning electron micrograph at 60× magnification of control, cross section of honey hard candy. White scale bar represents 100 μm. [B] = air bubbles, [E] = edge of the hard candy sample, [OL] = overlapping of layers.

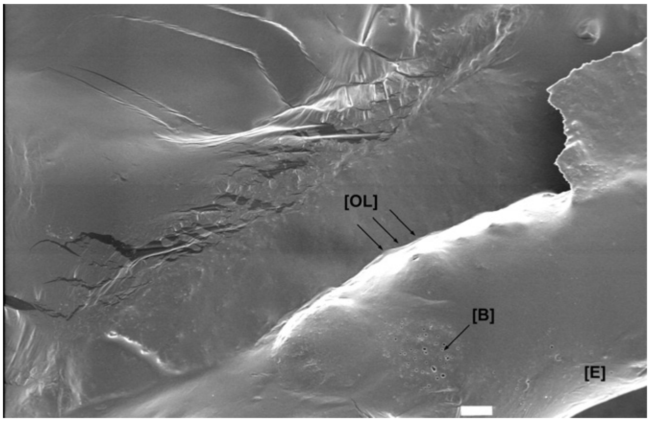

**Fig. 6.** Scanning electron micrograph at 60× magnification of control, cross section of honey hard candy. White scale bar represents 100 μm. [B] = air bubbles, [E] = edge of the hard candy sample, [OL] = overlapping of layers.

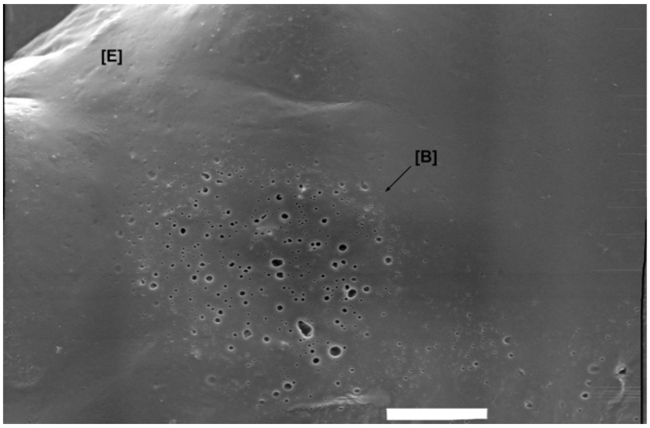

**Fig. 7.** Scanning electron micrograph at 200× magnification of control, cross section of honey hard candy. White scale bar represents 100 μm. [B] = air bubbles, [E] = edge of the hard candy sample.

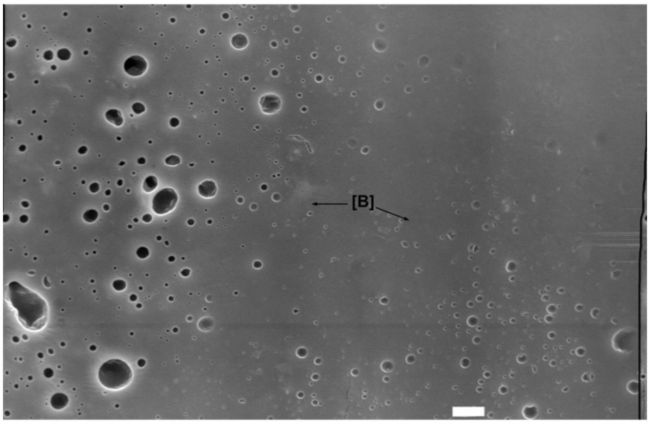

**Fig. 8.** Scanning electron micrograph at 600× magnification of control, cross section of honey hard candy. White scale bar represents 10 μm. [B] = air bubbles.

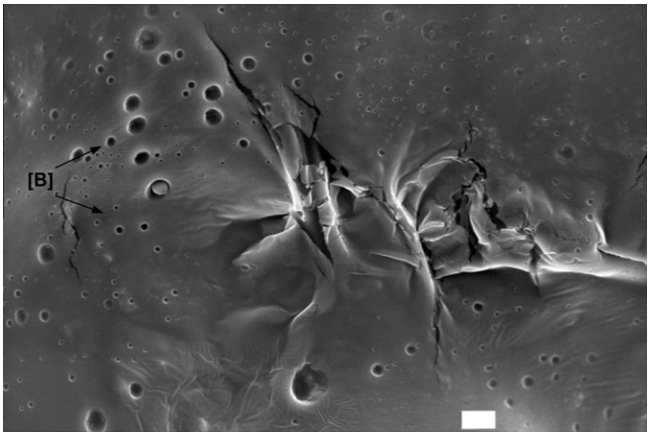

**Fig. 9.** Scanning electron micrograph at 600× magnification of control, cross section of honey hard candy. White scale bar represents 10 μm. [B] = air bubbles.

our previous results showed that the thermal conductivity of hard candy is the most relevant thermal property for the heat transfer process during the cooling stage of hard candies [23]. The behavior of the candy heat transfer model depends critically on the value of thermal conductivity, and has a weak dependence on the other parameters such as product density and heat capacity.

Regarding with the presence of air in solid matrixes, Sakiyama and collaborators [24] studied the air influence on hydrogels. The results revealed that for air-impregnated gels with low water content, the effective thermal diffusivities measured at 20 °C were in good agreement with the predicted values. For air-impregnated gels with high water content, the effective thermal diffusivities were well approximated by the predicted values up to 50 °C. At higher temperatures, the model tended to overestimate the effective thermal diffusivity especially for the gels with high porosity. On the other hand, Shariatt-Niassar and collaborators [25] concluded that the entrapment of fine air bubbles could not be avoided in practical food processes like extrusion.

Figs. 5 and 6 clearly show the presence of trapped air bubbles [B] at the nearby zones to hard candy edge. As was mentioned above, this trapped air has implications for the hard candies processing. Air bubbles appear in the candy dough due to a slowly cooling during the processing stage of dough tempering and kneading after the cooking stage, where the dough temperature goes from 140 °C to 85 °C.

The presence of air entrapped bubbles with higher magnifications can be seen from Figs. 7 to 9. Precisely, Fig. 7 shows a selected area of Fig. 6 while Fig. 8 refers to the same zone with higher magnification than Fig. 7. Fig. 9 exhibits another sample with the presence of air bubbles, in which the phenomenon is also observable in the nearby zone located between the crust and the center of the sample.

Another complication caused by the presence of entrapped air in food products is the determination of food thermal properties due to the need of high parameter precision for the control of the main processing parameters (temperature and velocity of cooling air, residence time). Limited experimental techniques with high accuracy are available to calculate thermal conductivity and diffusivity of solid foods. For this reason, it is common the application of different regression models for parameter estimations, which are then used for process modeling. A detailed review on several correlations can be found in Sweat [26] and Heldman [27]. The correlations developed by Choi and Okos [28] are the most widely used because they consider the dependence of the thermal properties as function of the moisture and they can be applied for a wide variety of food products. However, these correlations do not consider the effect of microstructural arrangements, which in many cases have significant influences [29]. Therefore, the use of such correlations introduces uncertainty in the estimation of thermal–physical properties.

In addition, large variations are expected due to the complex structure of foods, being in several cases multi-phase systems. Some structural models considering parallel, series, mixed or random phases for the estimation of thermal conductivity are reviewed by Aguilera and Stanley [29]. However, the effects of undesirable structural aspects on thermal property estimation, like the presence of trapped air bubbles, have not been widely considered.

The use of micrographics reveals the presence of trapped air. The subsequent step is to determine if the presence of this critical phenomenon influences the thermal conductivity. The analysis was done using the Choi and Okos's correlations [28]. It is expected, with the presence of air, that the real thermal conductivity will be lower than the estimated.

Images corresponding to multiple sections of the selected areas with bubbles were employed for characterization and quantification of the air content in the hard candies. The result of air content for all the samples examined expressed as mean value ± standard deviation was 5.71 ± 1.72%. When this value was taking into account to compute the thermal conductivity using Choi and Okos's correlation, the results showed that the actual thermal conductivity ($k_a$, contampling the air content) was lower than the one estimated without considering the air presence ($k_e$), however the value is included within the correlation standard error interval (±5%). The results are shown as follows:

$$k_a = 0.2729 \pm 0.0044\ \mathrm{W/m\ ^\circ C},$$
$$k_e = 0.2821 \pm 0.0141\ \mathrm{W/m\ ^\circ C}.$$

Thus, the presence of trapped air in hard candy can be neglected because its effect on the numerical value of the thermal conductivity decrease the same order of magnitude as the standard error (%) considered by the Choi and Okos's correlation.

## 4. Conclusions

In this paper the range of the transition glass temperature and the microstructure of hard candy honey flavored have been investigated. The glass transition temperature of hard candy honey flavored was calculated and its influence on cooling process and storage was also analyzed.

By applying DSC technique, it has been determined that the glass transition temperature range for hard candy honey flavored was 35.36 ± 1.48–36.37 ± 1.63 °C. From product quality point of view, the glass temperature ($T_g$) is important to determine the cooling operating conditions in order to obtain adequate temperature leaving the cooling tunnel. The maximum outlet temperature at the center of each hard candy article is 34 °C to reach the glassy structure. Also, $T_g$ is important to determine the storage conditions, in order to avoid crystallization problems and therefore improve product shelf life.

On the other hand, SEM images revealed undesired characteristic like the presence of trapped air within the candy matrix. The air content detected within the structure was 5.71 ± 1.72%, which produced a decrease in the value of the thermal conductivity obtained by Choi and Okos's correlation from $k_e = 0.2821 \pm 0.0141$ to $0.2729 \pm 0.0044$ W/m °C. However, it was concluded, that the thermal conductivity of hard candy honey flavored is not significantly affected by the presence of entrapped air within the matrix, due to the fact that this decrease is within the standard error of the correlation used.

In addition, with the help of SEM technique it was also observed overlapping of layers at samples edges showing a hygroscopic behavior which is one of the major responsible of the problem of ageing.

DSC and SEM techniques provided useful and necessary knowledge about the relationship among the microstructure, thermal properties, composition (in particular moisture) and processing aspects, especially at cooling stage and product storage. It is clear that glass transition temperature serves as a guide for quality aspects. Finally, the gained knowledge can be efficiently used not only to ensure a high product quality but also to develop a mathematical model to optimize the whole candy process. For instance, the $T_g$ value determined in this paper can be used as upper bound on the outlet temperature at the cooling tunnel. Moreover, proper assumptions to derive mathematical models can be considered from the obtained results. For example, to neglect the effect of air bubbles on the calculation of the candy thermal conductivity obtained at the same processing conditions.

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