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Wettability of starch-gellan coatings on fruits, as affected by the incorporation of essential oil and/or surfactants

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Abstract

Wettability of coating-forming systems (CFS) based on starch-gellan (80:20) blends, containing or not, emulsified/lecithin-encapsulated thyme essential oil (EO), was analysed in apple, tomato and persimmon fruit. Different concentrations (0-10^5 mg/L) of Tween 85 were incorporated into the CFS in order to know its potentially beneficial effect on the coating spreadability. These fruit skins exhibited high values of the surface tension dispersive component, while being low-energy surfaces (21-29 mN/m). Values of contact angle and surface tension of the starch-gellan solutions were positively affected by the addition of Tween 85 at $5 \cdot 10^4$ mg/L. However, it exerted a negative effect when the CFS contained emulsified or lecithin-encapsulated thyme essential oil. Likewise, wettability of starch-gellan coatings was notably improved with Tween 85 at $5 \cdot 10^4$ mg/L, whereas formulations containing emulsified or encapsulated EO did not require surfactant to improve their already good spreadability.

Keywords: cassava starch; contact angle; edible coating; surface properties; spreading coefficient.

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1. Introduction

One of the most important problems in fruit trading is their short shelf life, which produces heavy losses from harvesting to final consumption (Cerqueira, Lima, Teixeira, Moreira, & Vicente, 2009; Flores-López, Cerqueira, de Rodríguez, & Vicente, 2016). Their shelf-life can be prolonged by reducing fruit respiration or gas transfer rates through the control of factors, such as the composition of the atmosphere surrounding the fruit (O_2, CO_2 and ethylene), temperature, water vapour transfer rate or relative humidity (Lima et al., 2010).

The application of edible coatings, using biopolymers, as a postharvest technique for agricultural commodities, offers environmentally-friendly alternatives in order to solve these problems. Several studies have demonstrated that the application of polysaccharide-based coatings on fruits and vegetables, such as apple (Carneiro-da-Cunha et al., 2009; Mehyar, Al-Qadiri, & Swanson, 2014), strawberry (Garcia, Pereira, de Luca Sarantópoulos, & Hubinger, 2010; García, Martino, & Zaritzky, 2002; Ribeiro, Vicente, Teixeira, & Miranda, 2007), orange (Saberi et al., 2018), guava (Botelho, Rocha, Braga, Silva, & de Abreu, 2016; De Aquino, Blank, & De Aquino Santana, 2015) or tomato (Nawab, Alam, & Hasnain, 2017; Ortega-Toro, Collazo-Bigliardi, Roselló, Santamarina, & Chiralt, 2017), provides an extended shelf life while enhancing the product quality.

Starch is a promising polysaccharide for food coating/packaging purposes, when considering its filmogenic capacity, ready availability, renewability and low cost (Acosta, Jiménez, Cháfer, González-Martínez, & Chiralt, 2015). Starch-based coatings are colourless, odourless, have an oil-free appearance and exhibit low oxygen permeability which can contribute to reducing the respiration rate of the fresh products. It can be used in combination with other biopolymers in order to overcome some drawbacks, such as high water sensitity and water vapour permeability or the retrogradation phenomena during storage (Cano, Jiménez, Cháfer, Gónzalez, & Chiralt, 2014). In this sense, different microbial gums, such as gellan or xanthan gums, have been described as enhancers of the mechanical resistance of starch films, while limiting their water sensitivity and retrogradation (Arismendi et al., 2013; Kim, Choi, Kim, & Lim, 2014; Sapper, Talens, & Chiralt, 2019). Gellan gum at 10 and 20 % in starch blends improved the functional properties of the starch matrix, while also carrying active compounds (thyme essential oil) to better control the product shelf-life through their antifungal effect (Sapper, Wilcaso, Santamarina, Roselló, & Chiralt, 2018). The use of essential oils for decay control is often limited because of their sensory impact in fruit and phytotoxicity risks. The incorporation of these compounds to edible coatings could be an useful strategy to prolong the postharvest life of fresh produce, contributing to modulate the release kinetics of the active compound and maintaining a higher concentration of the antimicrobial agent on the fruit surface for a longer period, while inhibiting phytotoxicity by preventing the direct contact of the essential oil with the fruit skin through the encapsulating action of the polymer matrix. However, previous studies (Perdones, Chiralt, & Vargas, 2016) revealed high losses of the essential oil during the drying step of the aqueous film-forming emulsions, associated with the emulsion destabilization and steam drag evaporation at the film surface. These losses were limited when essential oil compounds were previously encapsulated in amphiphilic substances, such as lecithin, which can entrap the compounds in liposome structures (Sapper et al., 2018; Valencia-Sullca et al., 2016).

An important issue related with the effectiveness of edible coatings at preserving fruits and vegetables is the product surface wettability with the coating which determines the coating uniformity and thickness on the surface (Cerqueira et al., 2009; Park, 1999) and, thereby, its permeability and mechanical performance. The coating process involves the wetting of the surface to be coated, the possible penetration of the coating solution into the peel, followed by the potential adhesion between the coating solution and the food surface (Hershko, Klein, & Nussinovitch, 1996). In this sense, the fruit surface energy and liquid surface tension are controlling factors, affecting the contact angle and liquid spreadability on the solid surface (Hong, Han, & Krochta, 2004). Then, this analysis, which includes the estimation of the critical surface tension of the solid surface, is relevant to evaluate the effectiveness of the product wetting. Fernández & Khayet (2015) analysed and compared different surface free energy calculation methods in plant materials, concluding that three different liquids must be used in order to obtain coherent results and also suggested the standard use of the surface tension values obtained for water, glycerol and diiodomethane, which are often used for such purpose.

The wetting behaviour is influenced both by the chemical composition (e.g., polymer, plasticisers, surfactants, antimicrobials or antioxidants) and molecular interactions in the coating-forming solutions, and by the product surface interactions with the coating components (Basiak, Geyer, Debeaufort, Lenart, & Linke, 2019; Basiak, Lenart, & Debeaufort, 2018; Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011). Consequently, it is important to optimise the coating formulations in order to promote their spreading coefficient (W_s) on a determined surface. This coefficient is a function of the work of cohesion (W_c) in the liquid phase and the work of adhesion (W_a) between liquid and solid surface (Osorio et al., 2017). The effect of the composition of coating solutions on the wetting properties of different fruits and vegetables has been described by several authors. In this sense, Carneiro-da-Cunha et al. (2009) and Choi, Park, Ahn, Lee, & Lee (2002) reported that the addition of Tween 80 was effective in reducing the surface tension of different coating solutions, which improved the compatibility between the solution and the surface of the fruit skin. Otherwise, different formulations of galactomannans and glycerol coatings showed good values of spreading coefficient when applied on different tropical fruits (Cerqueira et al., 2009). Likewise, the addition of glycerol and cellulose nanofibres enhanced the wetting of banana and eggplant with coating formulations based on gelatin (Andrade et al., 2014). The addition of antioxidant extracts of mango seed to edible coatings of mango peel improved the surface properties and wettability on the peach surface (Torres-León et al., 2018). Interactions of carboxymethyl cellulose, glycerol and turmeric oil in cassava starch coating-forming solutions, modified wettability of fresh-cut “Fuji” apple (Sharif et al., 2019). Also, edible coatings based on sodium alginate, glycerol, sunflower oil and Span 80 presented good wettability on strawberry epicarp (Parreidt, Schott, Schmid, & Müller, 2018).

The aim of this study was to characterise the surface properties of apple, tomato and persimmon and to evaluate the wettability/spreading coefficient of the starch-gellan coating-forming liquids, containing, or not, free or lecithin-encapsulated thyme essential oil, as affected by the addition of different concentrations of Tween 85.

2. Materials and methods

2.1. Materials and reagents

Cassava starch (S) (Quimidroga S.A., Barcelona, Spain), low acyl gellan gum (G) (KELCOGEL F, Premium Ingredients, Murcia, Spain), non-GMO soy lecithin (L) with 45 g phosphatidylcholine/100 g lecithin (Lipoid P45, Lipoid GmbH, Ludwigshafen, Germany), thyme (*Thymus zygis*) essential oil (EO) (Plantis, Artesanía Agrícola SA, Barcelona, Spain), glycerol (Panreac Química S.A., Barcelona, Spain) and polyoxyethylenesorbitan trioleate (Tween 85) (T) (Sigma-Aldrich, Madrid, Spain), were used to obtain the coating-forming systems. Heptane (Sigma.Aldrich, Madrid, Spain), dimethyl sulfoxide (DMSO) and methanol (Panreac Química S.A., Barcelona, Spain) were used as reference compounds.

2.2. Preparation of the coating-forming systems

To obtain the coating-forming systems, starch (2 g/100 g solution) was dispersed in distilled water and heated to 95 ºC for 30 min using a water bath (Precisdig, J.P. Selecta, S.A., Barcelona, Spain), while hand stirring, to induce complete starch gelatinization. The gellan solution (2 g/100 g solution) was obtained under magnetic stirring at 90 ºC for 60 min using a magnetic stirrer (RCT basic, IKA®-Werke GmbH & Co. KG, Staufen, Germany). Both were cooled down to reach room temperature (about 25 ºC) and afterwards, glycerol was incorporated as plasticizer (0.25 g/g of polymer), on the basis of previous studies (Cano et al., 2015; Jiménez, Fabra, Talens, & Chiralt, 2012). The starch and gellan solutions were mixed in 8:2 ratio to obtain the solutions without essential oil (S:G formulations). The essential oil, used as an antifungal compound (0.5 g/g of polymer), was added either by direct emulsification or encapsulated in lecithin liposomes (ratio polymer: lecithin 1: 0.5). In the first case (S:G-EO formulations), the essential oil was incorporated directly and the dispersions were homogenized for 3 min at 13500 rpm using an Ultra Turrax rotor-stator homogenizer (DI 25 Basic, IKA®-Werke GmbH & Co. KG, Staufen, Germany). In the second case (S:G-EO-L formulations), the liposome dispersions were previously prepared and added directly to the polymer blend solution while kept under soft magnetic stirring for 2 h using a magnetic stirrer (RCT basic, IKA®-Werke GmbH & Co. KG, Staufen, Germany). Lecithin dispersions (LD) were prepared following the method described by Valencia-Sullca et al. (2016). Lecithin (5 g/100 g solution) was dispersed in water and stirred for at least 4 h at 700 rpm. The essential oil (5 g/100 g solution) was incorporated into the lecithin dispersion by using a sonicator

(Vibra Cell, Sonics & Materials, Inc., Newtown, USA) at 20 kHz for 10 min with pulses of 1 s. Then, the ratios polymer:lecithin:essential oil were 1:0.5:0.5 in S:G-EO-L formulations. Tween 85 was added to the different formulations at different concentrations from 0 to 10^5 mg/L of total solution. All of the solutions were degassed by using a vacuum pump (MZ 2C NT, Vacuubrand GmbH + CO KG, Wertheim, Germany).

2.3. Surface properties of the fruits

Apples (*Malus domestica* Borkh cv. Golden Delicious), tomatoes (*Lycopersicum esculentum* Mill.) and persimmons (*Diospyros kaki* Thunb. cv. Rojo Brillante) were purchased from a local market (Valencia, Spain). Fruits of uniform size, shape and colour and without any signs of mechanical damage were selected, cleaned with sodium hypochlorite solution (1 g/100 g solution) and dried at room temperature (about 25 ºC). To determine the contact angles, thin sections of the fruit skin were cut (2 cm x 2 cm) and placed on a glass plate to proceed with the measurements at 20 ºC.

2.3.1. Contact angle and surface tension measurements

The contact angle (θ) and liquid-vapour surface tension (γ_L) were measured by means of a Dynamic Contact Angle measuring devices and Tensiometer (OCA 20, DataPhysics Instruments GmbH, Filderstadt, Germany). The contact angles were measured by the sessile drop method (Kwok & Neumann, 1999), in which a droplet of the tested liquid was placed on the horizontal surface with a needle of 1.19 mm of internal diameter. Measurements were made in less than 10 s. The surface tension of the coating-forming systems was measured by the pendant drop method. Image analyses were carried out using SCA20 software. At least twelve replicates were obtained for each parameter and formulation.

2.3.2. Surface tension and critical surface tension of fruits skins

Surface tension of the fruit skins were determined through the measurement of contact angles (θ) on the fruit surface (Eq. (1)) of at least three different polar and nonpolar liquids: distilled water, dimethyl sulfoxide, methanol and heptane. Their surface tension (γ_L) parameters (values of polar (γ_L^p) and dispersive (γ_L^d) components) are shown in Table 1. According to Eq. (2) which describes the work of liquid-solid adhesion (W_a), the Eq. (3) can be obtained. From Eq. (3), the polar (γ_S^p) and dispersive (γ_S^d) contributions of the solid surface tension can be obtained by plotting the values of the dependent variable $\left(\frac{1+\cos\theta}{2}\frac{\gamma_L}{\sqrt{\gamma_L^d}}\right)$ vs. the independent variable $\left(\sqrt{\frac{\gamma_L^p}{\gamma_L^d}}\right)$, both calculated from the experimental values of θ of the different liquids with known values of γ_L, γ_L^p and γ_L^d.

$$cos\ \theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \tag{1}$$

$$W_a = W_a^d + W_a^p \leftrightarrow W_a = 2 \cdot \left(\sqrt{\gamma_S^d \cdot \gamma_L^d} + \sqrt{\gamma_S^p \cdot \gamma_L^p}\right) = \gamma_L(1 + \cos\theta) \tag{2}$$

$$\frac{1 + \cos\theta}{2} \cdot \frac{\gamma_L}{\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p} \cdot \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d} \tag{3}$$

2.3.3. Wettabilitty

The wettability of coatings on the fruit surface was determined as the spreading coefficient (W_s), depending on of the works of adhesion (W_a) (Eq. (4)) and cohesion (W_c)

(Eq. (5)), in terms of surface tensions at the interfaces SV (γ_S), LV (γ_L) and SL (γ_{SL}) and contact angle (Eq.(6)) (Rulon & Robert, 1993).

$$W_a = \gamma_L + \gamma_S - \gamma_{SL} = \gamma_L(1 + \cos\theta) \quad (4)$$

$$W_c = 2 \cdot \gamma_L \quad (5)$$

$$W_s = W_a - W_c = \gamma_{SV} - \gamma_{LV} - \gamma_{SL} = \gamma_{LV}(\cos\theta - 1) \quad (6)$$

2.4. Statistical analysis

Statistical analyses were performed through an analysis of variance (ANOVA) using Statgraphics Centurion XVI.II (StatPoint Technologies Inc., Warrenton, VA, USA). Fisher's least significant difference (LSD) procedure was used at the 95% confidence level.

3. Results and discussion

3.1 Fruit surface properties

The estimation of the critical surface tension (γ_C) of the different fruit skins was carried out by extrapolation from a Zisman plot (Zisman, 1964) (Figure 1). For a simple molecular liquid, γ_C is essentially independent of the nature of the liquid and only depends on the food surface (Andrade et al., 2014). The cosine of the contact angle obtained for the pure liquids on the fruit surface (Table 2) was plotted *vs*. the respective surface tension of the liquids, γ_L (Table 1). From the fitted straight lines ($r^2 > 0.944$), the intercept with $\cos\theta = 1$ corresponds to the γ_C values of each surface (Eq. (7)). This corresponds to the value of the surface tension (liquid/vapour), which would promote the best surface wettability. This method is applicable only for systems with a surface tension below 100 mN/m (low-energy surfaces). Thus, it is important to determine the surface energy of the target solid in order to verify its applicability.

$$\gamma_C = \lim_{\gamma_{LV}} \text{ as } \theta \to 0 \tag{7}$$

Table 1. Surface tension components of the reference liquids used for characterisation of the fruit surfaces (mN/m): surface tension (γ_L), dispersive (γ_L^d) and polar (γ_L^p) components.

Component	Compound			
	Water[a]	Methanol[b]	DMSO[b]	Heptane[b]
γ_L	72.1	22.5	44.0	20.1
γ_L^d	19.9	18.2	36.0	20.1
γ_L^p	52.2	4.3	8.0	0.0

[a] Data from Busscher, van Pelt, de Boer, de Jong, & Arends (1984).

[b] Data from Accu Dyne Test™ (2019).

Table 2. Contact angle (θ) values measured with the different pure liquids on the skin of apple, tomato and persimmon. Mean values and standard deviations (n=12).

Surface	Compound			
	Water	Methanol	DMSO	Heptane
Apple	80 ± 3	16 ± 5	37 ± 5	0
Tomato	95 ± 2	37 ± 4	64 ± 3	0
Persimmon	88 ± 5	21 ± 3	52 ±3	0

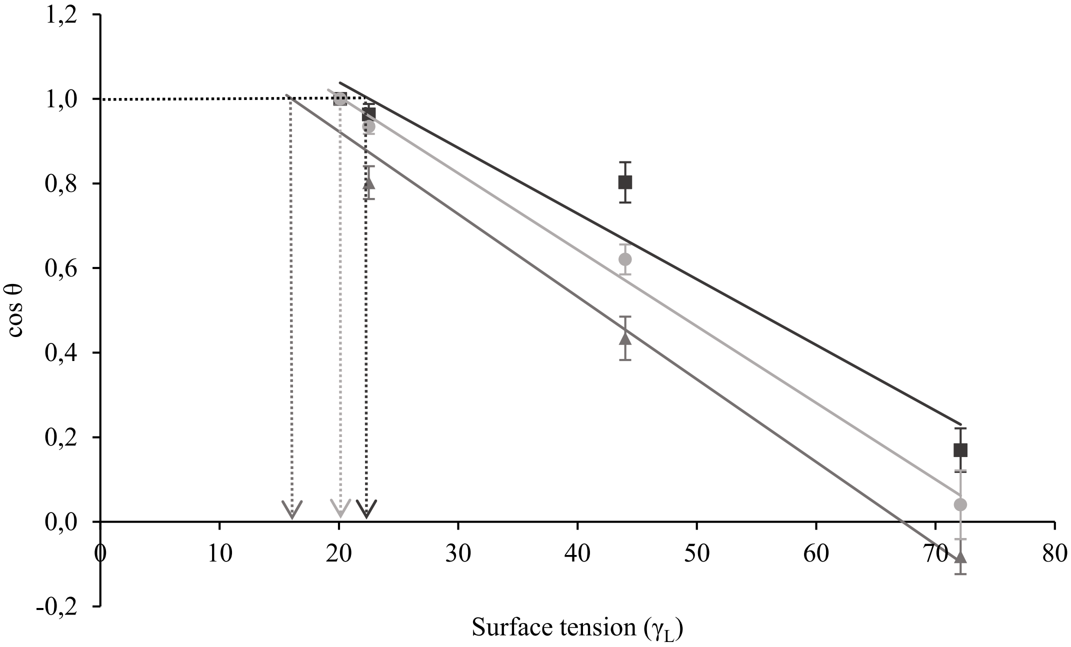

Figure 1. Zisman plot for apple (squares), tomato (triangles) and persimmon (circles) surfaces.

Table 3 shows the values of the critical surface tension of apple, tomato and persimmon surfaces. In general, the critical surface tension values are lower than the solid surface tension (Dann, 1970). This was verified in this study, as also reported by different authors for mango and apple skins (Lima et al., 2010), tomato and carrot (Casariego et al., 2008) and strawberry (Ribeiro et al., 2007).

Table 2 shows the values of contact angles of the different pure liquids on the surface of apple, tomato and persimmon fruits. From these values and the surface tension components of the liquids (Table 1), the independent $\left(\frac{1+\cos\theta}{2}\cdot\frac{\gamma_L}{\sqrt{\gamma_L^d}}\right)$ and dependent $\left(\sqrt{\frac{\gamma_L^p}{\gamma_L^d}}\right)$ variables of Eq. (2) were estimated. Eqs. (8) to (10) were fitted (Figure 2) to the respective data obtained for apple, tomato and persimmon surfaces.

$$\frac{1+\cos\theta}{2}\frac{\gamma_L}{\sqrt{\gamma_L^d}} = 3.1\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + 4.5;\ r^2 = 0.9246 \tag{8}$$

$$\frac{1+\cos\theta}{2}\frac{\gamma_L}{\sqrt{\gamma_L^d}} = 1.9\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + 4.3;\ r^2 = 0.9526 \tag{9}$$

$$\frac{1+\cos\theta}{2}\frac{\gamma_L}{\sqrt{\gamma_L^d}} = 2.4\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + 4.4;\ r^2 = 0.9554 \tag{10}$$

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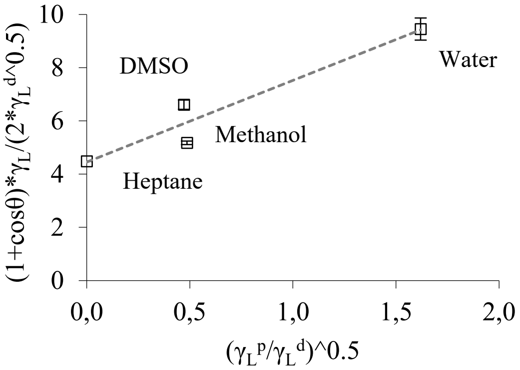
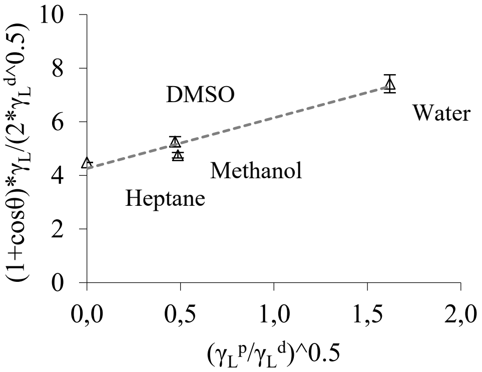
a)



b)



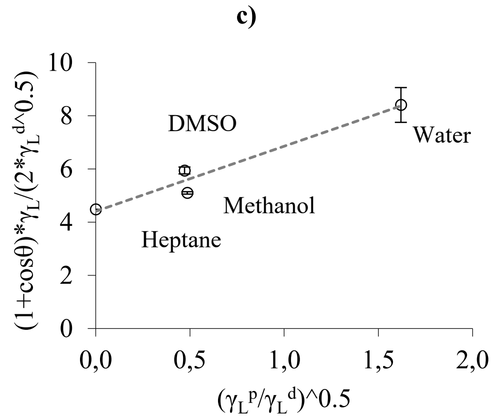


Figure 2. Plot and fitted straight line to calculate polar and dispersive components of the surface tension in a) apple, b) tomato and c) persimmon surfaces.

The slope and intercept of the fitted equations were used to estimate the values of the polar and dispersive components, respectively, as well as the total surface tension of the fruit surfaces. These values, also shown in Table 3, clearly demonstrate that apple, tomato and persimmon have low-energy surfaces (lower than 100 mN/m), and that their surface interactions with liquids would mainly be given by dispersion forces. This is coherent with the natural waxy coatings of the fruit, where non-polar components are the main constituents. Several authors reported the predominant cutin monomers and the main components of the cuticular waxes of apple (Belding, Blankenship, Young, & Leidy, 2019; Dong, Rao, Huber, Chang, & Xin, 2012; Ju & Bramlage, 2001; Morice & Shorland, 1973; Verardo, Pagani, Geatti, & Martinuzzi, 2003), tomato (Bauer, Schulte, & Thier, 2004; Kosma et al., 2010; Saladié et al., 2007), and persimmon (Tsubaki, Sugimura, Teramoto, Yonemori, & Azuma, 2013), where hydrocarbons, wax esters, free fatty acids, free alcohols and polar estolides, diols, aldehydes and ketones are present. Although, fruit cuticles show substantial variability according to species, genotypes within a given species, and stage of development (Lara, Belge, & Goulao, 2014), these are composed of polymer cutin and wax comprising a mixture of very-long-chain fatty acids and their derivatives, while also bioactive secondary metabolites such as triterpenoids are present (Trivedi et al., 2019). The non-polar nature of their main components gives rise to similar behaviour in the fruit surface tension. Due to the high values of the dispersive component of the surface tension, associated to the chemical characteristics of the cuticle constituents, these surfaces would have the ability to participate in non-polar interactions (Cerqueira et al., 2009). The tomato surface was the one that showed the lowest value of the polar component, and therefore, the most limited ability to participate in polar interactions with hydrophilic coatings. Values obtained for apple and tomato were in the range of those reported by other authors (Carneiro-da-Cunha et al., 2009; Casariego et al., 2008; Lima et al., 2010), although no previous studies were reported for persimmon.

Table 3. Values of the surface properties (n=12) determined for the skin of apple, tomato and persimmon (mN/m). The standard error for the intercept and slope of the fitted straight lines range between 0.3 and 0.5, determining the significant figures in the surface tension.

Fruit	Polar component $\left(\gamma_S^p\right)$	Dispersive component $\left(\gamma_S^d\right)$	Solid surface tension	Critical surface tension (γ_c)
Apple	9.4	19.8	29.2	22.7
Tomato	3.6	18.2	21.7	16.1
Persimmon	6.0	19.4	25.4	20.3

3.2. Fruit wettability

Values of the contact angles of the three formulations with the different amounts of Tween 85 are shown in Table 4. As concerns the formulations without Tween 85, the contact angle decreased when they contained essential oil, either emulsified or lecithin-encapsulated. This suggests that emulsified essential oil and liposomes affected the interactions of the coating-forming system with the fruit/air interfaces. These changes in the interfacial interactions are in agreement with the incorporation of lipid and surfactant compounds with different chemical affinity with the aqueous phase, fruit surface or air and the occurrence of interfacial adsorption of the components to reach the minimal free energy of the system. The lowest value was reached in all cases for persimmon, while more similar values were obtained for apple and tomato for every formulation. As expected, the incorporation of Tween 85 modified the values of the contact angles, depending on the concentration and coating composition. In general, the contact angle decreased as the concentration of Tween 85 rose, but the most significant change occurred at a high concentration level (about 10^4 mg/L). This suggests that interactions of the surfactant molecules within the system hindered the surface activity of the compound at low concentrations, which can limit their effectiveness at favouring the coating spreading on the fruit surface. In this sense, several authors (Eliasson, 1994; Ghiasi, Varriano-Marston, & Hoseney, 1982; Mira, Eliasson, & Persson, 2005; Wokadala, Ray, & Emmambux, 2012) have described the complexes of amylose with surfactants, which can give rise to low amounts of free surfactant molecules to act at surface level. On the other hand, when the essential oil is present in the system, the surfactant molecules could be predominantly adsorbed on the oil droplet surface, thus being less available for acting at the solid-liquid-vapour interfaces. For systems with lecithin-encapsulated essential oil, the surfactant molecules could interact with the lecithin membranes, which could also compromise the ability of the molecules to promote the liquid spreading on the fruit surface. The highest contact angle was obtained on apple skin with the starch-gellan dispersion without Tween 85.

Table 4. Contact angle (θ) values of the different coating-forming systems (S:G: starch-gellan formulation, S:G-EO: with emulsified essential oil, and S:G-EO-L: with lecithin encapsulated essential oil) on the skin of apple, tomato and persimmon as a function of the Tween 85 concentration (mg/L). Mean values and standard deviations (n=12).

Sample	Fruit	0	10^0	10^1	10^2	10^3	10^4	$5 \cdot 10^4$	10^5
S:G	Apple	$96 \pm 2^{g,3}$	$95 \pm 3^{fg,3}$	$94 \pm 2^{ef,2}$	$93 \pm 3^{e,2}$	$91 \pm 2^{d,2}$	$71 \pm 4^{c,3}$	$44 \pm 2^{a,2}$	$47 \pm 3^{b,2}$
	Tomato	$92 \pm 2^{de,2}$	$92 \pm 1^{de,2}$	$92 \pm 1^{e,2}$	$91 \pm 2^{d,2}$	$91 \pm 2^{de,2}$	$67 \pm 4^{c,2}$	$48 \pm 2^{a,3}$	$50 \pm 2^{b,3}$
	Persimmon	$67 \pm 3^{d,1}$	$68 \pm 4^{d,1}$	$75 \pm 5^{e,1}$	$77 \pm 6^{e,1}$	$86 \pm 3^{f,1}$	$52 \pm 4^{c,1}$	$42 \pm 3^{a,1}$	$46 \pm 2^{b,1}$
S:G-EO	Apple	$77 \pm 2^{f,3}$	$69 \pm 2^{e,3}$	$70 \pm 1^{e,2}$	$70 \pm 2^{e,2}$	$64 \pm 2^{d,2}$	$43 \pm 3^{a,2}$	$44 \pm 2^{b,2}$	$57 \pm 2^{c,3}$
	Tomato	$73 \pm 2^{e,2}$	$71 \pm 2^{d,2}$	$71 \pm 2^{d,2}$	$75 \pm 2^{f,3}$	$70 \pm 1^{d,3}$	$45 \pm 2^{b,3}$	$44 \pm 1^{a,2}$	$48 \pm 1^{c,2}$
	Persimmon	$68 \pm 2^{f,1}$	$66 \pm 2^{ef,1}$	$65 \pm 2^{de,1}$	$64 \pm 2^{d,1}$	$60 \pm 2^{c,1}$	$38 \pm 2^{b,1}$	$35 \pm 2^{a,1}$	$36 \pm 2^{a,1}$
S:G-EO-L	Apple	$74 \pm 2^{g,2}$	$67 \pm 3^{f,2}$	$64 \pm 4^{e,2}$	$53 \pm 2^{d,1}$	$53 \pm 4^{d,1}$	$38 \pm 3^{a,1}$	$45 \pm 2^{b,3}$	$50 \pm 2^{c,2}$
	Tomato	$79 \pm 2^{f,3}$	$75 \pm 2^{e,3}$	$73 \pm 2^{d,3}$	$69 \pm 2^{c,3}$	$70 \pm 2^{c,3}$	$49 \pm 3^{b,2}$	$42 \pm 1^{a,2}$	$50 \pm 1^{b,2}$
	Persimmon	$55 \pm 4^{cd,1}$	$57 \pm 3^{de,1}$	$57 \pm 1^{e,1}$	$60 \pm 2^{f,2}$	$55 \pm 2^{c,2}$	$38 \pm 1^{a,1}$	$39 \pm 2^{a,1}$	$41 \pm 2^{b,1}$

Different superscript letters within the same row indicate significant differences among formulations for a determined fruit ($p < 0.05$).

Different superscript numbers within the same column indicate significant differences among fruits for a determined Tween 85 concentration ($p < 0.05$).

Table 5 shows the values of the surface tension of the coating-forming systems as a function of the concentrations of Tween 85. It is remarkable that essential oil, either emulsified or encapsulated, significantly decreased the surface tension of the starch-gellan solutions, leading to values near the critical surface tension of the fruits. Then, no surfactant would be necessary to promote the coating spreading on the fruit surface in these cases. The surface activity of the essential oil could not be attributed to the amphiphilic nature of the essential oil components, but to the prevalent location of the essential oil droplets at the air-liquid interface, due to the hydrophobic nature of the essential oil dispersed droplets, with greater affinity with the air phase, as occurs in foams stabilised by fat globules (Eisner, Jeelani, Bernhard, & Windhab, 2007). When essential oil is encapsulated in lecithin liposomes, a similar effect could occur.

In the starch-gellan solution, the surface tension progressively decreased when the Tween concentration rose, but values close to the critical surface tension of the different fruits were only reached at the highest concentration of the surfactant. The decrease in the surface tension at this high concentration could be explained by the interaction of Tween 85 with the amylose molecules, as previously commented on, which limits its surface activity, forming the typical amylose-lipid complexes where the chain of the surfactant is included in the hydrophobic cavities of the amylose helical conformation (Marín, Atarés, Cháfer, & Chiralt, 2017). In fact, some authors report a lipid complexation capacity of amylose in the helical hydrophobic cavity of 10 g lipid/100 g amylose (Eliasson, 1994). Considering an amylose content of 10 g/100 g of cassava starch (Cano et al., 2014) and the ratios of starch-Tween in the coating-forming system, a total complexation could occur, at lower surfactant levels, without saturating the amylose complexation capacity. This could explain the lack of notable changes in the surface tension at relatively high surfactant concentration.

In contrast, the values of surface tension significantly increased in the formulation containing emulsified essential oil from a Tween 85 concentration of 10^3 mg/L. This behaviour suggests that, at lower concentrations of surfactant, the molecules preferably adsorbed at the oil-water interface, helping to stabilise the essential oil emulsion. When the oil-water interfacial area was saturated, the surfactant molecules displaced, at least partially, the oil droplets from the air-water interface, thus provoking a notable change in the surface tension. At the highest amounts of Tween, the surface tension is still higher than that of both the Tween-free emulsion and the critical surface tension of the fruits.

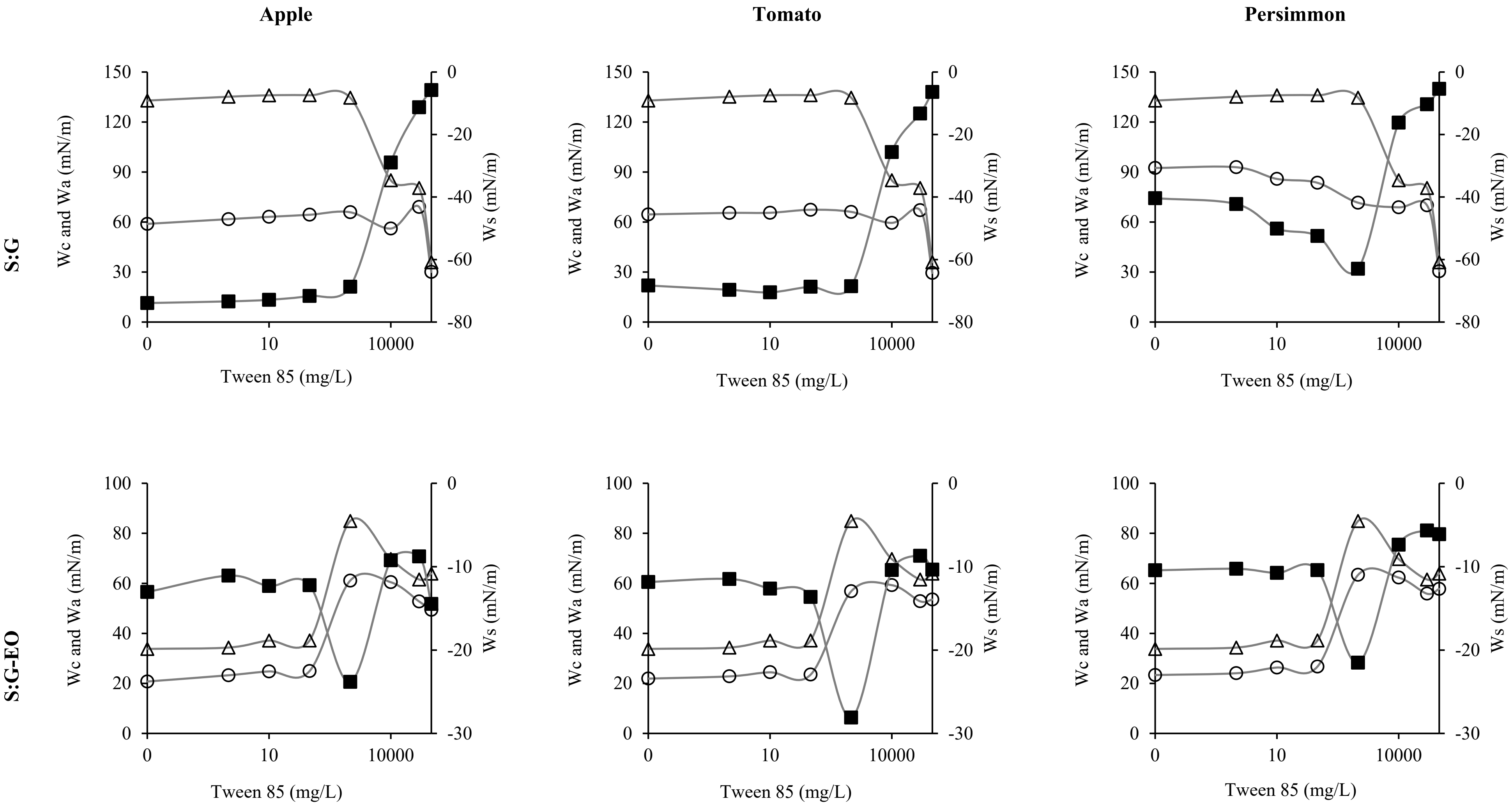
Therefore, in the formulation containing emulsified essential oil, the incorporation of the surfactant did not exert a positive effect on the spreading of the coating-forming system on the fruit. A similar phenomenon occurred in the coating-forming system with the essential oil encapsulated in lecithin liposomes, where the surfactant-free coating-forming system already had low surface tension. In this particular case, the surfactant molecules could participate in the structure of the liposomes helping to stabilise the oil droplets, thus developing a limited role in the water-air interface. Therefore, the interactions of the surfactant at different levels with the components of the coating-forming system limit its surface activity and its effectiveness in reducing the surface tension.

Table 5. Surface tension (γ_L) values of the different coating-forming systems (S:G: starch-gellan formulation, S:G-EO: with emulsified essential oil, and S:G-EO-L: with lecithin encapsulated essential oil) as a function of the Tween 85 concentration (mg/L). Mean values and standard deviations (n=12).

Sample	0	10^0	10^1	10^2	10^3	10^4	$5\cdot10^4$	10^5
S:G	66.4 ± 0.5^{d}	67.6 ± 0.4^{e}	68.0 ± 0.4^{f}	68.0 ± 0.3^{f}	67.3 ± 0.2^{e}	42.5 ± 0.5^{c}	40.2 ± 0.9^{b}	17.9 ± 0.5^{a}
S:G-EO	16.9 ± 0.2^{a}	17.2 ± 0.2^{a}	18.5 ± 0.1^{b}	18.6 ± 0.1^{b}	42.5 ± 0.4^{f}	34.9 ± 0.6^{e}	30.8 ± 0.8^{c}	31.9 ± 1.2^{d}
S:G-EO-L	18.4 ± 0.3^{a}	18.2 ± 0.1^{a}	18.0 ± 0.2^{a}	45.7 ± 0.6^{f}	44.7 ± 1.2^{e}	39.0 ± 0.7^{d}	32.8 ± 0.8^{b}	34.8 ± 0.5^{c}

Different superscript letters within the same row indicate significant differences associated to the Tween 85 concentration for a determined formulation ($p < 0.05$).

Figure 3 shows the obtained values of the W_a, W_c and W_s for the different fruits as a function of the Tween concentration. Negative values of W_s were obtained in every case, but in practical terms the closer the W_s values are to zero, the better the coating spreading. Therefore, in terms of wettability, the starch-gellan formulation without Tween presented the least favourable behaviour, whereas coating-forming systems with emulsified or encapsulated essential oil exhibited good wettability on the different fruit surfaces, with the closest-to-zero values of W_s. Although Tween incorporation at concentrations higher than 10^3 mg/L enhanced the wettability of starch-gellan systems on the three fruits, it did not improve the wettability of coating-forming systems containing essential oil at any concentration. In fact, a sharp decrease in the W_s of these coating-forming systems was observed when Tween was added at 10^2 - 10^3 mg/L, when the surface tension of these coating-forming systems increased, as commented on above. Therefore, the starch-gellan solution requires the addition of at least $5 \cdot 10^4$ mg/L of Tween to have a good wettability on the fruit surface, but the coating-forming systems with essential oil, emulsified or encapsulated in lecithin liposomes, did not require the incorporation of Tween 85 to improve their spreading on the fruit. On the contrary, at intermediate concentrations, a highly negative effect was observed.


Apple
Tomato
Persimmon
S:G
S:G-EO
Wc and Wa (mN/m)
Ws (mN/m)
Tween 85 (mg/L)
150
120
90
60
30
0
-20
-40
-60
-80
100
80
40
20
-10
-30
0
10
10000

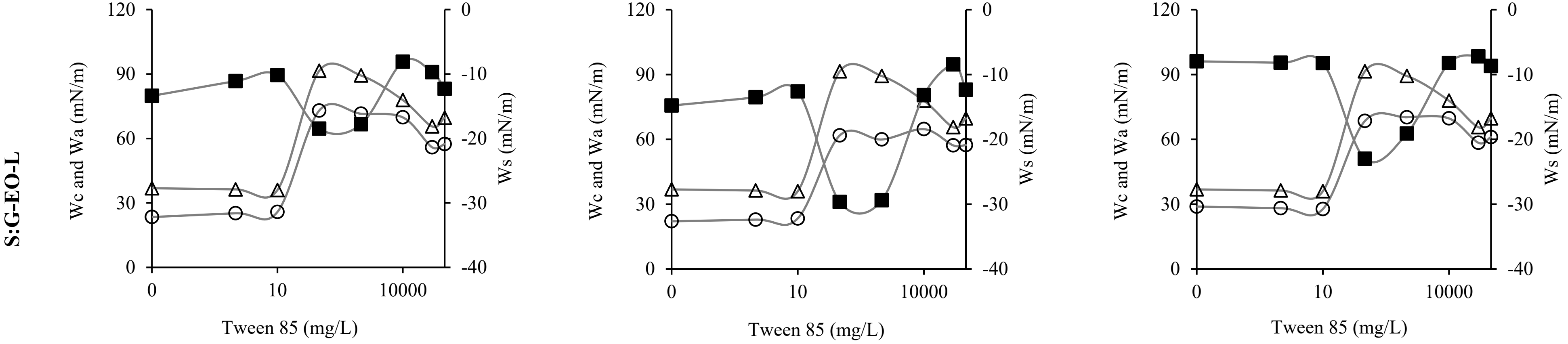


Figure 3. Spreading (W_s) (squares), adhesion (W_a) (circles) and cohesion (W_c) (triangles) coefficients as a function of Tween 85 concentration, obtained for the different coating-forming systems (S:G: starch-gellan formulation, S:G-EO: with emulsified essential oil, and S:G-EO-L: with lecithin encapsulated essential oil) for the apple, tomato and persimmon surfaces.

4. Conclusions

The skins of apple, tomato and persimmon were found to be of low-energy surfaces (lower than 100 mN/m), and the results of the polar and the dispersive components, demonstrate the ability of these surfaces to interact with non-polar liquids. The addition of Tween 85 positively influenced the contact angle and surface tension values of the starch-gellan solutions, but in the presence of thyme essential oil and lecithin, it had a negative impact depending on the concentration of the surfactant. Spreading coefficient was notably improved with Tween 85 at $5 \cdot 10^4$ mg/L in the starch-gellan formulations (values closer to zero). However, it had a negative effect on the already good spreadability of formulations containing free or lecithin encapsulated thyme essential oil.

These findings provide relevant information on surface properties of starch-gellan coating-forming solutions in view of their use as coatings for fruits. However, it would be necessary to analyse the effect of the coatings with Tween 85 on the preservation parameters of fruits, since this type of compound could also interact with the wax layer of the fruits, modifying their natural barrier capacity.

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