Acta Sci. Pol. Technol. Aliment. 22(2) 2023, 227–236
www.food.actapol.net pISSN 1644-0730 eISSN 1898-9594 http://dx.doi.org/10.17306/J.AFS.2023.1133

ORIGINAL PAPER

Received: 23.04.2023
Accepted: 25.06.2023

EFFECTS OF HEATING PROCESS ON KINETIC DEGRADATION OF ANTHOCYANIN AND VITAMIN C ON HARDNESS AND SENSORY VALUE OF STRAWBERRY SOFT CANDY

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ABSTRACT

Background. Strawberries are a good source of aroma, colour, and antioxidants (vitamin C and anthocyanins), which provide various health benefits. However, these antioxidants are sensitive to heat and can easily degrade during thermal processing. Their contents could be described by thermal kinetic models during the heating process for strawberry candy. The extent of heating temperature and time's effect on hardness and sensory value of the fruit candy would be evaluated.
Material and methods. The study aimed to investigate the effects of cooking temperatures (80–100°C) and times (8–22 min) on the quality parameters of strawberry fruit candy, including water content, hardness, anthocyanin and vitamin C levels, and sensory attributes.
Results. The results showed that temperature strongly influenced the changes in anthocyanin content, while time highly affected changes in vitamin C content during cooking. The degradation of anthocyanin and vitamin C could be described using the first-order reaction model. The results showed activation energy values of 614 kJ/mol and 429 kJ/mol, respectively, as determined by the Arrhenius model. The study found strong correlations between the quality parameters and the heating conditions. Heating at 90°C for 14 minutes resulted in the best sensory values and the highest anthocyanin and vitamin C levels.
Conclusion. The heating time of the strawberry mixture sharply caused a decrease in vitamin C content and an increase in hardness. Meanwhile, the heating temperature was a vital contributor to the reduction in anthocyanin, degradation of anthocyanin, and vitamin C in the strawberry mixture, and it can be described by the first-order reaction and Arrhenius model during the heating of the strawberry soft candy. The study highlights the potential for developing new food products from strawberries, carefully considering cooking to optimize quality parameters and preserve essential antioxidants.

Keywords: anthocyanin, degradation, hardness, heating process, kinetic, vitamin C

INTRODUCTION

Strawberries are a type of fruit that belong to the genus Fragaria in the rose family, *Rosaceae*. The most common type of strawberry grown commercially is the garden strawberry, which is a hybrid of two different species. Strawberries have a wide range of flavours, from very sweet to quite tart, depending on the specific cultivar (Kazim, 2016). They are an important commercial fruit crop grown in temperate regions all

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over the world, including in Vietnam, where they are mainly grown in highland areas in Dalat city.

Strawberries are also packed with vitamins, particularly vitamin C, which they contain in higher amounts than many other fruits, including oranges and pineapples. Vitamin C is an essential nutrient that is important for a variety of bodily functions, including supporting a healthy immune system, preventing infections, and reducing stress. It is a powerful antioxidant that can help protect cells from damage caused by harmful free radicals, and it also plays a role in the production of collagen, a protein that is essential for healthy skin, bones, and other tissues. Adequate intake of vitamin C has been linked to reduced risk of various diseases, including certain types of cancer and heart disease, and it may also help improve mental health by reducing stress and anxiety (Akhilender, 2003; Basu et al., 2014).

Strawberries are a rich source of anthocyanins. The bioactive compound is known for its antioxidant properties and has been linked to a variety of health benefits, such as reducing inflammation, improving heart health, and preventing chronic diseases such as cancer and diabetes. Anthocyanin is a natural, beautiful, and safe pigment (Montilla et al., 2011; Nabae et al., 2008; He and Giusti, 2010) with health-promoting properties (Patras et al., 2010). This compound helps to eliminate free radicals, prevents cancers, and reduces cholesterol and heart disease and diabetes type II (Felgines et al., 2006; He and Giusti, 2010; Ghosh and Konishi, 2007; Wu et al., 2006).

The confectionery industry has been undergoing a shift towards more natural and healthier options due to changes in consumer preferences and demands. This trend has led to the development of soft candies that are free from synthetic components and have a lower number of calories. In addition to these health considerations, consumers are also looking for soft candies that use natural ingredients, such as fruit juices and purees (Recep et al., 2022).

Strawberries are still widely used all over the world as an ingredient for confectionery due to their attractive bright red colour, sweet flavour, aroma, texture, juiciness, and taste. In addition to their use as fresh fruit, modern technology and other developments have also enabled strawberries to be processed into different forms, such as juice, jam, syrups, wine, and vinegar (Donoso, 2009). However, there is limited research available on the kinetic degradation of anthocyanin and vitamin C specifically in strawberry soft candy. However, bioactive compounds in strawberries are sensitive to thermal processing and can degrade (Kim et al., 2022). For example, vitamin C can be degraded during the pasteurization of juices such as oranges, lemon, grapefruit (Njoku et al., 2011) and pomegranate (Ranu and Uma, 2012). Anthocyanin content also decreased with increasing temperature during the pasteurization of juices from strawberries, blueberries, and red oranges (Patras et al., 2010). The degradation of vitamin C in grape juice could be described by the first-order model (Danişman et al., 2015). However, changes in vitamin C and anthocyanin during the heating of strawberry candy are important for gaining an understanding. Therefore, the objective of this study was to determine the degradation of vitamin C and anthocyanin during the heating strawberry candy. In addition, the changes in quality parameters of the candy (hardness and sensory values) were also evaluated for thermal effects on consumption.

MATERIALS AND METHODS

Materials

The main ingredients were fresh strawberry fruits (Dalat, Vietnam), gelatin powder (fish skin, France), and extra refined sugar (Bien Hoa, Vietnam).

Methods

Preparation of fruit candy. The strawberries were washed, and ground well. A mixture was prepared with strawberry puree (30%), gelatin (12%), sugar (50%), citric acid (0.5%), and water (7.5%). The mixture (150 g) was stirred and heated at different temperatures (80, 90, and 100°C) for different lengths of time (6, 10, 14, 18, and 22 minutes). After heating, the concentrate was filled into the silicon mould (equilateral triangle sides with 15 mm and height with 2 mm) and cooled for 20 hours in the refrigerator (5°C).

Moisture content. Moisture content (water content) was determined by heating in the oven at 105°C using the method AOAC (2004).

Anthocyanin content. The total anthocyanin content was determined according to the spectrophotometric pH-differential method (Lee et al., 2005). Briefly, an aliquot (1 mL) of the extract was mixed with 0.025 M potassium chloride buffer (pH 1.0, 4 mL) and 0.4 M sodium acetate buffer (pH 4.5, 4 mL), respectively. The absorbance of the mixture was measured at 510 and 700 nm using a UV-Vis spectrophotometer model U-2800A (Hitachi High Technologies America, Inc). Absorbance was calculated as A = [(A510 − A700) at pH 1.0] − [(A510 − A700) at pH 4.5] with a molar extinction coefficient of 26,900 for anthocyanin. The total anthocyanin content was calculated as cyanidin--3-glucoside equivalents using Equation 1:

$$X = \frac{A \times M \times DF \times V \times 10^3}{\varepsilon \times L \times m} \text{ (mg/L)} \quad (1)$$

Where *A*, absorbance; *M* the molecular weight of cyanidin-3-glucoside (449.2 Da); *DF*, the dilution factor; *V*, the final volume (mL); 10^3, the factor for conversion from g to mg; *ε*, the cyanindin-3-glucoside molar absorbance (26,900); *L*, the cell path length (1 cm), and *m*, sample weight (g).

Then, the total anthocyanin content (mg per 100 g dry weight) was calculated using the following Equation 2:

$$C = \frac{X \times V \times 100}{m \times (100 - w) \times 100^{-2}} \text{ (mg/100 g)} \quad (2)$$

Where, *C*, total anthocyanin content (mg cyanidin--3-glucoside /100 g dry weight); *X* (equation 1), anthocyanin in the extract solution (mg/*L*); *m* and *w*, sample weight (g) and moisture content (%); *V*, the extraction volume (L).

Vitamin C content. The vitamin C content was determined by a redox titration using iodine (Pietro et al., 2001). The content of vitamin C was calculated with the following Equation 3:

$$C = \frac{V \times V_1 \times 0.00088 \times 100}{V_2 \times m \times (100 - w) \times 100^{-2}} \text{ (mg/100 g)} \quad (3)$$

Where, *C*, vitamin C content (mg/100g); *V*, volume (mL) of iodine solution 0.01 N, V_1, volume (50 mL) of sample, V_2, volume (20 mL) for titration; m, sample weight (g); 0.00088, the weight of vitamin C to react with 1 mL of 0.01 N solution; and *w*, moisture content (%) of sample.

Hardness. Hardness of candy was determined by the texture analyser (Rheotex SD700, Sunscience, Japan). The sample was placed on the base plate of the analyzer with the cylinder probe (diameter = 5 mm), which was set to travel at a speed of 2 mm/s and a traveling distance of 4 mm. The penetration position of the candy was at the center of the sample being measured. The maximum compression force from the force deformation indicated the hardness of the sample.

Sensory evaluation. The attributes, namely, colour, texture, aroma, and taste, were evaluated using the method of Quantitative Descriptive Analysis (Poste et al., 1991). The twenty qualified panelists were staff and students of Can Tho University, who were chosen and asked to compare the coded samples.

The first-order reaction model. The degradation of anthocyanin orvitamin C and anthocyanin was calculated with Equation 4 (Labuza, 1984):

$$\ln\left(\frac{C}{C_0}\right) = -k \times t \quad (4)$$

Where, *C* and C_0, contents of anthocyanin (equation 3) or vitamin C (equation 4) at a heating time (minutes) *t* and initial time *t* = 0; *k*, the first-order rate constant (min^{-1}) of degradation of anthocyanin or vitamin C.

The Arrhenius model. The activation energy of thermal degradation was calculated with the Arrhenius model (Özşen and Erge, 2012), using Equation 5:

$$\ln(k) = \ln(k_{\text{ref}}) + \left[\frac{E}{R_T} \times \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \quad (5)$$

Where, E_a, degradation energy (kJ/mol); *k* and k_{ref} (min^{-1}), degradation rate constants at *T* (reaction temperature, °K) and T_{ref} (reference temperature, °K); and R_T = 8.314 J/°K.mol).

Data analysis

Data were statistically analyzed with an Analysis of Variance (ANOVA), Pearson correlation coefficients, and means were measured using Duncan's multiple range tests at $p < 0.05$ using Stagraphic Centurion 15. Significant differences were indicated by different letters in the same column.

RESULTS AND DISCUSSION

Effects of heating temperature and time on variance of hardness, moisture, anthocyanin, and vitamin C contents

Temperature and time had a significant and strong ($p < 0.001$) influence on variances of the quality parameters (hardness, moisture, anthocyanin, and vitamin C contents) whilst heating the strawberry fruit mixture. Interaction of temperature and time also significantly and weakly ($p < 0.05$) affected variances of these parameters during heating.

Table 2 showed that heating temperatures mainly influenced the variance of anthocyanin content at 53.36%. Heating time strongly affected the variances of moisture, hardness, and vitamin C contents at 61.30%, 64.24%, and 73.13%, respectively.

Averages of moisture content and hardness from different heating temperatures and times

Figures 1A and 1B showed that the strawberry fruit candy had lower moisture contents but higher hardness with increasing temperatures and times during heating. When the strawberry fruit mixture was heated at higher temperatures and for a longer time, water would evaporate and the moisture content of the strawberry candy decreased. As a result, increasing the dry matter of the candy contributed to an increase in the hardness of the strawberry candy. In addition, gelatin had enough temperature and time to swell, dissolve, and form gelation, which made the strawberry fruit candy harder and elastic. An increase in moisture content in candies was found to decrease the hardness of the candy (Figiel and Tajner-Czopek, 2006). Water is a constituent of food that affects food safety, stability, quality, and physical properties (Lewicki, 2004). The texture of finished products is significantly affected by water, its properties, and distribution in a product (Cornillon and Salim, 2002).

Table 1. Effects of heating temperature and time on variance for hardness, moisture, anthocyanin, and vitamin C contents of strawberry soft candy

Factors	Moisture, %	Hardness, N/cm^2	Anthocyanin, mg%/DWB	Vitamin C, mg%/DWB
Temperature	75.65***	5.89***	12,157.90***	87.76***
Time	64.82***	6.03***	5,152.78***	123.99***
Temperature × time	0.67*	0.13*	17.91*	3.10*
Error	0.23	0.02	7.66	0.14

Note: *** – $p < 0.001$; ** – $0.001 < p < 0.01$; * – $p < 0.05$.

Table 2. Variance components for hardness, moisture, anthocyanin, and vitamin C at different heating temperatures and times

Factors	Variance component (%)			
	Moisture, %	Hardness, N/cm^2	Anthocyanin, mg%/DWB	Vitamin C, mg%/DWB
Temperature	35.77	31.40	53.36	25.89
Time	61.30	64.26	45.23	73.13
Temperature × time	1.28	2.78	0.24	0.37
Error	1.66	1.56	1.16	0.61

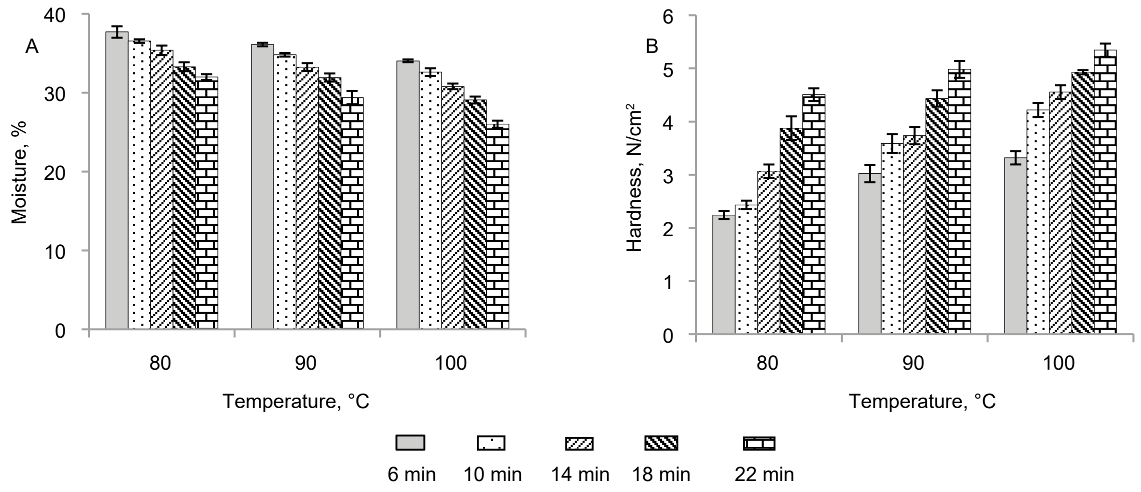

Fig. 1. Changes of moisture content (A) and hardness (B) of candy from different heating temperatures and times

Anthocyanin degradation in the fruit candy during heating

Anthocyanin (in dry weight basis, DWB) in the strawberry mixture was determined at different temperatures (80°C, 90°C, and 100°C) during heating times (Fig. 2A). The degradation of anthocyanin in the strawberry mixture was evaluated with the first order model to calculate the reaction rate constant k (Fig. 2B, Table 3) and the activation energy E_a (Table 3).

Figure 2 showed that anthocyanin was destroyed during heating at different temperatures and times. The higher the heating temperature was, the faster anthocyanin was degraded.

Table 3 showed that the coefficients of R_1^2 were always higher than 0.94. This means degradation of anthocyanin could be described with the first order reaction model to predict anthocyanin contents in the strawberry mixture at the given temperature with different times.

As expected, the higher the heating temperatures, the higher the degradation rate constants of anthocyanin in the strawberry mixture. Mishra et al. (2008)

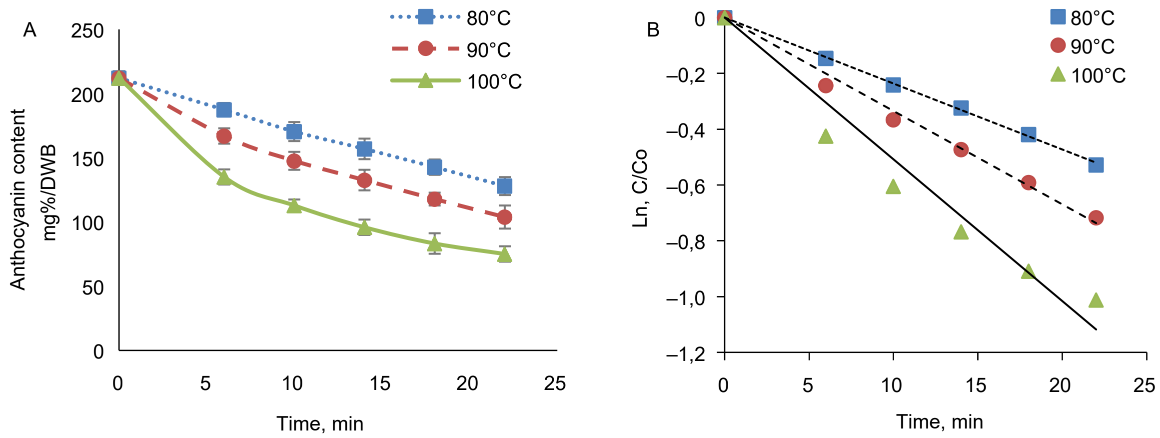

Fig. 2. Degradation of anthocyanin (A) was evaluated with the first order model (B) at different temperatures during heating

Table 3. Kinetic degradation of anthocyanin in strawberry mixture during heating

Heating temperature, °C	First order		Arrhenius model	
	K, min^{-1}	R_1^2	E_a, kJ/mol	R_2^2
80	0.023	0.99		
90	0.033	0.99	614	0.99
100	0.050	0.94		

Note: k – reaction rate constant; E_a – activation energy; R_1^2 and R_2^2 the R squared or the coefficient of determination of a linear regression for k and E_a, respectively.

reported that the degradation rate constant of anthocyanin in grape juice was 0.0607 min^{-1} at 110°C. Their temperature was higher than the temperatures of this study; therefore, their k was higher than the degradation rate constants of anthocyanin in the strawberry mixture during heating.

The dependence of the anthocyanins degradation on temperature was determined by calculating the activation energy (E_a) value 5 of the Arrhenius model based on the k values in Table 3. The activation energy for the degradation of anthocyanins in the strawberry mixture was determined as E_a = 614 kJ/mol at 80–100°C with R_2^2 = 0.99. This E_a value is higher than those reported for strawberry juice anthocyanin (72.00 kJ/mol) at 70–90°C (Patras et al., 2010), grape anthocyanins (72.74 kJ/mol) at 70–90°C (Hillmann et al. 2011). Moreover, Wang and Xu (2007) reported a lower E_a value (58.95 kJ/mol) for the degradation of blackberry anthocyanins at 60–90°C. This shows that the higher the activation energy value, the more difficult it was for the reaction to activate. That means the degradation of anthocyanins in the strawberry mixture was slower to rise in temperature than those of strawberry, blackberry, and grape juice anthocyanins. This could be explained as the viscous gelatin and sugar in the strawberry mixture protecting and making the anthocyanins more stable.

Vitamin C degradation in strawberry mixture during heating

Vitamin C contents (in dry weight basis, DWB) in the strawberry mixture were determined at different temperatures (80°C, 90°C, and 100°C) during heating times (Fig. 3A). The degradation of vitamin C in the strawberry mixture was evaluated with the first order model to calculate the reaction rate constant k (Fig. 3B, Table 4) and the activation energy E_a (Table 4).

Figure 3 showed that vitamin C was destroyed during heating at different temperatures and times. The higher the heating temperature and longer the time were, the more anthocyanins were degraded.

Table 4 showed that the coefficients of R_1^2 were always higher than 0.98. This means degradation of

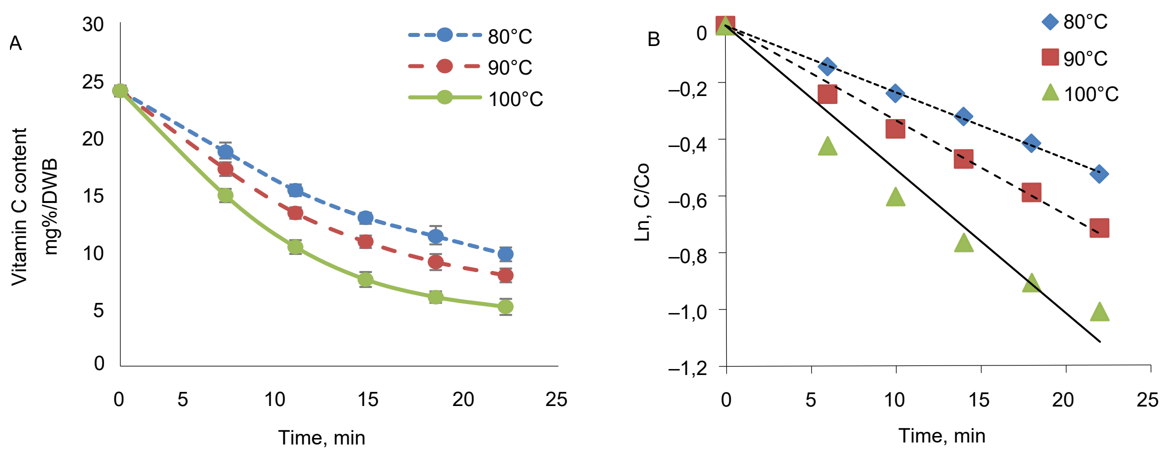

Fig. 3. Degradation of vitamin C (A) was evaluated with the first-order model (B) at different temperatures during heating

Table 4. Kinetic degradation of vitamin C in strawberry mixture during heating

Heating temperatures, °C	First order		Arrhenius model	
	k, min^{-1}	R_1^2	E_a, kJ/mol	R_2^2
80	0.043	0.99		
90	0.053	0.99	428.79	0.97
100	0.074	0.98		

Note: k – reaction rate constant; E_a – activation energy; $R_1^2$and R_2^2 the R squared or the coefficient of determination of a linear regression for k and E_a, respectively.

vitamin C could be described with the first-order reaction model to predict vitamin C contents in the strawberry mixture in a short time (22 minutes). Similarly, the thermal degradation of vitamin C in fruit juice followed the first-order reaction model (Bree et al., 2012).

As expected, with the higher heating temperatures, the degradation rate constants of anthocyanin in the strawberry mixture were higher. Ranu and Uma (2012) reported that the first-order degradation constants of vitamin C in pomegranate juice were 0.0034 and 0.0038min^{-1} at 80°C and 90°C, respectively. The first-order rate constant (k) for the thermal degradation of vitamin C in processed fruit products can vary depending on several factors, including the composition of the purees containing various amounts of antioxidants, sugars, and organic acids.

The dependence of the vitamin C degradation on temperature was determined by calculating the activation energy (E_a) value 5 of the Arrhenius model based on the k values in Table 4. The activation energy for the degradation of vitamin C in the strawberry mixture was determined as E_a = 428,79 kJ/mol at 80–100°C with R_2^2 = 0.97. This E_a value for the strawberry mixture is higher than E_a = 81.97 kJ/mol for pomegranate juice at 70–90°C (Ranu and Uma, 2012). This means the degradation of vitamin C in the strawberry candy was slower in relation to temperature elevations than those of other fruit juices. This can be explained by the viscous gelatin and sugar in the strawberry mixture possibly protecting and making vitamin C more stable.

Relationship between parameters

The Pearson's correlation coefficients used to test the statistical relationships between quality parameters (hardness, moisture, anthocyanin, and vitamin C values) of the strawberry fruit candy from the combined data set for different temperatures are presented in Table 5.

Hardness had a strong ($p < 0.001$) positive correlation with heating temperature and time. Furthermore, the moisture content of the candy was strongly correlated with its hardness. The study also found that an increase in the heating temperature and duration led to lower levels of anthocyanins and vitamin C in the strawberry candy. Interestingly, the study also reported a strong positive correlation between the contents of anthocyanins and vitamin C, suggesting that vitamin C may contribute to the stability of anthocyanins during thermal processing (Nguyen et al., 2022).

Overall, these findings highlight the importance of carefully controlling the processing conditions of strawberry candies to achieve desirable properties such as hardness, moisture, and nutrient content. Optimizing the heating temperature and duration can help to achieve these goals while minimizing the

Table 5. Correlation between quality parameters with heating temperatures and times

	Temperature	Time	Anthocyanin	Vitamin C	Hardness
Anthocyanin	–0.73***	–0.67***			
Vitamin C	–0.51***	–0.83***	0.94***		
Hardness	0.56***	0.80***	–0.94***	–0.94***	
Moisture	–0.60***	–0.78***	0.95***	0.93***	–0.95***

Note: *** – $p < 0.001$; ** – $0.001 < p < 0.01$; * – $p < 0.05$.

degradation of important nutrients like anthocyanins and vitamin C.

Effects of heating temperatures and time on sensory values of the strawberry candy

The heating process in the preparation of the strawberry candy caused the gelatin to swell and the sugar to dissolve, resulting in the formation of candy with desirable sensory properties such as colour, texture, aroma, and taste. The gelatin likely played an important role in the texture of the candy, as it is a protein that can form a gel-like structure when hydrated and heated. The sugar would have contributed to the sweetness of the candy and may have also played a role in its texture.

Table 6. Effect of heating process on sensory values of the strawberry candy

Temperature °C	Time* min	Sensory attributes			
		Colour	Texture	Aroma	Taste
80	6	4.28*[a]	2.80[c]	3.60[b]	3.00[c]
	10	4.21[a]	3.14[b]	3.76[b]	3.72[b]
	14	4.28[a]	3.64[b]	4.26[a]	3.93[b]
	18	4.36[a]	3.84[b]	4.14[a]	4.30[a]
	22	4.10[b]	4.16[a]	3.57[b]	4.26[a]
90	6	4.28[a]	2.86[c]	3.76[b]	3.27[c]
	10	4.21[a]	3.14[b]	4.19[a]	3.80[b]
	14	4.35[a]	4.30[a]	4.49[b]	4.42[a]
	18	4.11[b]	3.93[a]	3.57[b]	4.51[a]
	22	4.07[c]	3.64[b]	3.36[b]	3.68[b]
100	6	4.21[a]	3.14[b]	3.79[b]	3.86[b]
	10	4.10[a]	4.24[a]	4.19[a]	4.36[a]
	14	3.84[b]	4.12[a]	3.57[b]	4.64[a]
	18	3.60[b]	3.64[b]	3.36[b]	3.82[b]
	22	3.30[c]	3.26[c]	3.18[c]	3.02[c]

Note: * – mean value of three replications. The different letters that accompanied the mean values in the same column represented the difference at the 5% significant value ($p < 0.05$).

The heating conditions during the preparation of the strawberry candy were critical to achieving the desired sensory properties. Heating the mixture at 90°C for 14 minutes resulted in candy with a bright red colour, good aroma, elastic texture, and moderate sweetness. This suggests that this combination of temperature and time allowed for the gelatin to form a well-structured gel, the Maillard and caramel reactions to produce desirable flavour compounds, and the mixture to condense to a sweet enough level without overcooking. A moderate hardness can provide a pleasant chewing experience without being too hard or too soft. This can contribute to the consumer's overall enjoyment of the product. Additionally, the texture of the gelatin candy can affect its flavour release, which can also influence its sensory properties. Gelatin candy with moderate hardness was highly accepted in sensory evaluations, as there is often a correlation between textural properties and sensory attributes in gelatin candy (Tireki et al., 2021).

However, heating the mixture at lower temperatures and for shorter times did not allow for proper gelation, Maillard and caramel reactions, or sufficient concentration of the mixture, resulting in candy with poor texture, flavour, and sweetness.

On the other hand, boiling the mixture at higher temperatures for longer times resulted in candy with a harder texture and a sweeter taste due to excessive water loss and overcooking. This also led to a darker colour and less strawberry fruit aroma, as overcooking can lead to the degradation of some of the desirable flavour and aroma compounds.

These results highlight the importance of carefully controlling the heating conditions during the preparation of fruit candies to achieve the desired sensory properties.

CONCLUSION

The heating time caused more degradation of vitamin C and hardness of strawberry candy than the heating temperature. The extent of heating temperature influenced the reduction of anthocyanin much more than the heating time. The degradation of anthocyanin and vitamin C in the strawberry mixture can be described by the first-order reaction. The activation energy could be calculated by the Arrhenius model. The antioxidants in the viscous gelatin and sugar media were relatively stable during the heating process.

The findings suggest that a heating temperature of 90°C for 14 minutes was suitable for producing strawberry candy with the best sensory attributes and high levels of anthocyanin and vitamin C. This information could be useful in developing processing methods that preserve the nutritional and sensory qualities of other fruit purees containing anthocyanin and vitamin C as well.

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