TITLE: Development of low calorie jams with increased content of natural dietary fibre made from tomato pomace

AUTHORS: Miona Belović, Aleksandra Torbica, Ivana Pajić-Lijaković, Jasna Mastilović

This article is provided by author(s) and FINS Repository in accordance with publisher policies.

The correct citation is available in the FINS Repository record for this article.

NOTICE: This is the author’s version of a work that was accepted for publication Food Chemistry. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Food Chemistry, Volume 237, 15 December 2017, Pages 1226–1233. DOI: 10.1016/j.foodchem.2017.06.045

This item is made available to you under the Creative Commons Attribution-NonCommercial-NoDerivative Works – CC BY-NC-ND 3.0 Serbia
Development of low calorie jams with increased content of natural dietary fibre made from tomato pomace

Running title: Tomato pomace low calorie jams with increased dietary fibre content

Miona Belovića, Aleksandra Torbica, Ivana Pajić-Lijakovićb, Jasna Mastilovića

aUniversity of Novi Sad, Institute of Food Technology, Bul. cara Lazara 1, 21000 Novi Sad, Serbia
bUniversity of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

*Corresponding author: Miona Belović, Institute of Food Technology, University of Novi Sad, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia. Tel.: +381 21 485 3779.
E-mail address: miona.belovic@fins.uns.ac.rs
Abstract

In this study, four jam formulations were developed, starting with the basic formulation (Jam 1) containing sucrose and without added pectin. Sucrose was partially (50%) replaced by stevioside in formulations of Jam 2 and 3, while in Jam 4 sucrose was completely replaced by fructose and stevioside, making this formulation suitable for diabetic patients. Jam formulations 1 and 2, prepared without added pectin, were thermally stable in the temperature range of 25-90 °C, which indicate their potential use as fruit fillings. Jam formulations 3 and 4 were assessed by the sensory panel as more spreadable since tomato pomace particles are incorporated in pectin network which acts as a lubricant. Jam formulations were characterized by a lower total carbohydrate content (17.23-43.81%) and lower energy value (87.1-193.7 kcal/100 g) when compared to commercial products. Tomato pomace jams contained 15-20 times more dietary fibre than commercial apricot jam.

Keywords: jam; tomato pomace; dietary fibre; sweeteners; rheology; texture

Chemical compounds studied in this article:
Sucrose (PubChem CID: 5988); Fructose (PubChem CID: 5984); Pectin (PubChem CID: 441476); Stevioside (PubChem CID: 442089)
1. Introduction

Jam is one of the most popular fruit preserves, prepared by boiling fruit pulp with sugar (sucrose), pectin, acid, and other ingredients (preservative, colouring and flavouring materials) to a consistency firm enough to hold the fruit tissues in position (Besbes, Drira, Blecker, Deroanne, & Attia, 2009; Basu, Shivhare, Singh, & Beniwal, 2011). Total soluble solids content of the finished jam should be between 60% and 65% or greater and the product should contain at least 45% fruit (CODEX, 2009). Tomato is rarely used as an ingredient for jam production; with examples including two International Patents, one for common tomato jam (No. HUH3113 (A)) and other for low sugar tomato jam (No. KR20100105250 (A)), as well as jam made of green tomato fruits (Özdoğan & Yılmaz, 2011).

During industrial processing of tomato, approximately 4% (w/w) of total processed tomato is discarded (Del Valle, Câmara, & Torija, 2006; Kalogeropoulos, Chiou, Pyriocho, Peristeraki, & Karathanos, 2012). According to data presented in the paper by Van Dyk, Gama, Morrison, Swart, & Pletschke (2013), approximately 4.37-10.20 million tons of tomato waste was generated in the world in 2010. This waste material is called tomato pomace and consists mostly of skin, seeds, and vascular tissue, containing up to 60% of dietary fibre per dry weight (Al-Wandawi, Abdul-Rahman, & Al-Shaikhly, 1985; Del Valle et al., 2006). Tomato pomace has high moisture content (about 80%), similarly to other fruit and vegetable processing industry by-products, and therefore drying process (convection or freeze drying) is suitable for its preservation (Al-Wandawi et al., 1985; O'Shea, Arendt, & Gallagher, 2012). Beside dietary fibre, tomato pomace also represents
a source of bioactive phytochemicals, such as lycopene, β-carotene and phenolic compounds, predominantly hydroxycinnamic acids and flavonols (Kalogeropoulos et al., 2012).

According to the opinion of European Food Safety Authority (EFSA), dietary fibre is defined as non-digestible carbohydrates (non-starch polysaccharides, resistant starch and resistant oligosaccharides) plus lignin, and dietary fibre intake of 25 g per day is considered to be adequate for normal laxation in adults (Agostoni et al., 2010). Beside normal bowel function, consumption of dietary fibre provides other health benefits, of which lowering of blood glucose and cholesterol levels and prevention of colon cancer are the most important (Rodríguez, Jiménez, Fernández-Bolaños, Guillén, & Heredia, 2006). Additionally, the oligosaccharides and phenolic compounds associated with the dietary fibre improve its beneficial effects by adding prebiotic and antioxidant activity (Macagnan, da Silva, & Hecktheuer, 2016). Besides its nutritive value, dietary fibre can provide multiple technological properties when incorporated into food product: syneresis (water release from jam during storage) prevention and shelf life extension due to its water holding capacity, stabilization of foods with high fat content and emulsions due to its oil holding capacity, gel formation, thickening (viscosity increase), fat replacement, prevention of caking, as well as general improvement of textural and sensory properties of food (O'Shea et al., 2012).

Due to the growing health concerns and higher incidence of obesity, metabolic syndrome and diabetes, during the recent decades there has been an increase in interest for low-calorie food consumption (Souza et al., 2013; Abolila, Barakat, El-Tanaha, & El-Mansy, 2015). Low calorie food products can be made by incorporating combinations of
non-caloric and carbohydrate sweeteners, which are used for partial or full replacement of sucrose (Basu, Shivhare, & Singh, 2013). Although most of the sugars (sucrose, fructose and glucose) have energy value around 4 kcal/g, they differ by their glycaemic index (GI). Namely, glucose has the highest GI with a value of 100, followed by sucrose with 61-65 and fructose with a GI of 19-23 (Rubio Arraez, Sahuquillo, Capella, Ortolá, & Castelló, 2015). Therefore, fructose is the most commonly used sugar in jam formulations for people with diagnosed diabetes mellitus type 2. In addition, animal and human studies have demonstrated that fructose may play an active role in the increase of hepatic glucose uptake and the subsequent lowering of the glycaemic response to additional dietary carbohydrate (Heacock, Hertzler, & Wolf, 2002). Stevia is another natural sweetener, which is increasingly popular in the last years. It represents extract from the leaves of the plant *Stevia rebaudiana* (Bert.) which contains a high level of low calorie sweetening compounds, known as steviol glycosides (Lemus-Mondaca, Vega-Gálvez, Zura-Bravo, & Ah-Hen, 2012; Basu et al., 2013). Besides sweetening properties, stevia extracts possess antioxidant, antimicrobial and antifungal activity (Lemus-Mondaca et al., 2012).

Removal of sucrose from food formulations affects not only sweetness and flavour, but also browning, crystallization, structure, viscosity, moisture, osmotic pressure, fermentation etc. (Alonso & Setser, 1994). Fruit jam incorporating alternative sweetener should have similar textural and rheological characteristics, as well as sensory properties to that of the traditional product (Basu et al., 2013). This is commonly achieved by the application of low methoxyl (LM) pectins, which can form a gel in the presence of calcium ions. In this case, ionic linkages are formed via calcium bridges between
dissociated carboxyl groups, creating the so called ‘‘egg-box’’ model (Fraeye, Duvetter, Doungla, Van Loey, & Hendrickx, 2010). However, sugar (sucrose or fructose) also has to be added in the low-calorie jam formulations since it acts as a dehydrating agent for the pectin molecules, allowing closer contact between the pectin chains during jam manufacturing (Basu et al., 2011).

Bearing in mind all mentioned above, the aim of this study was to upgrade tomato processing by-products into value-added products by application of adequate technological processes. These products should be characterized by an increased content of dietary fibre originating from tomato pomace and lower energy value in comparison with commercial products. Since tomato jam is not produced commercially in Serbia, rheological measurements were employed to estimate the mechanical and thermal stabilities – parameters of special importance for processing and storage of developed products.

2. Materials and Methods

2.1. Material

For the manufacturing of low calorie jams, tomato pomace obtained from industrial plant (Zdravo Organic d.o.o., Selenča, Serbia) was lyophilized and ground as described in Belović, Pajić-Ljaković, Torbica, Mastilović, & Pečinar (2016). Commercially available sucrose, fructose and cinnamon were used in the jam manufacturing. Citric acid, calcium-
chloride (CaCl₂) and potassium sorbate were obtained from Lach-ner (Neratovice, Czech Republic). Low-methoxyl (LM) pectin (citrus-apple pectin, NECJ-A2) was obtained from Vinipex d.o.o. (Belgrade, Serbia). Stevioside was produced by Esarom GmbH (Oberrohrbach, Austria).

2.2. Basic jam formulation and manufacturing

Basic formulation (Jam 1) used for the manufacturing of low calorie jam from tomato pomace is presented in Table 1. Jam 1 (contains only sucrose as a sweetening agent) was created on the basis of previous researches (Belović et al., 2016) and using the general jam formulation given in Niketić-Aleksić (1988).

In the manufacturing process, all ingredients except water were mixed in an open stainless steel pan. After that, the water previously heated to 30 °C was added and mixed thoroughly with other ingredients. The obtained mixture was heated on a burner at low temperature, which was monitored during the process and regulated to remain in the range of 60-70 °C. This temperature was chosen bearing in mind that tomato pomace suspensions are stiffer when prepared at 60 °C in comparison with those prepared at 100 °C (Belović et al., 2016). Total soluble solids (TSS) content was also monitored during the process, which was stopped when TSS reached value of 48 °Brix as determined in previous experiments. After cooling to 30 °C, cinnamon was added. Samples were stored in a refrigerator at +4 °C in closed plastic jars prior to analyses.

2.3. Chemical analyses and determination of water activity (A_w)

7
Moisture content, total acids, protein, fat, and total dietary fibre content of low calorie jams made of tomato pomace were analysed according to Association Official of Analytical Chemists (AOAC 2000) methods 925.10, 925.53, 950.36, 935.38, and 985.29, respectively. Total sugars were determined by Schoorl method (AACC method 80-68.01). Total soluble solids (TSS) and pH value were measured instrumentally using table refractometer (ATR ST Plus, Schmidt + Haensch, Germany) and a pH meter with temperature probe (Denver Instrument, USA). The $A_w$ value of jam samples was measured using the portable $A_w$ meter Testo 205 (Testo AG, USA) equipped with a combined penetration tip with temperature probe according to the standard method (ISO, 2004).

2.4. Rheological analysis

Rheological characterization of low calorie jam samples was performed at 25 °C, with a Haake MARS rheometer (Thermo Scientific, Karlsruhe, Germany).

2.4.1. Flow curve measurements

Cylinder sensor system Z20 DIN (bob diameter = 20 mm and inner cup diameter = 21.7 mm, gap 4.20 mm) was used for the flow curve measurements. Flow curve measurements were carried out firstly by increasing the shear rate linearly from 1 to 100 s$^{-1}$ for 120 s, then maintaining it at 100 s$^{-1}$ for 120 s, and finally decreasing it linearly back to 1 s$^{-1}$ for additional 120 s. The hysteresis loop areas, $S$, were obtained as the
difference between the surface area enclosed by the up (ascending) curve and the surface area enclosed by the down (descending) curve in the shear rate range considered (Eq. 1).

\[ S = S_{up} - S_{down} \]  

(1)

where \( S \) is the hysteresis loop area, \( S_{up} \) and \( S_{down} \) are obtained surface areas under the ascending and descending flow curves, respectively.

Other flow curve parameters were calculated by fitting the experimental data for descending curve to Ostwald-de Waele relationship (Eq. 2).

\[ \tau = K \dot{\gamma}^n \]  

(2)

where \( \tau \) is the shear stress, \( \dot{\gamma} \) is the shear rate (s\(^{-1}\)), \( K \) the consistency index (Pa s\(^n\)) and \( n \) the flow index. Apparent viscosity was recorded from flow curve as a mean value at 100 s\(^{-1}\).

2.4.2. Yield stress measurements

In order to determine the yield stress, stress-controlled (CS) measurements (deformation/stress relationship) were performed using parallel plate sensor system PP35 (35 mm diameter and 1 mm gap). After a waiting period of 300 s, a logarithmical CS ramp in a shear stress range between 0.5 Pa and 100 Pa was measured within 180 s to obtain 50 data points. The intersection of the linear segments in log-log plot of
deformation versus stress values indicated the transition from elastic behaviour to flow and was considered as the yield stress value.

2.4.3. Oscillatory measurements

Oscillatory measurements of reconstituted tomato pomace were performed using parallel plate geometry PP35. Mechanical spectra (frequency sweeps) were recorded over the range 0.1-10 Hz at 1 Pa stress (which was within the linear viscoelastic region as determined by amplitude sweep). In order to detect changes in the rheological properties of jam samples during thermal treatment, temperature sweep tests were performed using the same geometry. The temperature of the Peltier plate on which the samples were placed was increased from 25 to 90 °C for 600 s, at a fixed stress of 1 Pa, with a frequency of 1 Hz. A cooling step followed the heating procedure at the same conditions in the temperature range 90 - 25 °C.

Solvent traps were used in all the tests to prevent sample drying. All the rheological measurements were performed in triplicates.

2.5. Texture analysis

Textural analysis of low calorie jams was carried out using TA.XT Plus Texture Analyser (Stable Micro Systems, England, UK) in order to determine its spreadability, since jam is consumed spread on bread. Spreadability was measured using TTC Spreadability Rig (HDP/SR), which consisted of female and male perspex cones with 45°
angle, using a 5 kg load cell. Spreadability parameters included hardness (N), stickiness (N), work of shear (J), and work of adhesion (J). Instrumental settings for spreadability test were taken from the sample project (CHEE2_SR.PRJ) of the software package (Texture Exponent Software TEE32, version 6.0.6.0, Stable Micro Systems, England, UK). Force calibration of the instrument was done prior to start of the experiment to minimize measurement error. Afterwards, the height calibration was done with return distance of 25 mm. The instrument was operated at pre-test speed = 1 mm/s, test speed = 3 mm/s, post-test speed = 10 mm/s, distance = 23 mm, and trigger force = 5 g. The tests were performed in triplicate.

2.6. Sensory analysis

Six expert panellists from the Institute of Food Technology (University of Novi Sad, Serbia), aged 25-50 years, with sensory experience in sensory profiling work with tomato products, performed the sensory analysis of low calorie jams. Panellists were initially provided with sensory terms of ketchup sensory profile used in previously published research (Törbica et al., 2016) but were told that they could keep, delete or add any terms as appropriate during the training sessions. A consensus approach was used to allow further discussion on each jam sample that was meant to be analysed later and to define the descriptors (Table 2). Once the descriptors were established, all samples were evaluated by the panel using an unstructured linear scale with the anchor points 0 – not perceptible and 100 – strongly perceptible. Jam samples were tempered for 30 minutes at room temperature (23 ± 2 °C) before filling in the three-coded plastic containers up to 2/3
level and presenting to the panel. Drinking water was provided for palate cleansing after each sample testing. The evaluation was performed in tasting booths with controlled environmental conditions (ISO, 2007).

2.7. Statistical analysis

Numerical data obtained by dynamic oscillatory measurements were analysed using Matlab R2011b by application of the modified fractional Kelvin-Voigt model equation as previously described in Belović et al. (2016).

3. Results and Discussion

3.1. Development of jam formulations

The basic formulation (Jam 1) described in Materials and Methods section was further modified to create jams with lower amount of sugar and calories, as well as jam suitable for consumption by the diabetic patients. These formulations are presented in Table 1.

Firstly, 50% of sucrose amount present in Jam 1 was substituted with stevioside, lyophilized tomato pomace and water in order to retain the same total amount of ingredients. The ratio of lyophilized tomato pomace and water (1:5.4) was taken from Jam 1 formulation to ensure that the whole amount of water present in the sample is
bound by the dietary fibre present in the tomato pomace. The amount of steviol glycoside used for the substitution of sucrose was calculated based on the fact that steviol, the most abundant steviol glycoside in the leaf of the plant, is 250–300 times sweeter than sucrose (Lemus-Mondaca et al., 2012). The obtained formulation was named Jam 2, and the process used for the manufacturing of this jam was the same as that used in Jam 1 (described in Materials and Methods section). Because the aim of the experiment was to obtain a jam with similar consistency and lower amount of sugar, evaporation was conducted on a burner until Jam 2 reached the same apparent viscosity at 100 s⁻¹ as Jam 1 (Table 3), since the consistency of Jam 1 was previously assessed as acceptable by sensory panel. The apparent viscosity was determined at a shear rate of 100 s⁻¹, since that value represents a shear rate encountered during pipe flow in food industry, consumption and spreading (Steffe, 1996). The final TSS content of Jam 2 was 30°Brix, and this value was further used for easier process monitoring.

Since Jam 2 had a slightly granular texture, it was presumed that addition of pectin could improve its textural properties. Therefore 1% LM pectin and CaCl₂ (120 mg of Ca²⁺ ions per 1 g of LM pectin, as described in Niketić-Aleksić (1988)) were added to the formulation of Jam 2 and the resulting product was labelled as Jam 3. The rheological properties of this jam were slightly different from the previous two, and it was concluded by sensory panel that apparent viscosity of Jam 3 at 100 s⁻¹ should be about 3 Pa s (Table 3). This value also corresponded to the TSS content of 30°Brix.

The creation of jam for people with diagnosed diabetes included replacement of sucrose by fructose and consisted of several steps. In the first step, the amount of sucrose in the Jam 1 formulation was substituted by the amount of fructose calculated on the
basis of sweetness index of fructose (1.6) (Zamora, Buratti, & Otero-Losada, 1998). In the next step, 50% of fructose amount was substituted with stevioside (amount calculated based on sweetness index), lyophilized tomato pomace and water in the ratio used in Jam 1 formulation (1:5.4). The consistency of these two formulations was assessed by sensory panel as not acceptable since it was more similar to pulp than to jam. In the final step, 1.25% of LM pectin and CaCl₂ were added in the ratio used in Jam 3 formulation (120 mg Ca²⁺ per 1 g of LM pectin) to obtain the acceptable consistency, which was also determined as the value of apparent viscosity at 100 s⁻¹ about 3 Pa s (Table 3).

Cinnamon was used in all jam formulations to mask potentially unpleasant bitter taste originating from phenolic compounds present in tomato pomace. Preservative (potassium sorbate) was added since products of with low soluble solids content, such as low calorie jams, are more prone to microbial spoilage than conventional products (Gajar & Badrie, 2002).

3.2. Rheological and textural properties

Rheological experiments represent useful tools for estimating mechanical and thermal stability of examined jam systems. Mechanical stability is important for jam storage, since products with insufficient mechanical stability are prone to syneresis and other structural changes which could potentially lead to rejection of product by consumers before the end of shelf life. Thermal stability is important when jam is applied as fruit filling in bakery products, either in the industry or in the household. Mechanical stability is assessed under: (1) low oscillatory strain condition within frequency sweep mode and
(2) steady shear conditions. Thermal stability is assessed under low oscillatory strain conditions within temperature sweep mode. Low oscillatory strain conditions are applied to examine systems viscoelasticity while steady shear conditions under shear rate in the range from 1 to 100 s\(^{-1}\) are applied to ensure flow of jam systems. Intensive energy dissipation during systems ordering in the direction of flow is quantified by viscosity as function of shear rate. Viscoelasticity could be assessed under low strain by measuring storage and loss moduli as function of: (1) frequency (frequency sweep mode), and (2) temperature (temperature sweep mode). Storage modulus represents a measure of reversible (elastic) structural changes while loss modulus represents a measure of irreversible (viscous) structural changes of examined systems. Irreversible structural changes can induce systems destabilization. Consequently, storage and loss moduli during frequency sweep and temperature sweep measurement ensure deeper insight into systems mechanical and thermal stabilities.

Jam systems 1 and 2 without pectin represent concentrated suspensions of tomato particles. Jam systems 3 and 4 are prepared with pectin which results in formation of network structure around the dispersed tomato particles. Tomato particles within the suspensions (systems 1 and 2) are more mobile than that within the pectin network (systems 3 and 4). Particles in suspension are disordered, while less mobile particles within the pectin network remain ordered under low oscillatory strain conditions at constant temperature. Disordered systems are stiffer than the ordered ones due to “shear thickening effects” pronounced under low strain conditions. Pectin addition restricts particle motion, and consequently the shear thickening effects for the systems 3 and 4.
The phenomenon is quantified by higher values of storage and loss moduli obtained for the jam suspensions relative to jam networks at constant temperature.

Jam suspensions without added pectin could be compared based on the proposed fractional Kelvin-Voigt model (Belović et al., 2016). This model is used to describe rheological behaviour of the jam systems under frequency sweep experiments (see Supplementary Figure 1). Jam 1 (only sucrose) is stiffer than Jam 2 (sucrose and stevioside). The stiffness is quantified by higher values of the model parameters elastic modulus ($G_e$) and effective modulus ($η$), and lower value of the damping coefficient ($α$) (Table 3). The partial substitution of sucrose (50%) by stevioside has caused softening of the system since lower amount of sucrose was available for the gelling of naturally present pectic substances in serum surrounding the tomato pomace particles. Lower amount of sucrose also caused a decrease of adhesion work in Jam 2 when compared to Jam 1 (Table 3). Jams with pectin show similar rheological behaviour. Higher concentration of pectin, equal to 1.25%, slightly increases the structure stiffness relative to pectin concentration of 1%. The increase of system stiffness is also reflected in the increase of values of textural properties, namely firmness and work of shear (Table 3). Due to the addition of pectin, the influence of fructose on system stiffness could not be estimated, although it was previously shown that gels prepared with fructose were weaker than those prepared with sucrose (Fraeye et al., 2010). Sugars generally reduce the water activity, which promotes pectin-pectin interactions rather than pectin-water interactions (Löfgren, Walkenström, & Hermansson, 2006).

However, intensive flow conditions obtained under steady shear measurement at constant temperature could orient tomato particles in the direction of flow, which induces
decrease of the flow resistance effects as well as the viscosity. Consequently, viscosity is lower for the suspensions (the systems without pectin) in comparison to the networks (systems with pectin) at the same shear rates along the entire flow curve (see Supplementary Figure 2). This is in accordance with the fact that less mobile particles entrapped within the pectin network could not orient in the direction of flow. Systems with pectin show higher hysteresis values during loading-unloading cycle compared to the systems without pectin (Table 3). Increase of the pectin concentration from 1% to 1.25% induces more intensive energy dissipation during loading-unloading cycle which results in formation of hysteresis.

Regarding the yield stress values, they are higher for the suspensions (the systems without pectin) due to the pronounced friction between the tomato pomace particles. Pectin acts like a lubricant and therefore networks (systems with pectin) have lower yield stress values (Table 3). Several models were applied on the flow curve results, and the best fitting was obtained by the application of Ostwald-de Waele model. Correlation coefficients \( r \) were lower for the suspensions due to high non-uniformity of tomato pomace particles. Consistency index of jam samples could be related to the sugar content; Jam 1 had the highest consistency index, Jams 2 and 3 had similar values, while Jam 4 had the lowest values. Flow behaviour index (deviation from the Newtonian flow) expressed similar trend; sample with the highest sugar content (Jam 1) had the lowest flow behaviour index values, while sample with the lowest sugar content (Jam 4) had the highest flow behaviour index values. The suspension-type systems generally showed higher deviations from the Newtonian flow when compared with network-type systems.
Temperature increase under constant oscillatory strain condition \( \omega = 6.26 \text{ rad/s} \) induces an additional thermal motion of particles. It is pronounced for the jam suspensions (Jam 1 and Jam 2) (Figure 1). These systems are stiffer due to thermally induced “thickening effects” relative to the systems with pectin. The phenomenon is quantified by higher values of the storage and loss moduli. Jam suspensions are thermally stable in the temperature range from 25 to 90 °C and show constant values of the storage and loss moduli with temperature increase. This is contrary to the research conducted by Sagdic et al. (2015) on the conventional rosehip marmalade, which showed that temperature increase caused lowering of storage and loss moduli values.

Jams with added pectin are softer than those without added pectin due to less mobility of tomato particles entrapped within the pectin network. These systems show constant values of the storage and loss moduli for the experimental temperatures up to 80 °C. Further temperature increase leads to breaking of the particle-pectin bounds and increase of the particle mobility. Increase of the particle mobility induces the systems stiffening due to “thickening effects” quantified by increase of the storage and loss moduli. Particle-pectin breaking bonds could not re-establish during temperature decrease. Consequently, the systems with added pectin expressed higher storage modulus values during temperature decrease compared to the same systems during temperature increase. Storage modulus of the systems with added pectin is similar to those for the systems without pectin obtained during temperature decrease. Loss modulus of the systems with pectin is higher than those obtained for the systems without pectin obtained during temperature decrease. Higher values of the loss modulus represent the consequence of additional
energy dissipation during particle-pectin bonds breaking obtained during temperature decrease.

Storage modulus is higher during temperature decrease relative to temperature increase for the systems without added pectin. This phenomenon represents the consequence of thermally induced irreversible structural changes of particles which induce their swelling. Loss modulus remains approximately the same during temperature decrease relative to temperature increase for the systems without added pectin. In contrary, increase of the storage and loss moduli during temperature decrease relative to temperature increase becomes significant for the systems with added pectin, which is caused by thermally induced breaking of the particle-pectin bonds. Increase of the pectin concentration from 1% to 1.25% induces increase of the storage and loss moduli during temperature sweep experiments.

3.3. Sensory properties

Sensory properties of low calorie jams prepared from tomato pomace are presented in spider plot (Figure 2). Syneresis was the most prominent in Jam 4, indicating that the lowest amount of water was bound due to the lowest sugar content. The results for viscosity obtained by sensory panel evaluation are in accordance with the results obtained by the rheological measurements. Namely, samples with added pectin (Jams 3 and 4) were assessed as more viscous than samples without added pectin (Jams 1 and 2). Spreadability could be related to the stickiness and work of adhesion obtained by the textural measurements, but opposite to the expectation that the stickier sample would be
less spreadable. Namely, the more adhesive samples are those containing pectin (Jams 3 and 4) and they are at the same time more spreadable, since tomato pomace particles are incorporated in pectin network which acts as a lubricant. On the other hand, the suspensions (Jams 1 and 2) have more granular structure, as expected.

The intensity of tomato odour could be related to the tomato pomace content in formulation – the higher the amount of tomato pomace, the more prominent tomato odour was present. Spicy odour is the most expressed in Jam 4, indicating that combination of fructose and stevioside has enhanced the odour of spices. Jam 1 (containing only sucrose) had more prominent spicy odour than the samples containing mixture of sucrose and stevioside.

The sample prepared with sucrose (Jam 1) was the sweetest, followed by the sample with 50% substitution of sucrose with stevioside and added pectin (Jam 3). Although sucrose was substituted by fructose in ratio given in the literature, Jam 4 was perceived as the least sweet. This could be explained by the fact that fructose in higher concentrations has lower sweetness index (Zamora et al., 1998). Jam 2 was assessed as the sourest, followed by the Jam 4. This could be explained by the fact that pectin masks sour taste, making Jam 3 perceived as sweeter than the corresponding formulation without added pectin (Jam 2). None of jam samples was assessed as bitter, although it was expected since tomato pomace contains phenolic compounds which could contribute to the bitterness. Aftertaste was present only in samples with added pectin, and it was more intensive in sample prepared with sucrose (Jam 3).

Tomato flavour is the most pronounced in Jam 2, probably since it contains less sugar than Jam 1 but does not contain pectin which masks the tomato flavour. Spicy flavour
was more prominent in samples without added pectin, indicating that pectin masks both tomato and spicy flavour.

3.4. Proximate composition and water activity

Since one of the aims of this study was to create value added products – jams with increased amount of dietary fibre, proximate composition of low calorie jams produced from tomato pomace was determined (Table 4). Besides its role in pectin gelling, sugar also acts as a preservative in gelled products, such as jams, by reducing the water activity in these products. Therefore, the water activity of low calorie jams was determined and is presented in Table 4.

All four jams were prepared with the total soluble solid content lower than in commercial products (CODEX, 2009). This has led to lower total carbohydrate content (17.23-43.81%) and lower energy value (87.1-193.7 kcal/100 g) of all jams when compared to commercial apricot jam (64.40% and 242 kcal/100 g, respectively) as defined by the USDA standard reference database. Energy value reduction obtained by the replacement of sucrose by natural sweeteners (stevioside and fructose) in basic (Jam 1) formulation is presented in Table 4, expressed as the percentage reduction of Jam 1 energy value. Reducing sugars present in jam formulations 1-3 are predominantly glucose and fructose originating from tomato pomace (Oms-Oliu et al., 2011). Due to its formulation, Jam 4 had the lowest energy value, roughly only 36% of commercial products. Jam 4 is also characterized by the lowest total carbohydrate content, comprised
almost only of reducing sugars due to the substitution of sucrose by fructose. Therefore Jam 4 is suitable for consumption by the diabetic patients.

All jam samples had roughly 2-3 times higher protein content than commercial apricot jam (0.70%) defined by the USDA standard reference database, which can be explained by the presence of tomato seeds from pomace. Fat content showed only small variations between the prepared jams. Low calorie jams produced from tomato pomace can bear the label “source of fibre” or “containing fibre” according to Regulation EC No 1924 (2006) on nutrition and health claims made on foods, since they contain more than 3 g/100 g or 1.5 g/100 kcal of dietary fibre. Namely, the formulated jams contain 15-20 times more dietary fibre than apricot jam (0.3 g/100 g) defined in the USDA standard reference database, and even 2.12-6.79 g of dietary fibre per 100 kcal of product. This indicates that significant part of calories (~17 kcal) in created products originates from proteins and dietary fibre, contrary to the commercial product in which calories originate almost exclusively from sugars.

Total acid content was highest in the Jam 4 as a consequence of formulation which included the highest amount of tomato pomace. pH values of all jam samples were in interval 3.5-3.6 (lower than 4.0), and therefore are considered microbiologically stable for more than one year if preservatives and pasteurisation are applied (Rajchl et al., 2010). pH values around 3.5 are also favourable for LM pectin gelling, since at low pH values carboxyl groups in LM pectin are protonated and can form hydrogen bonds independently of the presence of calcium salts (Fraeye et al., 2010). Jam products are considered safe from development of most bacteria when their water activity is lower than 0.86 (Besbes et al., 2009). However, A_w values of jams created in this study were
higher than 0.86 and especially high for products in which sucrose was substituted with other natural sweeteners (0.96), indicating that these products might have shorter shelf life due to the faster colonization of acidophilic microorganisms. Therefore, further studies should include the determination of the best preservation technique and shelf life of created products.

4. Conclusions

In this study, four jam formulations were developed: basic formulation (Jam 1) containing sucrose and without added pectin; Jam 2 in which sucrose was partially (50%) replaced by stevioside; formulation 3 in which 50% of sucrose was also replaced by stevioside but with added low-methoxyl pectin; and Jam 4 in which sucrose was completely replaced by fructose and stevioside, making this formulation suitable for diabetic patients. Jam formulations 1 and 2 were prepared without addition of gelling agents and represent concentrated suspensions of tomato particles. Jam formulations 3 and 4 were prepared with addition of low-methoxyl pectin which resulted in formation of network structure around the dispersed tomato particles. Mechanical and thermal stability of jams were estimated by application of low oscillatory strain and steady shear rheological measurement due to their importance for storage and processing. Jam suspensions (formulations 1 and 2) were thermally stable in the temperature range of 25-90 °C and showed constant values of the storage and loss moduli with temperature increase and decrease, indicating their potential use as fruit fillings. Jams prepared with LM pectin (formulations 3 and 4) were characterized by the higher work of adhesion.
Contrary to the expectations, these formulations were assessed by the sensory panel as more spreadable due to the fact that tomato pomace particles are incorporated in pectin network which acts as a lubricant. Jam formulations were characterized by the lower total carbohydrate content (17.23-43.81%) and lower energy value (87.1-193.7 kcal/100 g) when compared to commercial products. Tomato pomace jams contained 15-20 times more dietary fibre than commercial apricot jam. High water activity values of jams indicate that these products might have shorter shelf life due to the faster colonization of microorganisms.

Acknowledgements

This work is a result of research within the project “Development and utilization of novel and traditional technologies in production of competitive food products with added value for national and global market - CREATING WEALTH FROM THE WEALTH OF SERBIA” (grant number III46001), supported by the Ministry of Education, Science and Technological Development, Republic of Serbia. The authors would like to thank Vinipex d.o.o. for providing the LM pectin sample.

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

References


Figure captions:

Figure 1. Temperature change under constant oscillator strain condition (temperature sweep) for low calorie jams prepared from tomato pomace; a) storage modulus ($G'$); b) loss modulus ($G''$)

Figure 2. Sensory properties of low calorie jams prepared from tomato pomace

Supplementary material:

Supplementary Figure 1. Change of storage and loss moduli during frequency sweep mode (experimental data and model prediction) for the representative jam sample (Jam 3).

Supplementary Figure 2. Flow curves of low calorie jams prepared from tomato pomace presented on semi-log plot.
• Four low calorie jams were created from tomato pomace
• Jams contained 15-20 times more dietary fibre than commercial apricot jam
• Jams prepared without pectin were thermally stable from 25 to 90°C
• Jams prepared with pectin were assessed by the sensory panel as more spreadable
Table 1. Basic formulation (Jam 1) and developed formulations (Jam 2, 3 and 4) used for the manufacturing of low calorie jam from tomato pomace.

<table>
<thead>
<tr>
<th>Ingredients needed for manufacturing of approx. 100 g of jam</th>
<th>Jam 1</th>
<th>Jam 2</th>
<th>Jam 3</th>
<th>Jam 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.4</td>
<td>88.6</td>
<td>112.4</td>
<td>112.8</td>
</tr>
<tr>
<td>Lyophilized tomato pomace</td>
<td>13.4</td>
<td>16.4</td>
<td>16.4</td>
<td>17.6</td>
</tr>
<tr>
<td>Sucrose</td>
<td>38.4</td>
<td>19.2</td>
<td>19.2</td>
<td>-</td>
</tr>
<tr>
<td>Fructose</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>12.0</td>
</tr>
<tr>
<td>Stevia</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Citric acid (E 330)</td>
<td>0.72</td>
<td>0.72</td>
<td>0.72</td>
<td>0.72</td>
</tr>
<tr>
<td>LM pectin</td>
<td>-</td>
<td>-</td>
<td>1.44</td>
<td>1.80</td>
</tr>
<tr>
<td>CaCl₂</td>
<td>-</td>
<td>-</td>
<td>0.48</td>
<td>0.60</td>
</tr>
<tr>
<td>Cinnamon</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Potassium sorbate (E 202)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 2. Sensory descriptors and their definitions used for the sensory analysis of low calorie jams prepared from tomato pomace.

<table>
<thead>
<tr>
<th>Descriptor</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Intensity of syneresis: Evaluation of the amount of water separated on the jam surface.</td>
</tr>
<tr>
<td>Texture</td>
<td>Viscosity: Degree of resistance to flow. Evaluated by the rate of flow of liquid when sample is poured from a spoon.</td>
</tr>
<tr>
<td></td>
<td>Spreadability: Force needed to spread the jam into thin layer using a spoon.</td>
</tr>
<tr>
<td></td>
<td>Granularity: The perception of rough particles during consumption.</td>
</tr>
<tr>
<td>Odour</td>
<td>Tomato: Odours associated with fresh tomato evaluated by smelling.</td>
</tr>
<tr>
<td></td>
<td>Spicy: Odours associated with various spices evaluated by smelling.</td>
</tr>
<tr>
<td>Taste</td>
<td>Sweet: Basic taste produced by sugars and sweeteners.</td>
</tr>
<tr>
<td></td>
<td>Sour: Basic taste produced by acids.</td>
</tr>
<tr>
<td></td>
<td>Bitter: Basic taste produced by substances such as caffeine, quinine etc.</td>
</tr>
<tr>
<td>Aftertaste</td>
<td>Lingering taste in the mouth after swallowing.</td>
</tr>
<tr>
<td>Flavour</td>
<td>Tomato: Aromatics or volatiles associated with fresh tomato.</td>
</tr>
<tr>
<td></td>
<td>Spicy: Aromatics or volatiles associated with cinnamon.</td>
</tr>
</tbody>
</table>
Table 3. Flow curve parameters, modified fractional Kelvin-Voigt model parameters, and textural parameters of low calorie jams prepared from tomato pomace.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Jam 1</th>
<th>Jam 2</th>
<th>Jam 3</th>
<th>Jam 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield stress, $\tau_0$ (Pa)</td>
<td>426.40 ± 14.14</td>
<td>314.45 ± 37.69</td>
<td>30.87 ± 8.47</td>
<td>67.62 ± 18.75</td>
</tr>
<tr>
<td>Apparent viscosity at 100 s$^{-1}$ (Pa s)</td>
<td>2.040 ± 0.176</td>
<td>2.052 ± 0.240</td>
<td>3.275 ± 0.156</td>
<td>2.830 ± 0.314</td>
</tr>
<tr>
<td>Hysteresis loop area, S (Pa/s)</td>
<td>2094.0 ± 120.2</td>
<td>3228.0 ± 937.6</td>
<td>4415.5 ± 450.4</td>
<td>4050.5 ± 72.8</td>
</tr>
<tr>
<td>Consistency index, $K$ (Pa s$^n$)</td>
<td>113.27 ± 7.26</td>
<td>101.83 ± 14.96</td>
<td>102.42 ± 11.14</td>
<td>78.27 ± 10.85</td>
</tr>
<tr>
<td>Flow behaviour index, $n$ (-)</td>
<td>0.105 ± 0.006</td>
<td>0.133 ± 0.056</td>
<td>0.252 ± 0.021</td>
<td>0.271 ± 0.022</td>
</tr>
<tr>
<td>Coefficient of correlation, $r$</td>
<td>0.7572</td>
<td>0.7937</td>
<td>0.9239</td>
<td>0.9351</td>
</tr>
<tr>
<td>Elastic modulus, $G_s$ (Pa)</td>
<td>(0.40 ± 0.01)x10$^4$</td>
<td>(0.23 ± 0.01)x10$^4$</td>
<td>(0.06 ± 0.01)x10$^4$</td>
<td>(0.08 ± 0.01)x10$^4$</td>
</tr>
<tr>
<td>Effective modulus, $\eta$ (Pas$^n$)</td>
<td>(0.33 ± 0.01)x10$^4$</td>
<td>(0.15 ± 0.01)x10$^4$</td>
<td>(0.14 ± 0.01)x10$^4$</td>
<td>(0.10 ± 0.01)x10$^4$</td>
</tr>
<tr>
<td>Damping coefficient, $\alpha$ (-)</td>
<td>0.25 ± 0.01</td>
<td>0.29 ± 0.01</td>
<td>0.29 ± 0.01</td>
<td>0.29 ± 0.01</td>
</tr>
<tr>
<td>Firmness (N)</td>
<td>49.13 ± 1.44</td>
<td>32.03 ± 3.26</td>
<td>41.41 ± 0.78</td>
<td>35.50 ± 1.97</td>
</tr>
<tr>
<td>Work of shear (J)</td>
<td>0.043 ± 0.002</td>
<td>0.023 ± 0.002</td>
<td>0.038 ± 0.002</td>
<td>0.028 ± 0.002</td>
</tr>
<tr>
<td>Stickiness (N)</td>
<td>-12.14 ± 1.25</td>
<td>-7.25 ± 0.73</td>
<td>-18.22 ± 0.77</td>
<td>-15.96 ± 0.82</td>
</tr>
<tr>
<td>Work of adhesion (J)</td>
<td>-0.013 ± 0.001</td>
<td>-0.007 ± 0.001</td>
<td>-0.020 ± 0.003</td>
<td>-0.015 ± 0.003</td>
</tr>
</tbody>
</table>

Results are presented as means ± standard deviations of three replicates ($n = 3$).
Table 4. Proximate composition and water activity of low calorie jams prepared from tomato pomace

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Jam 1</th>
<th>Jam 2</th>
<th>Jam 3</th>
<th>Jam 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total soluble solids (°Brix)</td>
<td>48.33</td>
<td>30.94</td>
<td>30.73</td>
<td>24.26</td>
</tr>
<tr>
<td>pH value</td>
<td>3.55</td>
<td>3.57</td>
<td>3.50</td>
<td>3.56</td>
</tr>
<tr>
<td>Total acids as citric (%)</td>
<td>0.30</td>
<td>0.33</td>
<td>0.30</td>
<td>0.41</td>
</tr>
<tr>
<td>Total carbohydrates (%)</td>
<td>43.81</td>
<td>21.99</td>
<td>22.25</td>
<td>17.23</td>
</tr>
<tr>
<td>Total sugars (%)</td>
<td>43.81</td>
<td>21.99</td>
<td>22.25</td>
<td>17.23</td>
</tr>
<tr>
<td>Reducing sugars (%)</td>
<td>14.36</td>
<td>7.25</td>
<td>6.94</td>
<td>16.95</td>
</tr>
<tr>
<td>Sucrose (%)</td>
<td>28.82</td>
<td>14.00</td>
<td>14.54</td>
<td>0.26</td>
</tr>
<tr>
<td>Fats (%)</td>
<td>0.16</td>
<td>0.09</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>Proteins (%)</td>
<td>2.03</td>
<td>1.42</td>
<td>1.32</td>
<td>1.37</td>
</tr>
<tr>
<td>Dietary fibre (%)</td>
<td>4.44</td>
<td>5.44</td>
<td>5.50</td>
<td>5.91</td>
</tr>
<tr>
<td>Energy value (kJ/kcal per 100 g)</td>
<td>820.7/193.7</td>
<td>444.8/105.3</td>
<td>448.8/106.3</td>
<td>367.2/87.1</td>
</tr>
<tr>
<td>Energy value reduction (%)</td>
<td>0.0%</td>
<td>45.6%</td>
<td>45.1%</td>
<td>55.0%</td>
</tr>
<tr>
<td>Water activity</td>
<td>0.90</td>
<td>0.96</td>
<td>0.96</td>
<td>0.96</td>
</tr>
</tbody>
</table>

Values are expressed as a mean of three replications.