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Surface Free Energy Utilization to Evaluate Wettability of Hydrocolloid Suspension on Different Vegetable Epicarps

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Abstract: Surface free energy is an essential physicochemical property of a solid and it greatly influences the interactions between vegetable epicarps and coating suspensions. Wettability is the property of a solid surface to reduce the surface tension of a liquid in contact with it such that it spreads over the surface and wets it, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by an energy balance between adhesive and cohesive work. The spreading coefficient ($S_{cf/food}$) is the difference between the work of adhesion and the work of cohesion. Surface wettability is measured by the contact angle, which is formed when a droplet of a liquid is placed on a surface. The objective of this work was to determine the effect of hydroxypropyl methylcellulose (HPMC), κ-carrageenan, glycerol, and cellulose nanofiber (CNF) concentrations on the wettability of edible coatings on banana and eggplant epicarps. Coating suspension wettability on both epicarps were evaluated by contact angle measurements. For the ($S_{cf/food}$) values obtained, it can be concluded that the surfaces were partially wet by the suspensions. $S_{cf/food}$ on banana surface was influenced mainly by κ-carrageenan concentration, HPMC-glycerol, κ-carrageenan-CNF, and glycerol-CNF interactions. Thus, increasing κ-carrageenan concentrations within the working range led to a 17.7% decrease in $S_{cf/banana}$ values. Furthermore, a HPMC concentration of 3 g/100 g produced a 10.4% increase of the $S_{cf/banana}$ values. Finally, $S_{cf/fruit}$ values for banana epicarps were higher (~10%) than those obtained for eggplant epicarp, indicating that suspensions wetted more the banana than the eggplant surface.

Keywords: contact angle; edible coating; epicarp; spreading coefficient; wettability

1. Introduction

Edible coatings help to meet many challenges related to food preservation. They contribute to the extension of the shelf-life of fruits by reducing moisture and solute migration, gas exchange, respiration, and oxidative reaction rates. The functionality and performance of edible coatings depend on their mechanical, optical, and barrier properties, which in turn are related to film composition, its formation process, and the method of application on the food [1–3].

Edible coatings are made from biopolymer materials such as proteins (gelatin, casein, zein), polysaccharides (starch, cellulose, alginate), and lipids (beeswax, fatty acids). Cellulose derivatives such as hydroxypropyl methylcellulose (HPMC) are promising materials for edible coatings because they impart moderate strength, and they are resistant to oils and fats, as well as being flexible, transparent, odorless, tasteless, water-soluble, and moderate barriers to oxygen. However, they have poor barrier properties against water vapor transfer due to their hydrophilic nature [4–6]. Carrageenan is a generic term applied to a naturally occurring, commercially important family of hydrophilic polysaccharides extracted from a number of closely-related species of red seaweeds. Carrageenan have high molecular weight, as well as highly sulfated and linear molecules with a galactose backbone which are joined by alternating α (1→3) and β (1→4) glycosidic linkages. κ-carrageenan displays partial solubility in cold and full solubility in hot water. The most frequently used strategies to enhance barrier properties are the use of composites and multilayered films containing a high barrier film; however, both techniques present disadvantages [7]. A recent breakthrough in composite materials is the advancement of nanotechnology. Cellulose nanofibers (CNF) are more effective than their micro-sized counterparts in reinforcing polymers as they form a percolated network connected by hydrogen bonds, provided there is a good dispersion of the nanofibers in the matrix [8,9].

The coating process involves the wetting of the food surface to be coated by the coating formulation, possible penetration of the coating suspension into the peel, followed by a possible adhesion between the suspension and food surface [10]. Surface free energy is an essential physicochemical property of a solid and it greatly influences the interactions between vegetable epicarps and coating suspensions. Wettability is the ability of a solid surface to reduce the surface tension of a liquid in contact with it such that it spreads over the surface and wets it, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by an energy balance between adhesive and cohesive work. The spreading coefficient ($S_{cf/food}$) is the difference between the work of adhesion and the work of cohesion. Surface wettability is measured by the contact angle, which is formed when a droplet of a liquid is placed on a surface. The coating must be designed considering food surface properties (surface free energy), coating formulation properties (viscosity and surface tension), and the interfacial interaction between the food surface and coating suspension. The affinity between the food surface and coating formulation is fundamental in the coating design, considering that the effective spreading of a coating on a food is greatly influenced by the wettability of the surface by the coating formulation [11–14]. However, there are few studies in the scientific literature dealing with the study of the wettability properties of coating suspensions on food surfaces [11,14,15], even though an understanding of this property represents a way to improve and develop new surface and interface interactions by modifying the liquid and/or surface properties. Contact angle as a wetting phenomenon was defined in the early 1800s for solid, non-porous, and non-absorbent surfaces under equilibrium. The relationship for surface tension at a point of the three-phase contact line between a smooth, rigid, solid phase S, a liquid L, and its vapor V is described by the Young equation as:

$$\gamma_{LV} \cdot \cos\theta = \gamma_{SV} - \gamma_{SL} \tag{1}$$

where γ_{LV}, γ_{SV}, and γ_{SL} are the surface tensions (or surface free energy, mN·m^{-1}) of the liquid-vapor, solid-vapor, and solid-liquid interfaces, and θ is the contact angle. The angle value depends on the relative magnitude of the molecular forces acting within the liquid (cohesive) and between the liquid and the solid (adhesive), and spreading occurs when $\gamma_{SV} - \gamma_{SL} > \gamma_{LV}$.

Three parameters must be considered to establish the appropriate concentrations of the different components in an edible coating formulation to be applied on a food surface: The spreading coefficient ($S_{cf/food}$), the work of adhesion (W_A), and the work of cohesion (W_C). The spreading coefficient of a solid by a liquid considers the balance between the W_A of the liquid on the solid and the W_C of the liquid [14,15]. The control of adhesion and cohesive energies is very important because the former promotes the spreading of the liquid, while the latter promotes its contraction [13]. Thus, the work of adhesion and spreading coefficient may be used to predict the adhesion of materials, evaluating those factors that affect film adhesion on food surface.

The objective of this work was to evaluate the influence of HPMC, κ-carrageenan, glycerol, and CNF concentrations on the wettability of edible coatings on banana and eggplant epicarps.

2. Materials and Methods

2.1. Materials

Bananas and eggplants were purchased as fresh fruits from a local market (Santiago, Chile). The fruits were selected for their uniformity in ripeness, size, color, and absence of physical damage on their surface according to visual analysis. The fruits in their natural state without a cleaning step were cut in rectangular samples (1.5 cm × 2.5 cm). The surface free energies (γ_{SV}) of banana and eggplant epicarps are 39.29 and 33.06 mN·m^{-1}, respectively [11]. HPMC (Methocel E19 Food Grade M.W. 1261.45 g·mol^{-1}; η = 19 cP at 2% *w/w* and *T* = 20 °C) and κ-carrageenan (Carragel PGU 5289 Kappa I; ~800 mPa·s at 1.5% *w/w*) were obtained from Blumos (Blumos S.A., Santiago, Chile), and glycerol (G) was purchased from Sigma (Sigma-Aldrich, Santiago, Chile). Cellulose nanofibers (20–70 nm wide ribbons) were obtained from agroindustrial residues produced by *Gluconacetobacter swingsii* sp., as reported by Castro et al. [16].

2.2. Preparation of Coating Formulations

κ-Carrageenan (0.1–0.3% *w*/*w*) was dissolved in 2/3 of distilled water at room temperature (20 °C) under agitation (1100–1300 RPM) for 30 min. HPMC (1–5% *w*/*w*) was dissolved in 1/3 of distilled water by heating to 90 ± 2 °C under agitation using a magnetic stirrer (400 RPM). Finally, both glycerol (10–30% *w/w*) and CNF (1–5% *w*/*w*) were added at 40 °C, and this mixture was then sonicated in a bath type sonicator (Branson Model 2210, Danbury, CT, USA) for 30 min.

2.3. Wettability of Coating Formulations on Banana and Eggplant Epicarps

The wettability of the coating formulations on banana and eggplant epicarps was evaluated from contact angle (CA) measurements, based on the sessile drop method [17]. For each of the coating formulations, CA was measured at room temperature (20 °C) using an optical system comprised of a zoom video lens (Edmund Optics, Barrington, NJ, USA) connected to a Charge-coupled device (CCD) camera (Pulnix Inc., San Jose, CA, USA) operated via software. Contact angle was determined using ImageJ software (1.47v) with the plug-in Drop Shape Analysis. Small drops (~2 μL) were manually deposited using a precision microliter pipette on the fruit skins, and 10 measurements of both left and right drop CAs of the droplet were performed. Parameters like $S_{cf/food}$, W_A, and W_C were calculated from Equations (2)–(4), respectively:

$$S_{\frac{cf}{food}} = W_A - W_C \tag{2}$$

$$W_A = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV} \cdot (1 + \cos\theta) \tag{3}$$

$$W_C = 2 \cdot \gamma_{LV} \tag{4}$$

Surface tensions of the coating formulations were measured by the sessile drop method [14]. To validate the results, it was experimentally corroborated that the interfacial tension of the pure water/air system was 72.8 ± 0.3 mN·m^{-1}.

2.4. Statistical Design and Analysis

The Box-Behnke statistical screening design was used to evaluate main effects, interaction effects, and quadratic effects of the independent variables (HPMC, κ-carrageenan, glycerol, and CNF concentrations) on the wettability ($S_{cf/food}$, W_A, and W_C) of fruits with different surface free energies (banana and eggplant). The levels of the independent variables were 1 g, 3 g, and 5 g/100 g for HPMC concentration; 0.1 g, 0.2 g, and 0.3 g/100 g for κ-carrageenan concentration; 10 g, 20 g, and 30 g/100 g for the glycerol concentration, and 1 g, 3 g, and 5 g/100 g for the CNF concentration.

Response surface methodology was applied to analyze the effect of independent variables on response variables (W_C, W_A, and $S_{cf/food}$). A second-order polynomial model (Equation (5)) was used to predict the experimental behavior [18].

$$\hat{Y} = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum \sum_{i<j=1}^{k} \beta_{ij} X_i X_j, \quad (5)$$

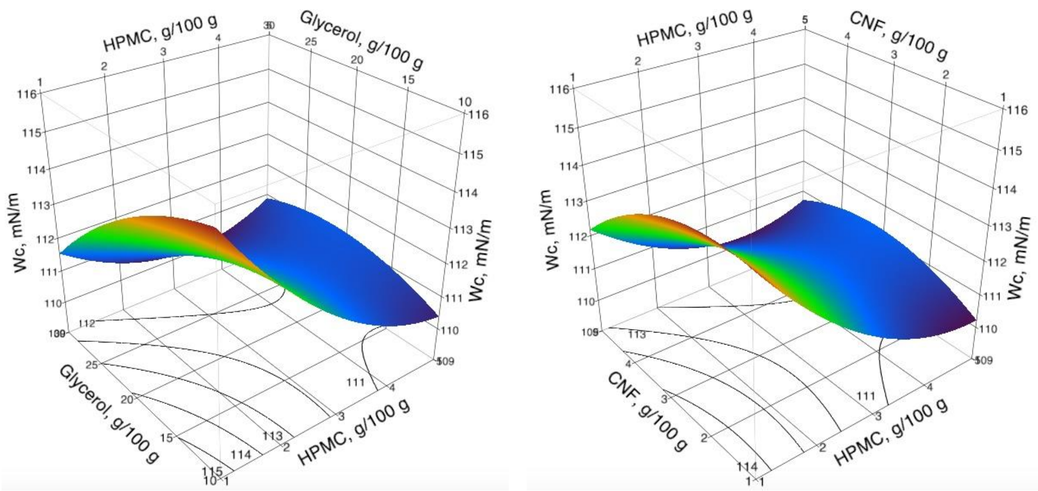
where $\hat{Y}$ is the predicted value of the response; β_0, β_i, β_{ii}, and β_{ij} are the regression coefficients for interception, linear, quadratic, and interaction effects, respectively; k is the number of independent parameters (k = 3 in this study), and X_i, X_j are the coded levels of the experimental conditions. Analysis of variance (ANOVA) was used to determine significant effects of HPMC, κ-carrageenan, glycerol, and cellulose nanofibers concentrations on $S_{cf/food}$, W_A, and W_C (95% confidence). The quality of the developed model was determined by the coefficients of determination (R^2) and root mean square error (RMSE). This study design was analyzed using JMP software (version 9.0.1, SAS Institute, Cary, NC, USA).

3. Results and Discussion

Cohesion work (W_C), adhesion work (W_A), contact angle (CA), and spreading coefficient values on banana ($S_{cf/banana}$) and eggplant ($S_{cf/eggplant}$) skins obtained for each coating formulation are shown in Table 1.

3.1. Cohesion Work (W_C) of Coating Formulations

ANOVA results showed that the W_C of the coating formulations was influenced significantly by the linear effect of HPMC concentration (p-value < 0.05). The variation of W_C with HPMC and glycerol concentrations is shown in Figure 1a, and variation of W_C with HPMC and CNF concentrations is shown in Figure 1b. An increase in HPMC concentration led to a decrease in W_C for all of the range of glycerol concentration evaluated, reaching a stable value around 110.5 mN·m^{-1}. It should be noted that W_C values are dependent only on the surface tension (see Equation (4)). HPMC is a highly surface-active macromolecule and therefore surface tension of aqueous HPMC suspensions decrease as the HPMC concentration increases [19].



(**a**) (**b**)

Figure 1. Response surface of W_C as a function of (**a**) HPMC and glycerol, (**b**) HPMC and cellulose nanofibers (CNF).

Table 1. Design matrix in the Box-Behnken model and response values obtained from experimental runs.

Run	Level of Variables				$W_C \pm$ SD mN·m^{-1}	Banana			Eggplant		
	HPMC	κ-C †	G *	CNF		CA ± SD	$W_A \pm$ SD mN·m^{-1}	$S_{cf/Banana} \pm$ SD mN·m^{-1}	CA ± SD	$W_A \pm$ SD mN·m^{-1}	$S_{cf/Eggplant} \pm$ SD mN·m^{-1}
S1	1	0.1	10	1	114.02 ± 2.27	49.0 ± 1.7	94.42 ± 2.78	−19.6 ± 0.51	61.5 ± 1.1	84.22 ± 1.93	−29.8 ± 0.34
S2	1	0.1	10	5	114.26 ± 2.64	65.0 ± 0.9	81.26 ± 1.51	−33.0 ± 1.13	67.2 ± 1.7	79.26 ± 2.81	−35.0 ± 0.17
S3	1	0.1	30	1	115.64 ± 3.47	45.4 ± 1.6	98.44 ± 2.76	−17.2 ± 0.71	59.2 ± 1.0	87.44 ± 1.72	−28.2 ± 1.75
S4	1	0.1	30	5	108.9 ± 2.38	39.8 ± 1.8	96.3 ± 3.03	−12.6 ± 0.65	49.8 ± 1.3	89.6 ± 2.27	−19.3 ± 0.11
S5	1	0.3	10	1	124.7 ± 1.85	51.9 ± 1.6	100.8 ± 2.32	−23.9 ± 0.47	48.3 ± 0.7	103.8 ± 1.17	−20.9 ± 0.68
S6	1	0.3	10	5	115.5 ± 2.06	53.5 ± 0.9	92.1 ± 1.58	−23.4 ± 0.48	53.4 ± 1.8	92.2 ± 2.98	−23.3 ± 0.92
S7	1	0.3	30	1	111.04 ± 2.56	60.8 ± 1.5	82.64 ± 2.51	−28.4 ± 0.50	59.9 ± 1.2	83.34 ± 1.96	−27.7 ± 0.60
S8	1	0.3	30	5	115.8 ± 2.95	49.1 ± 1.2	95.8 ± 1.85	−20.0 ± 1.10	53.9 ± 1.3	92.0 ± 2.27	−23.8 ± 0.68
S9	5	0.1	10	1	112.78 ± 2.49	47.0 ± 1.8	94.88 ± 2.76	−17.9 ± 0.27	61.6 ± 1.9	83.18 ± 2.92	−29.6 ± 0.43
S10	5	0.1	10	5	111.64 ± 2.52	50.5 ± 1.9	91.34 ± 3.13	−20.3 ± 0.69	57.7 ± 1.8	85.64 ± 2.91	−26.0 ± 0.39
S11	5	0.1	30	1	109.78 ± 2.46	50.1 ± 1.1	90.08 ± 1.77	−19.7 ± 0.61	59.1 ± 1.7	83.08 ± 2.77	−26.7 ± 0.31
S12	5	0.1	30	5	110.26 ± 3.11	57.5 ± 1.6	84.76 ± 2.61	−25.5 ± 0.50	58.0 ± 1.4	84.36 ± 2.46	−25.9 ± 0.65
S13	5	0.3	10	1	109.96 ± 3.34	56.7 ± 1.7	85.16 ± 2.88	−24.8 ± 0.46	64.8 ± 1.2	78.36 ± 1.90	−31.6 ± 1.44
S14	5	0.3	10	5	111.96 ± 3.33	57.3 ± 1.8	86.26 ± 2.88	−25.7 ± 0.45	56.6 ± 1.7	86.76 ± 2.81	−25.2 ± 0.52
S15	5	0.3	30	1	114.00 ± 2.68	61.4 ± 1.7	84.3 ± 2.98	−29.7 ± 0.30	61.6 ± 1.4	84.10 ± 2.40	−29.9 ± 0.28
S16	5	0.3	30	5	113.00 ± 2.69	53.9 ± 1.7	89.8 ± 2.75	−23.2 ± 0.60	55.3 ± 1.4	88.70 ± 2.20	−24.3 ± 0.49
S17	1	0.2	20	3	112.24 ± 2.31	58.0 ± 1.6	85.84 ± 2.84	−26.4 ± 0.53	59.0 ± 1.1	85.04 ± 1.90	−27.2 ± 0.41
S18	5	0.2	20	3	112.74 ± 2.96	66.8 ± 1.8	78.54 ± 2.83	−34.2 ± 0.13	57.3 ± 1.5	86.84 ± 2.57	−25.9 ± 0.39
S19	3	0.1	20	3	113.46 ± 2.42	53.8 ± 1.7	90.26 ± 2.70	−23.2 ± 0.28	50.0 ± 1.6	93.16 ± 2.71	−20.3 ± 0.29
S20	3	0.3	20	3	113.42 ± 2.42	58.4 ± 1.7	86.42 ± 2.58	−27.0 ± 0.16	44.8 ± 1.1	96.92 ± 1.84	−16.5 ± 0.58
S21	3	0.2	10	3	110.42 ± 1.91	53.5 ± 1.8	88.02 ± 3.07	−22.4 ± 1.16	64.7 ± 0.9	78.82 ± 1.47	−31.6 ± 0.44
S22	3	0.2	30	3	111.18 ± 2.13	51.8 ± 1.9	89.98 ± 2.93	−21.2 ± 0.80	60.5 ± 1.2	82.98 ± 2.07	−28.2 ± 0.60
S23	3	0.2	20	1	109.52 ± 2.95	62.5 ± 1.7	80.02 ± 3.00	−29.5 ± 0.50	69.6 ± 1.7	73.82 ± 2.80	−35.7 ± 0.15
S24	3	0.2	20	5	111.74 ± 2.76	62.8 ± 1.6	81.44 ± 2.49	−30.3 ± 0.27	53.5 ± 1.4	89.14 ± 2.44	−22.6 ± 0.32
S25	3	0.2	20	3	110.62 ± 2.40	53.9 ± 1.6	87.92 ± 2.71	−22.7 ± 0.31	55.8 ± 1.0	86.42 ± 1.66	−25.2 ± 0.74
S26	3	0.2	20	3	111.64 ± 2.33	54.7 ± 1.7	88.04 ± 2.91	−23.6 ± 0.58	56.2 ± 1.4	86.84 ± 2.48	−24.8 ± 0.15
S27	3	0.2	20	3	112.28 ± 2.82	54.5 ± 1.6	88.78 ± 2.84	−23.5 ± 0.20	56.6 ± 1.2	87.08 ± 2.21	−25.2 ± 0.61
S28	3	0.2	20	3	111.94 ± 1.91	54.9 ± 1.6	88.14 ± 2.80	−23.8 ± 0.89	55.5 ± 1.2	87.64 ± 2.19	−24.3 ± 0.28
S29	3	0.2	20	3	113.36 ± 2.76	55.4 ± 1.7	88.86 ± 2.92	−24.5 ± 0.16	56.5 ± 1.6	87.96 ± 2.90	−25.4 ± 0.34
S30	3	0.2	20	3	112.34 ± 2.44	54.8 ± 1.8	88.54 ± 2.89	−23.8 ± 0.45	56.9 ± 1.0	86.84 ± 1.83	−25.5 ± 0.61
S31	3	0.2	20	3	110.32 ± 2.25	55.2 ± 1.4	86.62 ± 2.42	−23.7 ± 0.17	55.5 ± 1.6	86.42 ± 2.88	−25.9 ± 0.63

Notes: κ-C †—† κ-carrageenan, and G *—* Glycerol; SD—Standard Deviation.

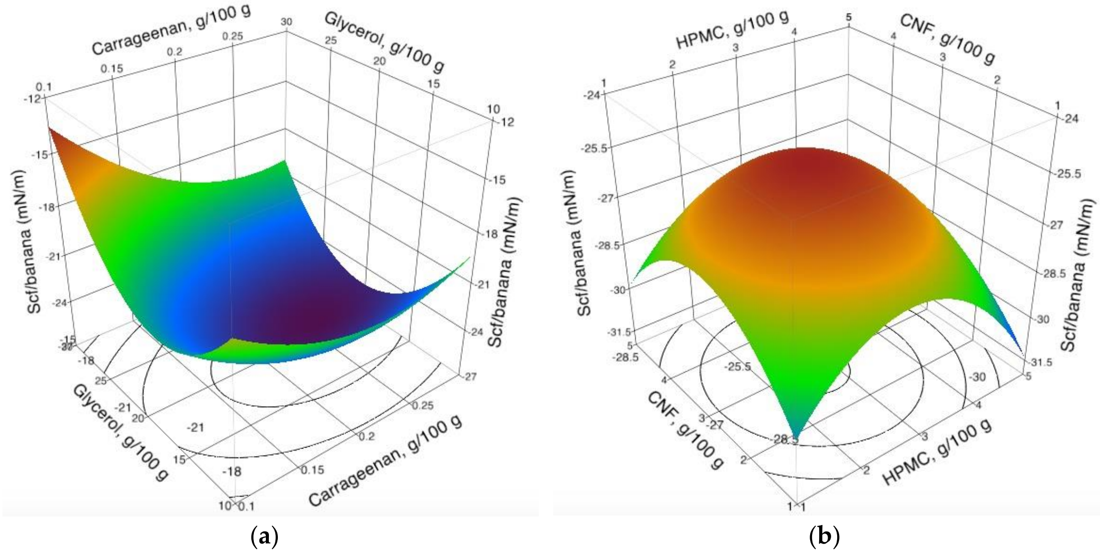
To obtain a better coating, it is important to select a coating formulation with a low cohesive energy (W_C) to obtain a better adhesion between the coating suspension and the fruit epicarp. As previously mentioned, it is possible to obtain a lower W_C when using 30 g/100 g rather than 10 g/100 g of glycerol. On the other hand, the application of 1 g/100 g HPMC led to a reduction of W_C values for the glycerol concentrations evaluated in this work, being noticeable for increasing glycerol concentration.

For CNF-HPMC (Figure 1b), W_C showed a similar behavior as the glycerol-HPMC interaction, where the presence of a solute such as CNF led to an increase in W_C; this behavior agrees with the fact that the nanocellulose fibers have a high surface tension (~60 mJ·m^{-2}), and the surface is highly hydrophilic [20].

3.2. Spreading Coefficient of Coating Formulations on Banana Epicarp

Analysis of variance (ANOVA) showed that $S_{cf/banana}$ is influenced significantly by κ-carrageenan concentration, by the interaction effect of HPMC-glycerol, κ-carrageenan-CNF, and glycerol-CNF, and by the quadratic effects of glycerol and HPMC concentrations (p-values < 0.05).

Figure 2 shows the surface response plot of the spreading coefficient ($S_{cf/banana}$) of the coating suspensions on banana epicarp. The evolution of $S_{cf/banana}$ as a function of κ-carrageenan-glycerol and HPMC-CNF concentrations are shown in Figure 2a,b, respectively. An increase of κ-carrageenan concentration from the low level (0.1 g/100 g) to the high level (0.3 g/100 g) led to a decrease of 17.7% in $S_{cf/banana}$ values at 3 g/100 g HPMC. Furthermore, the increase of glycerol concentration from the low level (10 g/100 g) to the medium level (20 g/100 g) produced a decrease of 28% in this parameter, which is the worst condition for wetting of this food surface. Thus, the desirable condition for a better wettability of banana surface is using a glycerol concentration of (30 g/100 g) for a κ-carrageenan concentration of 0.1 g/100 g.



(**a**) (**b**)

Figure 2. Response surface of $S_{cf/banana}$ as a function of (**a**) κ-carrageenan and glycerol, (**b**) HPMC and cellulose nanofibers (CNF).

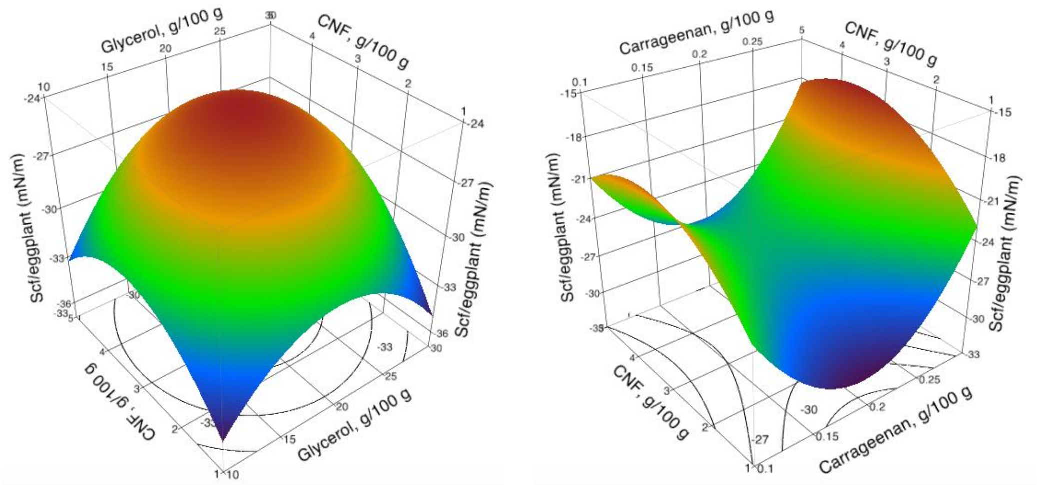
Finally, the change of HPMC concentration from the low level (1 g/100 g) to the medium level (3 g/100 g) led to an increase of 10.4% in $S_{cf/banana}$ values (~−25.4 mN·m^{-1}), and the CNF effect itself was lower than the other parameters evaluated. From the optimal analysis, the maximum of $S_{cf/banana}$ value was −13.03 mN·m^{-1} for 2.17 g/100 g of HPMC, 0.10 g/100 g of κ-carrageenan, 30.00 g/100 g of glycerol, and 2.85 g/100 g of CNF. It should be noted that the spreading coefficients obtained for HPMC coating formulations on banana epicarps in this study (ranging from −12.6 to −34.2 mN·m^{-1}) were higher than those reported in previous studies [11] for gelatin-based coatings (ranging from

−27.1 to −43.9 mN·m^{-1}), which indicates that the wettability of HPMC-based coating formulations on banana epicarps was higher than that of gelatin-based coating formulations.

3.3. Spreading Coefficient of Coating Formulations on Eggplant Epicarp

From ANOVA analysis, the surface showed that $S_{cf/eggplant}$ is influenced significantly by CNF concentration, quadratic effects κ-carrageenan, and glycerol concentration (p-values < 0.05).

Figure 3 shows the surface response of the spreading coefficient of the coating formulations on eggplant epicarp ($S_{cf/eggplant}$) as a function of glycerol-CNF (Figure 3a) and κ-carrageenan-CNF concentrations (Figure 3b). An increase in the CNF concentration from the low level (1 g/100 g) to the high level (5 g/100 g) led to an increase of 12.5% in $S_{cf/eggplant}$ values; similarly, an increase of glycerol concentration produced an increase of 14.3% in this parameter. Thus, there is evidence of a synergic effect of CNF-glycerol at 3 g/100 g and 20 g/100 g, respectively on $S_{cf/eggplant}$ when working at 3 g/100 g of HPMC obtaining a value around −25 mN·m^{-1}. However, the increase of κ-carrageenan concentration from the low level (0.1 g/100 g) to the medium level (0.2 g/100 g) led to a decrease of 40.1% in $S_{cf/eggplant}$ at 3 g/100 g of HPMC, becoming the worst condition for the wettability process. From the optimal analysis, the maximum of $S_{cf/eggplant}$ was −16.10 mN·m^{-1} for 1.19 g/100 g of HPMC, 0.30 g/100 g of κ-carrageenan, 19.98 g/100 g of glycerol, and 3.47 g/100 g of CNF. The wettability of HPMC-based coating formulations on eggplant epicarps was higher than that reported in the literature [11] for gelatin-based coating formulations, where the spreading coefficients ranged from −28.8 to −66.8 mN·m^{-1}.



(**a**) (**b**)

Figure 3. Response surface of $S_{cf/eggplant}$ as a function of (**a**) cellulose nanofibers (CNF) and glycerol, (**b**) κ-carrageenan and cellulose nanofibers (CNF).

An approximation was obtained from the contact angle evaluation ($\theta_{banana} < \theta_{eggplant}$) where the banana surface facilitated the wetting; this is probably due to the chemical cuticle composition. Eggplant cuticle is composed mostly of n-alkane groups such as n-hentriacontane (C_{31}) and triterpenoid alcohols (α- and β-amyrin) as predominant wax components [21], thus the presence of triterpenoid compounds such as ursolic acid may make the surface cuticle more difficult to wet [22], showing a tendency to form weak bonds through Van der Waals forces. Meanwhile, the banana cuticle surface is composed of ketones and aldehydes which can form hydrogen bonds [11]. Therefore, for those suspensions which present a surface tension less than the superficial free energy, there is a tendency to fully wet the surface, this may be expressed as $S_{cf/food} = 0$; in the case of partial wettability it may be expressed as $S_{cf/food} < 0$ [23,24]. The results obtained are in agreement with those expected because both eggplant and banana surface tension is above the surface free energy value (33.06 mN·m^{-1} and

39.29 mN·m^{-1}, respectively). However, the physical influence of the vegetable surface nature may be considered as another factor that influences the wettability phenomenon. Thus, the roughness presence may be considered and evaluated using surface entropy analysis [25]; also, the coating porosity could be obtained by etching and calculated as function of the mass fraction, and the coating volume fractions can be calculated using TEM [26]. Nevertheless, there are sophisticated methods for measuring texture properties associated with nature, origin, and depth of traps using *X*-ray-induced thermally stimulated currents (TSC) and thermoluminescence (TL) [27]. Other recent advances in surface inspection include computer vision and image processing techniques [28]. All mentioned techniques could be a feasible way of proving surface structure effects on wettability processes to be considered in future works.

4. Conclusions

It was possible to evaluate the work of cohesion and adhesion on vegetable surfaces with different free energy surfaces; coating formulations reinforced with nanofibers showed partial wettability, which was attributed to the chemical nature of the surfaces. According to statistical analysis, HPMC showed the major influence on the work of cohesion, decreasing its values with increasing HPMC concentration. In addition, in coated HPMC-based films, concentrations of glycerol, nanofibers, and κ-carrageenan showed a significant influence on the work of spreading, showing both synergistic and antagonistic effects under specific formulations. Finally, values for the spreading work for high free energy surface values were higher (around 10%) than those of low free energy values (represented by eggplant, with a free energy value of 33.06 mN·m^{-1}), which indicates that surfaces with high values of surface free energy show more affinity for these types of formulations.

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