Food texture design in sugar reduced cakes: Predicting batters rheology and physical properties of cakes from physicochemical principles

Stefano Renzetti [*], Ruud G.M. van der Sman

Wageningen Food and Biobased Research, Wageningen University & Research, Bornse Weilanden 9, 6700, AA, Wageningen, the Netherlands

ABSTRACT

Sugar reduction in bakery products such as pound cake is a challenging task due to the multiple functionalities of sugars. Sucrose affects flour pasting behaviour, starch gelatinization and protein denaturation temperatures and batter rheology. Hence, sugar replacement can substantially alter the structure and texture of the baked product. In this study, batter rheology, phase transitions during baking and the physical properties of the baked cakes were studied as affected by 50% sugar replacement. The novelty of the study lies on relating the physical properties of batter and cakes to three physicochemical parameters computed from the cake formulations: i) the volumetric density of effective H-bonding sites available in the sugar-water phase $\Phi_{w,eff}$; ii) the number of H-bonding sites effectively available for intermolecular interactions within the molar volume of a sugar $N_{OH,s}/v_s$ and iii) the volume averaged interaction parameter of the sugars with water χ_{eff}. Batter rheology and phase transitions during baking showed to be a linear function of $\Phi_{w,eff}$. Cake volume and crumb hardness were also controlled by $\Phi_{w,eff}$. Crumb cohesiveness was a non-linear function of $N_{OH,s}/v_s$. The water activity of cake batters and cake crumbs were a linear function of χ_{eff}. This relations were valid with mixtures of four different types of compounds: sucrose, xylitol, an oligofructose and L-proline. In conclusion, sugar replacement in cake can be optimized by matching the physicochemical parameters $\Phi_{w,eff}$, $N_{OH,s}/v_s$ and χ_{eff} of the sucrose reference. Since different mixture of ingredients can be used to obtain similar physicochemical parameters, the study suggests the possibility to uncouple the physical properties of cakes from nutritional composition with regards to added sugars. Hence, the approach provides opportunities to substantially increase the amounts of health promoting ingredients such as dietary fibres in sweet bakery products.

1. Introduction

Health organizations recommend free sugar (i.e. mono and di-saccharides) intake of maximum 10% of the total daily energy intake and preferably less than 5%. Currently, sugar intake contributes from 15 to 25% of the daily energy supply in several EU countries, among which 7.5–17% is from added sugars (Azaïs-Braesco, Sluik, Maillot, Kok, & Moreno, 2017). To fight the obesity and overweight epidemics, the food industry is urged to reformulate food by lowering free sugar contents (World Health Organization, 2017). However, sugar replacement is a challenging task due to the many functionality that sugar exerts in food (Clemens et al., 2016). This is particularly the case for sweet bakery products, where sugar contributes to taste, structure, texture, colour and shelf-life (Struck, Jaros, Brennan, & Rohm, 2014). In biscuits and cakes, the main reformulation challenge lies in mimicking the structure and texture (van der Sman & Renzetti, 2019) (van der Sman & Renzetti,

2020). These properties are controlled by sugar type and concentration via affecting dough rheology during baking, phase transitions and moisture distribution within constituents and phases (Donovan, 1977) (Pareyt & Delcour, 2008) (Slade, Kweon, & Levine, 2020) (van der Sman & Renzetti, 2019) (Wilderjans, Luyts, Brijs, & Delcour, 2013). Precisely matching the rheological behaviour and phase transitions during baking is required for optimal sugar replacement (Renzetti & Jurgens, 2016). In cake, this is particularly challenging, since the balance between flour, egg, and sucrose has been shown to be quite critical for achieving the optimal rheological behaviour, i.e. shear modulus, of the batter during baking (Mizukoshi, 1985). The formulation of cakes is in a region where a small change in the ratio of ingredients leads to quite substantial changes in the shear modulus during baking (Mizukoshi, 1985) and consequently on the final cake structure and texture (van der Sman & Renzetti, 2020). The effect of sucrose on cake batter rheology is via its effect on starch gelatinization and swelling and on protein denaturation

which is a pre-requisite for protein network formation in cake (Lambrecht, Deleu, Rombouts, & Delcour, 2018). Hence, mimicking the texture of sucrose containing cakes requires matching flour pasting behaviour (Louise Slade et al., 2020), the melting temperatures of starch and proteins in the cake batter formulation (Renzetti & Jurgens, 2016) and the moisture distribution (van der Sman & Renzetti, 2019) (van der Sman & Renzetti, 2020).

Despite the extensive literature on sugar functionality in bakery products, quantitative relations between sugar properties, product formulations and the physical properties of batters/doughs and of baked products have not been fully elucidated. Many studies have been performed in bakery products by mainly comparing the functionality of individual sugars and sugar replacers on a one-to-one replacement strategy in order to assess the similarities or differences with a sucrose reference (Kweon, Slade, & Levine, 2016a) (Kweon, Slade, & Levine, 2016b) (Kweon, Slade, Levine, Martin, & Souza, 2009) (Laguna, Vallons, Jurgens, & Sanz, 2013) (Martínez-Cervera, Salvador, & Sanz, 2014) (Pateras & Rosenthal, 1992). The weight-average molecular weight of the sugar-water solvent (Slade & Levine, 1988) (Slade et al., 2020) and the degree of polymerization (Tsatsaragkou, Methven, Chatzifragkou, & Rodriguez-Garcia, 2021) have been suggested as relevant intrinsic properties of sugars in relation to bakery applications. These insights support sucrose replacement by polyols with comparable molecular weight (M_w) (Laguna et al., 2013) (Martínez-Cervera et al., 2014). However, they do not yet provide sufficient and comprehensive guidance to optimally and substantially replace sucrose with dietary fibres or to develop novel replacement strategies and functional ingredients.

By reviewing the functionality of sucrose in cake and biscuits, we have recently suggested that sugars mainly act as plasticizers and humectants in relation to food structuring (van der Sman & Renzetti, 2019) (van der Sman & Renzetti, 2020). For the cake pound cake applications, the functionality of sucrose during mixing and baking are listed in Table 1 together with the suggested physical parameters which describe them. Within this framework, we have recently shown that the pasting viscosity of starch is controlled by an intrinsic property of the sugars (or sugars mixture), the $N_{OH,s}/v_s$ parameter, which represents the number of H-bonding sites effectively available for intermolecular interactions within the molar volume of a sugar (Renzetti, van den Hoek, & van der Sman, 2021). We have also shown that the volumetric density of effective H-bonding sites available in the solvent (i.e. the water-sugar mixture) $\Phi_{w,eff}$, controls starch pasting temperature (Renzetti, van den Hoek, et al., 2021), starch gelatinization temperature (van der Sman & Mauer, 2019) (Renzetti, van den Hoek, et al., 2021) and the denaturation temperature of egg white proteins and of gluten (Renzetti, van den Hoek, & van der Sman, 2020) (van der Sman & Renzetti, 2019). Finally, the hygroscopic properties of sugars and sugars mixtures have been described by the Flory-Huggins theory using a volume averaged interaction parameter of the sugars with water, i.e. χ_{eff} (van der Sman, 2013).

We have recently demonstrated for the first time that several classes

of sugar replacers, such as oligofructoses, polyols and amino acids, can be mixed together to modulate starch and protein thermal properties via controlling $N_{OH,s}/v_s$ and $\Phi_{w,eff}$ (Renzetti et al., 2020) (Renzetti, van den Hoek, et al., 2021). Therefore, multiple combinations of low and high M_w plasticizers can be potentially designed to optimally replace sucrose in a cake application (Jurgens, Noort, Renzetti, & de Harder, 2016) (Renzetti, van den Hoek, et al., 2021). This approach provides new opportunities beyond the current widespread use of sweeteners such as sorbitol, isomalt and maltitol (Luo, Arcot, Gill, Louie, & Rangan, 2019) (Woodbury, Grush, Allan, & Mauer, 2021), which have negative connotations among consumers due to their gastrointestinal side-effects (Rice, Zannini, Arendt E, & Coffey, 2020).

Against this background, the aim of this study was to demonstrate for the first time the use of $\Phi_{w,eff}$, $N_{OH,s}/v_s$ and χ_{eff} as physicochemical parameters to design the physical properties (i.e. volume, instrumental texture) of cakes directly from the starting formulations. To achieve this aim, we first demonstrate how the physicochemical parameters control flour pasting behaviour, cake batter rheology and the biopolymer phase transitions following on the structuring pathway in the supplemented state diagram of cake baking (Renzetti et al., 2020) (Renzetti, van den Hoek, et al., 2021) (van der Sman & Renzetti, 2020). Next, we show the relation between the physicochemical parameters and the physical properties of pound cake. In order to modulate $\Phi_{w,eff}$, $N_{OH,s}/v_s$ and χ_{eff}, sucrose was replaced by 50% using sugar replacers (i.e. plasticizers) from three different classes of compounds: xylitol (polyol), an oligofructose, L-proline and glycine (amino acids). The reformulation studied resulted in binary to quaternary mixtures of sugar and sugar replacers, in order to demonstrate the general applicability of the approach.

2. Theoretical background for quantitative description of sugar functionality in bakery applications

2.1. Effective number of H-bonding sites in sugar solution controlling phase transition of starch and proteins

The structuring of the cake batter emulsion into a solid sponge is controlled by the leavening action of gasses and the phase transitions associated with starch gelatinization and the thermosetting of gluten and egg white proteins (Renzetti et al., 2020) (van der Sman & Renzetti, 2020). The use of supplemented state diagrams is therefore instrumental in understanding the structuring process during baking (van der Sman, 2018). In recent studies (Renzetti et al., 2020) (Renzetti, van den Hoek, et al., 2021) (van der Sman & Renzetti, 2019) (van der Sman & Renzetti, 2020), we have shown that starch gelatinization temperatures, the thermosetting of gluten and the denaturation of egg white proteins can be described by an adapted Flory-Huggins theory for biopolymer melting according to:

$$\frac{1}{T_m} - \frac{1}{T_m^{\circ}} = \frac{R}{\Delta H_U} \frac{v_U}{v_W} \left[\Phi_{w,eff} - \chi_{p,eff} \cdot \Phi_{w,eff}{}^2 \right] \tag{1}$$

where T_m (K) is the melting temperature of the biopolymer in the system under consideration, T_m° (K) the melting temperature of the dry biopolymer, ΔH_U (kJ/mol) is the melting enthalpy per mole of the repeat unit of the biopolymer, v_U is the molar volume of the biopolymer repeat unit, v_w is the molar volume of water, $\Phi_{w,eff}$ is the volumetric density of effective H-bonding sites available in the solvent (i.e. the water-sugar mixture) for interaction with biopolymers, $\chi_{p,eff}$ is the FH solvent-biopolymer interaction parameter and R is the universal gas constant.

The $\Phi_{w,eff}$ is computed according to (van der Sman, 2016):

$$\Phi_{w,eff} = \Phi_w + \sum_i \Phi_{s,i} \frac{N_{OH,s} v_w}{N_{OH,w} v_s} \tag{2}$$

where Φ_w is the volume fraction of water, $\Phi_{s,i}$ that of the plasticizer and v_w and v_s are the molar volume of water and plasticizer, respectively,

Table 1
Sucrose functionality in pound cake and controlling parameter.

Sucrose functionality during mixing and baking	Controlling parameter
Enhances air incorporation during creaming due to its crystalline state	crystallinity
Limits biopolymer hydration and gluten network formation via its hygroscopic properties	χ_{eff}
Improves foam stability via viscosity enhancement	$\Phi_{w,eff}$
Controls water evaporation into the expanding bubble by influencing water activity	χ_{eff}
Controls cake volume by modulating starch gelatinization and protein denaturation temperatures	$\Phi_{w,eff}$
Controls cake texture by modulating starch pasting behaviour	$\Phi_{w,eff}$, $N_{OH,s}/v_s$
Enhances browning by Maillard reactions and caramelization	Reducing power
Controls shelf-life by contributing to lowering the water activity	χ_{eff}

obtained from the ratio of their molar weight over their mass density.

The $N_{OH,s}$ represents the number of H-bonding sites effectively available within the sugar for intermolecular interactions (van der Sman, 2016). For water holds $N_{OH,w} = 2$. $N_{OH,s}$ differs from the total number of hydroxyl groups in a molecule as it is corrected for intramolecular hydrogen bond interactions due to stereochemistry (Pawlus, Grzybowski, Paluch, & Wlodarczyk, 2012). For plasticizers such as amino-acids, sugars, polyols and sugar oligomers, $N_{OH,s}$ is inversely proportional to the glass transition temperature of the pure compound via:

$$\frac{1}{2}\frac{T_g - T_{g,w}}{T_g^\infty - T_{g,w}} = \left(\frac{1}{2} - \frac{N}{N_{OH,s}}\right) \tag{3}$$

where T_g is the glass transition temperature of the pure compound, $T_{g,w}$ is the glass transition temperature of pure water, T_g^∞ is the glass transition temperature of a compound of infinite size from a particular class of materials (van der Sman & Mauer, 2019) and $\frac{N}{N_{OH,s}}$ is the inverse of the number of hydroxyl groups per molecule.

The effective interaction parameter $\chi_{p,eff}$ in equation (1) is computed from (van der Sman, 2016):

$$\chi_{p,eff} = \chi_0 + (\chi_1 - \chi_0)\left(1 - \Phi_{w,eff}^2\right) \tag{4}$$

where $\chi_{0=0.5}$ is the interaction parameter of fully hydrated biopolymers (which is assumed to hold universally for all biopolymers), while χ_1 is the interaction parameter if the biopolymer is in the dry state. χ_1 is specific for each biopolymer.

2.2. Role of sugars in controlling flour pasting behaviour

From the $N_{OH,s}$ of sugars and sugar replacers, $N_{OH,s}/\nu_s$ is obtained where ν_s is the molar volume of the plasticizer. The $N_{OH,s}/\nu_s$ parameter is an intrinsic property of the plasticizer, which represents the number of H-bonding sites effectively available for intermolecular interactions within the molar volume of a sugar. We have recently shown that $N_{OH,s}/\nu_s$ controls the swelling behaviour of starch, as it controls peak viscosity and final viscosity obtained by rapid viscous analysis. In presence of mixtures of plasticizers, $N_{OH,s}/\nu_s$ is computed from (Renzetti et al., 2020):

$$\left(\frac{N_{OH,s}}{\nu_s}\right)_{eff} = \frac{\sum_i \Phi_s \frac{N_{OH,s}}{\nu_s}}{\sum_i \Phi_s} \tag{5}$$

where Φ_s is the volume fraction of each plasticizer in the mixture. Here, we suggest that $N_{OH,s}/\nu_s$ will also control the pasting behaviour of wheat flour.

2.3. Effect of sugars and sugar replacers on water activity

The water activity (a_w) of sugar solutions for individual compounds and mixtures has been described based on the Flory-Huggins Free Volume theory (FHFV) (van der Sman, 2013), including polyols (van der Sman, 2017) and amino acids (van der Sman et al., 2019), following on:

$$ln\,a_w = \ln(\Phi_w) + (1 - 1/N_s)(1 - \Phi_w) + \chi_s(1 - \Phi_w)^2 + F(\Phi_w) \tag{6}$$

where N_s is the ratio of molar volumes of solute versus water (ν_s/ν_w), χ_s is the Flory-Huggins interaction parameter of the solute with water and φ_w is the volume fraction of water. $F(\Phi_w)$ accounts for structural relaxation in the glassy state and the changes in hydrogen bonding between water and polymer in the semi-dilute regime. $F(\Phi_w)$ is calculated from:

$$F(\Phi_w) = \begin{cases} 0, & \text{if } T \geq T_g \\ -M_w y_s^2 \dfrac{\Delta C_{p,w}}{RT}\dfrac{dT_g}{dy_s}\dfrac{T - T_g}{T_g}, & \text{if } T \leq T_g \end{cases} \tag{7}$$

where M_w is the molecular weight of water, y_s is the mass fraction of the solute, T is the actual temperature. T_g is the glass transition temperature of the water-solute mixture as computed from Couchman-Karasz equation:

$$T_g = \frac{y_w T_{g,w}\Delta C_{p,w} + \sum_i y_{s,i}T_{g,s,i}\Delta C_{p,s,i}}{y_w\Delta C_{p,w} + \sum_i y_{s,i}\Delta C_{p,s,i}} \tag{8}$$

as we recently reported also for mixtures of sugars and sugar replacers included in this study (Renzetti et al., 2020). The value of $\Delta C_{p,s}$ is dependent on the class of plasticizers as previously reported (Renzetti et al., 2020).

$\frac{dT_g}{dy_s}$ is computed from (van der Sman & Meinders, 2011):

$$\frac{dT_g}{dy_s} = \frac{\Delta C_{p,s}C_{p,w}(T_{g,w} - T_{g,s})}{(y_w\Delta C_{p,w} + y_s\Delta C_{p,s})^2} \tag{9}$$

Equation (6) assumes that the interactions between sugars (and sugar replacers) is about zero. This is supported also by recent findings (Diarce, Gandarias, Campos-Celador, García-Romero, & Griesser, 2015) (Palomo Del Barrio, Cadoret, Daranlot, & Achchaq, 2016).

For predicting the a_w of mixtures of solutes in water, the Flory-Huggins interaction parameter χ_s in equation (6) is replaced by an effective parameter χ_{eff} representing the properties of the mixture, according to:

$$\chi_{eff} = \frac{\sum_i \Phi_{s,i}\cdot\chi_{s,i}}{\sum_i \Phi_{s,i}} \tag{10}$$

According to the proposed theory, we here suggest that the a_w of cake batters and crumb varying in sugar composition will be a function of χ_{eff}.

3. Materials and methods

3.1. Materials

Wheat flour Flamingo was from Meneba (Rotterdam, the Netherlands), the bakery fat trio Cake was from CSM Benelux BV (Goes, the Netherlands) and sodium bicarbonate and sodium acid pyrophosphate were from Budenheim (Budenheim, Germany). Fresh eggs and sugar (sucrose) were purchased at a local supermarket. The oligofructose FOS Actilight® 950P (FOS) was supplied by Tereos (Neuilly, France). Xylitol, L-proline and glycine were of analytical grade. The physicochemical properties of the sugars and sugar replacers in this study are reported in Table 2.

3.2. Methods

3.2.1. Moisture sorption behaviour of sugar replacers

The moisture sorption behaviour of xylitol and sucrose has been already described by (van der Sman, 2017) and that of glycine and L-proline by (van der Sman et al., 2019). The moisture sorption of FOS was determined following the method described by (Renzetti, Voogt,

Table 2
Physicochemical characteristics of the sugars and sugar replacers used in the study.

Compound	M_w (g/mol)	Density (kg/m³)	T_g (K)	$N_{OH,s}$	$N_{OH,s}/\nu_s$ (1000 mol/cm³)[c]	χ_s
Glycine	75	1660	220[a]	2.63	58.2	−0.2[d]
L-Proline	115	1370	250[a]	2.99	35.6	0[d]
Xylitol	152	1520	249	2.94	29.4	0.32
Sucrose	342	1550	336	4.48	20.3	0.51
FOS	605	1550	315[b]	4.66	11.9	0.62

[a,d] From (van der Sman et al., 2019).
[b] From (Renzetti et al., 2020).
[c] From (Renzetti, van den Hoek, et al., 2021).

Oliver, & Meinders, 2012). The sorption data were modelled following on equation (6), using the T_g of FOS as previously reported (Renzetti et al., 2020).

3.2.2. Cake batter preparation

The reference cake batter recipe used for preparing pound cake contained 244 g of each of the four main ingredients: flour, sugar, egg and margarine. Sodium bicarbonate (2 g) and sodium acid pyrophosphate (2.9 g) were added as leavening agents. Cake batter was prepared using a multi-stage mixing method. Margarine and sugar were mixed for 2 min at speed 3 in a Hobart N-50 electric mixer (St. Joseph, MI, USA). The fresh eggs were then poured into the mixer. After 30 s mixing at speed 2, sieved flour, sodium bicarbonate and sodium acid pyrophosphate were added and the batter was mixed for another 2 min at speed 2. Batter (400 g) was placed in baking pans (internal dimensions: length 150 mm, width 50 mm, height 60 mm). Cakes (3 per each set of baking) were baked in a deck oven Piccolo I (Spronk, Andelst, the Netherlands) for 60 min at 180 °C top and 160 °C bottom. After baking, the cakes were cooled for 60 min at room temperature and packed in plastic bags till evaluation. Baking tests were performed in duplicate for each variation.

For differential scanning calorimetry and rheological evaluation, batters were prepared without sodium bicarbonate and sodium acid pyrophosphate.

3.2.3. Studied variations in sugar composition

The study comprised 10 formulations with 50% sucrose replacement and a sucrose reference. The sucrose in the reference cake batter formulation was replaced using the sugar replacement compositions described in Table 3. Formulations included single sugar replacers or complex mixtures of 2–3 replacers. Xylitol and FOS were chosen as replacers since their $N_{OH,s}/v_s$ are almost equally distant from that of sucrose, while being lower and higher than sucrose, respectively (Table 2). Hence, formulations containing their mixtures could be computed in order to vary $\Phi_{w,eff}$ around the values of the reference cake. Additionally, xylitol is an interesting replacer since its relative sweetness is similar to sucrose (Struck et al., 2014). The sweet amino acids L-proline and glycine were selected as alternatives to polyols. As their $N_{OH,s}/v_s$ is much higher than xylitol, smaller amounts are needed to obtain similar ranges of $\Phi_{w,eff}$ in combination with FOS as compared to xylitol. Sugar reduced batter and cake samples were coded based on the sugar replacers used (F=FOS, G = Glycine, P = L-Proline and X = Xylitol) followed by the value of $\Phi_{w,eff}$ computed from the formulation. Based on the described theories, the supplemented state diagram for pound cake baking is constructed in Fig. 1 following on our recent studies (Renzetti et al., 2020) (Renzetti et al., 2021) (van der Sman & Renzetti, 2020). Assuming constant processing conditions, the supplemented state diagram suggests that variations in $\Phi_{w,eff}$ will affect the specific temperatures at which relevant phase transitions will take place during baking. Consequently, cakes with different structures and physical properties will be
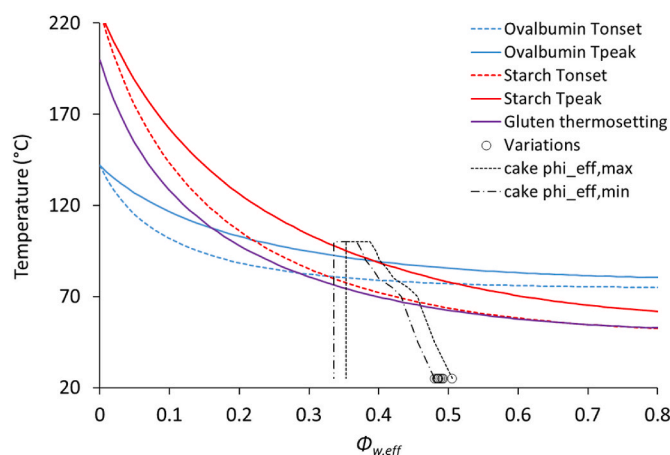

Fig. 1. Structuring pathway for cake batter during baking (black lines) as adapted from (Renzetti et al., 2020) (van der Sman & Renzetti, 2020), plotted on the state diagram along with egg white denaturation and starch gelatinization. The black lines represent the two extremes in value of $\Phi_{w,eff}$ (i.e. F_0.480 and X_0.505) within the study.

obtained. The formulations with FOS and xylitol alone represent the extremes in $\Phi_{w,eff}$ when 50% of sucrose is replaced by one or the other sugar replacer (Table 3).

3.2.4. Rapid viscosity analysis (RVA) of flour in sugar solutions

A Rapid Visco Analyser (Newport Scientific Pvt. Ltd., Warriewood, Australia) was used to determine the pasting properties of wheat flour in 50% sugar solutions based on the cake batter formulation in Table 3. The sugar concentration was chosen since the sugars in the water phase of the batter are around 50%. Flour suspensions of 8% dry matter (dm) in the different solutions were prepared for a total weight of 25.0 g. Samples were then subjected to the following time–temperature profile: hold at 50 °C for 1 min (mixing for 10 s at 960 rpm and then decrease to 160 rpm for the rest of the measurement), increase to 95 °C over 3 min 42 s, hold at 95 °C for 2 min 30 s, decrease to 50 °C over 3 min 48 s and hold at 50 °C for 2 min. The viscosity was expressed as centipoise (cP). Analyses were performed in duplicate, with a relative difference of <1% for all samples.

3.2.5. Thermal transitions in cake batter by differential scanning calorimetry

Differential Scanning Calorimetry (DSC) was performed using a TA Instruments Q200 type analyser. About 10 mg of batter was weighed and placed in a high pressure stainless steel pan. The pan was placed in the DSC together with an empty reference pan and equilibrated at 2 °C for 5 min. After equilibration the temperature was increased linearly with a rate of 7.50 °C/min from 2 °C till 160 °C. The onset of melting endotherms (T_{onset}) and peak temperature (T_{peak}) were determined using the

Table 3
Variations in sugar composition based on 100g batter formulation and the corresponding physicochemical parameters derived. Sugar reduced samples are coded based on the sugar replacers used (F=FOS, G = Glycine, P = L-Proline and X = Xylitol) followed by the value of $\Phi_{w,eff}$ computed from the formulation.

Variation	Sucrose (g/100g)	FOS (g/100g)	Glycine (g/100g)	L-Proline (g/100g)	Xylitol (g/100g)	$\Phi_{w,eff}$	$N_{OH,s}/v_s$ (1000xmol/cm³)	χ_{eff}
Ref	24.4					0.493	20.3	0.510
F_0.480	12.2	12.2				0.480	15.9	0.563
FP_0.484	12.2	10.7		1.5		0.484	17.5	0.520
FPX_0.484	12.2	10.3		1.0	0.9	0.484	17.7	0.523
FX_0.485	12.2	9.6			2.6	0.485	17.9	0.531
FGP_0.486	12.2	10.7	0.75	0.75		0.486	18.1	0.518
FG_0.488	12.2	10.7	1.5			0.488	18.6	0.516
FG_0.491	12.2	10.2	2			0.491	19.5	0.500
FX_0.495	12.2	5.1			7.1	0.495	21.2	0.476
FX_0.500	12.2	2.6			9.6	0.500	23.0	0.446
X_0.505	12.2				12.2	0.505	25.0	0.414

analysis tool available in the Universal Analysis software. Experiments were performed in triplicates.

3.2.6. Dynamic mechanical thermal analysis of dough

Dynamic Mechanical Thermal Analysis (DMTA) were performed using a TA-Instrumenst Dicovery HR-2 (DHR2) type rheometer equipped with a 25 mm parallel cross-hatched steel type plate geometry and an environmental test chamber. Samples were prepared without baking powder. After preparation, about 1 g of batter sample was placed on the lower plate of the rheometer and compressed until 1.025 mm. Batter excess was removed, silicon oil was applied to prevent sample drying, and dough was compressed until 1 mm. Before the measurement, the dough was rested for 5 min at 25 °C. Samples were oscillated at a frequency of 1 Hz with a constant strain amplitude of 0.004 and heated from 20 °C till 120 °C at a rate of 5 °C/min. The strain amplitude was selected within the linear visco-elastic region based on previous strain amplitude tests. Experiments were performed in triplicates.

The data retrieved from this experiment were the storage modulus at its minimum and at 95 °C (G'$_{min}$ and G'$_{95°C}$, respectively) and the corresponding tan δ (tan δ$_{G'min}$ and tan δ$_{95°C}$) and the onset temperature of structure formation, T$_{onset}$. The latter was determined as the intersection of the tangents of the baseline before the sudden increase in G' and the tangent of the steep G' profile after T$_{onset}$. From the retrieved data, the ratio G'$_{95°C}$/G'$_{min}$ was computed as measure of the extent of the mechanical response to the thermal sweep (Arufe et al., 2017).

3.2.7. Cake volume and specific volume

Cakes were evaluated the day after baking for volume with a rapeseed displacement method according to (Zanoletti et al., 2017). Loaf volume was determined on a total 6 cakes for each variation resulting from two separate baking tests.

3.2.8. Crumb instrumental texture, moisture content and water activity

Cake crumb texture was measured the day after baking by means of Texture Profile Analysis (TPA) using a TA-XT2i Texture Analyser from Stable Micro Systems (Godalming, Surrey, UK). The instrument was equipped with a 5 kg load cell and a 75 mm compression plate and performed as described in (Zanoletti et al., 2017) with some modifications. Briefly, cylindrical crumb samples of 30 mm diameters were cut out from the centre of cake slices of 20 mm thickness. Crumb specimen underwent two cycles of compression until 40% of deformation with 5 s rest time between compressions. Crosshead speed and trigger force were set to 2 mm/s and 0.05 N, respectively. For each variation, 3 crumb samples were collected from each of the 6 cakes, resulting in 18 measurements per cake type.

Moisture content of crumbs was measured in triplicate according to Approved Method 44-15.02 (AACC, 2001). About 5 g of crumb were collected from the centre of a slice and dried overnight in aluminum dishes in an oven at 105 °C. The filled dishes were cooled for 1 h in a desiccator before weight determination.

The a$_w$ was determined in triplicates using a Decagon Aqua Lab meter (Pullman, WA, USA) calibrated with a 8.57 M lithium chloride solution (a$_w$ = 0.5).

Cake crumb colour was measured with a Minolta CR310 Colour Meter (L*,a*, b* colour space). Twelve measurements per variations were performed.

3.3. Statistical analysis

Statistical evaluation (analysis of variance, ANOVA, with Tukey's-Test as post-hoc test at a significance level of p < 0.05) was performed with SPSS, correlation analysis and regressions were performed with Rstudio (RStudio version 1.1.463, Inc., Boston, MA, USA).

4. Results

4.1. Sorption isotherm of FOS

The moisture sorption behaviour of the FOS in this study is shown in Fig. 2. The sorption data obtained in the a$_w$ range from 0 to 0.95 could be well described by the FHFV model (van der Sman, 2017) following on equation (6) (R^2 = 0.998, p < 0.001). The physicochemical parameters used in the model are shown in Table 2. The highest value of χ$_s$ among the sugars and sugar replacers in this study indicated that the FOS was the least hygroscopic among the plasticizers used.

4.2. RVA

Variations in sugar and sugar replacers composition considerably affected the pasting properties of the cake flour, resulting in significant effects on pasting temperature and paste viscosity during the temperature cycle (Fig. 3 and Table S1). The effect depended on the specific sugar composition. We have recently shown that the gelatinization and pasting temperature of wheat starch in sugar solutions is controlled by $\Phi_{w,eff}$, the volumetric density of effective H-bonding sites available in the solvent (i.e. the water-sugar mixture) for interaction with biopolymers (Renzetti, van den Hoek, et al., 2021). The $\Phi_{w,eff}$ could well describe pasting temperature for all variations, except for those containing glycine as plasticizer (Fig. 3A).

All flour suspensions in the sucrose reduced solutions showed a significant decrease in the paste viscosity parameters with the exception of samples X_0.505 and FX_0.500, which showed a significant increase (p < 0.05) (Table S1). We have recently shown that the paste viscosity of wheat starch in sugars and sugar replacers solutions is controlled by $N_{OH,s}/v_s$ of the sugar mixture (Renzetti, van den Hoek, et al., 2021). This parameter is an intrinsic property of the plasticizer, which represents the number of H-bonding sites effectively available for intermolecular interactions within the molar volume of a sugar. All paste viscosity parameters were controlled by the $N_{OH,s}/v_s$ of the sugar mixtures, except for those containing glycine (Fig. 3B–F). Deviations may be related to the difficulty in more precisely estimating the T$_g$, and hence the $N_{OH,s}$ of glycine (van der Sman, van den Hoek, & Renzetti, 2020).

4.3. DSC of cake batters

The DSC of cake batters was performed to detect phase transitions related to starch gelatinization and proteins denaturation. All DSC traces showed an endotherm around 50 °C and another around 100 °C (data not shown). The first endothermic peak was compatible with melting of
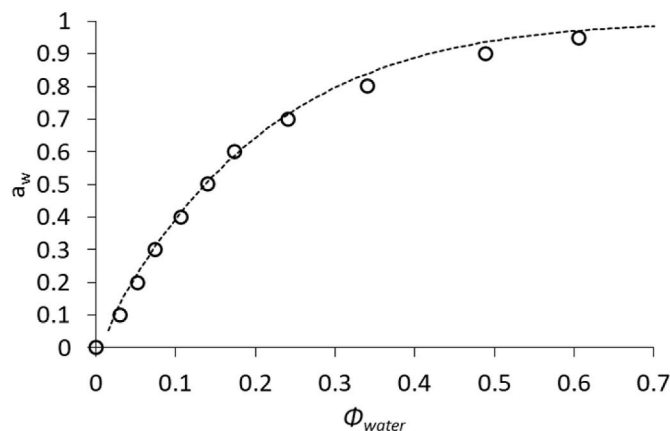
Fig. 2. Moisture sorption of FOS determined at 25 °C. Balck circles represent experimental data. The dotted line represent the prediction using the FHFV model described in equation (6).
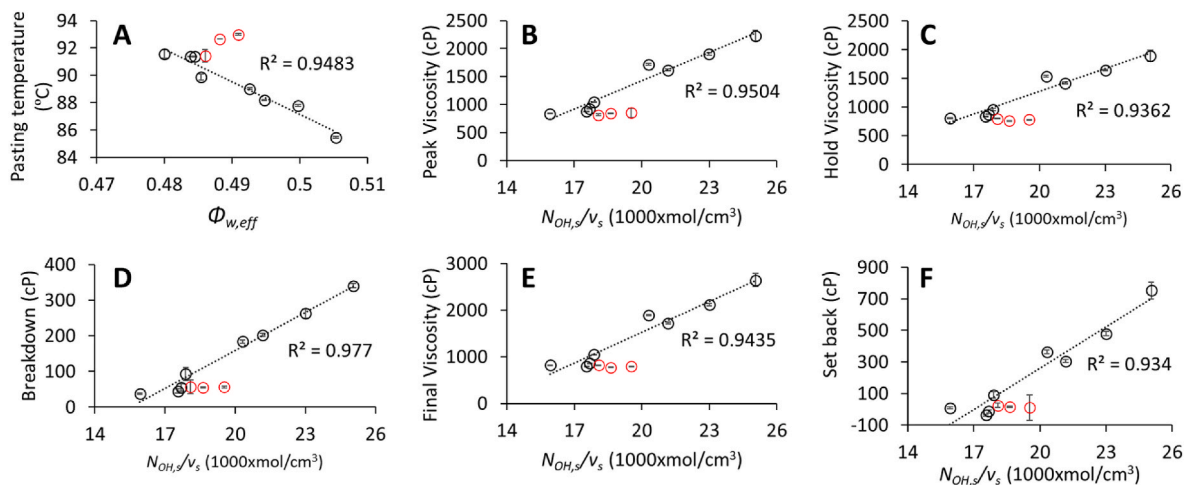
Fig. 3. Pasting properties of the cake flour (8% dry matter) as function of $\Phi_{w,eff}$ and $N_{OH,s}/\nu_s$ of the sugar solutions (50% w/w) used in the study. The red circles indicate formulations containing glycine. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the margarine in the formulation. The second endotherm is the combined events of starch gelatinization and egg denaturation (Wilderjans, Luyts, Goesaert, Brijs, & Delcour, 2010). The T_{onset} and T_{peak} associated to starch and protein melting were significantly affected by the sugar composition (Fig. 4 and Table S2). T_{peak} was well described by $\Phi_{w,eff}$ for the complex cake batter system. Similar results were found for T_{onset}. These results confirm our recent studies from which we constructed the state diagram for egg white proteins denaturation and starch gelatinization in sugars and sugar replacers solutions using $\Phi_{w,eff}$ (Renzetti et al., 2020) (Renzetti, van den Hoek, et al., 2021) (van der Sman & Renzetti, 2020). The state diagram of cake baking in Fig. 1 predicts sample X_0.505 as the formulation with lowest T_{peak} and sample F_0.480 the one with the highest, which agrees with experimental data (Table S2). Deviations were observed only for the formulations containing glycine.

4.4. Rheology cake batters during temperature sweep

The thermo-mechanical behavior of the different batters was investigated by DMTA. The technique provides insights in the visco-elastic properties of the dough (G′ and tan δ) as affected by key phase transitions. In general, G′ initially decreased going from 25 °C to 50 °C, approximately, due to fat melting and softening of the batter (Fig. 5A),
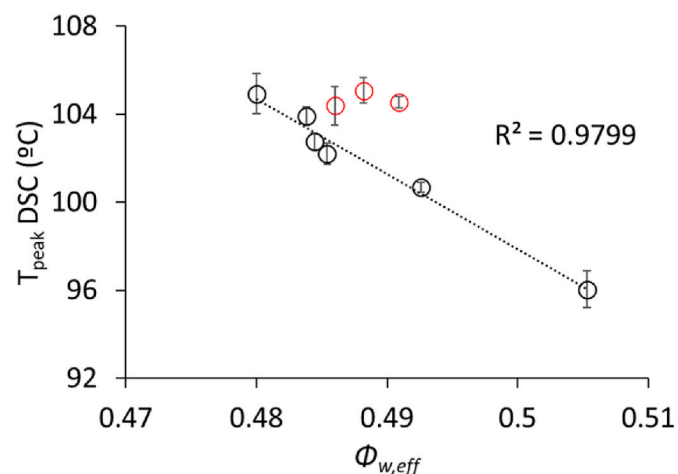

Fig. 4. Correlation between T_{peak} and $\Phi_{w,eff}$ for all formulations not containing glycine (p < 0.05). The red circles indicate formulations containing glycine. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

until reaching a minimum, i.e. G′$_{min}$. Significant differences in G′$_{min}$ could be observed (Table S2), thus indicating that sugars affected the batter rheology even before structure setting. However, no correlations were found between G′$_{min}$ and the physicochemical parameters $\Phi_{w,eff}$, $N_{OH,s}/\nu_s$ and χ_{eff}.

Just above 80 °C all batter samples showed a sharp increase in G′ with a concomitant decrease in tan δ (Fig. 5A). These changes can be associated with starch gelatinization and protein network formation (Renzetti et al., 2020) (van der Sman & Renzetti, 2020). The T_{onset} from DMTA analysis was significantly affected by the sugar replacement formulation (Table S2), with the results being only partially correlated with those from DSC ($R^2 = 0.693$, p < 0.00). The T_{onset} from DMTA could be well described by $\Phi_{w,eff}$ and χ_{eff} (Fig. 5B), with both parameters significantly contributing (p < 0.05 and 0.01, respectively). It should be noted that the DMTA detects changes in mechanical response as affected by phase transitions, while the DSC provides complementary information on the melting transitions. Hence, the T_{onset} in the DMTA is likely to be affected also by changes in the rheology of the batters. While $\Phi_{w,eff}$ modulates the phase transitions by controlling the solvent quality (Renzetti et al., 2020) (Renzetti, van den Hoek, et al., 2021) (van der Sman & Renzetti, 2019) (van der Sman & Renzetti, 2020), χ_{eff} relates to the moisture adsorption by the sugars and the hydration of the biopolymers. The latter is largely dictated by the interaction parameter χ_{eff} (Renzetti et al., 2020) (van der Sman & Renzetti, 2019) (van der Sman & Renzetti, 2020). In agreement with this hypothesis, the water activity of batters was significantly affected by sugar replacement (Table S2) and it was controlled by χ_{eff} ($R^2 = 0.943$, p < 0.01).

Significant effects were observed on both G′ and tan δ at 95 °C depending on the specific sugar replacement formulation (Fig. 5C and D and Table S2). The temperature was selected as representative of the latest stages of structure setting, as it is close to the maximum temperature reached in the core of the cake during baking. Overall, the changes in batter rheology during heating (i.e. G′$_{min}$, G′$_{95°C}$, tanδ$_{G'min}$ and tanδ$_{95°C}$) suggest an important role of the sugars also in controlling the extent of the biopolymeric network formed during baking and hence the final cake texture. The extent of network formation during baking of a bread dough has been recently described by the ratio G′$_{95°C}$/G′$_{min}$, with higher values indicating a higher sensitivity to the thermal process (Arufe et al., 2017). Here, G′$_{95°C}$/G′$_{min}$ was largely controlled by $\Phi_{w,eff}$ for all formulations, except those containing glycine (Fig. 5C). Similarly, also tan δ$_{G'min}$ and tan δ$_{95°C}$ were controlled by $\Phi_{w,eff}$ (Fig. 5D), thus confirming that the properties of the solvent (the water-sugar mixture) are critical in controlling the behaviour of the biopolymers in the batter matrix and consequently its rheology.
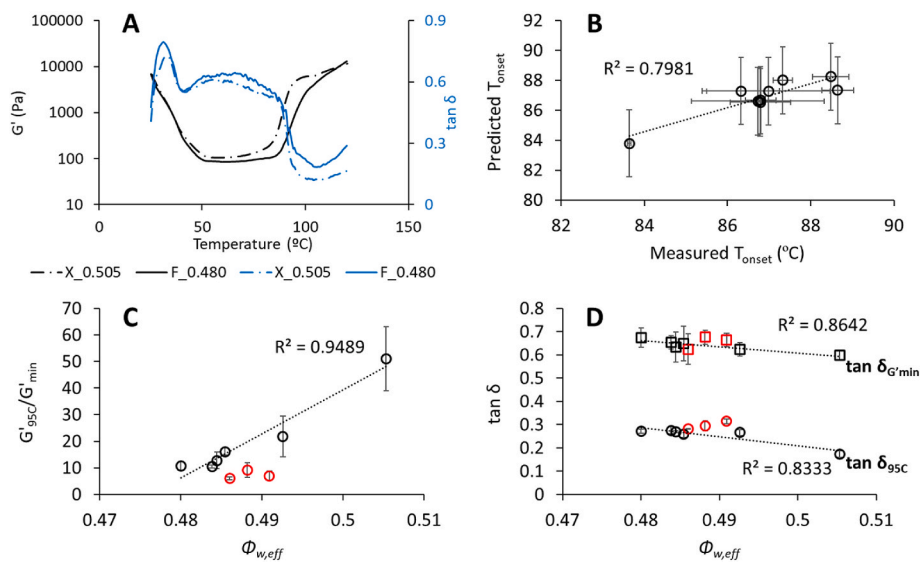
Fig. 5. DMTA of cake batters F_0.480 and X_0.505 showing the two extremes in the evolution of G′ and tan δ during a temperature sweep from 25 to 120 °C (A); Correlation between measured and predicted T_{onset} from DMTA as result of linear regression with $\Phi_{w,eff}$ and $\chi_{w,eff}$ (B); Correlation for G′$_{95°C}$/G′$_{min}$ (C) and tan δ (D) with $\Phi_{w,eff}$ for all formulations not containing glycine (p < 0.05). The red circles indicate formulations containing glycine. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

4.5. Cake volume

Sugar replacement resulted in cakes which varied in overall appearance, crumb structure and volume (Fig. 6A and B). The formulation with xylitol (i.e. sample X_0.505) showed the lowest volume (p < 0.05) while the one with FOS (i.e. sample F_0.480) resulted in the highest one (p < 0.05). For all variations the cake volume was controlled by $\Phi_{w,eff}$ (Fig. 6C; p < 0.05). Contrary to what earlier observed, the variations containing glycine could be also well described by the linear regression. Following on Fig. 1, a high $\Phi_{w,eff}$ resulted in an early structure setting during baking and consequently a low volume (as for sample X_0.505). On the contrary, a late setting determined a high cake volume, as observed for sample F_0.480. Gas bubble expansion occurs above 50 °C largely due to the production of CO_2 by the leavening agents and the thermal expansion of the gas bubble, well before the boiling point of water (van der Sman & Renzetti, 2020). The batter expansion is halted by the increased stiffness of the batter as a result of protein aggregation and starch swelling. Hence, a late occurrence of structure setting during baking provides more time for the expansion of the gas bubbles, which enhances cake volume.

4.6. Cake crumb properties

Sugar replacement resulted in significant changes in cake crumb a_w, instrumental texture and colour (Table 4). Several variations showed lower hardness than the reference cake (p < 0.05), except for samples X_0.505 and sample FX_0.500 which showed higher hardness. Crumb hardness was the highest when adding xylitol alone (sample X_0.505; p < 0.05). The reference cake showed the highest springiness, cohesiveness and resilience, while samples with highest glycine contents (i.e. samples FG_0.488 and FG_0.491) showed the lowest values for all these textural properties (p < 0.05). Springiness, cohesiveness and resilience were highly correlated with each other ($R^2 > 0.92$; p < 0.05). Also the crumb a_w varied significantly depending on formulation (Table 4), with xylitol addition (sample X_0.505) providing the lowest values and FOS (sample F_0.480) the highest one (p < 0.05). Crumb colour was also significantly affected (p < 0.05), remarkably for glycine containing formulations which were darker and with an increase in the red colour space.

Crumb hardness could be well described by the changes in $\Phi_{w,eff}$ (Fig. 7A; p < 0.05), except for the formulations containing glycine. The
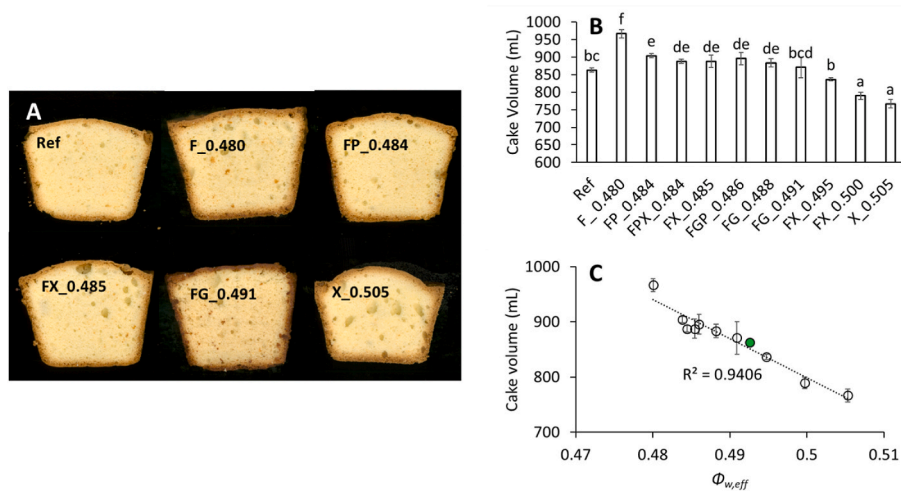

Fig. 6. Visual appearance of cake slices (A), measured variations in cake volume (B) and their correlation with $\Phi_{w,eff}$ (p < 0.05) (C). Green filled circle in (C) indicates the reference sample. Sugar reduced samples are coded based on the sugar replacers used (F=FOS, G = Glycine, P = L-Proline and X = Xylitol) followed by the value of $\Phi_{w,eff}$ computed from the formulation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4

Cake crumb properties: water activity, TPA texture and L*a*b colour space. Different letters in the same row indicate statistically significant differences (p < 0.05). Numbers in brackets indicate the standard deviation. Sugar reduced samples are coded based on the sugar replacers used (F=FOS, G = Glycine, P = L-Proline and X = Xylitol) followed by the value of $\Phi_{w,eff}$ computed from the formulation.

|	Ref	F_0.480	FP_0.484	FPX_0.484	FX_0.485	FGP_0.486	FG_0.488	FG_0.491	FX_0.495	FX_0.500	X_0.505
a_w	0.862bc (0.002)	0.874d (0.001)	0.869cd (0.003)	0.867cd (0.002)	0.869cd (0.001)	0.869cd (0.008)	0.864bc (0.009)	0.864bc (0.007)	0.864 ab (0.007)	0.870a (0.008)	0.847a (0.004)
Hardness (N)	7.2bc (0.1)	6.3a (0.1)	5.9a (0.1)	6.2a (0.0)	6.1a (0.0)	6.5 ab (0.2)	6.2a (0.1)	5.9a (0.2)	7.7c (0.4)	8.8d (0.5)	10.5e (0.5)
Springiness	0.843e (0.011)	0.807c (0.003)	0.809cd (0.000)	0.816cd (0.00)	0.818cd (0.004)	0.782b (0.00)	0.753a (0.001)	0.739a (0.001)	0.829de (0.006)	0.811c (0.028)	0.785b (0.009)
Cohesiveness	0.460g (0.001)	0.386cd (0.0030	0.403de (0.010)	0.401de (0.000)	0.415ef (0.001)	0.346b (0.005)	0.313a (0.003)	0.305a (0.005)	0.430f (0.007)	0.429f (0.015)	0.369c (0.000)
Resilience	0.168f (0.001)	0.129c (0.002)	0.137d (0.003)	0.137d (0.000)	0.143d (0.000)	0.115b (0.001)	0.103a (0.000)	0.101a (0.001)	0.151e (0.004)	0.150e (0.007)	0.125c (0.000)
L	82.0e (0.3)	81.0d (0.3)	81.1d (0.3)	81.0d (0.5)	82.0e (0.5)	79.2c (0.5)	77.5b (0.6)	76.6a (0.6)	82.1e (0.5)	82.3e (0.3)	81.9e (0.3)
a	0.8 ab (0.2)	1.4d (0.3)	1.3cd (0.2)	1.4d (0.2)	1.0bc (0.2)	2.7e (0.3)	4.0f (0.3)	4.5g (0.3)	0.7 ab (0.1)	0.6a (0.0)	0.9abc (0.2)
b	33.9 ab (0.3)	34.6d (0.3)	34.1abcd (0.4)	34.5cd (0.4)	33.9 ab (0.2)	34.5cd (0.2)	34.2abcd (0.3)	34.1abcd (0.3)<	34.3bcd (0.3)	33.8a (0.1)	34.0 ab (0.4)
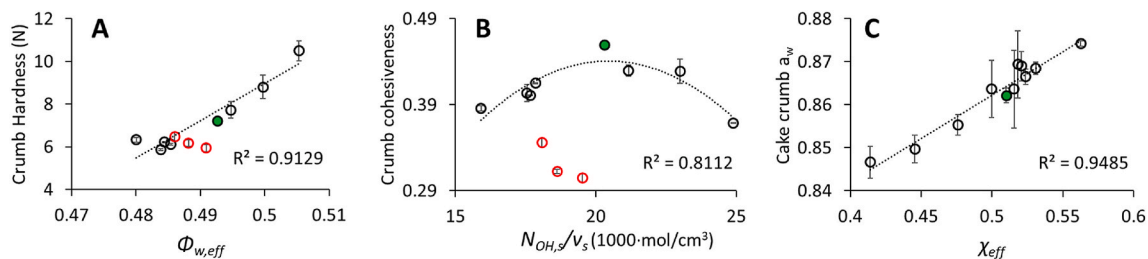
Fig. 7. Correlation of crumb hardness with $\Phi_{w,eff}$ (A) and of crumb cohesiveness with $N_{OH,s}/v_s$ (B) for variations not containing glycine (p < 0.05); correlation between crumb water activity and $\chi_{w,eff}$ (p < 0.05) (C). Green filled circle indicates the reference sample. The red circles in (A) and (B) indicate formulations containing glycine. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

hardness for those variations was inversely related to cake volume (R^2 = 0.75; p < 0.05). Crumb cohesiveness was a non-linear function of $N_{OH,s}/v_s$ with a maximum observed for the reference cake (Fig. 7B). Again, the variations containing glycine showed a distinct behaviour, which could not be related to $N_{OH,s}/v_s$. Finally, crumb a_w was well described by changes in χ_{eff} (Fig. 7C; p < 0.05).

5. Discussion

The main hypothesis of this study was that the effect of sugar replacement on the baking behaviour of batters and the physical properties of cakes is controlled by three main physicochemical parameters related to sugar functionality: $\Phi_{w,eff}$, χ_{eff} and $N_{OH,s}/v_s$. Compared to sucrose, xylitol and FOS display opposite physicochemical properties (Table 2). By replacing half of the sucrose with either xylitol or FOS, two extreme values for $\Phi_{w,eff}$, χ_{eff} and $N_{OH,s}/v_s$ were obtained, which were opposite to each other as compared to sucrose (i.e. samples F_0.480 and X_0.505 in Table 3). As a consequence, opposite effects on cake batter behaviour during baking (i.e. rheology, phase transitions and flour pasting) and on cake quality (i.e. volume and instrumental texture) would be expected. All other formulations were designed to have physicochemical properties distributed within the two extremes and closer to the sucrose reference by using combinations of FOS with xylitol or other low M_w plasticizers such as the amino acids. Hence, these formulations were expected to display properties which would be intermediate to those of FOS and xylitol alone. In fact, cake sample FX_0.495, having values of $\Phi_{w,eff}$, χ_{eff} and $N_{OH,s}/v_s$ close to the reference, showed similar physical properties as the reference cake (Table 4). On the contrary, samples F_0.480 and X_0.505 showed opposite characteristics compared to the cake reference.

In previous investigations (Renzetti et al., 2020; Renzetti, van den Hoek, et al., 2021), we have shown that the combination of low and high M_w plasticizers can be used to modulate the functionality of the sugar replacer mixtures to match that of sucrose with regards to bakery applications. Hence, this strategy can be potentially used to optimize sugar replacement while limiting the use of polyols and enhancing the use of dietary fibres. For such reason, sweet amino acids like L-proline and glycine were used in this study as alternatives to polyols. We have recently shown that these molecules have potential as sugar replacers, as they display a behaviour similar to carbohydrates regarding plasticizing and humectant properties (van der Sman et al., 2020). The results of this study indicated that L-proline could be used instead of xylitol within the theoretical framework to design the physical properties of cakes. In fact, formulations FP_0.484, FPX_0.484 and FX_0.485, having values of $\Phi_{w,eff}$, χ_{eff} and $N_{OH,s}/v_s$ close to each other, showed similar properties in batter rheology and in cake physical properties (Table S2 and Table 4, respectively). That was not the case for glycine, as flour pasting behaviour and cake instrumental texture could not be well described for the formulations containing this amino acid. In our recent studies (Renzetti et al., 2020) (Renzetti, van den Hoek, et al., 2021), the effect of glycine on the melting temperature of starch and egg white proteins could be well described by $\Phi_{w,eff}$ in binary system with water. However, glycine was not tested in presence of reducing sugars arising from the flour or from sugar replacers. The addition of glycine in the cake batters promoted a significant browning of the cake crumb (Table 4) due to its catalytic effect on Maillard reactions (Capuano, Ferrigno, Acampa, Ait-Ameur, & Fogliano, 2008), thus resulting in functionalities beyond the plasticizing aspects addressed in this study.

All the functionalities of dissolved sugar listed in Table 1 were well described by $\Phi_{w,eff}$, χ_{eff} and $N_{OH,s}/v_s$. The water activity of batters and of cake crumbs were well described by χ_{eff}, which could account for binary to quaternary mixtures of sugar and sugar replacers from different

classes of compounds (Fig. 7C). Hence, the functionality of sugar related to its hygroscopic properties, including the hydration of biopolymers, can be mimicked with sugar replacers by calculating this parameter directly form the batter formulation. As shown for FOS, the sorption behaviour could be well described by applying the FHFV (van der Sman, 2013). The χ_s of sugar replacers can be experimentally derived from their sorption isotherm following on equation (6). When their dry $T_g < T$ than the $F(\Phi_w)$ is zero and the sorption is fully described by χ_s.

Phase transitions controlling the setting of cake structure during baking were well described by $\Phi_{w,eff}$, with the exceptions of the formulations containing glycine. Recently, we have successfully applied this parameter for the prediction of starch gelatinization and protein denaturation temperatures in sugar (replacers) solutions (van der Sman & Mauer, 2019) (Renzetti et al., 2020) (Renzetti, van den Hoek, et al., 2021). The applicability of this parameter to a complex formulation such as a cake batter is of great relevance for sugar replacement purposes. In fact, computing $\Phi_{w,eff}$ directly from the formulation allows for precise control of the setting behaviour during baking (Fig. 1) and the final cake volume (Fig. 6C). It should be noted that phase separation in sugar-rich and biopolymer-rich phases occurs at high sugar concentrations and at high values $\Phi_{w,eff}$ as we recently suggested (Renzetti et al., 2020) (Renzetti, van den Hoek, et al., 2021). Therefore, experimental deviations from predictions may occur, as in such conditions the computed $\Phi_{w,eff}$ does not reflect the composition in the biopolymer-rich phase. In the pound cake formulation, the $\Phi_{w,eff}$ and the sugar concentration are around the onset of phase separation, and hence the phenomenon is limited (van der Sman & Renzetti, 2020).

The rheology of cake batters was assessed during temperature sweeps, thus simulating the changes in the mechanical responses associated to phase transitions during baking. The visco-elastic properties, i. e. tan δ, of cake were well described by $\Phi_{w,eff}$ for all formulations, except those containing glycine. Recently, the viscosity of sugar solutions and the dynamic viscoelastic properties of concentrated maltodextrins and starches mixtures have been shown to scale with T_g/T, the ratio between the glass transition temperature of the solution and the measuring temperature (van der Sman & Mauer, 2019) (Renzetti et al., 2020) (van der Sman, Ubbink, Dupas-langlet, Kristiawan, & Siemons, 2022). Our results are well in agreement with these recent findings, since the hydrogen bond density also controls the T_g of mixtures of biopolymers with sugars and water (Özeren, Guivier, Olsson, Nilsson, & Hedenqvist, 2020).

The extent of the mechanical response of the batter to the thermal process, i.e. the ratio $G'_{95°C}/G'_{min}$, was also well described by $\Phi_{w,eff}$ (Fig. 5C). The rheology of the cake batter during heating has been shown to play a critical role for its structure setting. A too-high shear modulus results in a tough cake, while a too-low shear modulus leads to cake collapse (van der Sman & Renzetti, 2020). Hence, the ratio $G'_{95°C}/G'_{min}$ can be seen as an indicator of the extent of structure formed during heating. The cake batter rheology has been shown to depend on the degree of protein aggregation (Mizukoshi, 1985). In the cake batter, all proteins present are involved in protein network formation during thermosetting (Lambrecht et al., 2018). The network is crosslinked via S–S bridges and hydrophobic interactions. The network appears to have a co-protein, with incorporation of gliadins and egg yolk proteins upon denaturation of ovalbumin (Deleu, Wilderjans, Van Haesendonck, Brijs, & Delcour, 2016) (Deleu et al., 2019) (Lambrecht et al., 2018). Thus, an early ovalbumin denaturation during baking provides with longer time for the co-proteins to aggregate in the network. We have recently demonstrated that $\Phi_{w,eff}$ controls the denaturation temperature of egg white proteins and gluten (Renzetti et al., 2020) (van der Sman & Renzetti, 2019). The results of this study demonstrate that $\Phi_{w,eff}$ also controls the phase transition in the cake batter (Fig. 4), where the dissolved sugars elevate both starch gelatinization and egg white proteins denaturation around the same temperature (85–90 °C) (Wilderjans et al., 2010) (van der Sman & Renzetti, 2020), resulting in a single endothermic peak. Overall, increasing $\Phi_{w,eff}$ promotes an earlier formation of the protein network (Fig. 1), resulting in increasing the $G'_{95°C}/G'_{min}$ ratio and lowering tan δ at 95 °C (Fig. 5D). These observations further demonstrate the validity of theoretical approach presented in this study.

The gelatinization and swelling behaviour of starch during cake baking has relevant contribution to crumb texture upon cooling (Wilderjans et al., 2010) (van der Sman & Renzetti, 2020). The importance of the starch phase in modulating crumb texture has been recently suggested also for bread crumbs, despite the presence of a permanent protein network such as gluten. Crumb cohesiveness and resilience depend more on starch gelatinization and swelling than on gluten aggregation (Renzetti, Theunissen, & Horrevorts, 2021) (Verbauwhede et al., 2018). In this study, the pasting properties of flour were significantly affected by the sugar compositions (Fig. 3). All pasting viscosity parameters were well described by $N_{OH,s}/v_s$ (Fig. 3B–F), confirming our recent findings on wheat starch in sugar solutions (Renzetti, van den Hoek, et al., 2021). Sugar reduced formulations with a NOH_s/v_s close to the value of the reference showed to most closely resemble its cohesiveness (Fig. 7B), thus supporting our original hypothesis. However, the non-linear dependency to $N_{OH,s}/v_s$ is not obvious and needs further investigations. For $N_{OH,s}/v_s$ values beyond that of the reference cake, cohesiveness may have been affected by an increased density of the cake crumb. Hardness linearly increased with increasing $\Phi_{w,eff}$ (Fig. 7A), which is associated with an increase in the volumetric density of H-bonding sites. This suggests that $\Phi_{w,eff}$ can be used to increase volume and crumb softness. The $\Phi_{w,eff}$ accounts for both water and sugars added. Therefore, designing the physical properties of cakes by changing the water content can be accounted for in our approach. This provides an additional mean to optimize the instrumental texture of cakes, including cohesiveness, which should be further investigated within the theoretical approach presented in this study.

6. Conclusion

This study demonstrated that three physicochemical parameters, i.e. $\Phi_{w,eff}$, $N_{OH,s}/v_s$ and χ_{eff}, control the rheology and thermosetting behaviour of sugar replaced cake batters and the physical properties of the resulting cake products. Since these parameters can be computed directly from the starting formulations, these principles enable to design the physical properties of cakes avoiding a "cook-and-look" approach. By matching the same physicochemical parameters of the reference product, similar instrumental texture and structural properties can be obtained with a substantial reduction in sucrose, with at least 50% replacement. Following on our recent work, we have demonstrated in a cake application that mixtures of plasticizers from different classes of compounds can be used to steer cake quality towards desired physical properties. In a companion paper (van der Sman, Jurgens, Smith, & Renzetti, 2022), we have shown that the same physicochemical parameters control both physical and sensory properties (i.e. mouthfeel) of sugar replaced biscuits. Overall, the forward-looking strategy that emerges from this study is the possibility to uncouple texture design from nutritional composition by using the here described physicochemical principles. In turn, this allows to design bakery products which are substantially reduced in sugar content while enriched in health promoting ingredients, such as dietary fibres. In the future, we aim to demonstrate that this principles can be extended to other classes of compounds and to broader reformulations targets, including sugar replacement beyond 50%.

CRediT authorship contribution statement

Stefano Renzetti: Conceptualization, Formal analysis, Visualization, Methodology, Writing - original draft, Writing - review & editing, Funding acquisition, **Ruud van der Sman:** Methodology, Writing -

review & editing.

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.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2022.107795.

References

Arufe, S., Chiron, H., Doré, J., Savary-Auzeloux, I., Saulnier, L., & Della Valle, G. (2017). Processing & rheological properties of wheat flour dough and bread containing high levels of soluble dietary fibres blends. *Food Research International, 97*, 123–132. https://doi.org/10.1016/j.foodres.2017.03.040

Azaïs-Braesco, V., Sluik, D., Maillot, M., Kok, F., & Moreno, L. A. (2017). A review of total & added sugar intakes and dietary sources in Europe. *Nutrition Journal, 16*(1), 1–15. https://doi.org/10.1186/s12937-016-0225-2

Capuano, E., Ferrigno, A., Acampa, I., Ait-Ameur, L., & Fogliano, V. (2008). Characterization of the Maillard reaction in bread crisps. *European Food Research and Technology, 228*(2), 311–319. https://doi.org/10.1007/s00217-008-0936-5

Clemens, R. A., Jones, J. M., Kern, M., Lee, S. Y., Mayhew, E. J., Slavin, J. L., et al. (2016). Functionality of sugars in foods and health. *Comprehensive Reviews in Food Science and Food Safety, 15*(3), 433–470. https://doi.org/10.1111/1541-4337.12194

Deleu, L. J., Luyts, A., Wilderjans, E., Van Haesendonck, I., Brijs, K., & Delcour, J. A. (2019). Ohmic versus conventional heating for studying molecular changes during pound cake baking. *Journal of Cereal Science, 89*. https://doi.org/10.1016/j.jcs.2019.01.008

Deleu, L. J., Wilderjans, E., Van Haesendonck, I., Brijs, K., & Delcour, J. A. (2016). Protein network formation during pound cake making: The role of egg white proteins and wheat flour gliadins. *Food Hydrocolloids, 61*, 409–414. https://doi.org/10.1016/j.foodhyd.2016.05.001

van Der Sman, R. G. M. (2017). Predicting the solubility of mixtures of sugars and their replacers using the Flory-Huggins theory. *Food & Function, 8*(1), 360–371. https://doi.org/10.1039/c6fo01497f

Diarce, G., Gandarias, I., Campos-Celador, García-Romero, A., & Griesser, U. J. (2015). Eutectic mixtures of sugar alcohols for thermal energy storage in the 50-90°C temperature range. *Solar Energy Materials and Solar Cells, 134*, 215–226. https://doi.org/10.1016/j.solmat.2014.11.050

Donovan, J. W. (1977). A study of the baking process by differential scanning calorimetry. *Journal of the Science of Food and Agriculture, 28*(6), 571–578. https://doi.org/10.1002/jsfa.2740280616

Jurgens, A., Noort, M. W. J., Renzetti, S., & de Harder, J. R. (2016). *Food products with reduced sugar content.* Patent No. WO 2016/171559 Al).

Kweon, M., Slade, L., & Levine, H. (2016a). Cake baking with alternative carbohydrates for potential sucrose replacement. I. Functionality of small sugars and their effects on high-ratio cake-baking performance. *Cereal Chemistry, 93*(6), 562–567. https://doi.org/10.1094/CCHEM-02-16-0032-R

Kweon, M., Slade, L., & Levine, H. (2016b). Cake baking with alternative carbohydrates for potential sucrose replacement. II. Functionality of healthful oligomers and their effects on high-ratio cake-baking performance. *Cereal Chemistry, 93*(6), 568–575. https://doi.org/10.1094/CCHEM-03-16-0056-R

Kweon, M., Slade, L., Levine, H., Martin, R., & Souza, E. (2009). Exploration of sugar functionality in sugar-snap and wire-cut cookie baking: Implications for potential sucrose replacement or reduction. *Cereal Chemistry, 86*(4), 425–433. https://doi.org/10.1094/CCHEM-86-4-0425

Laguna, L., Vallons, K. J. R., Jurgens, A., & Sanz, T. (2013). Understanding the effect of sugar and sugar replacement in short dough biscuits. *Food and Bioprocess Technology, 6*(11), 3143–3154. https://doi.org/10.1007/s11947-012-0968-5

Lambrecht, M. A., Deleu, L. J., Rombouts, I., & Delcour, J. A. (2018). Heat-induced network formation between proteins of different sources in model systems, wheat-based noodles and pound cakes. *Food Hydrocolloids, 79*, 352–370. https://doi.org/10.1016/j.foodhyd.2017.12.032

Luo, X., Arcot, J., Gill, T., Louie, J. C. Y., & Rangan, A. (2019). A review of food reformulation of baked products to reduce added sugar intake. *Trends in Food Science & Technology, 86*, 412–425. https://doi.org/10.1016/j.tifs.2019.02.051. April 2018.

Martínez-Cervera, S., Salvador, A., & Sanz, T. (2014). Comparison of different polyols as total sucrose replacers in muffins: Thermal, rheological, texture and acceptability properties. *Food Hydrocolloids, 35*, 1–8. https://doi.org/10.1016/j.foodhyd.2013.07.016

Mizukoshi, M. (1985). Model studies of cake baking-cake shrinkage and shear modulus of cake batter during baking. *Cereal Chemistry, 62*(4), 242–246.

Özeren, H. D., Guivier, M., Olsson, R. T., Nilsson, F., & Hedenqvist, M. S. (2020). Ranking plasticizers for polymers with atomistic simulations: PVT, mechanical properties, and the role of hydrogen bonding in thermoplastic starch. *ACS Applied Polymer Materials, 2*(5), 2016–2026. https://doi.org/10.1021/acsapm.0c00191

Palomo Del Barrio, E., Cadoret, R., Daranlot, J., & Achchaq, F. (2016). New sugar alcohols mixtures for long-term thermal energy storage applications at temperatures between 70 °C and 100 °C. *Solar Energy Materials and Solar Cells, 155*, 454–468. https://doi.org/10.1016/j.solmat.2016.06.048

Pareyt, B., & Delcour, J. A. (2008). The role of wheat flour constituents, sugar, and fat in low moisture cereal based products: A review on sugar-snap cookies. *Critical Reviews in Food Science and Nutrition, 48*(9), 824–839. https://doi.org/10.1080/10408390701719223

Pateras, I. M. C., & Rosenthal, A. J. (1992). Effects of sucrose replacement by poly dextrose on the mechanism of structure formation in high ratio cakes. *International Journal of Food Sciences & Nutrition, 43*(1), 25–30. https://doi.org/10.3109/09637489209027529

Pawlus, S., Grzybowski, A., Paluch, M., & Wlodarczyk, P. (2012). Role of hydrogen bonds and molecular structure in relaxation dynamics of pentiol isomers. *Physical Review E, 85*, 1–4. https://doi.org/10.1103/PhysRevE.85.052501, 052501.

Renzetti, S., & Jurgens, A. (2016). Rheological and thermal behavior of food matrices during processing and storage: Relevance for textural and nutritional quality of food. *Current Opinion in Food Science, 9*. https://doi.org/10.1016/j.cofs.2016.10.003

Renzetti, S., Theunissen, M., & Horrevorts, K. (2021). A systematic comparison of the intrinsic properties of wheat and oat bran fractions and their effects on dough and bread properties: Elucidation of chemical mechanisms, water binding, and steric hindrance. *Foods, 10*(6). https://doi.org/10.3390/foods10102311

Renzetti, S., van den Hoek, I. A. F., & van der Sman, R. G. M. (2020). Amino acids , polyols and soluble fibres as sugar replacers in bakery applications : Egg white proteins denaturation controlled by hydrogen bond density of solutions. *Food Hydrocolloids, 108*(May), Article 106034. https://doi.org/10.1016/j.foodhyd.2020.106034

Renzetti, S., van den Hoek, I. A. F., & van der Sman, R. G. M. (2021). Mechanisms controlling wheat starch gelatinization and pasting behaviour in presence of sugars and sugar replacers : Role of hydrogen bonding and plasticizer molar volume. *Food Hydrocolloids, 119*(May), Article 106880. https://doi.org/10.1016/j.foodhyd.2021.106880

Renzetti, S., Voogt, J. A., Oliver, L., & Meinders, M. B. J. (2012). Water migration mechanisms in amorphous powder material and related agglomeration propensity. *Journal of Food Engineering, 110*(2), 160–168. https://doi.org/10.1016/j.jfoodeng.2011.07.005

Rice, T., Zannini, E., Arendt, E. K., & Coffey, A. (2020). A review of polyols–biotechnological production, food applications, regulation, labeling and health effects. *Critical Reviews in Food Science and Nutrition, 60*(12), 2034–2051. https://doi.org/10.1080/10408398.2019.1625859

Slade, L., Kweon, M., & Levine, H. (2020). Exploration of the functionality of sugars in cake-baking, and effects on cake quality. *Critical Reviews in Food Science and Nutrition, 61*(2), 283–311. https://doi.org/10.1080/10408398.2020.1729694

Slade, L., & Levine, H. (1988). Non-equilibrium behavior of small carbohydrate-water systems. *Pure and Applied Chemistry, 60*(12), 1841–1864. https://doi.org/10.1351/pac198860121841

van der Sman, R. G. M. (2013). Moisture sorption in mixtures of biopolymer, Disaccharides and water. *Food Hydrocolloids, 32*(1), 186–194. https://doi.org/10.1016/j.foodhyd.2012.12.029

van der Sman, R. G. M. (2016). Sugar and polyol solutions as effective solvent for biopolymers. *Food Hydrocolloids, 56*, 144–149. https://doi.org/10.1016/j.foodhyd.2015.12.001

van der Sman, R. G. M. (2018). Progress in understanding of supplemented state diagrams of hydrophilic food materials. *Current Opinion in Food Science, 21*, 32–38. https://doi.org/10.1016/j.cofs.2018.05.006

van der Sman, R. G. M., Jurgens, A., Smith, A., & Renzetti, S. (2022). Universal strategy for sugar replacement in foods. *Food Hydrocolloids*, 1–22. *submitted*.

van der Sman, R. G. M., & Mauer, L. J. (2019). Starch gelatinization temperature in sugar and polyol solutions explained by hydrogen bond density. *Food Hydrocolloids, 94* (December 2018), 371–380. https://doi.org/10.1016/j.foodhyd.2019.03.034

van der Sman, R. G. M., & Meinders, M. B. J. (2011). Prediction of the state diagram of starch water mixtures using the Flory-Huggins free volume theory. *Soft Matter, 7*(2), 429–442. https://doi.org/10.1039/c0sm00280a

van der Sman, R. G. M., & Renzetti, S. (2019). Understanding functionality of sucrose in biscuits for reformulation purposes. *Critical Reviews in Food Science and Nutrition, 59* (14), 2225–2239. https://doi.org/10.1080/10408398.2018.1442315

van der Sman, R. G. M., & Renzetti, S. (2020). Understanding functionality of sucrose in cake for reformulation purposes. *Critical Reviews in Food Science and Nutrition*, 1–17. https://doi.org/10.1080/10408398.2020.1786003, 0(0).

van der Sman, R. G. M., Ubbink, J., Dupas-langlet, m., Kristiawan, M., & Siemons, I. (2022). Food Hydrocolloids Scaling relations in rheology of concentrated starches and maltodextrins. *Food Hydrocolloids, 124*(PB), Article 107306. https://doi.org/10.1016/j.foodhyd.2021.107306

van der Sman, R. G. M., van den Hoek, I. A. F., & Renzetti, S. (2020). Sugar replacement with zwitterionic plasticizers like amino acids. *Food Hydrocolloids, 109*(June), Article 106113. https://doi.org/10.1016/j.foodhyd.2020.106113

Struck, S., Jaros, D., Brennan, C. S., & Rohm, H. (2014). Sugar replacement in sweetened bakery goods. *International Journal of Food Science and Technology, 49*(9), 1963–1976. https://doi.org/10.1111/ijfs.12617

Tsatsaragkou, K., Methven, L., Chatzifragkou, A., & Rodriguez-Garcia, J. (2021). The functionality of inulin as a sugar replacer in cakes and biscuits; highlighting the influence of differences in degree of polymerisation on the properties of cake batter and product. *Foods, 10*(5). https://doi.org/10.3390/foods10050951

Verbauwhede, A. E., Lambrecht, M. A., Fierens, E., Hermans, S., Shegay, O., Brijs, K., et al. (2018). Thermo-reversible inhibition makes aqualysin 1 from Thermus aquaticus a potent tool for studying the contribution of the wheat gluten network to the crumb texture of fresh bread. *Food Chemistry, 264*, 118–125. https://doi.org/10.1016/j.foodchem.2018.05.014. November 2017.

Wilderjans, E., Luyts, A., Brijs, K., & Delcour, J. A. (2013). Ingredient functionality in batter type cake making. *Trends in Food Science & Technology, 30*(1), 6–15. https://doi.org/10.1016/j.tifs.2013.01.001

Wilderjans, E., Luyts, A., Goesaert, H., Brijs, K., & Delcour, J. A. (2010). A model approach to starch and protein functionality in a pound cake system. *Food Chemistry, 120*(1), 44–51. https://doi.org/10.1016/j.foodchem.2009.09.067

Woodbury, T. J., Grush, E., Allan, M. C., & Mauer, L. J. (2021). The effects of sugars and sugar alcohols on the pasting and granular swelling of wheat starch. *Food Hydrocolloids, 126*(December 2021), Article 107433. https://doi.org/10.1016/j.foodhyd.2021.107433

World Health Organization. (2017). *Taxes on sugary drinks: Why do it? World health organization.* https://apps.who.int/iris/handle/10665/260253.

Zanoletti, M., Marti, A., Marengo, M., Iametti, S., Pagani, M. A., & Renzetti, S. (2017). Understanding the influence of buckwheat bran on wheat dough baking performance: Mechanistic insights from molecular and material science approaches. *Food Research International, 102*. https://doi.org/10.1016/j.foodres.2017.09.052