Physicochemical characteristics of sauce model systems: Influence of particle size and extruded flour source

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Abstract

Physically modified extruded flours are suitable ingredients for cold preparation of products such as creams and sauces. The rheological and textural properties and stability of model sauces prepared with wheat and rice extruded flours with three different particle size fractions were assessed. All tested sauces showed non-Newtonian, shear-thinning and thixotropic fluid characteristics. Sauces made with rice extruded flours, with lower protein and amylose contents, presented lower shear-thinning behaviour, consistency index and yield stress than wheat based sauces. Rice sauces also displayed a less compact microstructure and lower viscoelastic character but a higher resistance to freeze-thaw process. Regarding particle size, the finest flours showed lower values of consistency index, yield stress, and G' and G'' moduli but led to higher syneresis. Overall, results proved that pregelatinised extruded flours can be used in sauces applications without heating, but their properties greatly depend on the cereal type and its particle size.

Keywords: white sauce; extrusion; flour; rheology; stability

1 Introduction

Sauces are a product of high added value and represent an important part of the human diet. Essentially, the formulation of sauces includes three main ingredients: water (or milk), starch (or flour) and oil. Among the different ingredients, starch plays a key role in the rheological and textural properties obtained. Therefore, in recent years, different studies have been focused on investigating the influence of the starch type in the microstructure and rheological properties of sauces (Arocas et al., 2009a, c), the sensorial properties (Arocas et al., 2010b), or even, in their interaction with hydrocolloids (Arocas et al., 2009b), proteins (Guardeño et al., 2012; Quiles et al., 2012) and other ingredients (Arocas et al., 2010a). Furthermore, during the last decade, the hectic lifestyle that people in western countries generally has led to a growing interest in convenience foods or foods that are quick and easy to prepare. These prepared products are frequently accompanied by sauces, in which starch plays an important functionality.

In terms of preparation, sauces need to be cooked to develop their viscous properties, based on the gelatinization of starch granules. To ease the preparation and remove or reduce this heating stage, pregelatinised starches and flours can be used. Hydrothermal treatments such as extrusion or drum-drying foster the gelatinization of the starch when this is subjected to enough heat and moisture, enabling the attainment of products with higher water absorption capacity and thickening power in cold temperatures (Chiu and Solarek, 2009; Doublier et al., 1986; Hagenimana et al., 2006; Martínez et al., 2014b). Therefore, pregelatinised flours represent an alternative to starchy products allowing the preparation of sauces with no need for heating. Drum-drying treated flours have higher viscosities and less starch solubilisation than extruded flours (Doublier et al., 1986). However, extrusion is a very versatile and relatively low cost process, with less environmental impact and less space requirements than drum-drying, in such a way that this technique is being widely used in the food industry. Added to starch gelatinization, a denaturation of proteins (Camire et al., 1990) and the formation of amylose-lipid complexes (Hagenimana et al., 2006) is also promoted, which will affect the rheological properties of the pastes. Furthermore, the particle size and the type of cereal used can also influence the properties of the extruded flours (Martínez et al., 2014a, b). In those works it was demonstrated that as extrusion intensity increased (i.e. barrel temperature and moisture content) higher gelatinization of starch was produced, but a minimum barrel temperature and feed moisture content were necessary to break the starch structure and induce gelatinization phenomena. When those processing requirements were met, an important increase in cold water absorption capacity and swelling power of the flours was found, being those values generally higher when using coarser flours (132-200 µm). In fact, due to this ability to absorb water at low temperatures, pregelatinised extruded flours have been used to improve the hydration in bread doughs (Martínez et al., 2013), as well as a fat replacements in mayonnaises (Román et al., 2015a) and cakes (Román et al., 2015b).

The rheological behaviour of emulsions, such as sauces, is a critical characteristic that must be studied as it is closely related to the sensory attributes, quality, and processing properties of a food product (McClements, 2005). Most importantly, it provides

fundamental insights into the structural organization and interaction between the components within the emulsion (McClements, 2005). Moreover, the stability towards freezing is also an important aspect to consider since many convenience foods containing sauces are preserved this way so as to extend their shelf life. In general, these sauce properties have been studied on different native or modified starches. Nevertheless, to the best of our knowledge, there are no studies based on the use of pregelatinised extruded flours for sauce development.

The objective of this study was to assess the effect of extruded flours of different particle sizes on the rheological characteristics and stability towards freezing of model sauces with no need for heating. To achieve this aim, two types of extruded flours were selected, wheat flour, as it is the most commonly used cereal in developed countries, and rice flour, the most commonly used gluten-free flour.

2 Materials and methods

2.1 Materials

The extruded rice and wheat flours used in this study commercially available as Ooc 190 and Toc 190, respectively, were provided by Molendum Ingredients (Zamora, Spain). The extrusion conditions were chosen according to the manufacturer expertise in order to ensure starch gelatinisation, and DSC analyses of the flours were carried out to confirm that gelatinisation was complete. In this way, when flour samples were analysed, a flat DSC curve with no endothermic peak in the range of starch gelatinization was observed, indicating that gelatinization was complete. The extrusion treatment was carried out in a single screw extruder Bühler Basf (Bühler S.A., Uzwil, Switzerland). The diameter of the extruder was 140 mm, the length to diameter (L/D) ratio of the extruder was 20:1 and the screw speed was 340 rpm. The diameter of the die hole and the number of holes used was 8 mm and 18 holes, respectively. The flours were extruded at a maximum barrel temperature of 160 °C, a feed rate of 500 kg/h and a feed moisture content of 25%. The extruded products were dried by convection air until reaching 10% moisture and then ground with a compression roller to a particle size below 200 µm. Each of the flours were sieved and separated into three fractions according to the amount of particles remaining on each sieve. The different particle sizes obtained were as follows: fine (less than 80 µm), intermediate (80-130 µm) and coarse (130-200 µm). The sieving process was performed with an Automatic Bühler MLI300B Sieve (Braunschweig, Germany) for 15 min. Each of the fractions was stored separately in sealed plastic bags until their analysis and use. Particle size of the flours was measured in duplicate with a laser diffraction particle size analyser (Mastersizer 3000, Malvern Instruments, Ltd., Worcestershire, UK) equipped with an Aero S unit. The mean diameter of equivalent volume D(4,3), which indicates the central point of the volume distribution of the particles, was recorded. For wheat extruded flours, D(4,3)values were 72.4 µm, 146.0 µm and 279.5 µm for fine, intermediate and coarse fractions, respectively. D(4,3) values of rice flours were 78.5 µm, 151.0 µm and 213.5 µm for fine, intermediate and coarse fractions, respectively.

2.2 Methods

2.2.1 Flour characterisation

The characterisation of the extruded flours was carried out before the preparation of the sauces. Flours were analysed following AACC Methods (AACC, 2012) for moisture, method 44-16.01 and protein method 46-30.01 with a Leco TruSpec device (Leco, St. Joseph, MI, USA). Amylose-amylopectin content was measured using Concanavalin A precipitation method (K-AMYL, Megazyme International, Wicklow, Ireland). Determinations were carried out in duplicate.

Water binding capacity (WBC) defined as the amount of water retained by the flour after it has been subjected to centrifugation was measured as described by method 56.30 (AACC, 2012). After centrifugation, the supernatant was decanted into an evaporating dish and the residue of the eppendorf tube was weighed (Wr). The weight of dry solids in the supernatant was recovered by evaporating the supernatant at 105 °C till constant weight. Water solubility index (WSI) was calculated as the amount of dry solids recovered in the supernatants divided by the initial sample weight in percentage (g/100g). Determinations were carried out in triplicate.

Pasting properties of flours were analyzed using the standard method (AACC 2012), (AACC 61-02.01) with a Rapid Visco Analyser (RVA-4) (Newport Scientific Pty Ltd., Warriewood, Australia) controlled by Thermocline software (Newport Scientific Pty. Limited, Warriewood, Australia) for Windows. All flours were run in duplicate.

2.2.2 Sauces preparation

Model sauces were prepared using flour (16.78%), sunflower oil (2.68%) and water up to 100%. It is noteworthy than extruded flours have less thickening power than the native ones after cooking (Martínez et al., 2014a, b), so it has been necessary to increase the flour content of the sauces to obtain a texture similar to conventional sauces. All the ingredients were placed in a food processor (Thermomix TM31, Wuppertal, Germany), and mixed at 1100 rpm and 30°C for 10 min. The resulting sauces were placed in glass beakers, covered with plastic film. Two sauces were prepared for each of the particle sizes of the two flours studied. In order to be able to study freshly prepared sauces, measurements were performed within the same day.

2.2.3 Sauces characterisation

2.2.3.1 Optical microscope observation

Sauces were examined with a DM750 microscope (Leica Microsystems, Wetzlar, Germany) with 20x times magnification, fitted with an EC3 video camera. Images were captured with LAS-EZ software (Leica Microsystems, Wetzlar, Germany). First of all, the sample was placed on a glass microscope slide and covered with a cover slip. The slides were compressed under a 1 kg weight for 2 minutes to create a sample layer of uniform thickness. Micrographs were performed on the freshly prepared sauces at least twice in two random points of each sample.

2.2.3.2 Rheological analysis

Rheological properties of sauces were determined with a Thermo Scientific Haake RheoStress1 rheometer (Thermo Fisher Scientific, Schwerte, Germany) and a Phoenix II P1-C25P unit to control the temperature, which was fixed at 30 °C for all analyses. All tests were monitored with RheoWin 4 Job Manager software and rheological parameters were calculated with Rheowin 4 Data Manager software (Thermo Fisher Scientific, Schwerte, Germany). All rheological measurements were performed twice on each freshly prepared sauce.

Flow behaviour

The flow behaviour measurements of sauces were carried out in control rate mode with a concentric cylinder system (Z34 DIN Ti). The shear rate was increased linearly from 1 to 100 s^{-1} for 200 s (up curve), then this shear rate (100 s^{-1}) was maintained for 150 s and was finally reduced to 1 s^{-1} in a further period of 200 s (down curve). This measurement is useful since it simulates the forces that food products (such as sauces) might experience during preparation and consumption, such as stirring, pouring, and mastication (Chung et al., 2013). Furthermore, this shear rate is within the range typically used to simulate oral conditions (McClements, 2005). The data of the up curve was adjusted to the Herschel-Bulkley equation since it was the best fit to the experimental data (\mathbb{R}^2 equal to or higher than 0.99):

 $\sigma \!\!= \sigma_o \! + K {(\dot{\gamma})}^n$

Where σ is the shear stress (Pa), $\dot{\gamma}$ is the shear rate (s⁻¹), K is the consistency index (Pa·sⁿ), σ_0 is the critical shear stress or yield stress (Pa) and n is the flow behaviour index. Moreover, the "relative thixotropic area" was calculated as the area between the rising and falling curves divided by the area under the up curve, which allows a correct comparison of the rate of internal structural breakdown in systems with different viscosities (Dolz et al., 2000).

Viscoelastic behaviour

The viscoelastic properties of sauces were measured with serrated titanium parallel plate with a diameter of 60 mm and a gap distance between plates of 1 mm. The sample surface exposed to air between the plates was covered with Panreac vaseline oil (Panreac Química SA, Castellar del Vallés, Spain) to prevent moisture loss. In order to determine the minimum resting time allowed to aid structure recovery and temperature equilibration in further analysis, a time sweep within the linear viscoelastic region (at a stress value within the linear viscoelastic region from the stress sweep) for 1800 s was carried out. After the time sweep, a resting time of 600 s was selected for all rheological tests. The linear viscoelastic region was determined by performing a stress sweep (0.01 to 10 Pa) at a frequency of 1 Hz. Subsequently, a dynamic frequency sweep was executed using a shear stress value within the linear viscoelastic region (previously established by the stress sweep), over a frequency range between 10 and 0.1 Hz. Viscoelastic parameters, such as storage modulus (G') and loss modulus (G"), were acquired. G' represents the energy stored in the material or that which is recoverable per cycle of deformation while G" is a measure of the energy which is lost as viscous dissipation per cycle of deformation.

2.2.3.3 Syneresis

Syneresis was assessed on the freshly prepared sauces on the same day and after storing the samples at -18° C for 24 h following the method of Heyman et al. (2010) with modifications. Samples of 15.00 g (W₀) of sauce were placed in falcon centrifuge tubes

(50 ml) and centrifuged for 15 min at 4000 \times g. The separated liquid was then removed and weighed (W₁). Syneresis was expressed as weight percent of the decanted liquid phase.

Syneresis= $(W_1/W_0) \ge 100$

To perform the measurement after freezing, samples were gradually thawed at room temperature during 2 h. Syneresis was carried out in duplicate for each of the sauces.

2.2.4 Statistical analysis

The obtained data was subjected to a one-way analysis of variance (ANOVA) using the LSD Fisher test (p<0.05). All analyses were performed with Statgraphics Centurion XVI software (StatPoint Technologies Inc., Warrenton, USA).

3 Results and discussion

3.1 Flour characterisation

Moisture, protein and amylose content of the different extruded flours are displayed in Table 1. In terms of moisture content, barely any significant differences were observed between the different flours studied and among the different particle size fractions of the rice samples, but for wheat flours slightly higher values of moisture content were detected for the finest particle sizes compared to the coarsest fraction. These small differences are due to the fact that the flours were previously dried to levels of 10% moisture content after being extruded.

Regarding amylose content, wheat flours presented more amylose than rice flours for each of the particle size fractions studied. Despite amylose content depends on the different varieties, amylose content is usually higher in wheat starches compared to rice starches (Waterschoot et al. 2015). Meanwhile, the intermediate particle size of both types of flour presented the lower values of amylose content. On the contrary, the protein content was significantly different for each type of flour and its particle size. In general, the protein content is higher for wheat flours compared to rice flours (Delcour and Hoseney, 2010). It is important to highlight the high protein content of the finest fraction of wheat flour (21.04g/100g) in comparison to the rest of the flours. The finest fraction of rice flour also presented the highest values of protein compared to the other two particle sizes. De la Hera et al. (2013) and Kim and Shin (2014), when assessing the protein content of the rice flour, obtained opposite results, reporting an increase in the protein content when the particle size was increased. However, the flours studied in those articles were not subjected to extrusion treatment. During extrusion treatment the gelatinisation and breakage of the starch granules as well as protein denaturation takes place, and the flour components are mixed together. In addition, flours were remilled after extrusion, thus, being able to alter the distribution of these components as a function of particle size. In this way, both protein denaturation during extrusion and further milling may have contributed to the increase in the amount of protein in the finest fractions. This fact may suggest that the weaker fractions of the extruded product, and therefore, the particles which break into smaller fragments, are those with a higher protein content and lower starch content.

Regarding water binding capacity of the flours, no great differences were observed between the extruded flours. Nevertheless, fine wheat presented the significantly lowest WBC value compared to the rest, which is likely to be attributed to its high protein content. Although proteins exhibit greater water absorption capacity than native starches (Manley, 2000), the extrusion process increases flours capacity to absorb water up to more than 500% due to starch gelatinisation (Martínez et al., 2014a). Therefore, higher protein content, and consequently lower starch content in this type of flours will reduce its water absorption capacity. WSI indicated that wheat extruded fractions were less soluble in water than rice counterparts which would suggest that rice flour was more degraded during extrusion treatment. In agreement with these results, Chinnaswamy and Hanna (1990) found that the more degraded samples after extrusion demonstrated higher solubility values and that water solubility increased with decreasing amylose contents.

3.2 Pasting behaviour of flours

The pasting behaviour of the flours studied is depicted in Figures 1a and 1b. All the samples exhibited very similar pasting profiles, with a cold peak viscosity before heating as a result of the pregelatinisation that occurred during extrusion process. These pasting profiles were similar to those obtained in other studies with extruded flours (Hagenimana et al., 2006; Martínez et al., 2014a, b). Extruded flours, as opposed to native flours, have the ability to absorb water and thicken at low temperature (Wolf, 2010). The peak viscosity provides a measure of the thickening power of the starch (Sanz et al., 2016). In general, wheat flours presented higher viscosity peaks than rice flours, which could be related to the higher solubility in water of rice extruded flours and also to the different starch structure of both flours. For both wheat and rice flours, the time needed to reach the peak viscosity was inversely related to the particle size, since fine flours needed less time to reach the peak than intermediate or coarse flours. This fact indicates that with great ease the fine particle sizes are hydrated, being associated with their higher surface to volume ratio. Fine flours also presented lower peak values compared to the other particle sizes, which may be to do with their higher protein content, and hence, lower starch content, being responsible for the peak viscosity. Furthermore, in the case of wheat extruded flours it is noteworthy that the cold peak viscosity was significantly higher for the intermediate fraction which could also be linked to its lower protein content (i.e. more pregelatinised starch able to absorb water) compared to the other particle size fractions.

After the cold peak was reached, a decrease in viscosity was produced when heating followed by a slight increase in viscosity during cooling. The retrogradation trend was scarcely observed during cooling, somewhat fostered during cooling after previous extrusion. Doublier et al. (1986) had already correlated the reduction in final viscosity and setback with the fragmentation of the amylose chains during extrusion, which might lose the ability to associate and retrograde during cooling. Furthermore, this slight increase in viscosity during the cooling stage should be mostly associated with the increase in viscosity linked to temperature reduction (Sanz et al., 2016). The viscosity profile after the peak was similar for all the rice flours, with no differences with regards to particle size. Conversely, for wheat flours, a lower viscosity profile was evident for the fine particle size, which may be related to its remarkably high protein content and then, low starch content, leading to a poorer thickening ability.

3.3 Microstructure of sauces

The microstructure of the sauces showed in Fig. 2 consisted of a network which was mainly composed of protein and the starch components forming the continuous phase, and some oil droplets immersed in the network. Similar structures were found in the microstructure of all the sauces regardless of the particle size used. Regarding the type of flour used for sauce making, it seemed that wheat sauce particles (a, b, c) were more aggregated forming a tightly packed network structure whereas the particles in rice sauces (d, e, f) seemed more dispersed giving rise to a less cohesive structure with some voids and apparently lower number of small oil droplets (see arrows). Guardeño et al. (2012) reported similar results for sauces made with the same amount of oil content. These authors observed that rice starch based sauces showed a greater degree of dispersion in the continuous phase, less capacity to swell and lower tendency to aggregate than corn starch sauces. Therefore, this less aggregated structure of rice sauces is expected to bring about a lower viscosity.

3.4 Flow behaviour

Herschel-Bulkley model was used to characterise the flow behaviour of sauces (Table 2). All the sauces exhibited non-ideal plastic behaviour, with a critical shear stress below which no flow was observed. Above this critical shear stress, all the sauces exhibited a non-Newtonian shear-thinning behaviour (n<1) in which the viscosity decreases as shear rate increases. Shear-thinning behaviour is characteristic for starch gels and more specifically for starch based sauces (Heyman et al., 2010; Mandala et al. 2004). The observed shear-thinning behaviour of sauces may be attributed to structural breakdown and evolution of the particle's alignment in the direction of flow followed by the decrease in physical interactions between adjacent polymer chains (Hosseini-Parvar et al. 2010). A greater shear-thinning behaviour was found with wheat sauces, with lower values of n as the particle size of the flour decreased. However, no differences were observed for the different particle sizes of rice flours. An increase in shear-thinning character indicates that more mutual entanglements were formed in the emulsion (Ma and Boye, 2013). A strong negative correlation (r = -0.850; p < 0.001) was found between this parameter and amylose content of the samples. The increase in shear-thinning character with increasing amylose content was generally attributed to an increase in entanglements between amylose chains, since the highly branched amylopectin was not expected to form effective entanglements (Willett et al., 1997). This theory is confirmed by the micrographs of the sauces previously explained, where wheat sauces, with higher amylose content, demonstrated a more compact structure.

The consistency coefficient K can be considered as a measure of the resistance to flow (Heyman et al., 2010). Consistency index was significantly higher for wheat sauces compared to rice ones, indicating a stronger structure of the sauce. In actual fact, other authors (Guardeño et al., 2012; Quiles et al., 2012) have related the increase in viscosity and consistency of sauces with the number and interaction or aggregation of the sauce components, in such a way that larger aggregates can be associated with higher viscosities. Mandala et al. (2004) also stressed that the resistance to shearing forces is increased as macromolecules' entanglements increase. Regarding the particle size of the

sauces, the finest flours led to the lowest values of K, but significant differences were only observed between the fine and the two coarsest fractions of wheat sauces.

The yield stress of a product is defined as the stress above which a material starts to flow. All sauces demonstrated yield stress (σ_0), which is perceived to be particularly important for salad dressings because it allows the retention of their ability to keep nonfluid on the salad surface (Liu et al., 2007). Yield stress or critical shear stress was also significantly higher for each of the particle sizes of the wheat sauces in comparison to rice sauces, following the trend observed by the consistency index. For other low-fat sauce model systems, Chung et al. (2013) found that suspensions containing thermally processed corn starch exhibited a critical shear stress around 25 Pa, similar to those obtained for rice extruded flours. Taking into account the different particle sizes, rice based sauces revealed that the yield stress significantly increased as the particle size increased also, suggesting that the intermolecular interactions in these samples might be stronger. Similar behaviour was observed for wheat sauces, with the finest particle size presenting the lowest value, but in this case the intermediate fraction presented the highest value. Therefore, it seems that finest particle sizes of the flours gave rise to weaker sauces, as the lowest values for consistency index and yield stress demonstrated. According to these results, Quemada (1988) pointed out that large particles occupy more space during aggregation than small particles, due to less efficient particle packing which leads to a higher volume occupation by these large particles, and they also give rise to an increase in flow resistance.

Time dependency of the sauces was evaluated by determining the relative thixotropic area. The results retrieved for the thixotropic area highlight that wheat samples displayed a greater thixotropic behaviour compared to rice samples, with no differences depending on the particle size. The lower value of relative thixotropic area of rice sauces indicates a more stable structure in response to agitation (Sanz et al., 2016), being much less sensitive to shearing. These results might be explained by the different microstructure of the sauces, indicating that, after removal of shear force, more time was necessary to rebuild the original structure of the more complex wheat sauces.

3.5 Viscoelastic behaviour

Oscillatory spectra of all the studied sauces were very similar to those obtained for other heated white sauces (Arocas et al., 2009c; Mandala et al., 2004). The mechanical spectra in Fig 3a and Fig 3b showed the existence of solid-like gels, with values of G' higher than those of G'' (see also supplementary material 1) and with both moduli, but mainly G'', depending on the frequency throughout the frequency range measured. Heyman et al. (2010) also reported that G'' always appeared to be more frequency dependent than G' in all the sauces studied, a typical trait of weak gels.

Rice sauces presented lower values for both G' and G" moduli compared to wheat based sauces, and a greater dependence on frequency. Sanz et al. (2016) related this behaviour to the poorer thickening ability of the starch described in the pasting properties. In this way, the lower values of the moduli for rice sauces are coherent with the lower cold peak viscosity observed in the pasting profile. Then, a poorer thickening power was found for rice flours in comparison to wheat flours. Furthermore, rice sauces revealed a clearly less elastic behaviour than wheat ones, with values of G' only slightly higher

than those of G". The smaller differences between the two moduli in rice sauces may indicate they were closer to the crossover, after which the liquid-like behaviour starts to be predominant, also denoting a less rigid structure. Karaman et al. (2013) reported that amylopectin fraction softens the structured behaviour, giving rise to lower values of G' compared to those which can be found in systems composed of starches with a greater amylose content. In this way, the greater amylose content in wheat flours than in rice flours most likely could have contributed to their greater elastic properties, since statistical correlations at 99.9% level were found for amylose and G' and G'' (r=0.788 and r= 0.765, respectively). Lu et al. (2009) also highlighted that gels with higher amylose content showed more independence from frequency, and the storage modulus became higher for higher amylose content samples.

In terms of particle size, for both moduli there were no great differences among the different fractions of wheat sauces, indicating the higher protein content did not affect the finest flour. On the contrary, for rice flours, as particle size increased the values of the moduli also increased, suggesting more interaction among the structural components of the sauces. This trend is also in concordance with what was reported by Sanz et al. (2016) since a greater thickening ability was found for coarser particle sizes.

3.6 Syneresis of sauces

One of the main phenomena observed after the freeze/thaw process is the appearance of syneresis, or released water, from the sauce structure which is, actually, a very negative quality factor. This water release negatively affects some texture attributes and a certain lack of homogeneity or a grainy mouth feel could be found (Ferrero & Zaritzky, 2000; Navarro et al., 1997). No water release was observed in any of the freshly prepared sauces (data not shown) suggesting a great initial stability of the sauces which can be associated with the high water absorption capacity of the pregelatinised starch presented in the extruded flours (Wolf, 2010). On the contrary, syneresis occurred after freeze/thaw process for all the sauces studied (Table 2). These results are consistent with those reported by Arocas et al. (2009a) in which no syneresis was found on fresh white sauces, but water was indeed released after freeze-thaw process. Rice flours led to higher freeze-thaw stability of their sauces, with values of syneresis significantly lower than those of wheat sauces for each of the particle sizes. Meanwhile, the finest particle size presented the highest values of syneresis for both types of flours studied. Rice sauces presented no significant differences among the two coarsest particle sizes, with the lowest water release. Nevertheless, for wheat sauces, the significantly lower values of syneresis were obtained for the intermediate particle size. Therefore, it seems that the larger volume occupation of coarser particles or the more reduced superficial area may have helped to avoid water release. Arocas et al (2009a) related the syneresis of the sauces to the viscoelastic properties of the starches used in their study, being the syneresis greater for the starches with higher G' and G" values. This could explain the greater syneresis found for wheat sauces compared to rice ones, but not the differences between the different particle sizes, which would confirm that the internal structure of the sauces also play an important role on the stability.

4. Conclusions

This study assessed the suitability of physically gelatinised extruded flours for the making of sauces with no need of heating. The results showed that it is possible to obtain model sauces with similar rheological properties to those obtained in other sauces which were heated to develop their viscous properties. Nevertheless, it is noteworthy that the finest particle sizes are not preferable for sauce making due to their weaker rheological behavior and higher syneresis. Results also suggested that wheat flours give rise to sauces with a more tightly packed network structure, while a more disperse and less cohesive structure is shown when using rice flours. These different structures greatly influenced the rheological properties of the sauces, leading to higher consistency and viscoelastic character for wheat based sauces, which will be reflected as an increase in the sensory consistency and pumping requirements. On the other hand, rice flours are less sensitive to shearing and release less water after freeze-thaw process.

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References

AACC (2012). Approved methods of the American Association of Cereal Chemists, Methods 44-15.02 (Moisture), 46-30.01 (Protein), 56-30.01 (Water Binding Capacity), 61-02.01 (Rapid Visco Analysis), 11th ed. American Association of Cereal Chemists, St. Paul, Minnesota.

Arocas, A., Sanz, T., & Fiszman, S.M. (2009a). Clean label starches as thickeners in white sauces. Shearing, heating and freeze/thaw stability. *Food Hydrocolloids*, 23, 2031-2037.

Arocas, A., Sanz, T., & Fiszman, S.M. (2009b). Improving effect of xanthan and locust bean gums on the freeze-thaw stability of white sauces made with different native starches. *Food Hydrocolloids*, 23, 2478-2484.

Arocas, A., Sanz, T., & Fiszman, S.M. (2009c). Influence of corn starch type in the rheological properties of a white sauce after eating and freezing. *Food Hydrocolloids*, 23, 901-907.

Arocas, A., Sanz, T., Hernández-Carrión, M., Hernando, I., & Fiszman, S.M. (2010a). Effect of cooking time and ingredients on the performance of different starches in white sauces. *European Food Research and Technology*, 231, 395-405.

Arocas, A., Sanz, T., Salvador, A., Varela, P., & Fiszman, S.M. (2010b). Sensory properties determined by starch type in white sauces: Effects of freeze/haw and hydrocolloid addition. *Journal of Food Science*, 75, 132-140.

Camire, M.E., Camire, A., & Krumhar, K. (1990). Chemical and nutritional changes in foods during extrusion. *Critical Reviews in Food Science and Nutrition*, 29, 35-57.

Chinnaswamy, R., & Hanna, M.A. (1990). Macromolecular and functional properties of native and extrusion-cooked corn starch. *Cereal Chemistry*, 67, 490-499.

Chiu, C., & Solarek, D. (2009). Modification of starch. In J. BeMiller, R. Whistler (Eds.), *Starch, chemistry and technology* (pp. 629-656). Academic Press, New York.

Chung, C., Degner, B., & McClements, D.J. (2013). Physicochemical characteristics of mixed colloidal dispersions: Models for foods containing fat and starch. *Food Hydrocolloids*, 30, 281-291.

de la Hera, E., Gómez, M., & Rosell, C.M. (2013). Particle size distribution affecting the starch enzymatic digestion and hydration of rice flour carbohydrates. *Carbohydrate Polymers*, 98, 421-427.

Dolz, M., González, F., Delegido, J., Hernández, M.J., & Pellicer, J. (2000). A time dependent expression for thixotropic areas. Application to Aerosil 200 Hydrogels. *Journal of Pharmaceutical Sciences*, 89, 790-797.

Doublier, J.L., Colonna, P., & Mercier, C. (1986). Extrusion cooking and drum drying of wheat starch, II. Rheological characterization of starch pastes. *Cereal Chemistry*, 63, 240-260.

Delcour, J.A., & Hoseney, R.C. (2010). Principles of Cereal Science and Technology. Third Edition. AACC International Inc, St. Paul, Minnesota, USA.

Ferrero, C., & Zaritzky, N.E. (2000). Effect of freezing rate and frozen storage on starch-sucrose-hydrocolloid systems. *Journal of the Science of Food and Agriculture*, 80, 2149-2158.

Guardeño, L.M., Hernando, I., Llorca, E., Hernández-Carrión, M., & Quiles, A. (2012). Microstructural, physical, and sensory impact of starch, inulin, and soy protein in lowfat gluten and lactose free white sauces. *Journal of Food Science*, 77, 859-865

Hagenimana, A., Ding, X., & Fang, T. (2006). Evaluation of rice flour modified by extrusion cooking. *Journal of Cereal Science*, 43, 38-46.

Heyman, B., Depypere, F., Delbaere, C., & Dewettinck, K. (2010). Effects of nonstarch hydrocolloids on the physicochemical properties and stability of a commercial béchamel sauce. *Journal of Food Engineering*, 99, 115-120.

Hosseini-Parvar, S.H., Matia-Merino, L., Goh, K.K.T., Razavi, S.M.A., & Mortazavi, S.A. (2010). Steady shear flow behavior of gum extracted from Ocimum basilicum L. seed: Effect of concentration and temperature. *Journal of Food Engineering*, 101, 236-243.

Karaman, S.,Yilmaz, M.T., & Kayacier, A. (2013). Mathematical approach for two component modeling of salep-starch mixtures using central composite rotatable design: Part II. Dynamic oscillatory shear properties and applicability of Cox–Merz rule. *Food Hydrocolloids*, 31, 277-288.

Kim, J., & Shin, M. (2014). Effects of particle size distributions of rice flour on the quality of gluten-free rice cupcakes. *LWT - Food Science and Technology*, 59, 526-532.

Liu, H., Xu, X.M., & Guo, Sh.D. (2007). Rheological, texture and sensory properties of low-fat mayonnaise with different fat mimetics. *LWT-Food Science and Technology*, 40, 946-954.

Lu, Z.H., Sasaki, T., Li, Y.Y., Yoshihashi, T., Li, L.T., & Kohyama, K. (2009). Effect of amylose content and rice type on dynamic viscoelasticity of a composite rice starch gel. *Food Hydrocolloids*, 23, 1712-1719.

Ma, Z., & Boye, J.I. (2013). Advances in the design and production of reduced-fat and reduced-cholesterol salad dressing and mayonnaise: A review. *Food and Bioprocess Technology*, 6, 648-670.

Mandala, I.G., Savvas, T.P., & Kostaropoulos, A.E. (2004). Xanthan and locust bean gum influence on the rheology and structure of a white model-sauce. *Journal of Food Engineering*, 64, 335-342.

Manley, D. (2000). Technology of Biscuits, Crackers and Cookies, Third edition. Woodhead Publishing Limited, Cambridge, UK.

Martínez, M.M., Oliete, B., Gómez, M. (2013) Effect of the addition of extruded wheat flours on dough rheology and bread quality. *Journal of Cereal Science*, 57, 424-429.

Martínez, M.M., Calviño, A., Rosell, C.M., & Gómez, M. (2014a). Effect of different extrusion treatments and particle size distribution on the physicochemical properties of rice flour. *Food and Bioprocess Technology*, 7, 2657-2665.

Martínez, M.M., Rosell, C.M., & Gómez, M. (2014b). Modification of wheat flour functionality and digestibility through different extrusion conditions. *Journal of Food Engineering*, 143, 74-79.

McClements, D.J. (2005). Food emulsions principles, practices, and techniques. Second Edition, CRC Press, Boca Raton, USA.

Navarro, A.S., Martino, M.N., & Zaritzky, N.E. (1997). Viscoelastic properties of frozen starch-triglycerides systems. *Journal of Food Engineering*, 34, 411-427.

Quemada, D. (1988). Rheological modelling of complex fluids. I. The concept of effective volume fraction revisited. *The European Physical Journal Applied Physics*, 1, 119-127.

Quiles, A., Llorca, E., Hernández-Carrión, M., Hernando, I. (2012). Effect of different cornstarch types in new formulations of gluten- and lactose-free white sauces with high protein content. *Journal of Food Quality*, 35, 341-352.

Román, L., Martínez, M.M., Gómez, M. (2015a). Assessing of the potential of extruded flour paste as fat replacer in O/W emulsion: A rheological and microstructural study. *Food Research International*. 74, 72-79.

Román, L., Santos, I., Martínez, M.M., Gómez, M. (2015b). Effect of extruded wheat flour as a fat replacer on batter characteristics and cake quality. *Journal of Food Science and Technology-Mysore*, 52, 8188-8195.

Sanz, T., Tárrega, A., & Salvador, A. (2016). Effect of thermally inhibited starches on the freezing and thermal stability of white sauces: Rheological and sensory properties. *LWT - Food Science and Technology*, 67, 82-88.

Waterschoot, J., Gomand, S.V., Fierens, E., & Delcour, J.A. (2015). Production, structure, physicochemical and functional properties of maize, cassava, wheat, potato and rice starches. *Starch/Staerke*, 67, 14-29.

Willett, J.L., Jasberg, B.K., & Swanson, C.L. (1995). Rheology of thermoplastics starch: effects of temperature, moisture content, and additives on melt viscosity. *Polymer Engineering and Science*, 35, 202-210.

Wolf, B. (2010). Polysaccharide functionally through extrusion processing. *Current Opinion in Colloid and Interface Science*, 15, 50-54.

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Sample	Moisture (g/100g)	Amylose (g/100g)	Protein (g/100g)	WBC (g/g)	WSI (g/100g)
Fine wheat	9.76b±0.11	28.11d±0.31	$21.04f \pm 0.04$	5.10a±0.04	19.94c±0.30
Intermediate wheat	9.15ab±0.08	24.30c±0.42	7.00a±0.05	6.11bc±0.03	12.92b±0.38
Coarse wheat	9.05a±0.10	27.63d±0.41	8.84d±0.09	6.44c±0.00	7.83a±0.88
Fine rice	9.85b±0.08	20.55ab±1.50	9.33e±0.02	$6.07b \pm 0.06$	20.92cd±0.40
Intermediate rice	9.62ab±0.05	17.86a±0.04	7.54c±0.01	6.14bc±0.16	21.87cd±0.70
Coarse rice	9.57ab±0.47	22.50bc±1.40	7.40b±0.05	6.38bc±0.20	22.82d±1.33

Table 1 Composition, water binding capacity and solubility of extruded flours

Mean values followed by the same letter in each column are not significantly different at $p \le 0.05$. WBC= Water binding capacity, WSI= Water solubility index.

Table 2 Parameters of Herschel-Bulkley equation, relative thixotropic area and freezethaw syneresis for the studied sauces

Sample	$K (Pa \cdot s^n)$	n	σ_{o} (Pa)	Thixotropic area (%)	Freeze-thaw syneresis (%)
Fine wheat	16.43b±1.73	0.380a±0.021	61.22d±1.38	34.46b±1.05	22.55d±3.64
Intermediate wheat	26.67c±2.58	0.388ab±0.021	121.85f±2.28	43.19b±4.17	14.14c±3.31
Coarse wheat	22.48c±1.13	$0.414b \pm 0.008$	109.83e±8.03	39.64b±3.79	19.14d±1.34
Fine rice	4.92a±0.43	0.578c±0.017	16.74a±1.73	18.85a±1.01	6.27b±0.94
Intermediate rice	6.37a±0.28	0.583c±0.010	26.42b±0.93	19.24a±0.97	2.13a±0.43
Coarse rice	7.96a±0.39	$0.564c \pm 0.008$	32.74c±1.28	21.48a±1.58	2.15a±0.56

Mean values followed by the same letter in each column are not significantly different

at p \leq 0.05. K= consistency index, n= flow behavior index, σ_o = critical shear stress



Fig 1. Pasting profiles of wheat (a) and rice (b) flours with coarse (black continuous line), intermediate (grey broken line) and fine (grey continuous line) particle sizes used in sauces making. Pointed line indicates the temperature profile. Fine, intermediate and coarse fractions correspond to particle sizes of 0-80 μ m, 80-130 μ m and 130-200 μ m, respectively.



Fig 2. Microphotographs of sauces made with wheat (a, b, c) and rice (d, e, f) flours with fine (a, d), intermediate (b, e) and coarse (c, f) particle sizes. The bar in the upper right side of each picture indicates a 100 μ m size. White arrows indicate oil droplets. Fine, intermediate and coarse fractions correspond to particle sizes of 0-80 μ m, 80-130 μ m and 130-200 μ m, respectively.



Fig 3. Storage (unfilled symbols) and loss (filled symbols) moduli as a function of frequency for wheat (a) and rice (b) sauces made with coarse (circle), intermediate (triangle) and fine (square) particle sizes. Fine, intermediate and coarse fractions correspond to particle sizes of 0-80 μ m, 80-130 μ m and 130-200 μ m, respectively.