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Static and advancing contact angles of water on dark chocolate

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ABSTRACT

This work investigated the wettability of dark chocolate by water, focusing on commercial and laboratory-produced chocolate. The study employed optical tensiometry to measure the static and advancing contact angle. Sessile drop experiments on commercial chocolate demonstrated that water was neither absorbed nor subject to evaporation during the measurement period. Chocolate with higher sugar content exhibited lower contact angles, that is a more hydrophilic character. Furthermore, the higher sugar content resulted in greater droplet spreading during the measurement time, leading to greater deviations from the ideal behavior, corresponding to smooth, chemically uniform, and inert surfaces. A more hydrophilic and less ideal character was also observed for non-tempered chocolate compared to its tempered counterpart. We hypothesized that the hydrophilic character of chocolate, among other factors, is conferred by sugar, which the wetting water can access through surface irregularities such as cracks and pores. This mechanism, which is introduced as a novel explanation of the phenomenon, was supported by NMR analysis of the liquid after contact with the chocolate, which showed sugar contamination. Such irregularities depend on the chocolate composition and process conditions and are exacerbated in poorly tempered chocolate. The difference between the advancing and static contact angle was larger for non-tempered samples, suggesting that surface non-idealities such as roughness and solid dissolution are more important in non-tempered samples. This research contributes to a deeper understanding of the wetting behavior of chocolate and opens the way to the use of contact angle measurements in the chocolate field as an easy-to-measure parameter for assessing chocolate surface characteristics and supporting quality-control practices.

1. Introduction

Chocolate is one of the most beloved confectionery products worldwide, prized for its glossy appearance, smooth texture, and rich flavor (Nujkić et al., 2024). These desirable attributes are closely linked to the microstructure of chocolate, which consists of fine solid particles (sugar, cocoa solids, and other solids depending on the type of chocolate) dispersed within a continuous fat phase (cocoa butter). During refining and conching, the size of the solid particles reduces, and fat coats these particles to ensure a smooth texture and appropriate flow properties. Proper tempering promotes the formation of stable cocoa butter V crystals, resulting in a dense and uniform fat crystal network that enhances gloss, snap, and shelf stability (Stobbs et al., 2025; Beckett, 2011). These quality attributes are negatively affected by inadequate refining, conching, or tempering, which can disrupt the internal fat crystal network and particle dispersion. The resulting structural heterogeneities may ultimately manifest at the chocolate surface, providing insight into its structural state and processing quality. Chocolate surface characteristics depend on formulation and processing conditions and may range from smooth and uniform to heterogeneous, with pores, cracks, and partially exposed particles. Microscopy and microstructural studies have revealed partially coated solid particles, particularly in poorly tempered chocolate as well as surface irregularities of micrometer dimensions (Konar et al., 2024; Rousseau, 2016). The degree of particle coating and surface uniformity is influenced by formulation and processing parameters: higher fat content promotes more effective coating (Afoakwa et al., 2009), smaller and well-distributed particle sizes favor smoother coverage (Glicerina et al., 2014), and appropriate refining, conching, and tempering are essential for dispersing fat and minimizing voids and defects (Afoakwa et al., 2007; Beckett, 2011). Consequently, the surface structure of chocolate reflects its internal fat crystal network and particle distribution.

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When this structural balance is disturbed, quality defects may arise. One of the most common is blooming, which appears as white, chalky streaks or patches on the chocolate surface (Lonchampt and Hartel, 2006). Blooming can be categorized into fat bloom and sugar bloom. Fat bloom occurs when cocoa butter crystals migrate to the surface and recrystallize, often due to improper tempering (Widlak and Hartel, 2012). Sugar bloom results from condensation of moisture on the chocolate surface, leading to dissolution and recrystallization of sugar (Lonchampt and Hartel, 2006). Both forms significantly affect sensory appeal and consumer perception of quality.

As emphasized in recent reviews (Rossi et al., 2018), contact angle analysis—i.e., the measurement of the angle formed between a liquid droplet and a solid surface as an indicator of wettability—represents a promising, non-destructive approach for probing food surface characteristics, yet its potential remains underexplored within the broader field of food materials science. In chocolate, wettability measurements may provide insight into surface composition, structural heterogeneity, and interfacial interactions.

The effects of composition and process conditions on chocolate surface behavior have traditionally been evaluated using indirect or structural techniques rather than direct wetting measurements. Common approaches include microscopic observations (optical microscopy or scanning electron microscopy, SEM) to identify sugar bloom formation and surface heterogeneities (Lonchampt and Hartel, 2006; Rousseau, 2016), surface topography analyses such as atomic force microscopy (AFM) or profilometry to quantify roughness and micro-scale irregularities associated with exposed or recrystallized sugar (Beckett, 2011; Konar et al., 2024), and moisture sorption analyses and controlled humidity cycling to assess sugar dissolution and recrystallization tendencies (Lonchampt and Hartel, 2004; Afoakwa, 2010). While these techniques provide valuable information on chocolate microstructure, surface morphology, and moisture sensitivity, they primarily offer localized or structural descriptors of the surface. On the other hand, contact angle measurements investigate the macroscopic wetting response resulting from the combined effects of surface chemistry, roughness, and heterogeneity, thereby providing complementary information on liquid-solid interactions that is not directly accessible through microscopy or topographical analysis alone.

Despite the effectiveness of established structural and moisture-based techniques, many of these methods are time-consuming, require specialized instrumentation, or are not readily applicable for routine or rapid quality assessment in industrial environments (Beckett, 2011; Afoakwa, 2010). In contrast, contact angle measurements offer a rapid, non-destructive, and surface-sensitive approach that can be performed with minimal sample preparation and small liquid volumes. Because wettability directly reflects the balance between hydrophilic and hydrophobic surface domains, contact angle measurements are particularly well suited to capture specific quality-related attributes such as tempering state, fat crystal coverage and surface stability (Reinke et al., 2015). While contact angle does not capture all aspects of chocolate quality (e.g., flavor or aroma), it could provide a quantitative and reproducible indicator of surface properties that are relevant to appearance, shelf life, and process consistency in industrial production.

Reinke et al. (2015) conducted the only comprehensive investigation of chocolate wettability to date, demonstrating that contact-angle measurements can provide valuable insight into chocolate surface properties and their dependence on tempering, surface roughness, and liquid characteristics. However, several aspects of chocolate wetting remain unresolved, particularly regarding how formulation variables, and surface interactions such as partial solid dissolution, contribute to the measured contact angles.

These open questions motivated the present study. We employed water wettability measurements as a tool to characterize the surface state of chocolate, investigating dark chocolates differing in fat content as well as tempered and non-tempered samples. Wettability measurements were complemented by compositional analysis of the aqueous phase after controlled water contact to further examine water–chocolate surface interactions.

2. Theoretical background on wettability

The wettability of a surface is quantitatively characterized by the equilibrium contact angle, with lower contact angles indicating higher wettability and greater spreading of a liquid across the surface. The contact angle, denoted as θ, is the equilibrium angle formed at the point where the liquid, solid, and gas phases meet. The relationship at this three-phase boundary is described for ideal surfaces by the Young Equation (Fig. 1):

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta_Y$$

Here, γ_{LV} represents the surface tension of the liquid, γ_{SL} is the interfacial tension between the solid and the liquid, γ_{SV} is the solid's surface tension (or surface free energy), and θ_Y is the so-called Young's contact angle.

Contact angles are usually measured with optical tensiometers, which operate by capturing high-resolution images of a sessile droplet and fitting its profile to theoretical drop-shape models. These instruments also provide the droplet volume and the baseline, i.e., the liquid–solid interfacial width of the line used as the reference for geometrical fitting. The Young equation is strictly valid only for an ideal surface, defined as one that is perfectly smooth, chemically homogeneous, and that neither dissolves nor undergoes chemical reactions with the contacting liquid. In practice, most real surfaces deviate from these conditions to some extent. As a result, the contact angle that a liquid forms with a surface at the equilibrium state, the apparent contact angle (θ), is different from θ_Y. Another aspect of real surfaces is the existence of not just one equilibrium contact angle but rather a range of stable contact angles. From an energy point of view, this corresponds to the existence of multiple local energy minima where the system can be in mechanical equilibrium. Such minima depend on the droplet's history and surface features, such as chemical heterogeneity and roughness. The entire range of apparent contact angles for a sample surface can be captured by measuring dynamic (advancing and receding) contact angles (Fig. 1). The advancing contact angle is defined as the angle formed between the tangent to the liquid droplet's surface and the solid surface at the point of contact, specifically when the droplet is increasing in volume. This measurement is obtained using the needle-in method, where a droplet of liquid is placed on a surface, and a needle is inserted into the droplet to steadily inject more liquid, causing the droplet's volume to increase. Initially, as the volume increases, the contact angle rises while the baseline remains stable. Eventually, the contact angle stabilizes, and the baseline begins to advance on the surface, indicating that the advancing contact angle has been reached (Ho et al., 2008; Kwok and Neumann, 1999). The receding contact angle is determined by a process that is essentially the reverse of measuring the advancing contact angle. In this method, liquid is withdrawn from a stationary droplet. Initially, both the volume of the droplet and the contact angle decrease, while the baseline remains unchanged. Eventually, the contact angle stops decreasing and stabilizes again. The receding contact angle is defined as the point at which the contact angle becomes stable, and the baseline length either decreases or starts to recede. On highly heterogeneous, rough, or chemically evolving surfaces, the contact line may remain strongly pinned during liquid withdrawal, making the receding contact angle difficult to measure reproducibly (Korhonen et al., 2013). The difference between the advancing and receding contact angles is known as contact angle hysteresis. The highest possible apparent contact angle corresponds with the advancing contact angle, and the lowest possible apparent contact angle corresponds with the receding contact angle (Zhao and Jiang, 2018). A perfectly uniform and smooth surface theoretically exhibits a contact angle hysteresis of 0°. Higher hysteresis values are generally linked to increased surface heterogeneity, and conversely, lower values indicate a more homogeneous surface. Factors

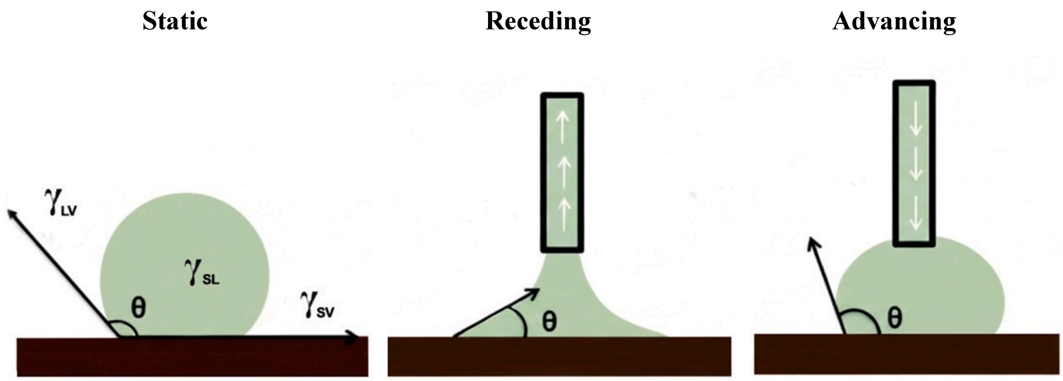

Fig. 1. Apparent static, receding and advancing contact angle (Adapted from Chang and Liu, 2023).

contributing to hysteresis often include surface roughness and variations in chemical composition (Huhtamäki et al., 2018).

3. Materials and methods

3.1. Materials

Four commercial dark chocolate bars of the same brand (Novi, Italy) with distinct labeled cacao solids content (70%, 80%, 88% and 99%) were purchased from a local supermarket in Viterbo, Italy. Their macronutrient content in terms of fat, carbohydrate, and sugar, as stated on the product label, is reported in Table 1. Cocoa powder containing 20-22% cocoa butter was supplied by Beppiani Cioccolato shop (Borgo Valbeluna, Italy). Sugar (sucrose) and vanilla powder were purchased from a local supermarket (Viterbo, Italy). Sunflower lecithin and cocoa butter (60% saturated fatty acids, melting point 33-36 °C) were kindly donated by Casa Optima S.p.A. (San Clemente, RN, Italy).

3.2. Dark chocolate production

A model dark chocolate formulation (35% cocoa butter, 45% cocoa powder, 19% sugar, 0.9% lecithin and 0.1% vanilla) was developed in this work, consistent with typical dark chocolate compositions (Svanberg et al., 2011) and legal definition of cocoa solids content (chocolate should contain not less than 35% cacao dry solids; Directive 2000/36/EC, 2000). Lecithin was mixed manually with the cocoa butter that had been previously melted at 45 °C, and the resulting blend was then transferred into a refiner (model no. 507, Diamond Custom Machines Corp., Hillsborough, NJ, USA). Then, the machine was turned on, and the solid ingredients were added gradually. Chocolate ingredients were refined for 5 h. After refining, the mixture was molded into polycarbonate molds and kept in the fridge overnight.

3.2.1. Tempering operation

The next day, the non-tempered samples were set aside, and the remaining chocolate was tempered by Kenwood cooking chef XL machine (New Lane, Havant, England). First, the chocolate was portioned into three parts of identical weight. Then, 1/3 of the chocolate was used as the seeds, added to the remaining 2/3 of it previously poured into the machine, and melted at 50 °C for an hour. Then the mixture was stirred continuously by the agitator blade to make the temperature uniform as it was cooling down, thanks to the heat exchange with the environment. When the temperature reached 27 °C, the chocolate was reheated to approximately 31−32 °C to eliminate any remaining unstable crystal forms. Finally, the chocolate was allowed to cool again to 27 °C. Then the machine was stopped, and the mixture was formed into the molds. The tempering process took approximately 30 min (Stobbs et al., 2025).

The molds were placed into plastic bags, sealed, and kept overnight in a refrigerator (4 °C). The molded chocolate was removed and stored at room temperature in the dark in sealed plastic bags and containers to protect it from the environment's humidity for future experiments.

Table 1
Gross composition of the different commercial chocolate bars, as reported on product labels; sugars are included within total carbohydrate.

Type of chocolate bar	70% Dark chocolate	80% Dark chocolate	88% Dark chocolate	99% Dark chocolate
Fat (g/100 g)	44	53	54	54
Total carbohydrate (g/100 g)	36	27	21	16
Sugar (g/100 g)	28	17	10	1.5

3.3. Contact angle and surface tension measurement

The sessile drop and dynamic contact angle protocols were applied to measure static and advancing contact angles of the pieces of chocolate by means of an automated optical tensiometer (model Theta flex, Biolin Scientific, Espoo, Finland). The instrument primarily comprised an automated pipettor, a sample holding plate, and a high-speed camera that was fitted with a microscope objective. For static contact angle measurements, the method used by Moreira et al. (2024) was used with slight modification. A droplet of deionized water was placed onto the surface of the chocolate sample using a 300 μL plastic pipette tip (Neptune, Germany). Advancing contact angle was measured by constantly increasing the volume of the initially deposited droplet of water (initial volume 4-5 μl) on the surface of chocolate by a needle tip (23G, D'encre Colle Lubrifiant, China) with reference to a modified version of the method used by Daghigh Shirazi et al. (2024). Although we attempted to measure the receding angles, the contact line remained pinned, a common issue (Korhonen et al., 2013), which ultimately impaired the measurement. Surface tension measurements of liquids were carried out using the optical tensiometer by using the pendant drop method according to the manufacturer's instructions.

Images of the droplet were taken by the high-speed camera. The instrument software could set the value of several operational parameters. In particular, the initial drop volume and image acquisition rate were set in the range 4 - 8 μl and at 1.4 fps for both contact angle and surface tension measurements.

At least three measurements were taken for each sample, and the average of these values was calculated. To ensure that the samples were acclimated to room temperature conditions, they were maintained in the measurement environment for a minimum of 1 h before the contact angle assessments. The data were analyzed using the instrument's proprietary software, One Attension (version 4.1.2). In addition to the measurement of the contact angles, the software was able to measure the droplet volume and the baseline width, that is, the width of the contact line between the drop and the solid surface.

3.4. NMR analysis

Proton NMR analysis was performed to qualitatively and semi-quantitatively identify which water-soluble compounds migrated from the chocolate into the aqueous phase after contact and to compare the relative extent of dissolution among the different samples, based on the presence and relative intensities of characteristic signals. A 10 μl drop of deionized water was withdrawn by a PR-100 pipettor (Rainin, USA) assembled with 200-μL volume tip and manually deposited on the surface of the chocolate pieces. After 60 s of deposition, the water drop was collected by a syringe equipped with a needle. When the sample volume reached about 1 ml, some of it was used to determine its surface tension by the pendant drop method using the optical tensiometer, which was performed immediately, and the remaining solution was stored in a freezer at −20 °C until NMR analysis. Frozen samples were thawed, added with deuterium oxide (D_2O, 10% v/v) and transferred into 5 mm-NMR sample tubes (Nihonseimitsu Scientific Co., Tokyo, Japan) at a final volume of 600 μl. 1H NMR spectra were acquired on a Bruker Avance instrument operating at 400 MHz (Bruker Biospin, Germany) and at 25 ± 1 °C. Samples were locked on deuterium signal of D_2O and the magnetic field homogeneity was optimized for each sample. The spectral width was 4807 Hz, and 32 k data points were collected using the standard Bruker NOESY pulse sequence (noesypr1d) and collected after a 100 ms mixing period. The water suppression was achieved using continuous wave irradiation. All spectra were recorded using 64 transients, a relaxation delay of 2 s, and an acquisition time of 4 s. Processing (phase and spectra baseline correction) was performed with 1D NMR Manager software (ACD/Labs, Toronto, Canada). Free induction decays (FID) were zero-filled to 64 k data points and multiplied by an exponential function equivalent to 0.2 Hz line broadening before Fourier transformation.

3.5. Experimental outline

The first step of this study involved setting up a protocol for the study of the wetting behavior of dark chocolate through static contact angle measurement and exploring the wettability as a function of cacao solid content. The four different commercial dark chocolates (70%, 80%, 88% and 99%) were used for this aim. Subsequently, 80% dark chocolate was produced in tempered and non-tempered form, and its wetting behavior was studied at several time intervals after production (2, 10 and 20 days) by static and advancing contact angle measurements. Further characterization experiments concerned the study of mass transfer from the chocolate surface to the deposited water droplet, due to the contact between the two phases, through nuclear magnetic resonance (NMR) and surface tension analysis of the deposited liquid after the contact with the chocolate.

3.6. Statistical analysis

Drop contact angles, volume, and baseline as a function of time were acquired by the tensiometer and exported as Excel® files. Data was imported into JMP Pro version 18.2.0 (SAS Institute, Cary, NC, USA) for visualization and statistical analysis. Measurements of static and dynamic contact angles were replicated both within the same piece of chocolate and across different pieces. At least three replicates for each chocolate sample were carried out. Two sample t-tests, two-way ANOVA tests and Fisher's multiple comparison tests were carried out by JMP Pro software.

4. Results and discussion

4.1. Sessile drop experiments

An optical tensiometer enables the measurement of several key parameters that help characterize the interaction between a liquid and a solid surface over time. The most important of these is the contact angle, although the droplet's baseline and volume also provide valuable insights. These parameters were collected over time and analyzed in this work for both sessile drop and dynamic contact angle experiments.

4.1.1. Wettability results for commercial chocolate samples

Fig. 2 shows the wettability results for the commercial chocolate samples with various cacao solids content (70%, 80%, 88% and 99%), by reporting the static contact angle, the drop volume, and the baseline as a function of time. The static contact angle plot (Fig. 2A) shows a contact angle that for all chocolate samples is high at the beginning and then decreases as function of time. For an ideal surface, the contact angle stabilizes much faster and reaches a mechanical equilibrium value. On the contrary, for real surfaces, several phenomena such as water absorption or surface modification can alter the liquid-solid, solid-vapor or liquid-vapor interactions, causing the droplet to spread further and the contact angle to decrease as a function of time. The observed decrease in contact angle cannot be attributed to water evaporation or absorption since the drop volume is almost constant over time for all the conditions examined (Fig. 2B). The decrease in contact angle is associated with an increase in baseline (Fig. 2C), which means that the drop spreads on the surface as a function of time. The decrease of the contact angle as a function of time, which can be quantified by the difference between the initial and final value of the contact angle, under these circumstances is called spreadability (Reinke et al., 2015). While the general wettability behavior does not seem to depend on the pipetted volume of the drop, there is a clear effect of the type of chocolate. Moving from low to high cacao solids, the contact angle curves assume higher values, and at the same time, the droplet spreading decreases. Thus, the increase of the cacao solids content leads to an increase of the hydrophobicity of chocolate and a decrease of the interaction between water and chocolate (less drop spreading). The increase in cacao solids thus enhances the chocolate surface's ideal behavior and hydrophobicity. We can hypothesize that the non-ideal behavior and hydrophilic character of chocolate are affected by the sugar content, which decreases with the increase of cacao solids. Sugar is soluble in water and hydrophilic (Reinke et al., 2015). Thus, in addition to the more hydrophilic character of the surface, it could be responsible for the interaction of the solid with water (solid dissolution) and the chemical heterogeneity of the surface, both characteristics of non-ideal surfaces.

To test the statistical significance of the effect of the type of chocolate and initial drop volume on the contact angle, volume, and baseline data, the data collected at 60 s were analyzed (Fig. 3).

A two-way analysis of variance was applied to the data acquired at 60 s from deposition (Table 2). The analysis revealed that at 5%-confidence level, the initial volume of the drop did not affect the contact angle, but just the drop volume and baseline (as can be expected). The type of chocolate had a highly significant effect on both contact angle and baseline, as emerged from visual inspection of Fig. 2. These results show that in the range of drop volume tested (4-8 μl), the drop volume did not affect contact angle measurements.

4.1.2. Wettability results for laboratory-made tempered and non-tempered chocolate

Fig. 4 shows two images of sessile drops of water after 60 s from deposition for tempered and non-tempered chocolate in sessile drop experiments. The behavior of the water droplet on the two surfaces was very different. Tempered chocolate repelled water, behaving as a hydrophobic surface, with a contact angle greater than 90°. On the contrary, the non-tempered chocolate behaved like a hydrophilic surface, the contact angle being far less than 90°.

Fig. 5 shows the time course of the tensiometer measurements obtained for tempered and non-tempered chocolate as a function of storage time. The contact angle data (Fig. 5A) for the tempered chocolate is similar to the data obtained for the commercial chocolate. While the contact angle for tempered chocolate showed a minimal decline as a

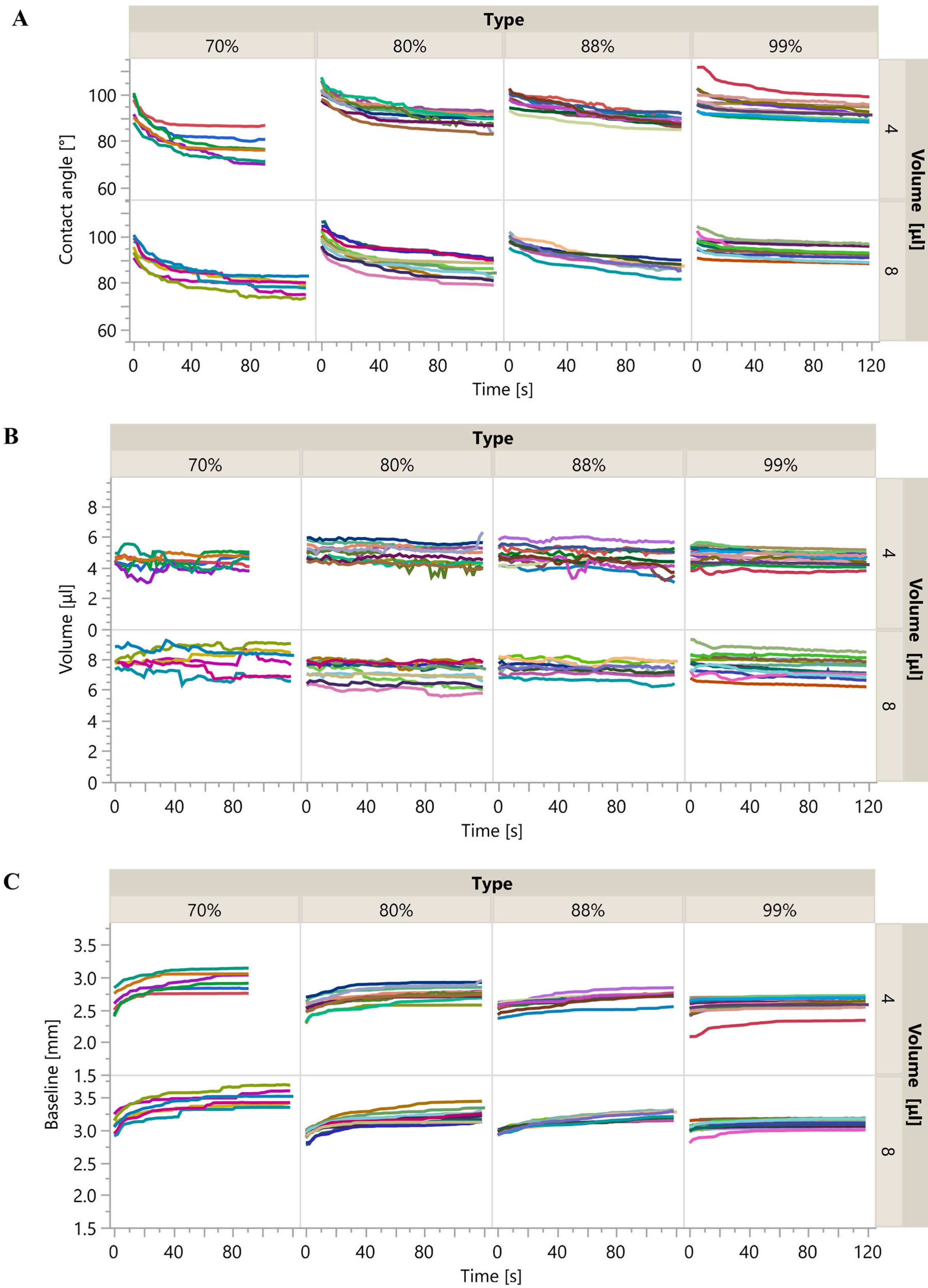

Fig. 2. Contact angle (A), volume (B), and baseline (C) of the water droplets as a function of time for chocolate with different contents of cacao solids (70%, 80%, 88%, 99%) in static contact angle tests.

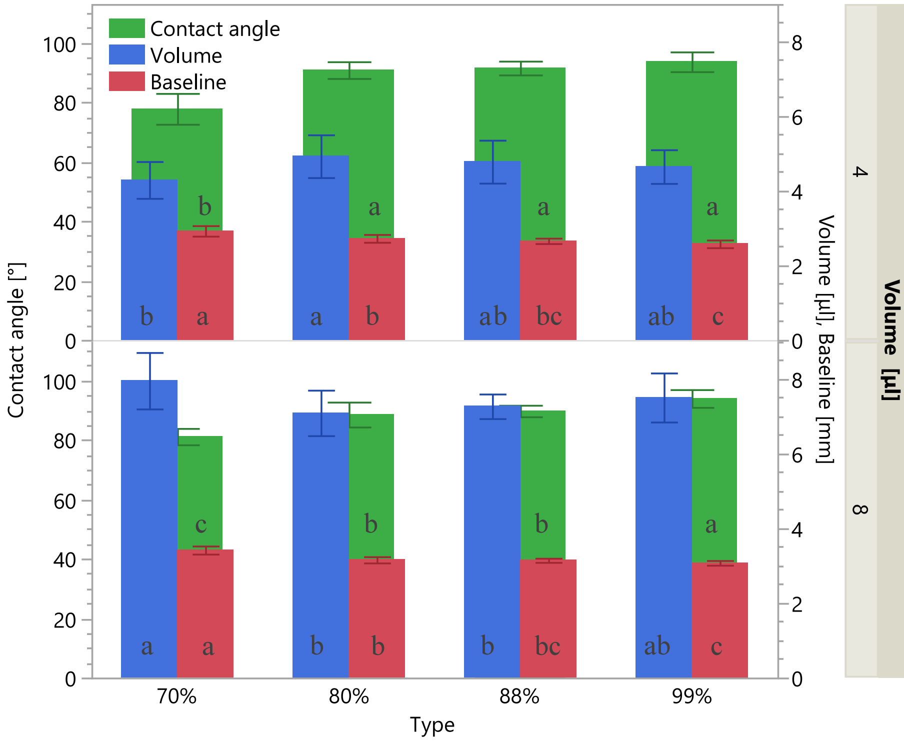

Fig. 3. Mean contact angle, volume, and baseline of the water droplets at 60 s from deposition for chocolate with different content of cacao solids (Type) in sessile drop experiments. Error bars indicate the standard deviations across replicates. Within each variable, means labeled with different letters differ significantly across chocolate type (Fisher's method, α = 0.05).

Table 2
Analysis of variance of contact angle, volume, and baseline data at 60 s as a function of initial drop volume and chocolate type: effect (Type, Volume and the two-way interaction Type*Volume), degrees of freedom (DF), sum of squares (SS), mean sum of squares (MS), F-ratio (F_0), p-value.

	Effect	DF	SS	MS	F_0	P-value
Contact angle	Type	3	1679.20	559.73	53.80	<0.0001
	Volume	1	0.13	0.13	0.01	0.9122
	Type*Volume	3	69.83	23.27	2.24	0.0919
Volume	Type	3	0.13	0.04	0.13	0.9386
	Volume	1	137.36	137.36	435.62	<0.0001
	Type*Volume	3	4.60	1.53	4.86	0.0041
Baseline	Type	3	0.97	0.32	39.30	<0.0001
	Volume	1	4.04	4.05	493.36	<0.0001
	Type*Volume	3	0.01	0.004	0.50	0.6855

function of time, from 101.22 to 90.91°, the value obtained for non-tempered chocolate declined much faster, from 73.20 to 42.03, showing a much higher spreadability. The volume of the droplets (Fig. 5B) on both surfaces was almost constant as a function of time, confirming that neither evaporation nor water absorption occurred. The baseline width did not change much for tempered chocolate but increased as a function of time for the non-tempered samples (Fig. 5C), indicating that the droplet spread on the chocolate surface during measurements. The trend of the graphs is very similar to the corresponding trend for the commercial chocolate samples, where the non-tempered and the tempered samples behaved respectively like sugar-rich and sugar-poor chocolate. The hydrophilic and non-ideal behavior of non-tempered chocolate was similar to the 70%-dark chocolate, which showed the highest spreadability among the commercial samples studied. Also, a higher variability of replicated measurements on non-tempered chocolate can be observed (Fig. 5), due to the less ideal nature of the surface.

Fig. 6 reports the results of sessile drop experiments at 60 s, to allow a

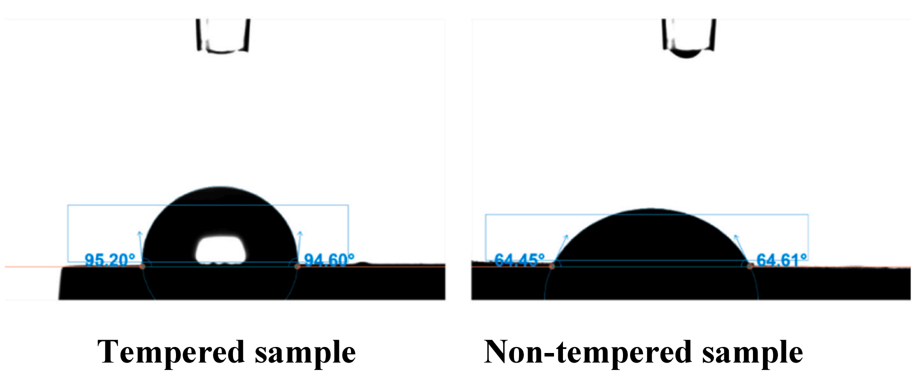

Fig. 4. Pictures of water droplets for tempered and non-tempered laboratory chocolate taken after 60 s from deposition in static contact angle tests after ten days from production.

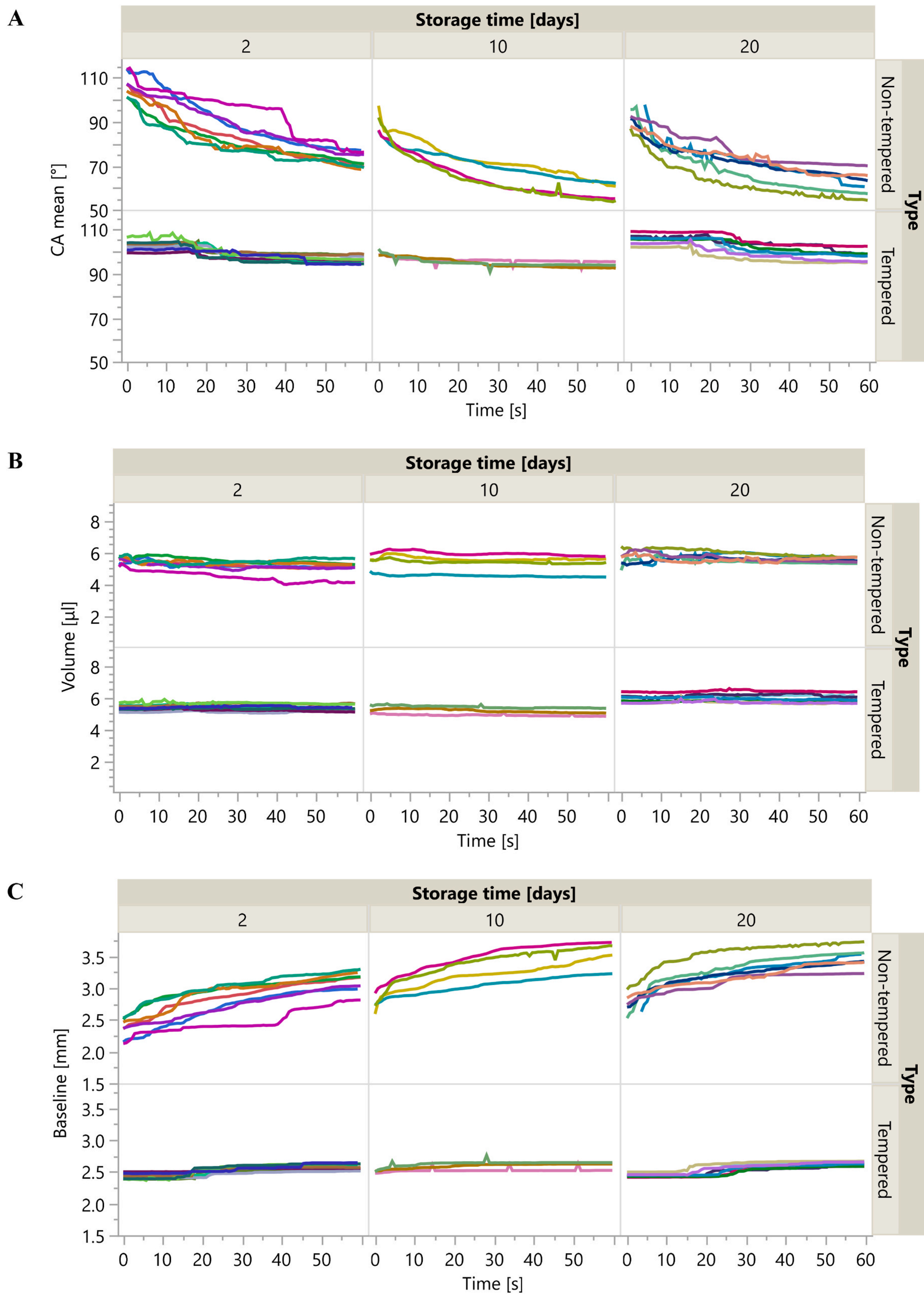

Fig. 5. Contact angle (A), volume (B) and baseline (C) as a function of measurement time for tempered and non-tempered chocolate samples at different storage times (2, 10 and 20 days) in static contact angle tests.

statistical comparison among the different conditions. The statistical analysis confirmed that the contact angles and baselines are different for tempered and non-tempered samples, for each storage time. The effect of storage time was significant for both conditions. The tempered chocolate exhibited a stable contact angle and baseline as a function of storage time, with a significant small effect. For the non-tempered samples, the effect of time was significant and much more important, with the data at 2 days from production being statistically different than the data at other times. In summary, while the tempered chocolate appeared more stable as a function of storage time, the non-tempered samples changed notably from day 2 to day 10 and then remained the same.

4.2. Advancing contact angle experiments

Fig. 7 shows two images of advancing contact angle experiments on tempered and non-tempered chocolate. The more hydrophilic nature of non-tempered chocolate is evident.

Fig. 8 reports the results of the advancing contact angle experiments. Contrary to the sessile drop experiments, the contact angle measured during the movement of the drop (Fig. 8A) reaches a steady state while the baseline is expanding (Fig. 8B) as a function of time. Another difference compared to sessile drop experiments is that the difference between the advancing contact angle of tempered and non-tempered chocolate is less important. The static contact angle at 60 s and the advancing contact angle (taken as the value at 50 s from deposition) are plotted in Fig. 9 and reported in Table 3. The contact angle data for the tempered samples showed almost the same values for both advancing and static methods at identical storage times, their difference being 9.8, −0.9 and −3.1° respectively at 2, 10 and 20 days of storage (Table 3). This was not the case for the non-tempered samples, which experienced a difference between the advancing and static contact angles of 23.3, 15.9, and 16.7° respectively for 2, 10, and 20 days of storage (Table 3). In short, changing the type of contact angle measurement test (advancing method) tended to produce higher values than the static method for non-tempered samples. The above-calculated differences do not represent the so-called hysteresis, defined as the difference between the advancing and the receding contact angle (the latter was not reported in this work since it was difficult to measure). However, it can be considered an indicator of contact-line pinning and deviation from ideal Young-type wetting behaviour on smooth, chemically homogeneous, and inert surfaces.

With regards to the effect of storage time on the advancing contact angle, also in this case, the tempered chocolate was much more stable, with approximately constant values, while for the non-tempered samples, it decreased from day 2 to day 10 and then remained almost constant afterward. This behavior of the non-tempered chocolate is in line with the results of the sessile drop experiments.

4.3. NMR analysis and surface tension of liquid after contact with chocolate

To study the interaction of the chocolate surface with the liquid used to study its wettability, in particular to check if any dissolution of the solid occurred, we conducted NMR analysis and surface tension of water droplets that had been in contact with the chocolate surface of tempered and non-tempered samples for 60 s. Since we suspected that some sucrose could migrate from the surface to the liquid, we tested also a 10% (w/w) solution of sucrose in water.

Fig. 10A shows the NMR spectrum for the 10% sucrose solution, where all the sucrose characteristic NMR resonances can be seen (Yusuf et al., 2021). The spectra acquired for the solutions obtained from non-tempered (Fig. 10B) and tempered chocolate (Fig. 10C) show the same pattern as Fig. 10A, thus confirming the presence of sugar in both samples, but the intensity of the peaks is much higher (more than one order of magnitude higher) for the non-tempered chocolate (the peak at 3.70 ppm, excluding the water peak, presented the highest relative intensities of 15.2, 13.9 and 0.23 respectively for the sucrose solution, the

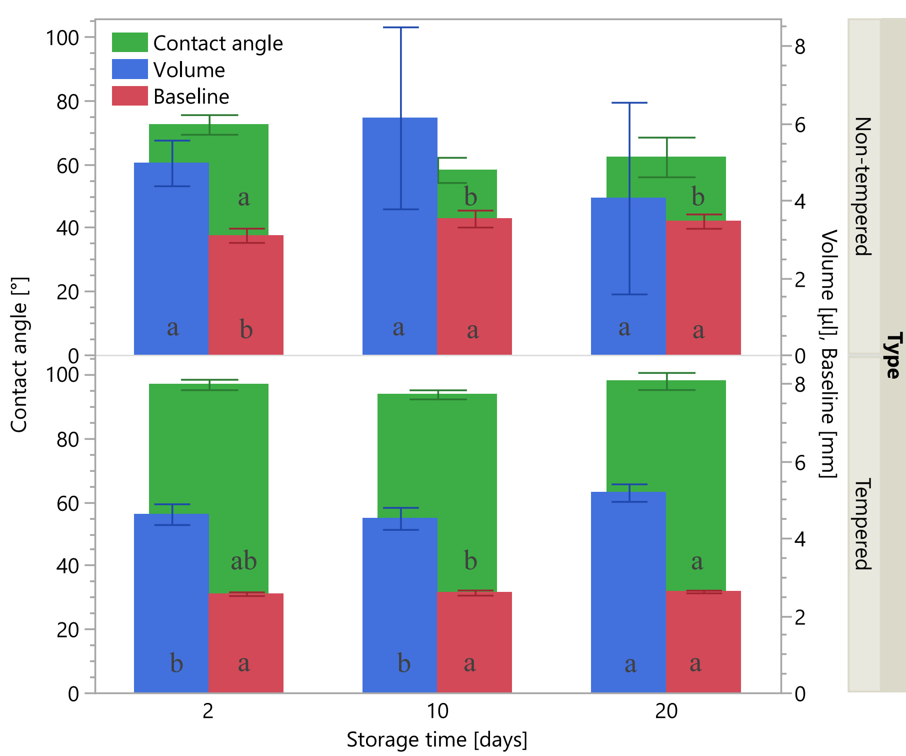

Fig. 6. Mean contact angle, volume and baseline at 60 s for tempered and non-tempered chocolate samples at different storage times (2, 10 and 20 days) in static contact angle tests. Error bars indicate the standard deviations across replicates. Within each variable, means labeled with different letters differ significantly across storage times (Fisher's method, α = 0.05).

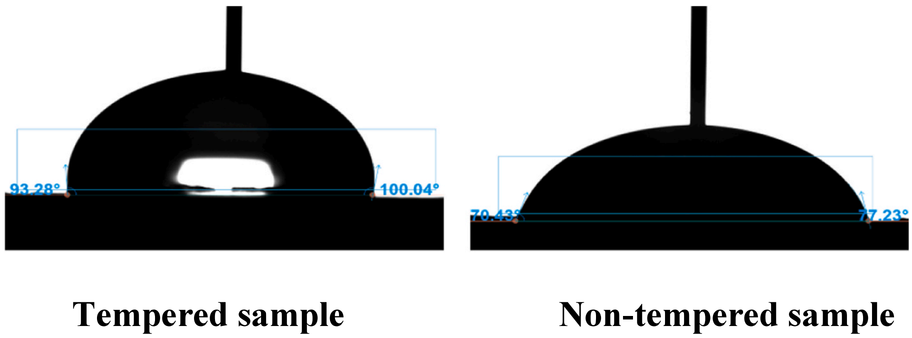

Fig. 7. Pictures of water droplets for tempered and non-tempered laboratory chocolate taken after 50 s from deposition in advancing contact angle tests after ten days from production.

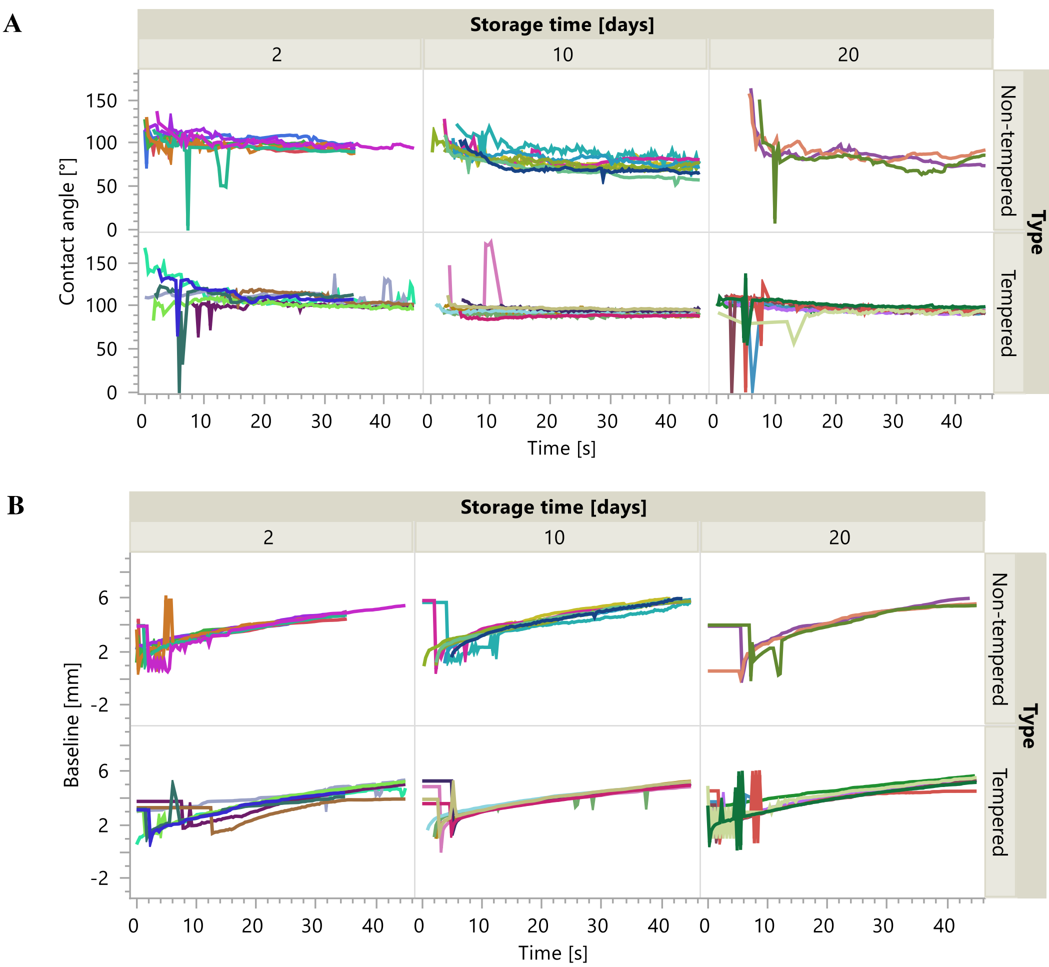

Fig. 8. Advancing contact angle (A) and baseline (B) as a function of storage time (2, 10, and 20 days) for tempered and non-tempered chocolate.

non-tempered chocolate and tempered chocolate), thus confirming a higher sugar content in the aqueous samples obtained from non-tempered chocolate compared to the tempered samples. The surface tension of the liquids after contact with chocolate differed by less than 1 mN/m from or practically coincided with that of pure water for non-tempered or tempered chocolate, respectively.

4.4. Discussion

To the best of our knowledge, only two studies focused on the wettability of chocolate with water or other liquids. Lapčík et al. (2017) studied the effect of cacao butter on the wetting of milk and dark chocolate, while Reinke et al. (2015) used contact angle measurements to explore surface alterations in pure cocoa butter and conventional chocolates. Consistent with our sessile-drop experiments on commercial chocolates, Lapčík et al. (2017) reported that the static contact angle of dark chocolate increased with rising cocoa butter content (and corresponding reduction in sugar). Their samples with 45%, 40%, and 35% cocoa butter showed contact angles of 93.8°, 88.5°, and 81.7°, respectively. Although the authors used slightly different formulations and protocols and did not report fat content explicitly, their trend matches ours: reducing fat content from 54 to 44% led to a decrease in static contact angle from 93.9° to 79.6° (average of 8- and 4-μL droplets) (Fig. 3).

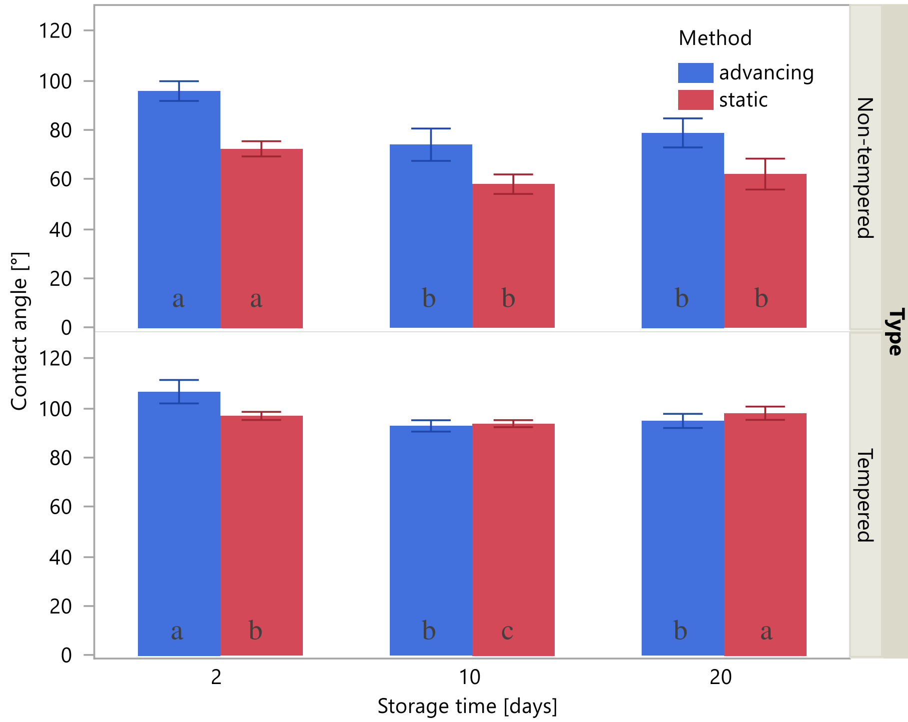

Fig. 9. Mean advancing, and static contact angle at 60 s for tempered and non-tempered chocolate. Error bars indicate the standard deviations across replicates. Within each variable, means labeled with different letters differ significantly across storage times (Fisher's method, α = 0.05).

Table 3
Advancing, static contact angle at 60 s, and their difference for tempered and non-tempered chocolate at 2, 10, and 20 days after production. Means and standard deviations of replicated measurements are reported. Degrees of freedom (DF) and p-value for 2-sample t-tests assuming unequal variances are reported. The asterisk indicates a statistically significant difference between advancing and static contact angles at a fixed storage time (α = 5%).

Type	Storage time [days]	Advancing contact angle [°]	Static contact angle [°]	Difference [°]	DF	P-value
Non-tempered	2	95.7 ± 4.0	72.4 ± 3.1	23.3*	9.9	<0.0001
Non-tempered	10	74.1 ± 6.5	58.1 ± 3.9	15.9*	9.3	0.0005
Non-tempered	20	78.8 ± 5.9	62.2 ± 6.2	16.7*	4.6	0.0149
Tempered	2	106.7 ± 4.7	96.9 ± 1.6	9.8*	7.6	0.0010
Tempered	10	92.8 ± 2.3	93.7 ± 1.4	−0.9	6.3	0.4910
Tempered	20	94.9 ± 2.8	98.0 ± 2.7	−3.1	10.9	0.0690

Reinke et al. (2015) measured the static contact angle and the tilting contact angles (roll-off or sliding angles) of pure cacao butter and dark chocolate as a function of several factors: pre-crystallization state (tempering, non-tempering), test liquid (water, diiodomethane, ethylene glycol), surface roughness (several levels of roughness), and storage time and temperature (fresh, 1 week at 20 °C, 1 week at 30 °C). They showed that the wetting behavior of cacao butter-based food composites is complex and is influenced by multiple factors. In particular, storage conditions did not significantly influence the wetting behavior within one week, suggesting that its surface structure remains stable. Non-tempered samples, however, displayed greater droplet spreading and larger changes in contact angle over time. Tempered samples also exhibited higher contact angles than non-tempered ones.

Our results are broadly consistent with those of Reinke et al. (2015): tempered samples were more stable over time, whereas non-tempered chocolates showed greater spreading and lower contact angles. However, our interpretation differs partly from theirs, as discussed below.

Reinke et al. (2015) explained their findings through surface heterogeneity (roughness and chemical heterogeneity) and molecular rearrangement at the surface due to different cacao butter polymorphs. They suggested that non-tempered cocoa butter has higher surface energy and therefore lower water contact angles. Based on tilted-angle comparisons, they hypothesized that solid dissolution might influence wetting by reducing the liquid's surface tension through cacao butter contamination, although they acknowledged that further study was needed.

In this work, we propose that surface irregularities arising from incomplete coating of sugar and cocoa particles by the fat phase play a key role. These irregularities may expose hydrophilic solid particles to the test liquid, influencing the observed wetting behavior. The increasing contact angle and decreasing spreadability observed in dark chocolates with lower sugar content can be explained by a more uniform hydrophobic surface: as sugar content decreases, the hydrophobic character increases and chemical heterogeneity decreases, reducing spreadability.

The strong differences we observed between tempered and non-tempered samples over time likely arise from the combined effects of cocoa butter polymorphism, surface roughness, chemical heterogeneity, and solid dissolution. As noted by Reinke et al. (2015) and Keijbets et al. (2009), non-tempered cocoa butter has higher surface energy than tempered cocoa butter, which explains its lower contact angle.

Contact angle theory also predicts that for liquids with θ > 90°, increasing roughness leads to an increase in apparent contact angle while the opposite happens for contact angles lower than 90° (Wenzel, 1949; Falzer et al., 2001). Reinke et al. (2015) confirmed this behavior for chocolate.

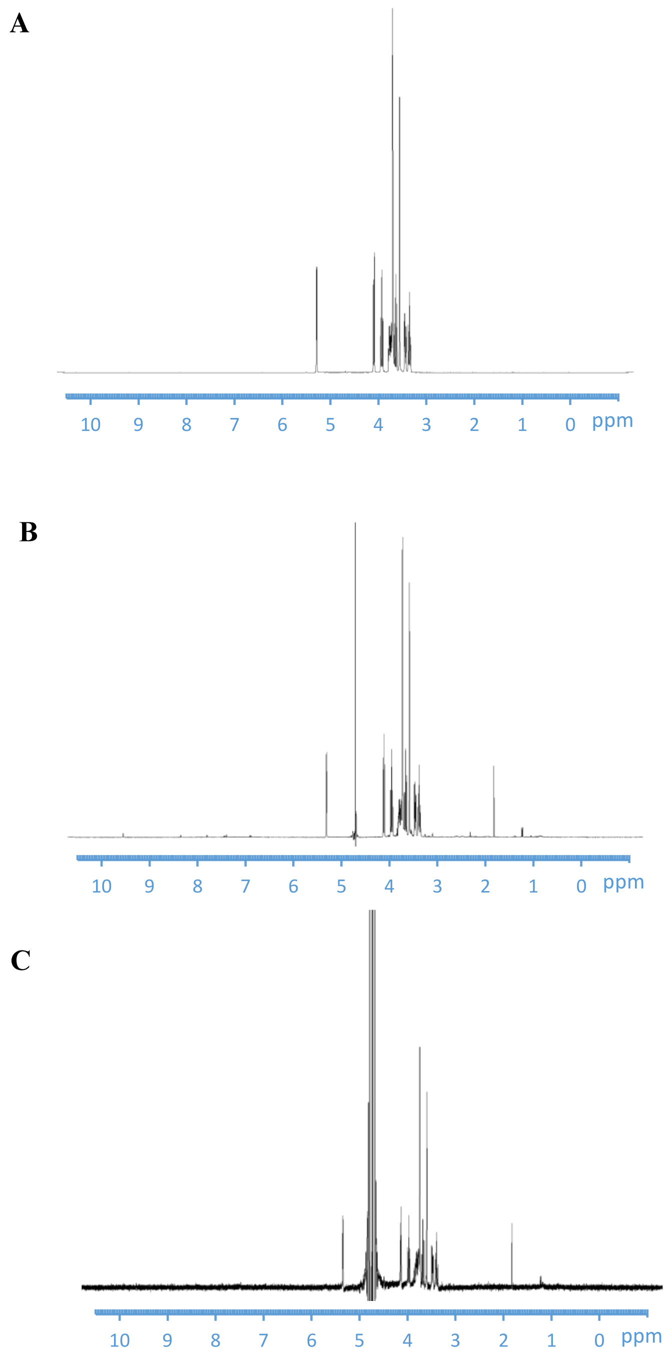

Fig. 10. NMR spectrum for 10% sucrose solution (A), non-tempered (B) and tempered chocolate (C).

However, since non-tempered chocolate is rougher but exhibits lower contact angles than tempered chocolate (which has a contact angle higher than 90°), roughness alone cannot explain the trend. When the higher surface energy of non-tempered cocoa butter is considered together with its greater roughness, the observed contact angle reduction becomes more understandable. Greater spreadability of droplets over time, especially on non-tempered chocolate, can also be attributed partly to roughness.

Chemical heterogeneity and solid dissolution, also mentioned by Reinke et al. (2015), contribute further. Chemical heterogeneity refers to a surface that is composed of different chemical regions, each with distinct surface energies. This variability affects how liquids interact with the surface, especially how they wet, spread, or recede and is a key factor in interpreting contact angle measurements, often producing contact angle hysteresis (Extrand, 2003). In non-tempered chocolate, the formation of pores and cracks makes the surface less consistent and more heterogeneous. Furthermore, with the exposure of sugar and cacao solids to water, the surface becomes more hydrophilic (both sugar and cacao solids are hydrophilic; Reinke et al. (2015)) leading to smaller contact angles.

Our NMR studies confirm higher sugar migration from the surface into the liquid in non-tempered samples, demonstrating that hydrophilic solid dissolution governs the interaction and proving that sugar contaminates the liquid through cracks, pores or uncoated solid particles. Reinke et al. (2015) mentioned the possibility that the test liquid could dissolve cacao butter, lowering the surface tension of the liquid. Our results show that their hypothesis does not hold. This was further proved by the surface tension measurements of the liquids after contact with the surface, which showed that surface tension did not change much compared to the value of pure water, the slight increase in surface tension expected from dissolved sucrose (Matubayasi and Nishiyama, 2006) being negligible.

Contact angle difference between advancing and static contact angles was more pronounced for non-tempered chocolate, confirming that chemical heterogeneity, roughness, and solid dissolution effects are more significant in these samples (Huhtamäki et al., 2018). Tempered chocolate forms smoother surfaces with fewer exposed particles and reduced dissolution, owing to its stable cocoa butter polymorphs and the absence of fat migration during storage. This results in reduced hysteresis, since on smooth surfaces the advancing angle approximates Young's angle (Ho et al., 2008; Kwok and Neumann, 1999). In contrast, non-tempered chocolate undergoes fat migration, surface roughening, and microcrack formation (Dahlenborg, 2014; Stobbs et al., 2025), exposing sugar to the droplet during both static and advancing measurements. Stobbs et al. (2025) linked crack formation to stress relief during the uncontrolled growth of cocoa butter crystals and to fat bloom. Their finding that tempered chocolate forms fewer cracks and withstands stress better supports our interpretation.

Regarding storage time, Reinke et al. (2015) observed minimal surface changes after 1 week at 20 °C for tempered samples, while non-tempered samples showed noticeable alterations. Our results confirm this trend: changes in static and advancing contact angles occurred primarily in non-tempered chocolate, were evident between days 2 and 10, and became negligible thereafter. This suggests that, under room-temperature storage, surface evolution in chocolate occurs mainly within the first 2–10 days after production.

The interpretation of the wettability results in this study relies on the presence of surface irregularities such as pores, micro-cracks, and incomplete fat coating, which are known to arise from chocolate formulation and processing conditions. Although these features are well documented in the literature for chocolate systems, they were not directly characterized in the present work. This represents a limitation of the study and should be acknowledged. Nevertheless, the proposed mechanism is supported indirectly by the observed trends in static and advancing contact angles, as well as by complementary NMR results, which together indicate differences in fat distribution and surface exposure of hydrophilic domains. Future work could combine contact angle measurements with direct surface characterization techniques, such as SEM to visualize surface morphology, AFM or profilometry to quantify surface roughness, and correlate these parameters more directly with wetting behavior. In addition, calibrated quantitative NMR or complementary analytical methods could be employed to determine absolute sugar concentrations in the aqueous phase. Such an integrated approach would enable a more direct validation of the relationship between surface microstructure, fat coverage, and wettability in chocolate systems.

Moreover, it should be noted that the present study is limited to dark chocolate formulations. While the mechanisms proposed, such as the influence of surface irregularities, fat coverage, and hydrophilic sugar domains on wettability are expected to be relevant in principle to other chocolate types, differences in composition may lead to different quantitative outcomes. For example, milk and white chocolates contain higher sugar content, milk solids, and lower cocoa solids, which affect fat-sugar-protein interactions and the distribution of surface hydrophilic and hydrophobic domains (Afoakwa, 2010; Beckett, 2011). As a result, contact angles and advancing/receding behaviors may differ from those observed in dark chocolate. Therefore, the conclusions of this study should be interpreted specifically in the context of dark chocolate, while future studies could investigate the applicability of these mechanisms across other chocolate types.

4.5. Conclusion

Our findings show that surface changes of dark chocolate can be monitored through contact angle measurements and that combining static and advancing contact angle measurements provides valuable insights into the physical properties of chocolate. In particular, the contact angle strongly depends on the tempering process and allows distinction between tempered and non-tempered samples, with static contact angles differing by approximately 24.5, 35.6 and 35.8° and advancing angles by 11.0, 18.7 and 16.1° between these conditions after 2, 10 and 20 days from production, respectively. This differentiation is crucial, as our results demonstrated that the tempering process plays a significant role in minimizing the susceptibility of dark chocolate surfaces to alterations, which are often linked to fat blooming, a common issue in chocolate quality. The present study provides experimental evidence, supported by complementary compositional (NMR) analysis, that the hydrophilic character of chocolate surfaces is influenced by sugar exposure. This effect is likely associated with solid sugar particles that are not fully covered by cacao butter due to pores and cracks or incomplete coating. Such surface irregularities, shaped by processing conditions, create pathways between hydrophilic sugar domains and the contacting liquid, thereby influencing the resulting wetting behavior. By relating wettability measurements to compositional evidence of sugar dissolution, this work contributes to a more direct experimental validation of previously proposed mechanisms linking surface heterogeneity to hydrophilicity in chocolate systems. We also extended the physical chemistry concept of ideal surfaces (smooth, chemically homogeneous, and inert) to chocolate, which can be approximated by a surface uniformly covered by a continuous fat layer and free of structural irregularities. Nevertheless, the study has certain limitations. Receding contact angles could not be measured reproducibly due to strong contact-line pinning, and direct surface imaging techniques were not employed to visualize microstructural features. Future work should therefore combine wettability analysis with surface characterization methods such as SEM, AFM, or profilometry to directly correlate microstructural features with wetting behavior. In addition, quantitative determination of dissolved sugars in the aqueous phase would further strengthen comparisons across samples. Such integrated approaches would enhance the understanding of the relationship between surface microstructure, fat coverage, sugar exposure, and wettability, ultimately supporting the use of contact angle measurements as practical indicators of chocolate surface state and processing quality.

CRediT authorship contribution statement

Zohreh Baratian Ghorghi: Writing – review & editing, Methodology, Investigation, Data curation. **Judicaelle Labelle Akana Donkem:** Methodology, Investigation. **Leonel Cedrick Mafotang Tsague:** Methodology, Investigation, Data curation. **Fernando Porcelli:** Methodology, Investigation, Data curation. **Marcello Fidaleo:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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