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Coating development with modified starch and tomato powder for application in frozen dough

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ABSTRACT

The Central Composite Rotatable Design (CCRD) with variables developed modified ascorbic acid (AA) starch coating added with tomato powder (TP): ascorbic acid and tomato powder. The CCRD verified the effects on the coating's properties: surface tension, electrical conductivity, viscosity and ζ-potential. Specific volume, hardness and Scanning Electron Microscopy with Energy-Dispersive Spectroscopy evaluated the optimized coating efficiency on the frozen dough in storage. A significant ($p < 0.05$) influence of AA and TP was observed in all parameters, as there was an increase in surface tension, viscosity and electrical conductivity with an increase in the independent variables. The optimized edible coatings were EC1 – 1.8% AA/4.0% TP and 2.2% AA/5.0% TP. The coated frozen dough promoted breads with a greater specific volume and less hardness than the breads produced by uncoated frozen dough. The EDS analysis showed the presence of K, S, Ca and P minerals, proving coating mobility into the dough.

1. Introduction

Bread is a product of wheat flour fermentation by yeast, and is widely consumed as a staple food across many cultures and countries worldwide (Arendt & Zannini, 2013). Dough is a comprehensive network containing wheat flour, water, and other ingredients. Gluten in wheat flour is a crucial protein to form a viscoelastic structure in dough and bread (Peng, Li, Ding, & Yang, 2017). The functionality of the gluten network developed through mixing is crucial for gas retention and the final structure of bread (Gao, Koh, Tay, & Zhou, 2017).

For economic reasons, the dough-freezing technique is commonly employed in bakery businesses (Halagarda, 2017). As such, bakery products can be prepared quickly and on demand, thus minimizing the cost of unsold products (Giannou, Kessoglou, & Tzia, 2003). Nevertheless, there are several issues connected with this technology, i.e. loss of dough strength caused by the formation of ice crystals, decreased retention capacity of CO_2, longer fermentation time, reduced viability and yeast activity. These may lead to reduced volume and deterioration in the texture of a baked product (Steffolani, Ribotta, Perez, Puppo, & Leon, 2012). During proofing, the gas production rate depends on the activity of baking yeast (Saccharomyces *cerevisiae*), while the dough expansion rate is determined by both the gas production and the gas transfer rate (Gao et al., 2017). In this way, frozen storage can reduce the yeast population which affects the final quality of the bread, making it necessary to develop technologies that reduce the impact of freezing on the structure and quality of bread dough.

Research on edible coatings and films has been intense in recent years. Application of edible coatings (EC) confers a more natural appearance to food products, and environmental impact reduction by decreasing the use of oil-derived plastic packaging materials (Dangaran, Tomasula, & Qi, 2009). EC can offer biocompatibility, aesthetic appearance, barrier properties, no toxicity, low cost, and can be used as additive carriers such as colorants, flavors, antioxidants, or antimicrobials (Vásconez, Flores, Campos, Alvarado, & Gerschenson, 2009). Starches are attractive biopolymer candidates for replacing a part of synthetic polymers in coatings since starch will increase the biodegradability of the final products and lower the material costs (Rahmat, Rahman, Sin, & Yussuf, 2009). Starch-based films are widely used because they are transparent, odorless, tasteless, and good CO_2 and O_2 barriers (Jiang, Neetoo, & Chen, 2011; Neetoo, Ye, & Chen, 2010). Modified starches have been used to develop biodegradable films for food packaging because they present better physical, optical, morphological, mechanical, and barrier properties when compared to native starch films (Fonseca et al., 2015). Coatings with modified corn starch by the action of ascorbic acid and added with powder tomato, when applied in frozen bread dough are able to improve physical properties

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and characteristics in the crust color. The use of ascorbic acid on the starch modification promotes improvements in the starch technological quality. Thus, the addition of functional powder components, such as tomato, can provide improvements in the general aspects of product quality (Galvão, Zambelli, Araújo, & Bastos, 2018).

The consumption of tomato and tomato-based products have been associated with a lower risk of developing certain types of cancers such as digestive tract and prostate cancer, which may be due to the ability of lycopene and other antioxidant components (Beecher, 1998). The increasing interest in the antioxidant activity of lycopene (the most abundant carotenoids in tomatoes), its bioavailability in the heating process (Alvarenga et al., 2017), and other functional components have been promoting tomato and tomato-based product consumption (Tapiero, Townsend, & Tew, 2004). Thus, the aim of this study was to develop edible corn starch coatings modified with ascorbic acid and added tomato powder for application on frozen bread dough to improve quality.

2. Materials and methods

2.1. Tomato powder preparation

Freshly harvested tomato (*Solanum lycopersicum* L.) fruit at the mature stage of ripening was purchased from a local market in Fortaleza. The fruits were chosen considering uniformity in color, size, and absence of blemishes, mechanical damage, or fungal infection. After washing, the tomatoes were dried (Quimis Corporation, São Paulo, Brazil) in an oven at 50 °C for 16 h. The dried tomatoes were then pulverized using an electric grinder and particles smaller than 149 μm were separated by passing through a standard sieve (U.S. No. 100). The obtained tomato powder was used to make the edible coating solution.

2.2. Corn starch modification

Corn starch was dissolved in distilled water in proportions of 1:1 until complete homogenization, containing different concentrations of ascorbic acid through a Central Composite Rotatable Design (CCRD) (Table 1). The solution was dried at 50 °C for 8 h in the forced air circulation oven. The modification that occurs in the starch is chemical, according to the review of Masina et al. (2017) with adaptations.

2.3. Preparation of coating solutions

Coating solutions were prepared according to Choulitoudi et al. (2016). First, Modified Corn Starch (MCS) was dissolved in distilled water (15 g/L) under magnetic stirring at 80 °C. The MCS solution was mixed by magnetic stirring with 20.2% glycerol (v/v). Emulsions were obtained by adding tomato powder in MCS solutions according to CCRD. Homogenization of the emulsions was performed by a high-speed homogenizer (CAT Unidrive 1000, Paso Robles, California) at 200 rpm for 5 min at room temperature. The emulsions remained for 15 min at room temperature to exhaust air bubbles formed during homogenization. The amounts of ascorbic acid and tomato powder used in the preparations of each formula were selected according to Table 1.

Table 1
Central Rotating Compound Project (CCRD) with uncoded and coded variables, these are presented in parentheses.

Edible Coatings	Independent Variables	
	Ascorbic Acid (mL/100 g of Starch) - X_1	Tomato Powder (g/100 g of starch) - X_2
1	1.0 (−1)	5.0 (−1)
2	1.0 (−1)	10.0 (+1)
3	2.0 (+1)	5.0 (−1)
4	2.0 (+1)	10.0 (+1)
5	0.80 (−1.41)	7.5 (0)
6	2.20 (+1.41)	7.5 (0)
7	1.5 (0)	4.0 (−1.41)
8	1.5 (0)	11.0 (+1.41)
9	1.5 (0)	7.5 (0)
10	1.5 (0)	7.5 (0)
11	1.5 (0)	7.5 (0)

2.4. Coating quality analysis

2.4.1. Surface tension

The surface tension of the coating solution was measured by the pendant drop method using the Laplace-Young approximation (Song & Springer, 1996) using a Du Nouy tensiometer (Lauda Command model TD 1 C). After insertion of the ring in the tensiometer, the samples were transferred to chemical cells, which were embedded in the equipment platform. This platform was then suspended until the ring became immersed in the liquid. The platform was slowly lowered and the value recorded on the equipment display.

2.4.2. Electrical conductivity

Solution conductance was analyzed using the mCA-150 conductivity meter, with cell constant k = 1.0504. The measurement consisted of inserting the electrolytic cell in the coating solutions.

2.4.3. Rheological properties

The rheological properties of the edible coating solutions were studied to investigate the flow behavior of blends, which is an important factor for food coating materials. Rheological parameters (shear stress, shear rate, apparent viscosity) of edible coating solution blends were measured using a Brookfield Engineering lab DV-III Rheometer. The edible coating solution was placed in a small sample adapter. The viscometer was operated between 10 and 50 rpm and shear stress, shear rate, apparent viscosity data were obtained directly from the instrument. The SC4-21 spindle was selected for measurement. Rheological measurements were made at different concentrations of ascorbic acid and tomato powder.

2.4.4. The ζ-potential

The ζ-potential (mV) was measured by phase-analysis light scattering (PALS) with a Zetasizer Nano-ZS laser diffractometer (Malvern Instruments Ltd, Worcestershire, UK). It determines the electrical charge at the interface of the droplets dispersed in the aqueous phase.

2.4.5. Statistical analysis

The CCRD was performed to obtain a second order model to predict the quality of the dough and bread as a result of ascorbic acid and tomato powder addition into the edible coating formulas. This model can be observed by the following equation:

$$y = \beta_0 + \sum_{i<j} \beta_{ij} x_i x_j + \sum_{j} \beta_{jj} x_j^2 + \varepsilon \tag{1}$$

Where y is the predicted response (dough and bread quality variables), β_0 is the global mean, β_j is the linear coefficient, β_{ij} is the coefficient of interaction, β_{jj} is the quadratic coefficient, ε is the error of the model, and x_i and x_j are the coded values of the independent variables.

The experimental data were analyzed using Statistica software version 9.0 (Statsoft, Inc., Tulsa, OK, USA). Analysis of variance (ANOVA) tables were generated, and the effect and regression coefficients of individual linear, quadratic and interaction terms were determined. The quality-of-fit of the equation model was expressed by the coefficient of determination (R^2), and its statistical significance was determined using the F-test. For validation of the statistical results, the observed values of edible coatings variables were compared with the predicted values obtained by the experimental models. The optimized

Table 2
Regression models for the response variables of edible coatings processed with different levels of ascorbic acid and tomato powder.

	Surface Tension ($mN\,m^{-1}$)	Eletric Conductivity (μScm^{-2})	Apparent Viscosity (mPa s)	ζ-potential (mV)
Intercept	78.55*	886.37*	8.19*	−6.57*
Ascorbic Acid (X_1)	2.53*	−9.14	8.02*	1.10*
Ascorbic Acid²	−3.55*	53.63*	4.92*	0.77*
Tomato Powder (X_2)	2.98*	122.03*	3.54*	−3.11*
Tomato Powder²	−2.71*	−3.12	2.31	−1.74*
Ascorbic Acid x Tomato Powder (X_1X_2)	−3.29*	−27.45	1.67	0.98*
R^2	0.829	0.949	0.894	0.918
p (Model)	< 0.0006	< 0.0029	< 0.0130	< 0.0001

* Values significantly different at $p < 0.05$.

independent variables were X_1 (Ascorbic Acid), X_2 (Tomato Powder) for the dependent responses, Y_1 (Surface Tension), Y_2 (Electrical Conductivity), Y_3 (Apparent Viscosity), and Y_4 (ζ-potential). The complete design consisted of 11 combinations performed in standard order (Table 1).

2.4.6. Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS)

The surface of optimized coating solutions, control and coated bread, and tomato powder were observed using an INSPECT S50 Scanning Electron Microscope (at a low energy of 10 kV). The samples were deposited on carbon tapes and coated with gold using vapor deposition techniques. The surface was scanned using magnification between 5,000× and 40,000×. The relative contents of the elements in the coatings, tomato powder and bread were investigated by energy-dispersive spectroscopy (EDS, Oxford Model 7537, England).

2.4.7. Fresh dough preparation and frozen storage shelf-life

The test baking formula used for the control bread was: flour (300 g, 14% moisture basis), fat (30 g), refined sugar (15 g), compressed yeast (11 g) and salt (6 g). Yeast was added in the form of suspension. The dough formed after mixing was placed in a baking pan and proofed for 90 min at 28 °C and 75% relative humidity (RH). The dough was molded in a dough molder, so that they have a length of 15 cm, a height of 4 cm and a width of 3 cm, weighing approximately 250 g. After molding, the doughs were immersed in the edible coating solutions according to the experimental design, where they remained for 3 min. The excess solution was removed by gravity for 1 min. After immersion, the dough was placed in lightly greased pans and set for final proofing for another 36 min at 28 °C ± 2 °C and 75% RH. After final proofing, the bread dough was baked at 220 °C for 20 min. The loaves were removed from the pans and cooled at room temperature (T = 25 ± 2 °C). Bread characteristics were tested two hours after the loaves were removed from the oven.

After removal of the excess from the edible coating solution, the doughs were placed in polyethylene containers and placed in a freezer with an average temperature of −18 °C and then stored for 15, 30, 45 and 60 days. The control breads were storage in the same way. After the storage period, the doughs were thawed for two hours, proofed and baked under the conditions outlined in the method described above. The freezing conditions were the same for all bread samples, and this technique is the one used by most bakeries in Brazil, thus simulating commercial operating conditions (Zambelli, 2015).

2.4.8. Specific volume

The bread was weighed after cooling and its volume (cm^3) was determined by the rapeseed displacement method. The specific volume (cm^3/g) was calculated as loaf volume/bread weight (AACC, 2000).

2.4.9. Bread hardness

Bread Hardness was performed using a TA-XT2i texture analyzer (Stable Micro Systems, Surrey, UK) equipped with a 25 kg load cell and a 35 mm aluminum cylindrical probe. Three bread slices (25 mm thickness) taken from the center of each loaf were used to evaluate the physical crumb texture. The settings used were a test speed of 5 mm/s with a trigger force of 0.98 N to compress the middle of the bread crumb to 50% its original height. Wait time between first and second compression cycle was 5 s (Licciardello, Cipri, & Muratore, 2014).

2.4.10. Image analysis (L*, a* and b*)

For the bread image analysis, slices of 50 × 50 mm were first cut from the center of the bread samples using a metal template (Peressini & Sensidoni, 2009). Slice images were captured using a 48.50 flatbed HP Photo Scanner (Hewlett–Packard, Palo Alto, CA) and saved in JPG format. Using Image J software, an image of 500 × 500 pixels was selected from the center of the bread samples and a feature analysis was performed in this area. RGB color space was converted into L*a*b* space. L* is the sample index in the brightness variable between the zero to 100 (pure black, pure white). A* index showed a significant amount of color close to green and red, b* index close to blue and yellow, while a* and b* ranged between −120 and +120.

2.4.11. Shelf-life statistical analysis

Results of the shelf-life study were analyzed in triplicate. The data tests were statistically analyzed by using Statistica software version 9.0 (Statsoft, Inc., Tulsa, OK, USA), and the Tukey test was used to determined significant difference between samples. In the regression analysis, a $p < 0.05$ was considered significant.

3. Results and discussion

The experimental design generated eleven experimental runs (Table 1 (combinations)). Each model created from the responses was shown to be significant with p value ($p < 0.05$). The lack of fit for each model was insignificant, with values ranging from $p > 0.3995$ to $p > 0.7849$. Finally, satisfactory coefficients (R^2) were received for each parameter (Table 2). According to the response surface (Fig. 1a), there was no direct correlation between the ascorbic acid level on starch modification and tomato powder levels and the surface tension of edible coatings. Increasing tomato powder levels while ascorbic acid was added up to 1.0% promoted an elevation in the surface tension of edible coatings at intermediate values (80–75 $mN\,m^{-1}$) (Fig. 1 a).

The use of ascorbic acid in concentrations higher than 2.0% combined with tomato powder levels above 8% promoted a significant increase in surface tension to values above 85 $mN\,m^{-1}$ (Fig. 1a). However, a reduction of the surface tension occurs to below 70 $mN\,m^{-1}$ in tomato powder levels below 5.0% at any addition of ascorbic acid. This is probably due to the increase in the number of hydrogen bonds between the ascorbic acid molecules and the coating particles, since such interactions reflect the increase in the value of the intermolecular forces at the fluid surface and consequently in the surface tension. In view of this, it can be seen that there is a required minimum concentration of particles in the coating to increase its surface tension. (Seric, Afkhami, & Kondic, 2018).

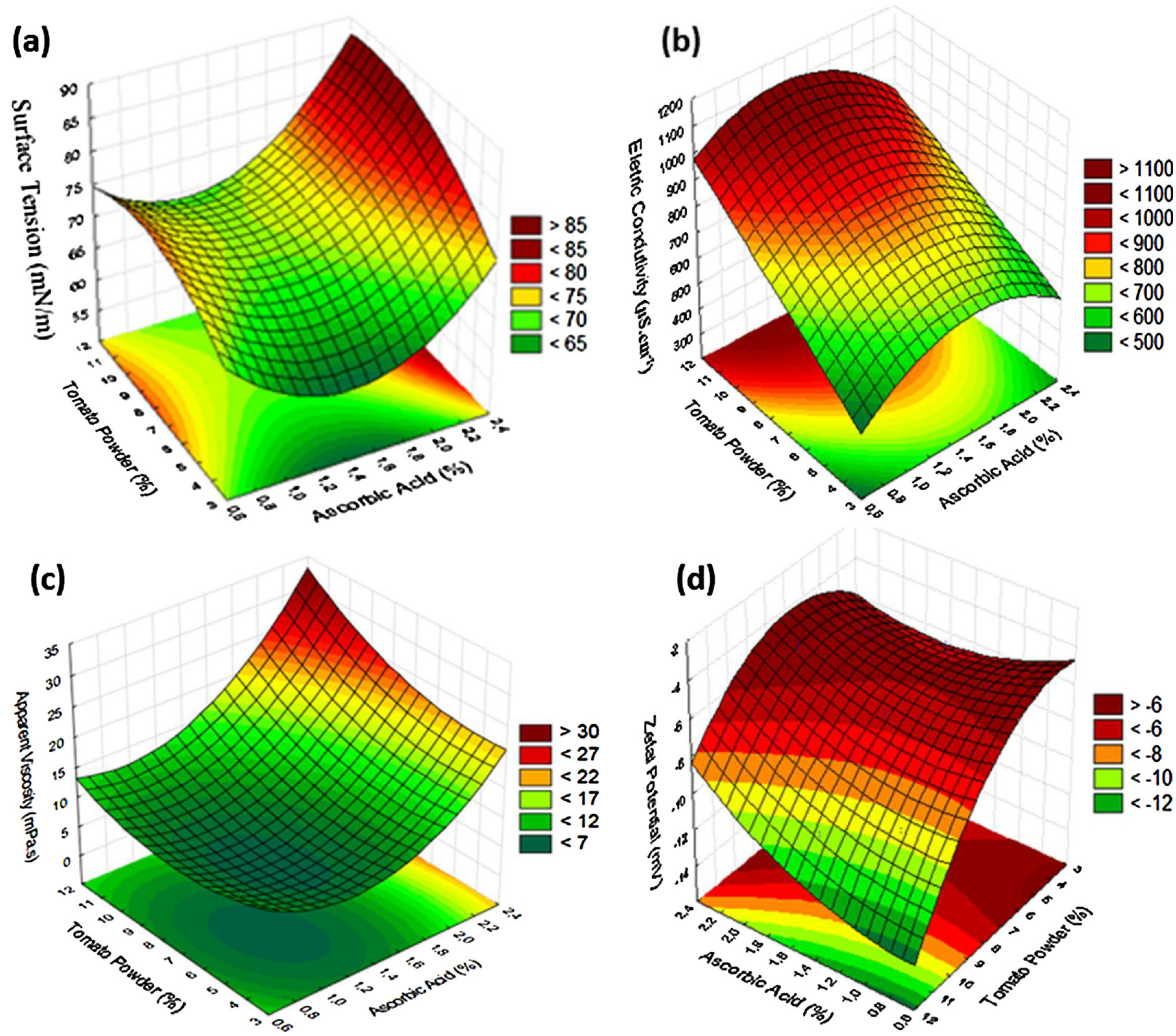

Fig. 1. Characteristics of coating solutions in relation to the effects of ascorbic acid and tomato powder concentrations on a) surface tension of the coating solution, b) electric conductivity, c) apparent viscosity, and d) Zeta Potential.

The performances of edible coatings not only depend on the employed coating methods, but also the properties of the coating materials (type, amount, density, viscosity, and surface tension). Many natural materials have the potential to make well performing edible coatings, including proteins, polysaccharides, and lipids (Al-Hassan & Norziah, 2012). In this method, a thin membranous film is formed over the product surface by directly dipping the dough into the aqueous medium of coating formulations, then removing it and allowing it to air dry (Skurtys et al., 2010). In this way, we can infer that the surface tension of the coating solution can directly influence the solution's ability to penetrate deeper layers of dough, thereby improving its protection capacity.

Surface tension is a contractive tendency of the surface of a liquid drip that allows it to resist an external force. Zhong, Cavender, and Zhao (2014) indicated a surface tension of 78.411.6 ^{1} and 26.7 mN m^{-1} of edible coatings with chitosan, sodium alginate and soy protein isolated, respectively, which indicated that the cohesion of edible coating with chitosan was the highest. Choi, Park, Ahn, Lee, and Lee (2002) obtained surface tension of 70.9 and 61.5 mN m^{-1}, respectively, using 1.5% chitosan and 1% alginate coating solution. In this way, the addition of ascorbic acid in the corn starch modification (a component of the edible coating), and the tomato powder increases the coating cohesion.

Fig. 1b shows the effect of acid ascorbic concentration and tomato powder on the edible coating electrical conductivity. It is indicated that the electrical conductivity depends more on the tomato powder concentration rather than ascorbic acid concentration. In low values of the tomato powder concentration, the electrical conductivity increased and then decreased up to 1% and over 2.0% ascorbic acid concentration (Fig. 1b). However, in high values of tomato powder (> 9.0%) concentration, the electrical conductivity is greater than 900 µS cm^{-2}, independent of the ascorbic acid concentration in the starch modification. Once in aqueous suspension, the ascorbic acid molecules must be partially dissociated. In addition, high values of electrical conductivity are to be expected due to the strong electrolytes present in tomato powder.

The apparent viscosity of edible coatings was influenced by the ascorbic acid starch modification and tomato powder addition. All edible coatings presented the Herschel-Bulkley rheology model; this behavior was observed in several starch gels and viscoelastic gluten-free doughs (Correa, Añón, Pérez, & Ferrero, 2010). The apparent viscosity increased with the ascorbic acid concentration due to the corn starch modification increase (Fig. 1c). Fig. 1c shows a minimum point (apparent viscosity less than 7 mPa s) in the range of 4.0%–8.0% on the response surface of tomato powder correlated with ascorbic acid modified starch in the proportions of 0.82% to 1.4%. At ascorbic acid concentrations of greater than 1.6%, the coating solutions showed a significant increase in viscosity (Fig. 1c). This increase is not desired for the coating solutions since they need to have low apparent viscosity to facilitate their flow on all the dough surfaces and to present penetration power through the dough pores. This was supposedly due to specific attractive interactions between side groups on the polymer chains (Walstra, 2003).

The ζ-potential behavior is shown in Fig. 1d and showed a smaller magnitude (−4.74 ± 0.85 mV to −11.08 ± 0.31 mV). It was found that the zeta potential of the solutions at high tomato powder levels (7.0%) at ascorbic acid concentrations below 2.1% was between −6.00 mV and −7.00 mV, and the potential zeta was below −6.00 mV when the ascorbic acid concentration was higher than 2.2%.

According to McClements (2012), the magnitude of the ζ-potential indicates the degree of electrostatic repulsion between adjacent and similarly charged particles in the dispersion. When ζ-potential is small near to 0.00 mV, attractive forces may exceed this repulsion and the colloid may break, so it shows a tendency to flocculate or precipitate. Through the response surface, it can be verified that an increase of the zeta potential occurs above the 7.0% level of tomato powder, favoring the stability of the edible coating solutions. According to Durigon, Souza, Carciofi, and Laurindo (2016), the short dispersion times observed in tomato powder samples indicate that this powder has high wettability. According to Hogekamp and Schubert (2003), the greater the diameter and particle porosity, the shorter the dispersion time as it facilitates water penetration into the particle voids. Thus, the particle size of the tomato powder favors stability in the edible coating solution, consequently contributing to improve the nutritional value.

In general, tomato powder reduces the zeta potential, which suggests its anionic nature and increases the electrical conductivity due to the presence of dissolved solids, thereby facilitating a transfer of electric particles. The ascorbic acid increases the zeta potential and reduces the electrical conductivity, and both increase the apparent viscosity of edible coating solutions. The viscosity is a parameter directly related to the fluid resistance to flow, so that the higher the viscosity, the greater the resistance, which is also related to the penetration, which decreased with increasing fluid viscosity, verifying an inverse relationship between viscosity and penetration (Chorilli, Zague, Scarpa, & Leonardi, 2007).

Therefore, from the results of the CCRD data the response surfaces were generated (Fig. 1) based on the optimized conditions of the edible coating properties resulting in the coating solutions EC1 - 1.8% ascorbic acid and 4.0% tomato powder; and EC2 - 2.2% ascorbic acid and 5.0% tomato powder. The frozen dough storage presented a significant influence ($p < 0.05$) on the specific volume of breads (Fig. 2). Therefore, the breads made from coated EC1 and EC2 dough presented higher specific volume than the breads made from uncoated dough. This behavior can be explained by some phenomena; first, the nutrients (corn starch and tomato powder) present in edible coatings promote yeast growth. The acid treatment on the corn starch modification probably promoted its hydrolysis in glucose molecules, thus facilitating access to yeast, as suggested by Kim, Maeda, and Morita (2006) for enzymatic starch degradation. Moreover, the coatings may have promoted a protective action on the gluten network against frozen storage damage due to the formation of a surface layer, which reduced the moisture loss to the external medium; this behavior can be performed by glycerol and ascorbic acid present in the coating formulation. According to Rocca-Smith et al. (2016), wheat gluten films could be thus applied as food coatings or edible films on naturally gluten containing foods (e.g. bakery products) in order to slow down mass transfer phenomena such as water and oxygen, which are known to decrease the food quality. The rate of the specific volume decrease was higher in the uncoated dough. In the coated doughs, this decrease was lower when using the EC2 coating. According to Wang et al., the frozen dough storage and thawing showed different degradation kinetics and contributed to reduced bread loaf volume. In this way, the use of edible coatings with ascorbic acid on corn starch modification and tomato powder in the frozen dough was beneficial for the quality maintenance of the bread made from frozen dough for up to 60 days. This behavior can be performed by glycerol and ascorbic acid present in the coating formulation.

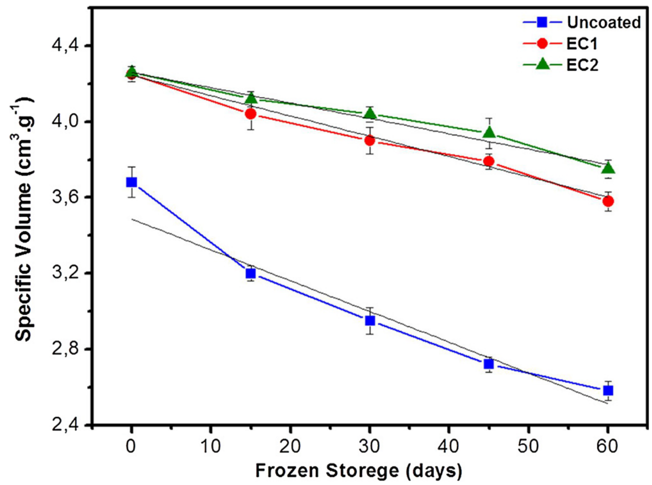

Fig. 2. Variation of specific volume of the breads with the storage time. Subtitle: EC1 (1.8% ascorbic acid and 4.0% tomato powder) and EC2 (2.2% ascorbic acid and 5.0% powdered tomatoes) are solutions that resulted from optimized conditions of response surfaces solutions.

Actually, for some additives whose role is to improve dough properties such as hydrocolloids and emulsifiers (Hejrani, Sheikholeslami, Mortazavi, & Davoodi, 2017), the use of edible coatings with modified corn starch and tomato powder can be a natural and more economical alternative to be applied in this product. In this coating, the glycerol acted with emulsifier, besides its main function of plasticizer. The parameters of bread crumb color and texture were also modified according to the application of the edible coating and frozen storage time (Table 3). For non-frozen dough, the bread presented reduced luminosity when coated; when the higher level of tomato powder was used, the luminosity and red tendency were lower due to the pigments present in tomato powder. According to Carrillo-López and Yahia (2012), ripe tomato fruits accumulate large amounts of red linear carotene (lycopene), which gives a red coloration to breads through the edible coatings. Davoodi, Vijayanand, Kulkarni, and Ramana (2007) suggest that the quality of tomato powder is influenced by the long-term storage conditions, including factors such as light, oxygen and moisture which accelerate the changes in the tomato powder quality during storage, which could be observed in this study.

A darkening of the control bread was observed during the frozen dough storage, while the coated breads presented an increase in luminosity, probably due to the degradation of the carotenoid pigments present in the tomato. This corroborates the results obtained for parameter a* and b*, which showed a reduction in the red tonality and an increase in the yellow. Uniformly distributed gas cells produced during the end of fermentation and early cooking tend to reflect light instead of absorbing it and provide a whiter appearance in contrast to the few large gas cells due to the weakening of the gluten matrix, which gives a darker appearance to the nucleus (Rosell & Gómez, 2007). Therefore, by color analysis it is possible to prove that there was no degradation of gluten in the loaves during the period of 60 days of freezing at −18 °C, because the parameter L * (dough luminosity) increased from 66.48 to 74.15. In this way, it can be inferred that the applied edible coatings promoted preservation of the gluten network.

According to Purlis (2011), breads with luminosity close to 70.00 have good sensorial acceptance. Therefore, values below 60.00 result in excessive darkening. Within this view, the control and coated breads have good coloring characteristics after 60 days of frozen storage. The bread hardness generally increased during the storage time of the

Table 3
Color parameters and hardness of breads made from frozen dough uncoated and coated.

Frozen storage time (days)					
Samples	0	15	30	45	60
L*					
Control	77.38 ± 0.29 ^{a}	73.91 ± 0.57 ^{a}	73.22 ± 0.07 ^{a}	70.77 ± 0.31 ^{b}	69.43 ± 0.22 ^{b}
EC1	66.48 ± 0.13 ^{b}	69.33 ± 0.15 ^{b}	71.19 ± 0.13 ^{b}	72.33 ± 0.10 ^{a}	74.15 ± 0.19 ^{a}
EC2	57.77 ± 0.17 ^{c}	61.20 ± 0.13 ^{c}	63.49 ± 0.18 ^{c}	64.28 ± 0.13 ^{c}	65.44 ± 0.15 ^{c}
a*					
Control	−7.96 ± 0.12 ^{a}	−6.55 ± 0.15 ^{c}	−5.12 ± 0.11 ^{c}	−4.33 ± 0.19 ^{c}	−3.82 ± 0.13 ^{c}
EC1	3.55 ± 0.22 ^{b}	3.04 ± 0.11 ^{b}	2.85 ± 0.12 ^{b}	2.34 ± 0.18 ^{b}	1.92 ± 0.11 ^{b}
EC2	3.70 ± 0.28 ^{b}	3.55 ± 0.19 ^{a}	3.28 ± 0.14 ^{a}	3.01 ± 0.11 ^{a}	2.85 ± 0.15 ^{a}
b*					
Control	20.09 ± 0.18 ^{a}	23.99 ± 0.18 ^{a}	24.19 ± 0.15 ^{a}	25.44 ± 0.12 ^{a}	26.17 ± 0.19 ^{a}
EC1	5.90 ± 0.29 ^{b}	6.85 ± 0.09 ^{b}	7.44 ± 0.19 ^{c}	8.17 ± 0.14 ^{c}	9.85 ± 0.12 ^{b}
EC2	6.70 ± 0.21 ^{c}	7.75 ± 0.10 ^{c}	8.33 ± 0.12 ^{b}	9.75 ± 0.12 ^{b}	10.27 ± 0.11 ^{c}
Hardness (g)					
Control	85.04 ± 0.12 ^{a}	95.87 ± 0.18 ^{a}	111.35 ± 0.12 ^{a}	129.66 ± 0.28 ^{a}	158.13 ± 0.17 ^{a}
EC1	75.02 ± 0.18 ^{b}	82.21 ± 0.15 ^{b}	91.98 ± 0.18 ^{b}	104.15 ± 0.13 ^{b}	121.33 ± 0.11 ^{b}
EC2	71.99 ± 0.09 ^{c}	75.99 ± 0.09 ^{c}	84.75 ± 0.09 ^{c}	99.31 ± 0.20 ^{c}	111.84 ± 0.14 ^{c}

EC1 (1.8% ascorbic acid and 4.0% tomato powder) and EC2 (2.2% ascorbic acid and 5.0% powdered tomatoes) are solutions that resulted from optimized conditions of response surfaces solutions. Different letter in the same column indicates significant statistical differences (Tukey's test, $p < 0.05$). L* measure of darkness to lightness (a greater value indicates a lighter color); a* value indicates redder color; b* value indicates more yellow color. N = 5 (mean ± standard deviation).

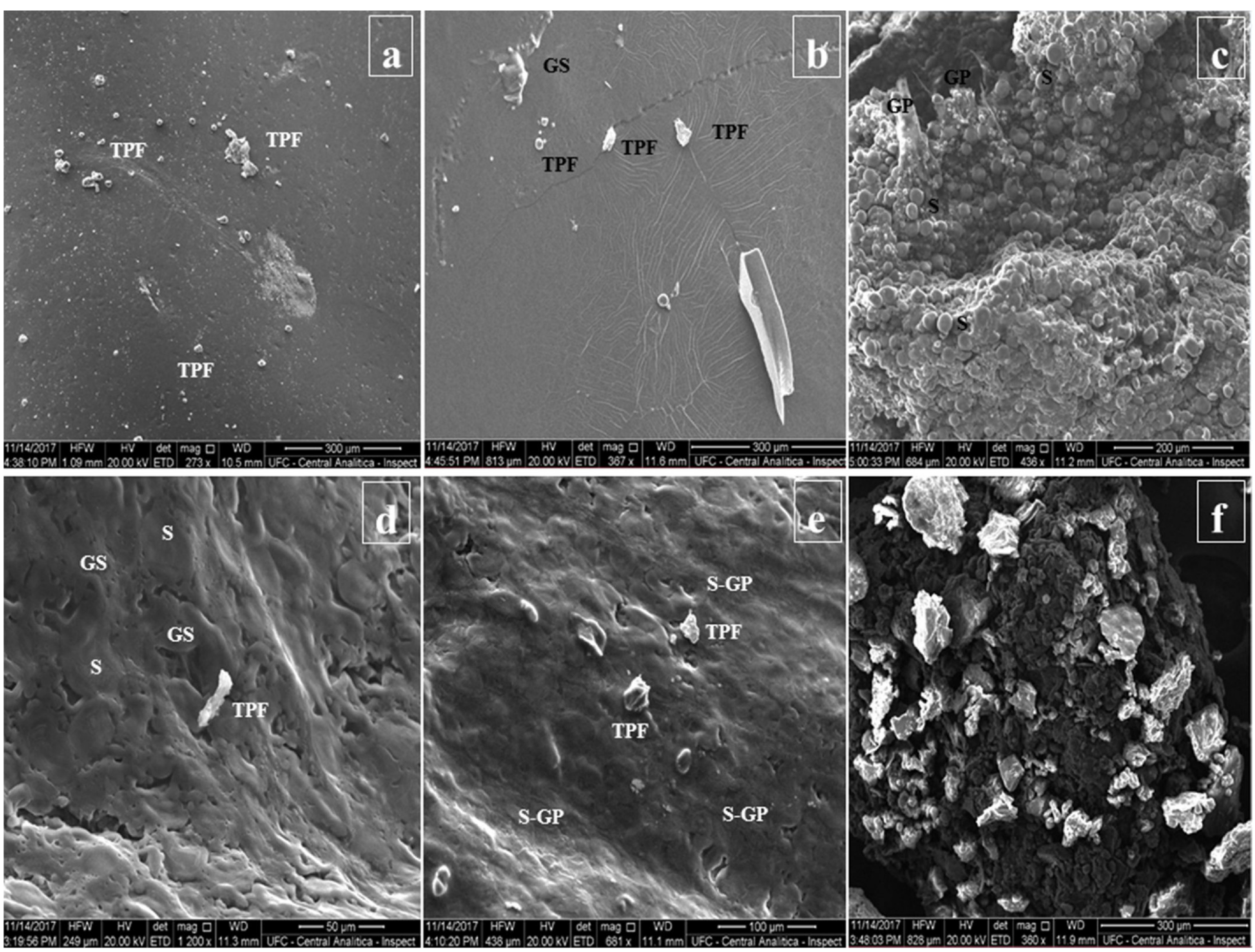

Fig. 3. Scanning Electron Microscopy (SEM) of a) EC1 solution, b) EC2 solution, c) fresh control bread, d) EC1 fresh bread, e) EC2 fresh bread and f) tomato powder. TPF: tomato powder fragments; GS: gelatinized starch; GP: gluten protein; S: starch; S-GP: Starch-Gluten Protein Complex.

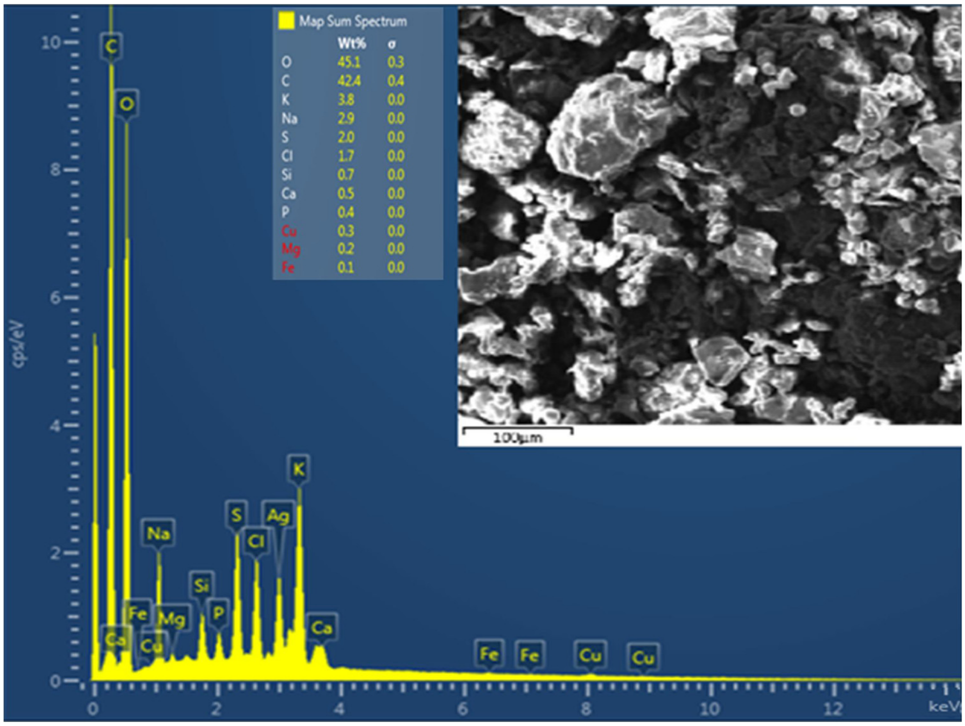

Fig. 4. Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS) analysis of tomato powder.

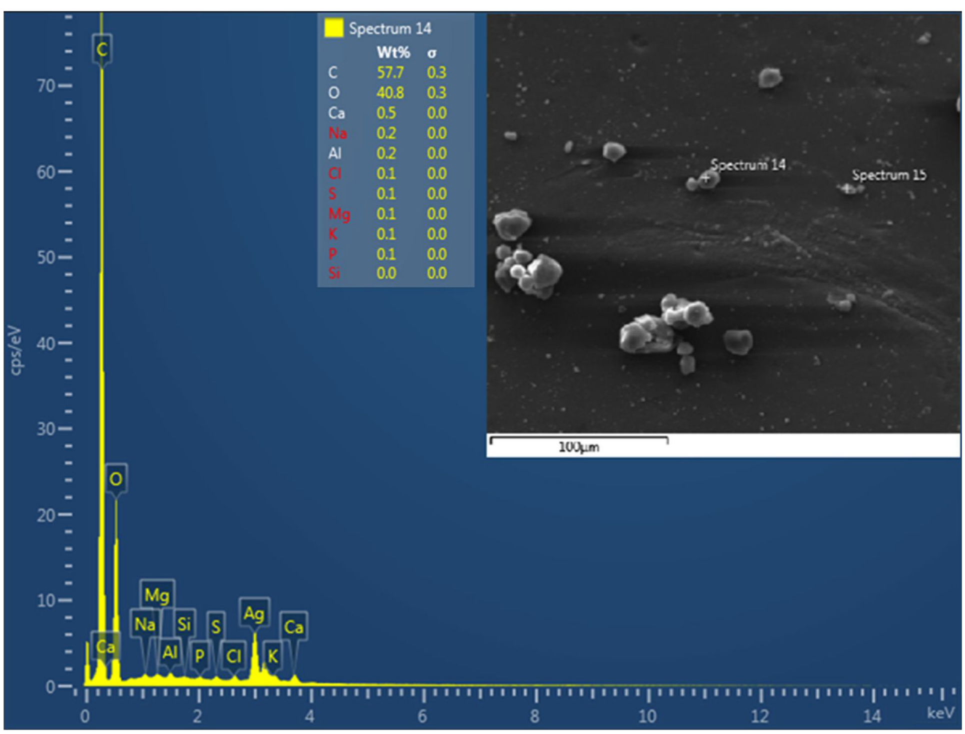

Fig. 5. Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS) analysis of EC1 solution.

frozen dough. However, it was observed that the pasta coated with edible modified corn starch with ascorbic acid and powdered tomato produced loaf of lower hardness (71.99 and 111.84 g in the 0 to 60 days of freezing, respectively) when compared to control bread ranging from 85.04 and 158.13 g in the 0 to 60 day freeze period, respectively (Table 3).

According to Gharaie, Azizi, Barzegar, and Aghagholizade (2015) and Morimoto, Tabara, and Seguchi (2015), this behavior resembles that promoted by hydrocolloids added in formulations of dough as gums, thus exhibiting an anti-staling effect. Fig. 3 shows the SEM of: (a) EC1 solution, (b) EC2 solution, (c) fresh control bread, (d) EC1 fresh bread, (e) EC2 fresh bread and (f) tomato powder. In a comparative study between Fig. 3a and b, we can identify fragments of tomato powders on the edible coating surface (confirmed by the EDS analysis below); however, cracks in its surface can be seen in Fig. 3b, probably caused by the greater amount of ascorbic acid used in the starch

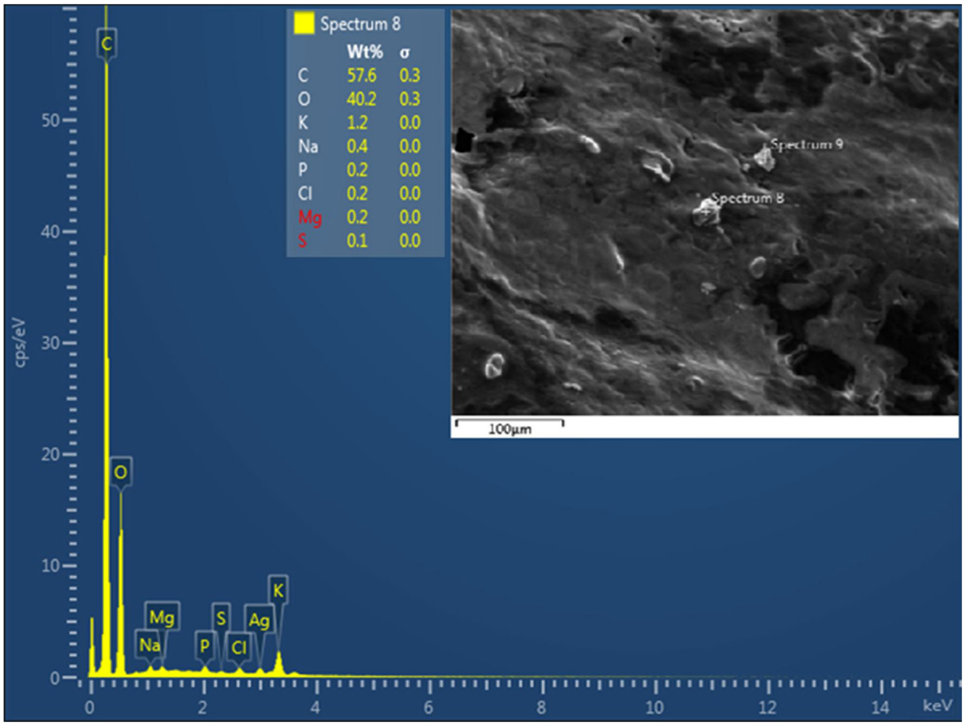

Fig. 6. Scanning electron microscopy (SEM) and dispersive energy spectroscopy (EDS) analysis of fresh bread coated with the EC2 solution.

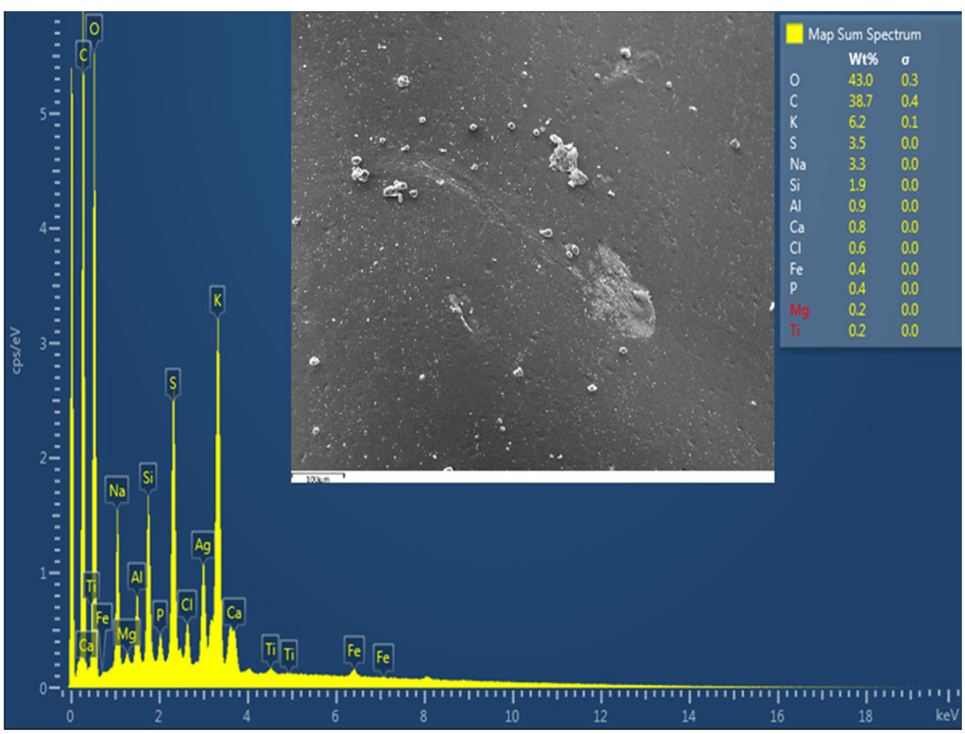

Fig. 7. Scanning Electron Microscopy (SEM) and Energy-Dispersive Spectroscopy (EDS) analysis of EC2 solution.

modification (Kim, Park, & Kim, 2017). In addition, gelatinized starch spots can be observed.

Scanning Electronic Microscopy analysis showed starch and protein are the main building structures of the flours in control bread (Fig. 3c). However, in bread coated with the edible coating (Fig. 3d and e), it is possible to observe that the gluten network and the starch exhibit greater interaction, which justifies the higher specific volume obtained by these breads. This behavior can be attributed to the coating promoting greater moisture to the dough, as well as corroborating the fermentative process as previously described which provides a more homogeneous gluten-starch interaction. The increase of dough moisture from the fermentative point of view is beneficial because it assists in the activity of the yeasts in this process and improves the water mobility, according Xiong, Zhang, Niu, and Zhao (2017). Fragments of tomato powder were observed in both breads and confirmed through EDS analysis, showing that the edible coating showed the ability to

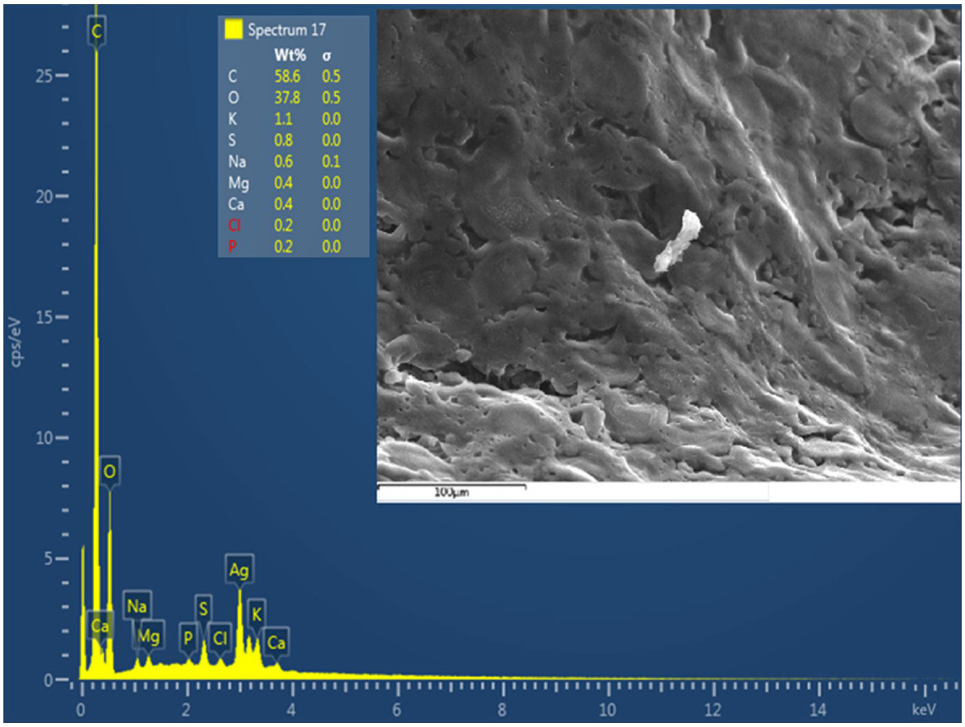

Fig. 8. Scanning electron microscopy (SEM) and dispersive energy spectroscopy (EDS) analysis of fresh bread coated with the EC1 solution.

penetrate the product.

Tomato powder particles (Fig. 3f) were spherical and flake-like particles after milling, tending to agglomerate because of high specific surface area and hygroscopicity, as suggested by Durigon et al. (2016), Liu, Cao, Wang, and Liao (2010) and Goula, Adamopoulos, and Kazakis (2004). The EDS analysis of tomato powder (Fig. 4) showed K, Na, S, Ca and P mineral content and traces of Cu, Mg and Fe. This result is in agreement with those obtained by Salem, Albanna, and Awwad (2016), Costa, Baeta, Saraiva, Verissimo, and Ramos (2011) and Sanders, Grayson, and Monaco (1981). Figs. 5 and 6 shows the EDS analysis for the EC1 coating sample and for the bread coated with the EC2 coating. The EDS of EC2 solution and bread coated with EC1 solution are present in Figs. 7 and 8 respectively. It was possible to observe the presence of tomato powder fragments, as well as the presence of the minerals intrinsic to their addition in both the coating and the bread after baking. This result shows the ability of the edible coating to penetrate into the dough structure during the fermentation and delivery steps.

4. Conclusion

The ascorbic acid in the corn starch modification and tomato powder in edible coating formulations contributed to the zeta potential, surface tension, electrical conductivity and apparent viscosity of the edible coatings. Both contributed to an apparent viscosity increase, while tomato powder reduced the zeta potential and ascorbic acid promoted its increase. The ascorbic acid increased the electrical conductivity and tomato powder produced an inverse effect.

Application of the optimized edible coatings in frozen dough promoted an increase of the useful life of the products, reducing the firmness and browning of the breads when compared to the uncoated bread until 60 days of frozen storage, and may be a viable alternative for the use of additives in frozen dough.

The SEM/EDS analysis showed that the minerals present in tomato powder are present in the edible coating as well as in the bread after the delivery step, thus improving the nutritional quality of the final product.

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