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ORIGINAL PAPER

Study of Spray System Applications of Edible Coating Suspensions Based on Hydrocolloids Containing Cellulose Nanofibers on Grape Surface (*Vitis vinifera* L.)

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Abstract

An edible coating is a useful technology to preserve fruit quality by covering them with a protective layer which improves the appearance and provides a semipermeable barrier for gases and water vapor transfer, allowing extension of their shelf life. In this study, edible coatings based on hydroxypropyl methyl cellulose, *k*-carrageenan, glycerol, and cellulose nanofibers were formulated. The operational conditions of the spray system were studied to obtain a coating with optimal adhesion on grape (*Vitis vinifera* L.) surface. Furthermore, the physico-chemical properties of grapes covered with edible coatings were evaluated during refrigerated storage. A full factorial 2^3 experimental design was applied, where liquid suspension flow (1–5 L h^{-1}), air pressure (50–200 kPa), and height of impact (0.3–0.5 m) were evaluated as independent variables, whereas the percentage of coating and thickness of coating was the response variables. Both mechanical and physico-chemical properties were evaluated during 41 days in both coated and uncoated grapes as shelf life criteria. Throughout the storage time, noticeable changes in pH and total soluble solids were not found in grapes covered with edible coatings and they showed the highest stability for the evaluated mechanical properties. Moreover, coated grapes showed final weight loss and water vapor permeability values of approximately 30 and 34% lower, respectively, than uncoated grapes, suggesting a shelf life extension.

Keywords Edible coating · Hydrocolloid · Spray system · Grape

Introduction

Nowadays, consumers are looking for healthy and natural products which lead to consumption of minimally processed fruits and vegetables and seeking the fresh–cut quality of these products on the basis of appearance and freshness at purchase time (Ghidelli et al. 2014; Rojas-Graü et al. 2009). However, due to highly perishable properties of fruits and vegetables, preservation technologies must be developed and adopted to provide a healthy, additive-free, microbiologically safe, and high-quality product for consumers. Edible coating technology is a feasible, alternative, and promising technology which gives protection, improving appearance, reducing vapor and air transfer between fruit and environment, decreasing also respiration rate, enzymatic activities, and water losses (Embuscado et al. 2009; Moalemiyan et al. 2012; Villalobos-Carvajal et al. 2009). One of the advantages of using edible coatings is that a number of active ingredients may be incorporated into the polymer matrix and consumed with the food; thus, it could enhance safety and even nutritional and sensory attributes. The nature of the matrix might vary in nature and chemical composition, such as polysaccharides, proteins, lipids, and composite (Dave et al. 2017; Z. Deng et al. 2017; Dhall 2013). The use of polysaccharide-based coatings in food products could offer new opportunities to develop novel food packaging systems (Otoni et al. 2017); derivatives of cellulose could be used such as methylcellulose (MC), hydroxypropyl cellulose (HPC), hydroxypropyl

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methylcellulose (HPMC), chitosan, carboxymethyl cellulose (CMC), and microcrystalline cellulose (MCC), which have unique and specific physical, chemical, and colloidal properties and ability to form coatings (Cazón et al. 2017; Suppakul et al. 2010). Although the polysaccharides above mentioned are based on a (1 → 4)-ß-D-glucopyranosyl backbone, they possess different substituent groups. For instance, CMC is polyanionic when dissolved in aqueous solution, due to its carboxylic substituent. Meanwhile, chitosan is polycationic when dissolved in a slightly acidic aqueous solution, due to its protonated amine groups, and polyelectrolytes. CMC and chitosan are more polar than the neutral MC and HPMC, which, in turn, are even slightly hydrophobic due to their alkyl chain substituents (Arnon et al. 2015). HPMC, a water soluble cellulose ether hydrocolloid with good film forming properties and tasteless, yields coatings which are flexible, odorless, water soluble, resistant to oils and fats, and show good oxygen and aroma barrier properties (Navarro-Tarazaga et al. 2011; Rubilar et al. 2015) being suggested to be used as ingredient in edible coating. The degree of substitution, types of functional group substitution, and chain length of this polymer affect permeability, mechanical properties, and water solubility; its application imparts both moisture and barrier (oxygen and hydrophobic compounds) characteristics. Although it is possible to develop coatings using only HPMC, they show high tensile strength, low elongation, and high water permeability, being necessary to incorporate within the matrix some agents to improve flexibility and barrier properties such as gums and cellulose nanofibers (CNFs) (Menegalli 2017). Thus, its mixture with type K carrageenan, a natural hot water (65–75 °C) soluble hydrophilic gum that forms a strong and thermal reversible rigid gel, under appropriate proportions delays moisture losses and avoids oxidation (Osorio et al. 2011; Rubilar et al. 2015). Moreover, the incorporation of CNFs into the matrix is also a way to improve coating barrier properties. Their morphology gives them a high surface energy, and they can form a tight network when changing to solid state due to the high number of hydroxyl groups at their surface (Lavoine et al. 2014).

The methods of coating application directly affect its adhesion, and the application onto foods products may be performed through dipping, brushing, panning, fluidized bed, electrostatic, spraying, electrospray, etc. All these techniques exhibit several advantages and disadvantages and the selection of an appropriate method depends on the characteristics of food, coating materials, intended effect of the coating, cost (Andrade et al. 2012), and configuration of processing. For example, when using dipping method, the suspension can dilute the outer layer of the food surface and degrade its functionality; also, the natural wax layer of fruits and vegetables could be removed after dipping (Baldwin et al. 2011). Hence, both methodology and adhesion of coating onto food surfaces still need to be studied and improved. An alternative arises from using spraying technique, which is among the most commonly used methods, at continuous configuration, to coat foods due to the development of high pressure spray applicators and air atomizing systems. Some coating applications, using spray system, are common in several processes such as to coat beef tenderloins, pork loins, salmon fillets, chicken breasts, bakery products, and fruit-based salads (Andrade et al. 2013). Besides, a fluidized bed processor coupled with spraying nozzle as an alternative to a tumbling vessel for coating puffed wheat particles with a sweet chocolate cover has been utilized (Solis-Morales et al. 2009).

Therefore, the objective of this research was to determine the operational conditions of the spray system to obtain an optimum coating adhesion on grape (*Vitis vinifera* L.) surface and its consequent effects on shelf life and physical properties when it is covered with an edible coating formulated with hydroxypropyl methyl cellulose, *k*-carrageenan, glycerol, and cellulose nanofibers.

Materials and Methods

Materials

Grapes (*Vitis vinifera* L.) were purchased at the local market (Santiago, Chile). Selection criteria were uniform size (minor semi-axis length 9.49 ± 0.11 mm and major semi-axis length 14.11 ± 0.15 mm), shape (prolate spheroid approximation), color (green characteristic), non-mechanical, and non-fungi injuries (by visual inspection). Hydroxypropyl methylcellulose (HPMC Methocel E19 Food Grade M.W. 1261.45 g mol^{-1}; η = 19 cP at 2% (*w*/*w*) and $T = 20$ °C; Dow Wolff Cellulosic; Bolmitz, Germany), and *K*-carrageenan (Gelcarin. GP 911 ~ 800 mPa·s at 1.5% (*w*/*w*), FMC BioPolymer, USA) were donated by Blumos Chile S.A. Glycerol was purchased from Sigma (Sigma-Aldrich, Santiago, Chile). Cellulose nanofibers (CNFs) (20–70 nm wide ribbons) were obtained from agroindustrial residues produced by *Gluconacetobacter swingsii* sp. (Castro et al. 2011).

Suspension Preparations

A suspension of 2 L total volume was prepared where 0.2% (*w*/*v*) of *k*-carrageenan was dissolved into 400 mL distillated water under agitation (1100–1300 rpm) for 30 min. Then, 4% (*w*/*v*) HPMC was dissolved into 1.2 L distillated water at 90 ± 2 °C under agitation (400 rpm) using a magnetic stirrer (Pobel, Model: HASM-50, Korea). Finally, both suspensions were mixed, and 10% (*w*/*w*) glycerol and 1% (*w*/*w*) CNFs were added at 40 °C under continuous stirring (Remi Motors, Model: RQ121-D, India) for 2 h at 800 rpm. Lastly, the suspension was stored for 24 h at 25 ± 2 °C.

Applications of Edible Coating Suspension

Spray System and Operational Conditions

Formation of edible coating on the fruit surface was performed using a pilot spray system (Andrade et al. 2013) as depicted in Fig. 1. Grape sample ($n = 30$) was selected randomly to undergo spray application. In the atomization process, the flow rates (1; 5) L h^{-1} were controlled with a rotameter coupled to the line and suspension blended in a hermetic tank (2.5 L). A spraying device (Spraying System S.S. Co, VA67255–60° SS) and air atomizing caps (S.S. Co, VF2850–SS) were utilized. Experimental runs correspond to a full factorial design 2^3 and the operational variables studied were as follows: flow rate (1; 5) L h^{-1}, pressure (50; 200) kPa, and height (0.3; 0.5) m. Samples were exposed to the spray application system during 20 s for each combination. Then, the samples were stored under atmospheric conditions (22 ± 2 °C) for 1 h and later stored at refrigeration conditions (4 ± 0.5 °C).

Coating Thickness Determination

Grapes covered by the edible coatings were stored at − 18 °C for 24 h; these samples were subjected to three 0.1-mm thickness cross-sectional cuts and analyzed with an optical microscope (A. KRÜSS Optronic, MBL2000, Germany) equipped with a video eyepiece (A. KRÜSS Optronic, VOPC93, Germany). Coating thickness measurements were determined using ImageJ 1.46r program (Schneider et al. 2012). As the program gives measurements as pixel numbers, a calibration was necessary to convert to metric system.

Coated Grape External Surface Determination

A known volume of suspension was applied to coat a certain portion of the grape surface; the application of the suspension on the grape surface was controlled for coating 0, 25, 50, and 100% of the total grape surface. The non-coated surface was protected with an impermeable coating material. Grapes were weighed previously to the spraying process and after applying the suspension without impermeable coating. The outer surface of the grapes was approximated a prolate spheroid in shape. A curve fitting procedure was applied to the grape surface coated v/s weight of the suspension spent in coating the surface.

Textural and Physico-Chemical Analysis of Grapes as Function of Storage Time

Both textural analysis (stiffness and work ratio) and physico-chemical properties (total soluble solids, pH, and maturity index) were evaluated after the spraying process at days 0, 4, 7, 10, 12, and 14. To evaluate a maximum period for shelf life, a final evaluation was performed at day 41 of storage. Samples were stored at 22 ± 2 °C for 1 h and then kept overnight at refrigeration temperature (4 ± 0.5 °C); uncoated grapes were used as control.

Determination of Grape Weight Loss

Around 0.3 kg of coated and uncoated grapes were stored at 4 ± 0.5 °C and weighed at days 0, 4, 7, 10, 12, 14, and 41 of storage (ISHIDA, ISH IPC1, England). Weight differences between coated and uncoated grapes were considered as total weight loss and expressed as a percentage (Gol et al. 2013).

Total Soluble Solids, pH, Titratable Acidity, and Ripeness Index Determination of Coated and Uncoated Grapes Samples

TSS analysis was carried out using a refractometer (RHB-32, Labtec, Chile, ± 0.2%) according to AOAC–932.12 standard methods; TA was measured according to AOAC–947.05 method. pH was measured using a pH-meter (Milwaukee Instruments, MI 150, USA) according to AOAC–981.12 standard methods. Ripeness index was expressed as TSS/TA ratio (Wanitchang et al. 2010).

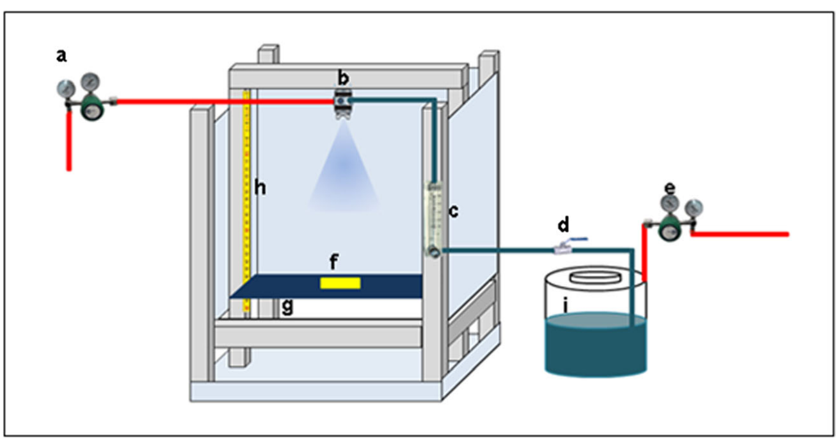

Fig. 1 Experimental setup of the pilot level spraying system. **a** Air control and manometer, **b** spraying device, **c** rotameter, **d** ball valve, **e** liquid regulator and manometer, **f** grape samples, **g** mobile flat plate, **h** height measurement meter, and **i** storage tank

Water Vapor Permeability

Around 0.3 kg of coated and uncoated grapes was weighted. The samples, stored at 4 ± 0.5 °C, were exposed to a controlled 76% relative humidity (RH) environment and evaluated every day during 14 days. The water vapor transmission rate (WVTR) was measured gravimetrically using a modification of the "cup method", following the ASTM Standard Test Method E96/E96M (ASTM) (Rubilar et al. 2015).

WVTR was determined as the ratio between the slope of the weight gain curve (S) and the coating area according to eq. (1):

$$\mathrm{WVTR} = \frac{\mathrm{S}}{\mathrm{A}} \tag{1}$$

where S is the slope of the weight change against time curve (kg s^{-1}) and Ais the exposed coating area (m^2) at constant temperature andRH (%). The WVP can be calculated from the WVTR (Cazón et al. 2017) according to eq. (2):

$$\mathrm{WVP} = \mathrm{WVTR} \cdot \frac{\varepsilon}{\Delta \mathrm{P}} \tag{2}$$

where εis the mean thickness of the coating (m) and ΔPis the partial pressure difference across the coating (Pa).

Physical and Mechanical Properties of Coated and Uncoated Grapes

Textural analysis was carried out using a texture analyzer machine (Zwick Roell, KAD–Z, Germany) according to the Puncture Test EN 14477 (En 2004) with some modifications. Samples were punctured with a pointed tip (0.8 mm diameter) at a constant speed of 0.5 mm s^{-1} until the plunger reached 4 mm depth into the grape sample. Stiffness (N m^{-1}) was determined from the slope of the stress-distance curves and work ratio (W1/WT) was calculated from W1, which denotes the work involved in penetrating through the edible coating plus cuticle system, and WT denotes the total work needed to reach 4 mm depth into the grape pulp.

Statistical Analysis of Data

Analysis of variance (ANOVA) test was used coupled to the Multiple Range Tukey's test to analyze the data, using GraphPad Prism v.4.0 (GrapPad System Inc.). A 2^3 randomly full experimental design was applied in triplicate. Differences between the mean values of the measured properties were compared using multiple-range Tukey's test. Besides, desirability index (DI) function was utilized as method for multicriteria optimization (Dodson et al. 2014; Trautmann and Weihs 2006). A significance level $\alpha = 0.05$ was used.

Results and Discussion

Spraying System Operation

Thickness of Edible Coating

Thickness of grape edible coatings varied from 24.26 ± 0.88 to 38.47 ± 1.35 (μm) according to the response surface (Fig. 2a, b). Statistical analysis for thickness indicated that flow rate, pressure, and impact height showed significant differences ($p < 0.05$). Figure 2b also shows that at the highest level of impact height (h = 0.5 m), there was a proportional relationship between coating thickness and pressure at the lowest flow rate level. However, at the lowest height level impact (h = 0.3 m) for all flow rate range, the thickness decreased when the pressure increased (Fig. 2b). Therefore, the positive effect of height may be attributed to the higher spreading capacity of the fluid, which is associated with a good adhesion between surface and suspension. Thus, these results showed that the kinetic energy associated to the droplet is low enough for spreading through the surface, avoiding the splashing phenomenon (Xu 2007); furthermore, it was shown that the increase in the Weber number had a positive influence on the maximum spread factor for both purple cabbage and banana epicarps (Andrade et al. 2012), when using a similar suspension composition. Pressure and flow rate showed strong influence ($p < 0.05$) on coating thickness (Fig. 2b), where an increase in mean grape coating thickness from 35 to 40 μm was observed at low levels of suspension flow rate (1 L h^{-1}) and high-pressure levels (200 kPa).

In general, when both pressure increases and flow rate decreases through spray-nozzle system, there is a drop size decrease (Fossen and Schümann 2017; Nuyttens et al. 2007). This fact allowed to obtain a homogenous liquid distribution on the grape surface, covering those interstitial zones between droplets. In addition, rheological behavior of the coating forming suspension played an important role in the drop impact process, specifically on spreading and thickness along with impact time until steady state was reached (An and Lee 2012); this may have improved both adhesion and layer-layer coating formation over time. From this study, it was confirmed that both impact velocity and suspension apparent viscosity (with shear thinning characteristics) had noticeable effects on drop spreading, but they had a minor effect on surface wettability. Therefore, an increase in both suspension flow rate and pressure was expected to result in the decrease of the edible coating thickness.

Percentage of Coated Surface by Edible Coating

The fruit-coated surface percentage varied from 47.5 ± 1.59 to 80.33 ± 0.32% since total experimental design proposed.

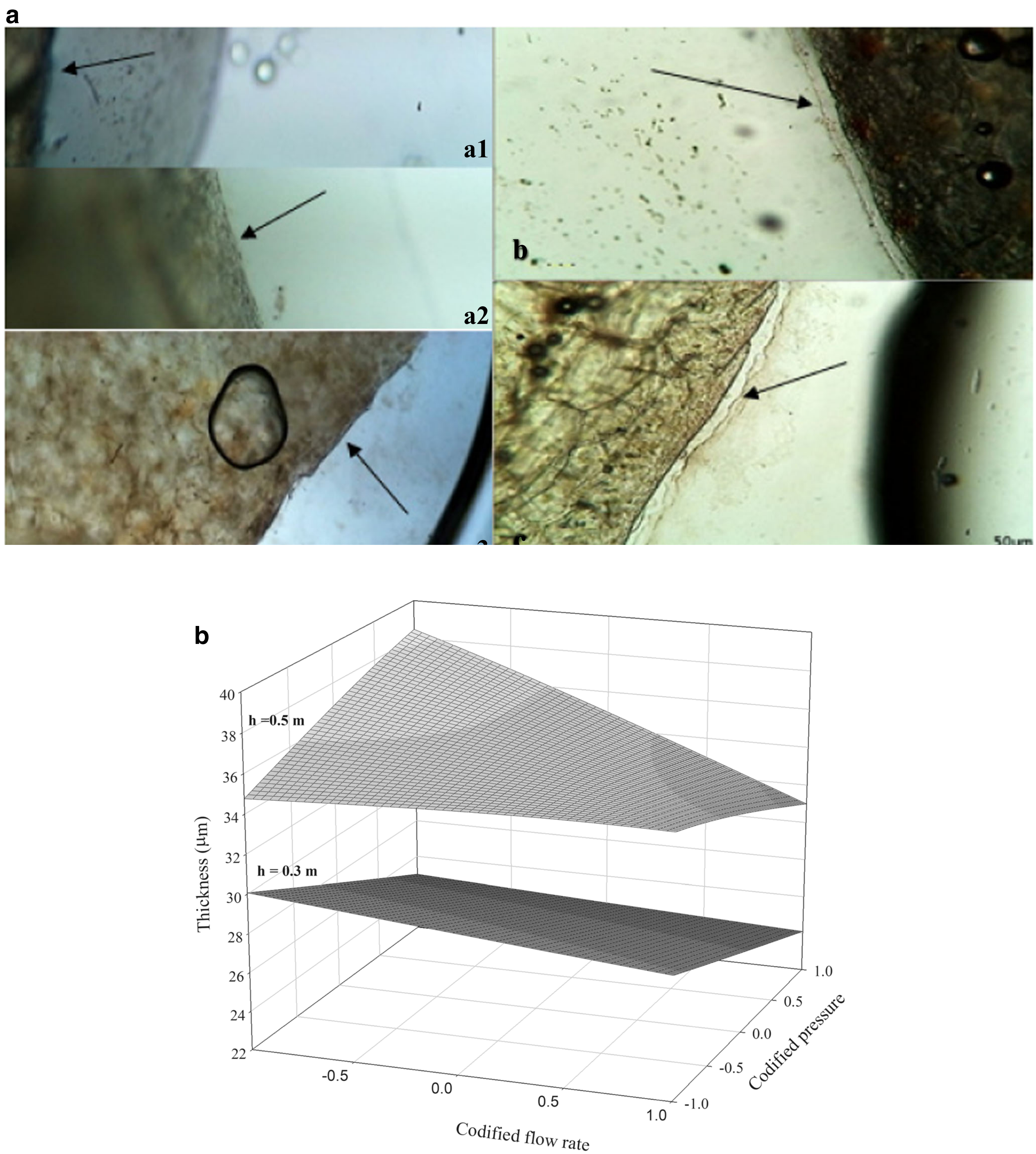

Fig. 2 **A** Optical microscopy (10×) image of grape surfaces showing absence (a1, a2, and a3) and presence (b, c) of the edible coating. **B** Surface response on grape surface thickness as function of both codified suspension flow rate and codified pressure for edible coating at 0.3 and 0.5 m of height

Statistical analysis showed that air pressure and the relation between air pressure and impact height had a significant effect on the coated surface percentage ($p < 0.05$). Air pressure was the variable that had the major effect on the coated surface area, and when the pressure was operated at the lowest level, the coated surface area decreased about 17% with respect to the highest level used (200 kPa). The pressure effect could be related with the drop size, since the higher the pressure, the lower the drop size and the higher the grape surface area to be impacted and coated by the suspension increased as described in the literature (Andrade et al. 2012). If both suspension flow rate and height of impact are varied, as shown in Fig. 3, at high

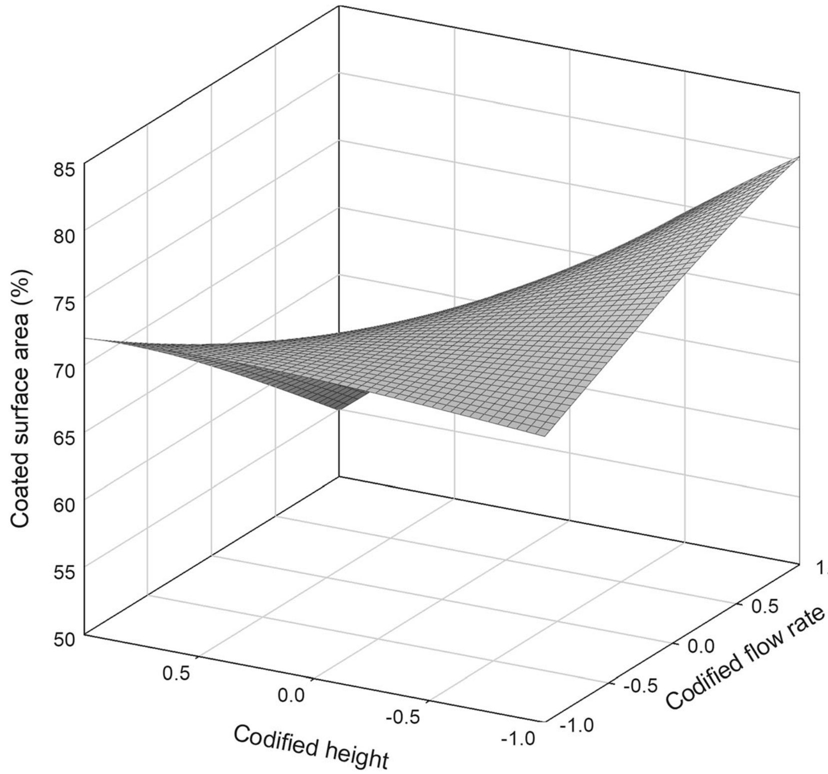

Fig. 3 Surface response of coated grape surface (%) as function of both codified suspension flow rate and height of the spray nozzle at the highest level of pressure (200 kPa)

pressure levels, the maximum fruit surface coated was obtained when working at low suspension flow rate and high impact height.

The results indicated that there was synergistic effect between suspension flow rate and height at 200 kPa, leading to an increase in the coated grape surface. The stable coated surface was obtained when working at low constant suspension flow rate (1 L h^{-1}) for all height levels at the highest pressure (200 kPa), which may be attributed to a good mixture between the suspension and the pressurized air inside the internal chamber. However, high values of coated surface (about 81%) were also obtained when working at high values of suspension flow rates (5 L h^{-1}), showing an opposite behavior to that described above, possibly due to an earlier and direct contact between the involved phases, resulting in a direct wetting of the surface (Perfetti et al. 2011). Thus, the formation of a complete drop within the distance between the nozzle and the grape surface is clearly a function of the pressure of the air in the aspersion system, good mixture of the coating forming suspension with the pressurized air and the non-Newtonian nature of the coating forming suspension (Osorio et al. 2018).

Operational Conditions of the Spray System

The optimization of the operational conditions of the spray system had the objective of maximizingthe response variables (coating thickness and covered surface). According to the statistical evaluation of the response variables, the optimum values for coating thickness (38.5 μm) and covered surface (72.0%) were obtained when working at a flow rate of 1 L h^{-1}, air pressure of 200 kPa, and height of impact of 0.5 m. The trend shown in Fig. 4 for surface response associated to desirability index of grapes indicates that they were between 0.4 and 0.8 at the highest height level, whereas at lowest height level, they were between 0.08 and 0.24. These differences could be attributed to the type of energy involved, physical properties of the fluids, spray system configuration, and time of exposure (Movahednejad et al. 2010). The impact velocity of the droplets on the grape surface was related to the droplet potential energy and the air pressure, whereas the spreading phenomenon was a function of the surface and liquid momentum. The operational conditions of the spray system played an important role on both the percentage of coated surface and the coating thickness on the grape surface due to the ratio nozzle-food distance and coated surface by a homogeneous suspension (Khan et al. 2012).

There was a clear effect of both potential and kinetic energy associated to the liquid drop impact in the analysis of surface response. According to the literature, the undesirable splashing phenomenon on the grape surface usually takes place at relatively high drop impact velocities, and it is accompanied by the production of tiny drops (Liang and Mudawar 2016). This phenomenon is crucial for atomization, but it is often detrimental in coating processes, such as ink jet printing and pesticide delivery (Bird et al. 2009) and may be influenced by apparent viscosity and surface tension. Additionally, high surface tension has been reported to inhibit splashing regardless of whether the target surface is dry or

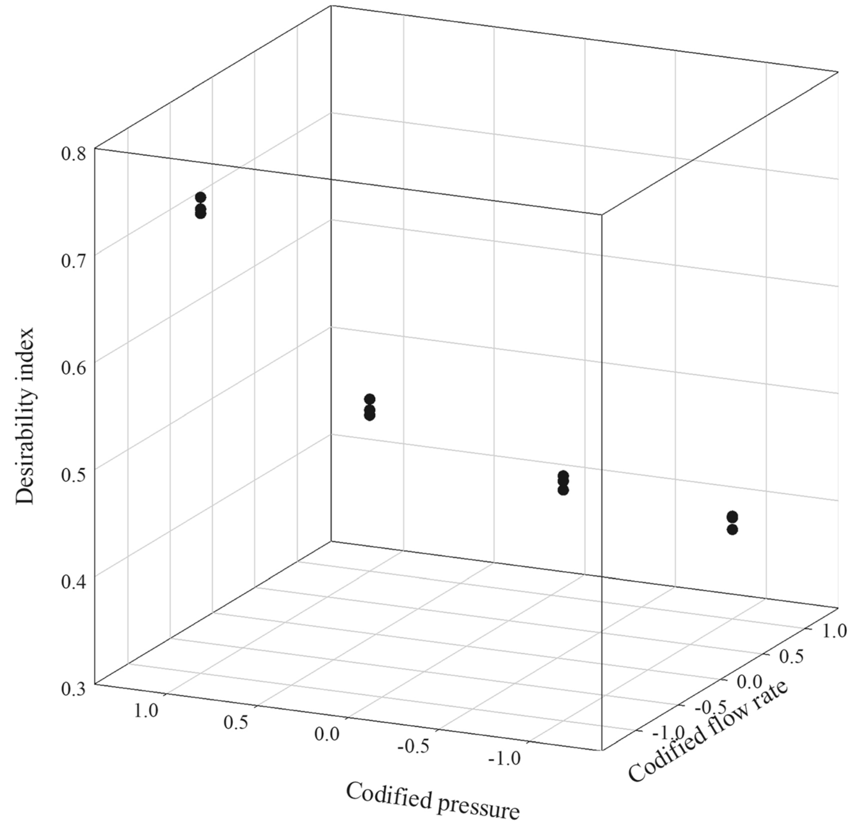

Fig. 4 Desirability index as function of both codified suspension flow rate and codified pressure at the highest level of height (0.5 m)

coated with a thin liquid coating (Vander Wal et al. 2006). Thus, this study has considered only solid–liquid interactions for the drop impact processes, being an ideal representation of the physical phenomenon. Moreover, an additional consideration to be taken into count for further studies should be grape curvature. Although single drop research provides a logical foundation for mechanistic understanding of multi-drop impact, the models and correlations developed for single drops cannot be extrapolated to multi-drop impacts (Ghielmetti et al. 1997; Liang and Mudawar 2016). In the real situation, it is convenient to establish that the energies involved in the process should be mainly focused on spreading rather than on splashing phenomena.

In summary, working under the operational conditions defined in this study (flow rate of 1 L h^{-1}, air pressure of 200 kPa, and height of impact of 0.5 m), it was possible to form potential homogeneous size drops inside the mixing chamber with pressurized air in the spray system, leading to an increase of the ratio surface–volume of the formed drops; the height of impact had a positive effect on the distribution of the drops ejected from the spray system device onto the grape surface.

Textural and Physico-Chemical Analysis

Weight Loss Table 1 shows the weight loss evolution of coated and uncoated grapes throughout the storage at 4 °C. All the samples showed an increasing trend in weight loss with storage time, and significant differences ($p < 0.05$) between coated and uncoated grapes were found at the end of the storage period (day 41), when the uncoated grapes showed a weight loss of 5.1 (30% higher than the coated ones), denoting the protective role of the edible coating and its effectiveness as water barrier. Weight loss in fruits has associated with respiration processes and evaporation of water from fruit (Amarante et al. 2001). The acceleration of weight loss found in uncoated grapes on the last day of storage may be due to an increase in their metabolic activity related to tissue senescence at long storage times. This was slowed down by the coating

Table 1 Loss weight (%) for coated and uncoated grapes with storage time

Days	Coated ± SD (%)	Uncoated ± SD (%)
4	0.6 ± 0.2a,x	0.6 ± 0.2a,x
7	0.8 ± 0.4a,x	0.7 ± 0.3a,x
10	0.9 ± 0.2a,x	1.2 ± 0.2a,x,y
12	1.2 ± 0.2a,x	1.3 ± 0.3a,x,y
14	1.2 ± 0.2a,x	1.7 ± 0.3a,y
41	3.6 ± 0.3b,y	5.1 ± 0.5a,z

Different letters show statistical differences for treatment (a, b) and storage time (x, y, z) ($p < 0.05$)

SD standard deviation

application, as reported in previous studies, where edible coatings provided an effective water vapor barrier when applied on muscatel grapes (Pastor et al. 2011; Sanchez-Gonzalez et al. 2011).

The coated grapes did not exceed the weight loss reported as acceptable limit for table grapes and other fruits (5%) (Y. Deng et al. 2006; Valenzuela et al. 2015) throughout the storage time. Similar results have been reported by Pastor et al. (2011), where muscatel grapes coated with 5% HPMC dispersion by dipping, showed significantly lower weight loss (3–4%) than uncoated grapes (over 5%) after 21 days of storage (1–2 °C and 85–90% RH), although in that case, the weight loss took place mainly during the first 7 days of storage. Therefore, the protective role of edible coating was clearly shown in this study.

Total Soluble Solids, pH, and Maturity Index No significant differences in TSS were found between coated and uncoated grapes throughout the storage time ($p > 0.05$), and therefore, an effect of coating application on TTS was not observed. Similar results have been reported for Pastor et al. (2011) for muscatel grape, where the application of 5% HPMC coatings did not have any significant effect on TSS. However, the content of TTS slightly increased with time in both coated (16.8–17.8%) and uncoated (16.7–18%) grapes. This slight increase observed in the TSS values may be mainly associated to water loss from bulk to environment, leading to an increase of soluble solid concentration (Rolle et al. 2015). Figure 5a shows the evolution of pH values for coated and uncoated grapes during the storage. An effect of coating application on pH values was not detected, and significant differences in pH values between coated and uncoated samples were also found at day 14 ($p < 0.05$). Furthermore, a slight increase of pH values was found for both coated (3.70–3.74) and uncoated (3.68–3.81) grapes throughout the storage time (Fig. 5a). This slight increase in pH value is a consequence of the maturity of grapes and may be mainly attributed to the formation of non-soluble potassium bitartrate ($KC_4H_5O_6$) associated to exchange of protons of tartaric acid with potassium cations (Zoecklein et al. 2010), leading to a decrease in the concentration of free acid.

Figure 5b shows the maturity index of both uncoated and coated grapes throughout the storage period at 4 °C. The maturity index, characterized by metabolic activities and sugar conversion from sucrose to simple sugars (glucose and fructose), varied from 32 to 36 ($p < 0.05$) for coated and from 32 to 40 ($p < 0.05$) for uncoated grapes throughout the storage. However, as in the case of TSS, an effect of the coating application was not observed ($p > 0.05$). According to Zoffoli and Latorre (2011), the consumer acceptability is mainly determined by sugar contents in the range 15–17% and maturity index (TSS/TA) higher than 20. Therefore, neither coated nor uncoated grapes obtained in this study were in the range of minimal required acceptability. However, uncoated grapes showed a faster maturity process than coated, in agreement with the results obtained for other fruits during storage with different types of edible coatings (Gao et al. 2013).

Water Vapor Permeability The coated grapes had significantly lower ($p < 0.05$) WVP values ($2.50 \cdot 10^{-14} \pm 1.45 \cdot 10^{-16}$ kg s^{-1} m^{-1} Pa^{-1}) than the uncoated samples ($3.78 \cdot 10^{-14} \pm 4.54 \cdot 10^{-15}$ kg s^{-1} m^{-1} Pa^{-1}), showing the effectiveness of the edible coating as water barrier. In this study, the synergistic relation between the grape natural barriers and the edible coatings with HPMC and CNFs allowed to decrease around 1.5 times the WVP, with the consequent shelf life extension of the coated grapes. The same behavior has been reported in the literature (Villalobos-Carvajal et al. 2009), where carrot slices coated with HPMC-based edible coatings showed higher WVTR resistance than the uncoated samples. Besides, CNFs played an important role in promoting WVTR resistance through the coating matrix. Thus, the presence of impermeable crystalline cellulose is thought to increase tortuosity in coating matrixes, leading to slower diffusion processes and, hence, lower water permeability. However, the incorporation of CNF particles at high ratio (HPMC/CNF = 3:0.4) into HPMC coatings has been reported to increase the water diffusion coefficient of HPMC/CNF coatings and diffusivity (Bilbao-Sainz et al. 2011).

Mechanical Properties Table 2 shows values obtained for stiffness and work ratio (W1/WT) for coated and uncoated grapes. Coated grapes showed stiffness values from 498.9 ± 71.1 to 404.8 ± 96.5 N m^{-1}, and no significant differences were found with storage time ($p > 0.05$). In addition, uncoated grapes showed stiffness values between 800.7 ± 125.4 and 327.7 ± 52.7 N m^{-1}, with significant differences with storage time ($p < 0.05$). The sharp decrease in stiffness values for uncoated grapes was in agreement with the natural maturity process of grapes, in agreement with pH values and maturity index. However, at early storage stages, the work ratio (W1/WT) involved in passing through the system cuticle—coating was higher for coated than uncoated grapes, showing a clear effect of the presence of the edible coating on the mechanical resistance properties. Throughout the storage period, a slight increase in W1/WT ratio was observed for both coated and uncoated grapes, which may be attributed to chemical changes inside the fruit at the pulp level or cuticle probably as a consequence of insufficient flexibility of the cutin (Heredia 2003). Hence, these values gave an idea about the maintenance of fruit firmness, related to control of weight loss and/or the modification of the internal atmosphere of the fruit as reported in the literature (Fagundes et al. 2015). Furthermore, the coated grapes showed a lower stiffness percent change with the time (~ 18.7%) than uncoated grapes (~ 59.1%), which is in agreement with the dehydration process observed in uncoated

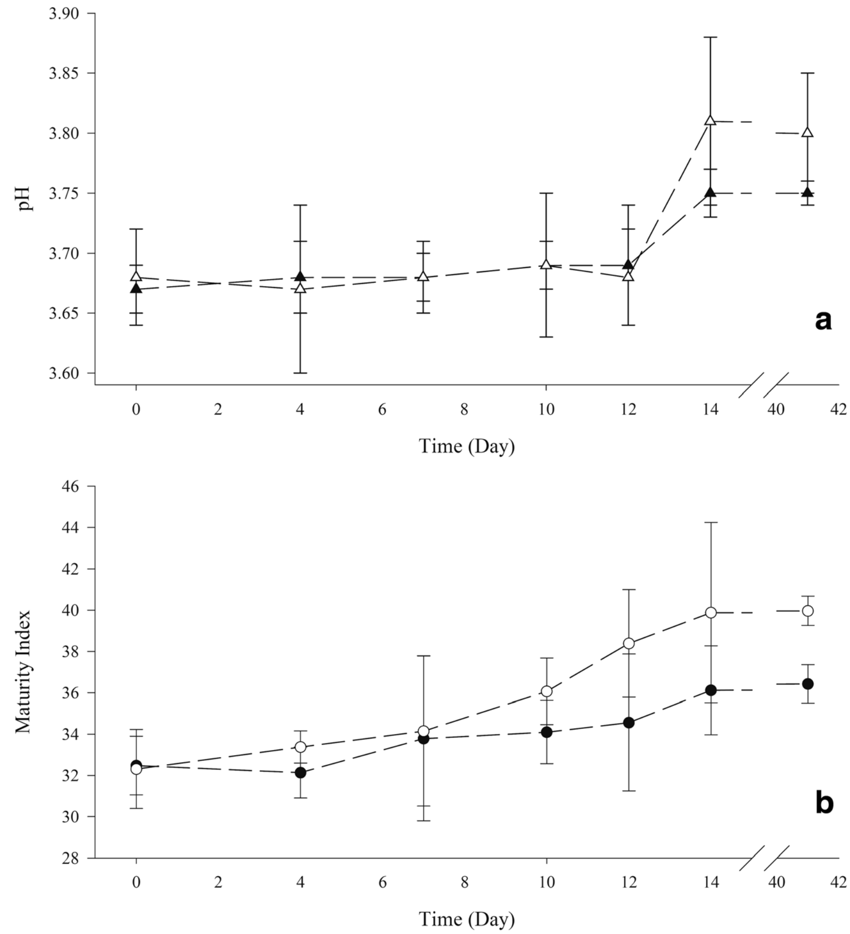

Fig. 5 **A** pH (▲: coated; △: uncoated) and **B** maturity index (●: coated; ○: uncoated) of grapes as function of storage time

grapes. These results are in agreement with Sanchez-Gonzalez et al. (2011), where muscatel grapes coated with a 1% HPMC dispersion maintained firmness better than uncoated ones. However, in contrast with this result, Pastor et al. (2011), working with the same cultivar but with a 5% HPMC dispersion, did not find any significant difference in the mechanical properties between coated and uncoated grapes, suggesting that the physicochemical properties of the coating dispersions may impact the coating thickness and, therefore, the equilibrium moisture content of the coatings. In conclusion, coated grapes showed the highest stability for the evaluated mechanical properties, suggesting that the presence of edible coating could positively affect their shelf life.

Conclusions

Edible coating based on HPMC, k-carrageenan, glycerol, and cellulose nanofibers was successfully applied by spray technology on grape surfaces, obtaining a coating thickness between 24.2 ± 0.9 (μm) and 38.5 ± 1.4 (μm). Regarding the

Table 2 Values of stiffness ($N\ m^{-1}$) and W1/WT (%) for coated and uncoated grapes with time ($n = 30$ samples)

	Coated		Uncoated	
Day	Stiffness ± SD ($N\ m^{-1}$)	W1/WT ± SD (%)	Stiffness ± SD ($N\ m^{-1}$)	W1/WT ± SD (%)
0	498.9 ± 71.1a,x	13.1 ± 0.7a,x	800.7 ± 125. 4a,y	6.9 ± 0.1a,y
4	463.6 ± 88.2a,x	14.3 ± 0.3b,x	613.5 ± 169.7b,y	6.8 ± 0.1a,b,y
7	503.5 ± 125.7a,x	12.5 ± 0.2a,c,x	416.5 ± 41.1c,x	14.0 ± 0.3c,y
12	463.4 ± 152.6a,x	15.6 ± 0.4d,x	350.9 ± 39.3c,d,y	17.4 ± 0.5d,y
41	404.8 ± 96.5a,x	18.9 ± 0.8e,x	327.7 ± 52.7d,e,x	13.6 ± 0.4c,e,y

Different letters show statistical differences for days (a, b, c, d, e) and treatment (x, y) ($p < 0.05$)

SD standard deviation, *W1* work involved penetrating through the edible coating plus cuticle system, *WT* total work needed to reach 4 mm depth into the grape pulp operational conditions, the distance between grape surface and spray nozzle was the main processing factor, followed by air pressure and suspension flow rate. Pressure influenced mainly the effectively coated surface. The optimal operational conditions, based on the optimization analysis, were suspension flow rate of 1 L h^{-1}, air pressure of 200 kPa, and spray nozzle height of 0.5 m. The stable adhesion of the edible coating on the grape surface had a direct effect on their physico-chemical properties. The edible coating designed in this study showed high water barrier properties, and the coated grapes had a weight loss lower than 5% as critical quality parameter at the end of the storage (day 41), together with low water vapor permeability and stable mechanical properties, leading to a shelf life extension compared to uncoated grapes. Further studies should be necessary to evaluate the microbiological and physico-chemical properties of coated grapes under different commercial temperatures at refrigeration storage conditions.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no conflict of interest.

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