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THE IMPACT OF SUNFLOWER AND RAPESEED LECITHIN ON THE RHEOLOGICAL PROPERTIES OF SPREADABLE COCOA CREAM

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THE IMPACT OF SUNFLOWER AND RAPESEED LECITHIN ON THE RHEOLOGICAL PROPERTIES OF SPREADABLE COCOA CREAM

Abstract

The rheological properties of spreadable cocoa cream containing lecithin of different origins (sunflower, rapeseed and soy lecithin) were investigated within this research. A laboratory ball mill was used to produce creams containing varying amounts of lecithin (0.3, 0.5 and 0.7 wt%). The effect of milling time was also studied (between 30, 40 and 50 minutes).

Comparison between the different origins of lecithin revealed sunflower lecithin to be lower in viscosity than soy or rapeseed lecithin. Sunflower and rapeseed lecithins have a higher phosphatidilcholine content than soy lecithin. Increasing the lecithin concentration decreased the crystallization rate and increased the peak and conclusion temperatures in the cream fat phase. The type of lecithin used had no significant influence on the fat phase viscosity. It is found that the optimal rheological properties of spreadable cocoa cream can be achieved using 0.5 wt% of soy and rapeseed lecithin or 0.7 wt% of sunflower lecithin and 40-min milling time.

Keywords: spreadable cocoa cream, phospholipids, crystallization kinetics, rheology, particle size distribution

Chemical compounds: Phosphatidylcholine (PubChem CID: 45266626), Phosphatidylinositol (PubChem CID: 46931112), PE – phosphatidylethanolamine (PubChem CID: 57339246), Phosphatidylserine (PubChem CID: 6323481), Phosphatidylglycerol (PubChem CID: 446440)

1. Introduction

Phospholipids play an important role as biochemical intermediates to aid the growth and functionality of plant cells. The common vegetable lecithin contains primarily phosphatidylcholine (PC), phosphatidylethanolamine (PE) and phosphatidylinositol (PI). It is produced commercially from oil-containing seeds, such as soy, sunflower kernels and rapeseed (Nieuwenhuyzen and Tomas, 2008). During oil processing, phospho- and glycolipids must be removed from oils in order to stabilize them against sedimentation and also to enable further refining steps (Penci et al., 2010). Lecithin is a by-product of the vegetable oil-refining process and can be defined as a mixture of acetone insoluble polar lipids and vegetable oil alongside other minor components. Commercial lecithin is mostly obtained from soy oil, typically containing between 0.5 and 3% of phospholipids (Doig and Diks, 2003). The functional

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properties of lecithin are mainly caused by a surface-active character of its phospholipids. They consist of a glycerol backbone esterified with two fatty acids and a phosphate group which may be esterified with monovalent alcohols (for example choline or ethanolamine), or polyvalent alcohols (such as glycerol or inositol) (Arnold et al., 2013). As an amphipathic molecule, lecithin has found numerous applications in the food industry, mainly as an emulsifier and stabilizer (Fernandes et al., 2012). Lecithin helps to provide a smooth texture to foods and serves as an emulsifying agent in the manufacture of chocolate, bakery products, margarines, and mayonnaise (Cabezas et al., 2009; Ramadan, 2008). One of the most traditional applications of lecithin is its use in chocolate production. Regarding its rheological properties, chocolate represents a complex dispersed matrix of sugar, cocoa particles, milk ingredients and cocoa butter (Bueschelberger, 2004). Unlike chocolate, spreadable cocoa cream does not contain cocoa butter but cheaper vegetable fats and may also contain vegetable oil to improve its spreadability. Cocoa cream ideally features good spreadability across a wide temperature range (ranging between ambient to fridge temperature), a rich creamy taste, smooth homogeneous structure with no fat-phase separation, and good oxidative stability (Pajin, 2014). Cocoa cream, much like chocolate, has a non-uniform particle size distribution and it exhibits thixotropic properties characterized by a plastic flow and yield stress (Pajin et al., 2013). In general, the addition of lecithin to oil-based suspensions causes adsorption of surface-active components on the surface of suspended particles, reducing the surface roughness. This minimizes the friction between the particles, which in turn results in both a decrease in the yield stress and viscosity until a minimum limit is reached. A further increase in the lecithin concentration adds to the yield stress but does not lead to a further reduction in viscosity (Arnold et al., 2013). Lecithin is added in relatively small amounts (0.1–2%) as an emulsifier in food formulations; these concentrations do not generally impact on the colour, odour and flavour of the product (Oke et al., 2010).

To date, no scientific literature sources have so far published any results that involve testing the physical properties of chocolate and cocoa-based confectionery products formulated from lecithin of different origins. Considering that soy lecithin is the most frequently used emulsifier in the food production, and furthermore that the widespread production of sunflower and rapeseed oil presents an opportunity to use lecithin from these sources, the aim of this study was to a) produce a variety of spreadable cocoa cream fat phase containing either sunflower or rapeseed lecithin and to then compare their crystallization kinetics and rheological behaviour with spreadable cocoa

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cream fat phase containing more commonly used soy lecithin and b) investigate the further impact of each lecithin type on the rheological properties of the spreadable cocoa cream, optimizing to factor both the amount of lecithin and the milling time in the laboratory ball mill simultaneously.

2. Materials and methods

2.1. Materials

The raw materials used in the spreadable cocoa cream production were a cocoa-cream mass, refined by a 3-roll mill in industrial conditions, consisting of powdered sugar (Crvenka JSC, Serbia), cocoa powder (Centroproizvod JSC, Serbia), milk powder (Imlek JSC, Serbia), and the NTFCP (non-trans fat intended for cream production) vegetable fat (Dijamant JSC, Serbia). The NTFCP fat characteristics, i.e. its fatty acid composition, solid fat content at different temperatures and thermal properties are given in our previous research (Lončarević et al., 2013). Sunflower oil (Dijamant JSC, Serbia) was used to improve the cream spreadability, while vanilla powder and hazelnut extract (VK Aromatics, Serbia) were added as flavours. The native soy, sunflower and rapeseed lecithin (Victoriaoil JSC, Serbia) were used as emulsifiers.

The composition of the spreadable cocoa cream included: powdered sugar 50 wt%, vegetable fat 24 wt%, refined sunflower oil 6 wt%, cocoa powder 7 wt%, milk powder 12 wt%, lecithin 0.3–0.7 wt%, vanilla flavour 0.06 wt% and hazelnut flavour 0.04 wt%.

2.2. Process Method

Initially, the influence of different amounts of soy, sunflower and rapeseed lecithin on the crystallization and rheological properties of the cream fat phase was investigated according to the following scheme:

Fat phase of spreadable cocoa cream									
Type of lecithin	Soy lecithin - soy			Sunflower lecitin - sun			Rapeseed lecitin - rape		
Concentration (wt%)	0.3	0.5	0.7	0.3	0.5	0.7	0.3	0.5	0.7
Sample	$soy_{0.3}$	$soy_{0.5}$	$soy_{0.7}$	$sun_{0.3}$	$sun_{0.5}$	$sun_{0.7}$	$rape_{0.3}$	$rape_{0.5}$	$rape_{0.7}$

Fat and oil ratios were calculated based on the composition of the spreadable cocoa cream.

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A mixture of fat and oil with lecithin was homogenized at 20 ºC using a homogenizer Ultraturrax T-25 (Janke Kunkel, Germany) with a rotation speed of 6000 rpm for 5 min.

The spreadable cocoa cream samples were produced in a laboratory ball mill (Mašino Produkt, Serbia), with a capacity of 5 kg. The ball mill contains a double-jacket cylinder, 0.25 m in diameter and 0.31 m in height (0.0152 m^3 in volume), with 30 kg of water-resistant steel balls sized 9.1 mm in diameter and a vertical shaft with horizontal arms. It is equipped with a recirculation pump and a temperature control system made up of a water jacket with a temperature sensor and thermo-regulators controlled by an electric board.

The samples were prepared using different amounts of soy, sunflower and rapeseed lecithin (0.3; 0.5 and 0.7 wt%) and variable milling time (30, 40 and 50 min) for each applied concentration, as shown below:

Standard spreadable cocoa cream with soy lecithin									
wt%*		0.3			0.5			0.7	
Min**	30	40	50	30	40	50	30	40	50
Sample	soy$_{0.3}$30	soy$_{0.3}$40	soy$_{0.3}$50	soy$_{0.5}$30	soy$_{0.5}$40	soy$_{0.5}$50	soy$_{0.7}$30	soy$_{0.7}$40	soy$_{0.7}$50
Spreadable cocoa cream with sunflower lecithin									
wt%*		0.3			0.5			0.7	
Min**	30	40	50	30	40	50	30	40	50
Sample	sun$_{0.3}$30	sun$_{0.3}$40	sun$_{0.3}$50	sun$_{0.5}$30	sun$_{0.5}$40	sun$_{0.5}$50	sun$_{0.7}$30	sun$_{0.7}$40	sun$_{0.7}$50
Spreadable cocoa cream with rapeseed lecithin									
wt%*		0.3			0.5			0.7	
Min**	30	40	50	30	40	50	30	40	50
Sample	rape$_{0.3}$30	rape$_{0.3}$40	rape$_{0.3}$50	rape$_{0.5}$ 30	rape$_{0.5}$ 40	rape$_{0.5}$ 50	rape$_{0.7}$ 30	rape$_{0.7}$ 40	rape$_{0.7}$ 50

At the beginning of production, the fat, oil and lecithin were homogenized in the laboratory ball mill for 5 min, after which the cocoa-cream mass was added alongside the hazelnut and vanilla flavours. The temperature in the ball mill was set at 40 °C, with a rotation speed of 50 rpm. Following the chosen milling time, the cream samples were placed into sterile plastic cups and capped with plastic lids. The temperature of the cream dosing was 35 ºC.

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2.3. Phospholipid composition

The phospholipid composition of the different types of lecithin investigated was determined by means of the ^{31}P NMR technique by the Spectra Service GmbH (Cologne, Germany). All spectra were acquired using the NMR spectrometer Avance III 600 (Bruker, Germany), magnetic flux density 14.1 Tesla QNP cryo probe head, equipped with the automated sample changer Bruker B-ACS 120. The software used for acquisition was Intel Core2 Duo 2.4 GHz with MS Windows XP and Bruker TopSpin 2.1. The latter was used for processing as well.

2.4. Crystallization kinetics

The crystallization rate of the cocoa cream fat phase under static conditions was followed by measuring the changes of the solid fat content (SFC) as a function of time using the Bruker minispec mq 20 NMR Analyzer pulse device (Bruker, Germany). Approximately 3 g of a melted fat sample was put into the glass NMR tube and heated for 30 min at 60 ºC to destroy the crystal structure. The sample was subsequently placed directly in a water bath at a crystallization temperature of 20 ºC. The SFC measurements were taken at one-minute intervals within the duration of 1 h.

2.5. Thermal properties

The differential scanning calorimetry DSC 910, the Thermal analyzer 990 and the Dynamic mechanical analyzer (Du Point Instruments, USA) were used to determine the thermal profile of the cream fat phase samples. Having weighed 5 mg of the fat sample into aluminum pans, the pierced covers were sealed in place. An empty, hermetically sealed aluminum pan was used as a reference. The samples were analysed by being heated from 10 ºC to 100 ºC with a heating rate of 5 ºC per minute.

2.6. Rheological properties

The rheological properties of pure lecithin, the fat phase and finally the spreadable cocoa cream samples were determined by the rotational rheometer Rheo Stress 600 (Haake, Germany).

The flow curves were carried out at 35 ºC using a concentric cylinder system (sensor Z20 DIN). The shear rate was first increased from 0 s^{-1} to 100 s^{-1}, then kept constant at a maximal speed of 100 s^{-1} and eventually reduced from 100 s^{-1} to 0 s^{-1}, each time within 180 s.

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Dynamic oscillatory measurements were performed for determining the elastic modulus G' and the viscosity modulus G" of the cream fat phase. On the basis of the determined linear viscous elastic (LVE) regime the measurement conditions were defined: x (angular frequency) within the interval of 6.28 to 62.8 rad/s (frequency 1–10 Hz) under the constant shear stress of 1 Pa. The ratio between the viscous and elastic portions of a rheological system possessing viscoelastic properties was defined by the parameter tanδ (Pajin et al., 2013):

$\tan\delta = G''/G'$

2.7. Particle size distribution

The influence of the milling time on the particle size distribution in the spreadable cocoa cream samples was determined using the Mastersizer 2000 laser diffraction particle size analyzer equipped with the Hydro 2000 μP dispersion unit (Malvern Instruments, England). The spreadable cocoa cream sample was dispersed in sunflower oil at the ambient temperature (20±2 °C) and added until an adequate obscuration was obtained (10-20%). The results were quantified as the volume-based particle size distribution by means of the Mastersizer 2000 software.

2.8. Statistical analysis

The results of the cream fat phase analyses and particle size measurements of the cream samples were statistically tested using the ANOVA method and the means were compared by the one- and two-factor analyses at variance with subsequent comparisons applying Duncan's test at a significance level of 0.05 using the Statistica 12.0 software (Statsoft, USA).

The results of the rheological parameters of the spreadable cocoa cream samples containing soy, sunflower and rapeseed lecithin were statistically analysed using the polynomial regression equation: $z = b_0 + b_1x + b_2y + b_{11}x^2 + b_{12}xy + b_{22}y^2$, in accordance with the factorial design of experiment 3^2. The response function z represents the parameters (thixotropic curve area, Casson viscosity and Casson yield stress), b_0-b_{22} are regression coefficients of the polynomial equation, while the independent variables x and y represent the concentration of the lecithin and the milling time, respectively.

3. Results and discussion

3.1. Phospholipid composition

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The phospholipid composition of lecithin usually depends on the type of oil from which the lecithin was obtained, and the processing conditions (Arnold et al., 2013), whilst the fatty acid composition is similar to oil (Nieuvenhuzen and Tomas, 2008). Our previous research (Lončarević et al., 2013) confirmed that sunflower lecithin, like sunflower oil, does not contain α-linolenic acid, whereas soy and rapeseed lecithin contain over 6% of ω-3 fatty acids.

The phospholipid composition of soy, sunflower, and rapeseed lecithin is shown in Table 1. The total phospholipid content may vary depending on the amount of residual oil in the lecithin. The soy lecithin had the highest phospholipid content (45.79%/lecithin), followed by rapeseed lecithin (44.61%/lecithin), and sunflower lecithin (42.02%/lecithin). All three lecithin types contained the highest proportion of PC, where the rapeseed and sunflower lecithin had approximately the same content of PC calculated in relation to the total content of phospholipids (40.93%/lecithin and 40.53%/lecithin, respectively), followed by soy lecithin (34.76%/lecithin). Helmerich and Koehler (2003) compared the methods for the quantitative determination of phospholipids in lecithin and ^{31}P NMR determination showed the highest PC share in native sunflower lecithin (40.08%/lecithin), followed respectively by soy lecithin (39.72%/lecithin) and rapeseed lecithin (35.94%/lecithin) calculated in relation to the total phospholipid content. The lecithin obtained from sunflower oil contained the highest proportion of PI, even 31.76%/lecithin, while the content of PI in the soy lecithin amounted to 17.49%/lecithin. On the other hand, soy lecithin was characterized by the highest PE (24.60%/lecithin), PA (11.00%/lecithin), and APE (5.46%/lecithin) content. PS dominated in the sunflower lecithin (2.07%/lecithin) and PG in the rapeseed lecithin (1.83%/lecithin). Lysophospholipids accounted for less than 1%/lecithin, with the exception of 2-LPC in the sunflower and rapeseed lecithin, which was 1.17%/lecithin and 1.88%/lecithin, respectively, while LPS was not detected.

3.2. Crystallization kinetics

Since the final product quality is influenced by its fat phase and the processing conditions, it is very important to focus on the fat crystallization kinetics. An investigation of Foubert et al. (2002) and Pajin et al. (2007) showed that the fat crystallization kinetics under isothermal conditions can be described by the Gompertz mathematical model:

$$S(t) = a \cdot \exp\left(-\exp\left[\frac{\mu \cdot e}{a}(\lambda - t) + 1\right]\right)$$

where *S* is the solid fat content (SFC, %) at time *t* (min), *a* is the value for S when *t* is approaching infinity (%), *μ* is the maximum crystallization rate (%/min), and *λ* is a parameter proportional to inductive time (min). The parameters

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of this model were determined based on experimental data by means of nonlinear regression for all fat phase samples. The determination coefficient (R^2) indicates how the experimental data fits the Gompertz mathematical model. The parameters of the Gompertz mathematical model were determined by means of nonlinear regression based on the experimental data for SFC as a function of time at a crystallization temperature of 20 ºC. The obtained parameters, including the estimates of 95% confidence interval, are shown in Table 2.

In general, during crystallization at 20 °C the smallest amount of solid fat was formed in the fat phase samples containing the soy lecithin (14.50–14.83%), whereas the largest amount was formed in those with the rapeseed lecithin (16.40–16.71%). The smallest lecithin amount resulted in higher crystallization rate value, compared to the samples with 0.5 and 0.7 wt% of lecithin, indicating the presence of less liquid triglycerides during the crystallization of the cream fat phase after the production. The highest μ value was determined in the sample containing 0.3 wt% of the rapeseed lecithin (1.01 %/min). The parameter λ varied in 0–0.74min interval and it can be assumed that the induction period was negligible, indicating that the crystallization centers were formed very quickly. The high values of the determination coefficient (R^2) (0.97–0.99) indicated that the application of the Gompertz mathematical model for describing experimental data by means of the theoretical curve was justified.

3.3. Thermal properties

DSC parameters – the onset temperature (T_{onset}), the peak temperature (T_{peak}), and the conclusion temperature (T_{end}) are presented in Table 2. The cream fat phase began to melt within a temperature range between 35.15 ºC–35.61 ºC. The type and amount of lecithin had no impact on this parameter. On the other hand, an increase in the amount of all examined types of lecithin increased T_{peak} (with the exception of sample $rape_{0.5}$), and T_{end} temperatures. Considering the fact that the crystallization rate decreased with an increase in the amount of lecithin, it can be concluded that a higher lecithin amount resulted in the formation of larger crystals during the crystallization process.

3.4. Rheological properties

3.4.1. Rheological properties of lecithin

Fig. 1a represents the flow curves of all examined types of lecithin, while their rheological parameters are presented in Table 3. The soy, and rapeseed lecithin exhibited a thixotropic flow, whilst the applied shear rates resulted in a minimal destruction of the internal structure of the sunflower lecithin, showing the lowest values of all rheological

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parameters ($p<0.05$). The soy lecithin has the highest yield stress value (6.78 Pa) compared to the sunflower (0.80 Pa) and rapeseed lecithin (3.98 Pa). Soy lecithin also has the highest value of viscosity at the maximum shear rate (13.78 Pas), which significantly differs ($p<0.05$) from the viscosity of the sunflower lecithin (4.97 Pas) and does not statistically differ ($p<0.05$) from the viscosity of the rapeseed lecithin (12.13 Pas). Although showing different flow curves, the values of the thixotropic curve area of the soybean and rapeseed lecithin (3737 Pa/s and 3602 Pa/s, respectively) do not significantly differ ($p<0.05$).

3.4.2. Rheological properties of the spreadable cocoa cream fat phase

The thixotropic curves of the spreadable cocoa cream fat phase are presented in Fig. 1b, c, d. The data in Table 3 showed that a mixture of fat and sunflower oil with 0.5 wt% of the soy lecithin had the lowest value of the thixotropic curve area (4493 Pa/s), which indicates the greatest micro-structural homogeneity, and spreadability compared to the other samples. The sample with 0.5 wt% of soy lecithin had significantly ($p<0.05$) lower value of the yield stress (7.23 Pa) compared to both the samples containing 0.3 and 0.7 wt% of soy lecithin, and also all sunflower lecithin samples. The increase in concentration from 0.5 to 0.7 wt% was followed by increase in values of the thixotropic curve area irrespective of the lecithin type. However, varying the amount of lecithin had no significant ($p<0.05$) effect on the viscosity at the maximum shear rate, which ranged from 0.59 to 0.69 Pas.

The rheological measurements in our recent research (Lončarević et al., 2013) showed that a concentration of 0.5% of soy, sunflower, and rapeseed lecithin improved the homogeneity and spreadability of pure fat, while the addition of all three investigated lecithin types at a fixed concentration of 0.7% caused the opposite effect by increasing both complexity and viscosity of the system.

The measurements performed in the LVE range provided determination of G' and G" moduli without destroying the system. Fig. 1e, f, g show the elastic (G') and viscous (G") moduli of the cream fat phase with the addition of different amounts of soy, sunflower, and rapeseed lecithin. In general, at lower frequencies the viscous (G") modulus in all the samples was more pronounced. At the certain frequency the curves overlapped, after which the elastic modulus (G') was more dominant than the viscous modulus (G"). The data presented in Table 3 show the values of the tanδ **(**G"/G'), which were below 1, with no significant differences ($p<0.05$) among the samples.

3.4.3. Rheological properties of the spreadable cocoa cream

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Fig. 2 presents the flow curves of the cream samples, where the largest area was obtained for those containing 0.3 wt% of any lecithin type, indicating the highest complexity, and the lowest homogeneity of the system. The rheological parameters, presented in Fig. 3, indicated the differences among the samples, depending on the type and concentration of lecithin, as well as the milling time in the laboratory ball mill. The samples with 0.7 wt% of lecithin have the highest Casson yield stress and the lowest Casson viscosity, since a higher amount of lecithin led to a better emulsification of solids with a lower share of the free fatty phase. This resulted in a more homogenous and compacted system. Increasing the milling time within specified concentration of lecithin generally resulted in increased Casson viscosity in all the samples.

Regarding the samples of the spreadable cocoa cream containing the soy lecithin, it is evident that the sample with 0.5 wt% of soy lecithin, and under a retention time of 40 min in the ball mill exhibited the most homogeneous structure and a minimal complexity of the system compared to the other soy lecithin-containing cocoa cream samples. This was manifested by the lowest thixotropic curve area (3109 Pa/s) compared to all other samples with soy lecithin. This sample also has a lower yield stress (34.40 Pa) in comparison to the samples with the same concentration of the soy lecithin which were milled for 30 and 50 min.

A concentration of 0.5 wt% of sunflower lecithin was sufficient to cover all solid particles in the spreadable cocoa cream samples. The sample milled for 40 min had the smallest thixotropic curve area when compared to the samples with 0.5 wt% of the sunflower lecithin that were milled for 30 and 50 min in the ball mill. The highest amount of sunflower lecithin resulted in a further reduction of the rheological parameters. The sample with the maximum amount of the sunflower lecithin ($sun_{0.7}40$) had the lowest value of the thixotropic curve area (2733 Pa/s), and the lowest value of Casson viscosity (2.20 Pas) compared to the other sunflower lecithin-containing cocoa cream samples.

For the samples using rapeseed lecithin, the lowest thixotropic curve area (3631 Pa/s) and the yield stress (31.04 Pa) were achieved with 0.5 wt% of rapeseed lecithin and a retention time of 40 min in the ball mill.

Fig. 4 shows 3D contour diagrams (obtained by regression analysis) to consider lecithin concentration, type and milling time influence on the rheological parameters of the spreadable cocoa cream samples. 0.5 wt% of soy lecithin, or 0.7wt% of sunflower lecithin in combination with the milling time from 30 to 40 min, provided the

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lowest thixotropic curve area for the spreadable cocoa cream samples produced. Furthermore, 0.5 wt%-0.6 wt% of rapeseed lecithin in combination with 40-min milling time in the ball mill resulted in the smallest thixotropic curve area. The spreadable cocoa cream sample containing soy lecithin had the lowest Casson yield stress achieved with a concentration of 0.3 wt% of lecithin in combination with 30-min milling time. The reduction of Casson viscosity was obtained by increasing the concentration of the soy lecithin and decreasing the milling time. The Casson yield stress had a minimum value in the cream containing 0.4-0.5 wt% of the sunflower lecithin within the milling time of 30 to 40 min or 0.4-0.5 wt% of the rapeseed lecithin and a minimal milling time. The maximum concentration of the sunflower and rapeseed lecithin, and the milling time of 30 to 40 min provided the lowest Casson viscosity.

Regression analysis of the influence of the concentration of lecithin and milling time on the rheological parameters show that a combination of 0.5 wt% of lecithin alongside a milling time of 40 min provided the spreadable cocoa cream with appropriate rheological properties, whereas the sample with soy lecithin has the lowest value of Casson viscosity in relation to the samples with sunflower and rapeseed lecithin. On the other hand, the addition of 0.7 wt% of lecithin increased the yield stress of all the samples but did not lead to the formation of lamellas, since the Casson viscosity did not increase in comparison to the samples with 0.3 and 0.5 wt% of lecithin. Moreover, the spreadable cocoa cream sample produced with 0.7 wt% of sunflower lecithin under 40 min milling time had the lowest values for the thixotropic curve area, and the lowest Casson viscosity compared to the samples with sunflower lecithin.

3.5. Particle size distribution

The influence of milling time on the particle size distribution of spreadable cocoa cream is presented in Fig. 5. The obtained results in terms of d(0.1) showed a relatively uniform particle distribution in all the cream samples. The parameter d(0.1) ranged from 2.94 to 3.59 μm, meaning that 10% of the volume distribution of the samples were smaller than the particular d(0.1) value. The milling time affected parameters d(0.5) and d(0.9), regardless of the type or amount of lecithin used. Decreasing d(0.5) and d(0.9), while increasing the retention time in the laboratory ball mill affected the rheological properties of the spreadable cocoa cream in terms of increasing the Casson viscosity. Afoakwa et al. (2008) investigated the effects of particle size distribution and composition on the rheological properties of dark chocolate, where it was observed that an increase in particle size resulted in a decrease in Casson plastic viscosity due to an increased number of particles, and points of contact between them.

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Lecithin concentration had no impact on d(0.5) and d(0.9). However, it was evident that the samples with the highest lecithin concentration in combination with 50-min milling time had the lowest parameter d(0.5) (ranging from 12.43 μm in $soy_{0.7}50$ to 12.88 in $sun_{0.7}50$). Also, the samples with 0.7 wt% of lecithin had a lower d(0.9) compared to the samples with 0.3 wt% of each lecithin type used (with the exception of $sun_{0.7}50$).Considering all samples, 50% of the volume distribution was smaller than 16.45 μm, which was the highest value for d(0.5) achieved in $soy_{0.3}30$. The parameter d(0.9) indicated that 90% of the volume distribution of all the samples milled for 30 min were smaller than 69.66 μm, while 10% were larger. On the other hand, 90% of the volume distribution in all the samples milled for 40 and 50 min were smaller than 66.25 μm and 55.81 μm, respectively.

4. Conclusion

The main objective of the study was to compare the phospholipid composition, the rheological behavior and the emulsifying properties of soy lecithin (which is considered a superior emulsifier in the confectionery industry) with sunflower and rapeseed lecithin.

The results showed that the investigated lecithin types have different phospholipid compositions with a higher PC content in the sunflower and rapeseed lecithin compared to the soy lecithin. On the other hand, soy and rapeseed lecithin have very similar consistency unlike sunflower lecithin which has a lower viscosity.

A lecithin concentration of 0.5 wt% improved the homogeneity and spreadability of the cream fat phase, whilest 0.7 wt% lecithin increased the complexity of the system with no influence on its viscosity. The Gompertz mathematical model showed the lowest crystallization rate and amount of formed solids in the fat phase for samples containing soy lecithin and the highest for samples containing rapeseed lecithin. The cream fat phase samples with lower crystallization rates had higher peaks and conclusion temperatures. 0.5 wt% of soy and rapeseed lecithin with 40-min milling time provided the lowest complexity, adequate values of the Casson yield stress, and viscosity in the spreadable cocoa cream, while 0.7 wt% of the sunflower lecithin and a retention time of 40 min in the ball mill resulted in both the lowest viscosity and complexity of the system.

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7. Figure captions

Fig 1. Flow curves of: a) Pure lecithin; Flow curves of the cream fat phase with different amount of: b) soy lecithin, c) sunflower lecithin, and d) rapeseed lecithin; Viscous (G'') and elastic (G') moduli of the cream fat phase with e) soy, f) sunflower, and g) rapeseed lecithin

Fig. 2. Flow curves of spreadable cocoa cream with different amount of: a) soy, b) sunflower, and c) rapeseed lecithin

Fig 3. Rheological properties of spreadable cocoa cream: a) thixotropic curve area, b) Casson yield stress, and c) Casson viscosity

Fig 4. Contour 3D diagrams to show the influence of independent variables on: a) thixotropic curve area, b) Casson yield stress, c) Casson viscosity

Fig 5. Particle size parameters of the spreadable cocoa cream: a) d(0.1), b) d(0.5), and c) d(0.9)

8. Tables

Table 1. Phospholipid composition of soy, sunflower, and rapeseed lecithin

Table 2. Parameters of the Gompertz mathematical model and the cream fat phase thermal properties

Table 3. Rheological properties of the lecithins and the cream fat phase

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Phospholipid	Phospholipid content (%/total phospholipids)		
	Soy lecithin	Sunflower lecithin	Rapeseed lecithin
PC	34.76	40.53	40.93
1-LPC	0.12	0.13	0.19
2-LPC	0.85	1.17	1.88
PI	17.49	31.76	24.78
LPI	0.91	0.98	1.19
PE	24.60	14.40	16.93
LPE	0.63	0.43	0.76
PS	1.23	2.07	1.25
LPS	n.d.	n.d.	n.d.
PG	1.30	0.81	1.83
DPG	1.02	1.49	1.24
PA	11.00	3.28	6.75
LPA	0.03	0.08	0.16
APE	5.46	2.63	1.55
Other	0.23	0.22	0.51
Total phospholipids (%/lecithin)	45.79	42.02	44.61

n.d. - not detected

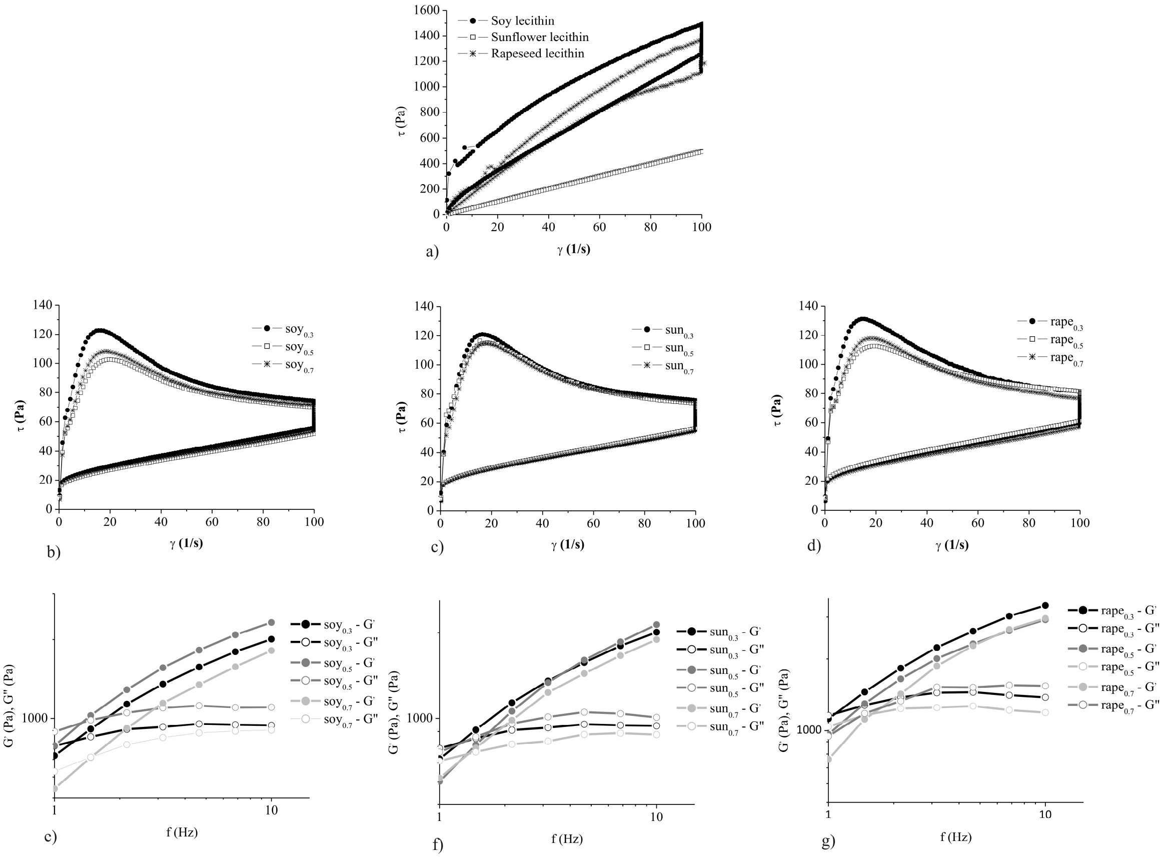
PC – phosphatidylcholine, LPC – lyso-phosphatidylcholine, PI – phosphatidylinositol, LPI – lyso-phosphatidylinositol, PE – phosphatidylethanolamine, LPE – lyso-phosphatidylethanolamine, PS – phosphatidylserine, LPS – lyso-phosphatidylserine, PG – phosphatidylglycerol, PA – phosphatidic acid, LPA – lyso-phosphatidic acid, APE - allyl pentaerythritol

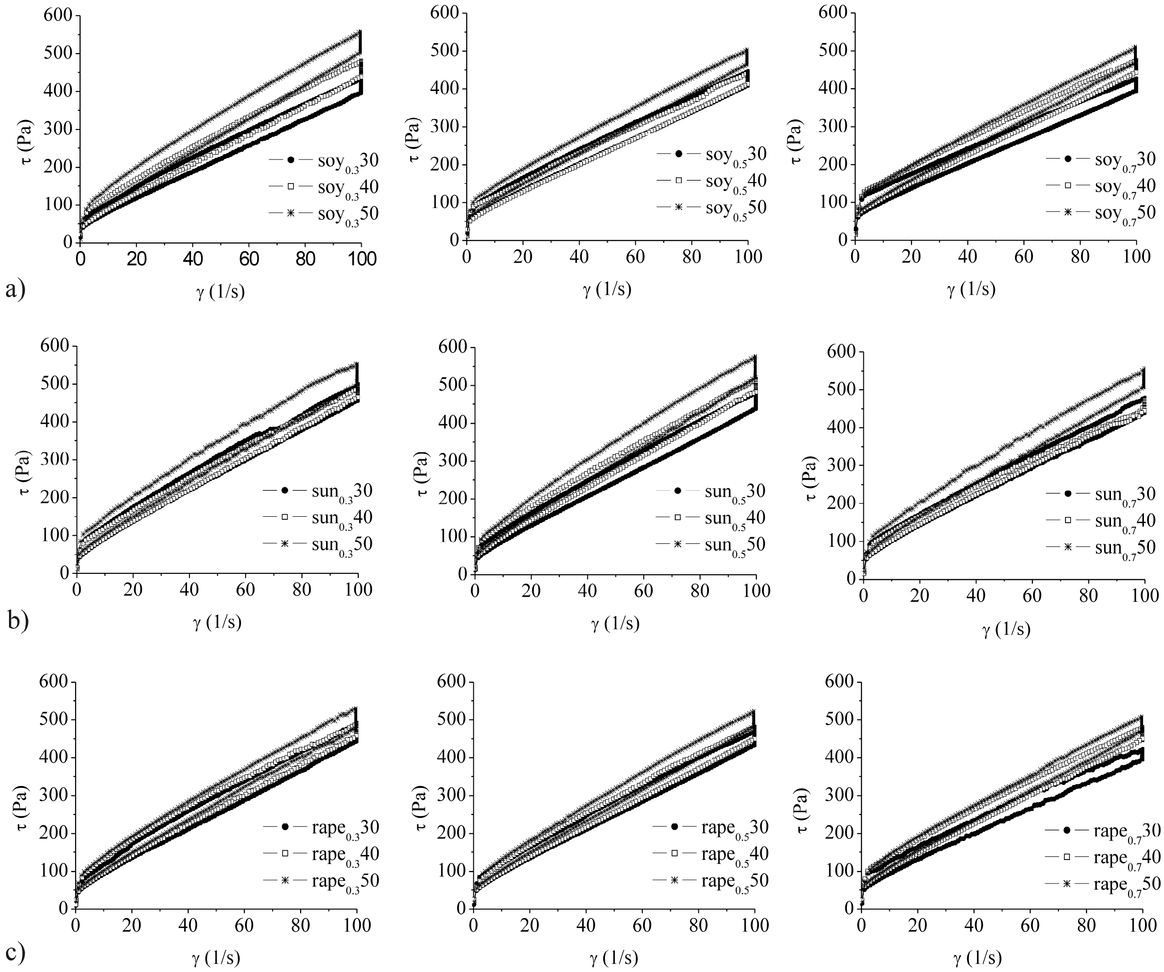
	Crystallization kinetics				Thermal properties		
Sample	**a (%)**	**μ (%/min)**	**λ (min)**	**R^2**	**T_{onset} (ºC)**	**T_{peak} (ºC)**	**T_{end} (ºC)**
$soy_{0.3}$	14.44	0.81	0.12	0.99	35.52	42.28	48.75
$soy_{0.5}$	14.70	0.79	0	0.98	35.27	43.26	49.17
$soy_{0.7}$	14.50	0.74	0.45	0.99	35.54	45.67	49.84
$sun_{0.3}$	14.83	0.96	0.74	0.99	35.17	42.01	48.32
$sun_{0.5}$	14.63	0.78	0.11	0.97	35.55	42.46	49.59
$sun_{0.7}$	16.52	0.83	0	0.99	35.53	45.22	51.27
$rape_{0.3}$	16.61	1.01	0	0.99	35.15	41.98	49.16
$rape_{0.5}$	16.71	0.97	0	0.98	35.61	45.94	50.97
$rape_{0.7}$	16.40	0.89	0	0.99	35.25	42.49	51.42

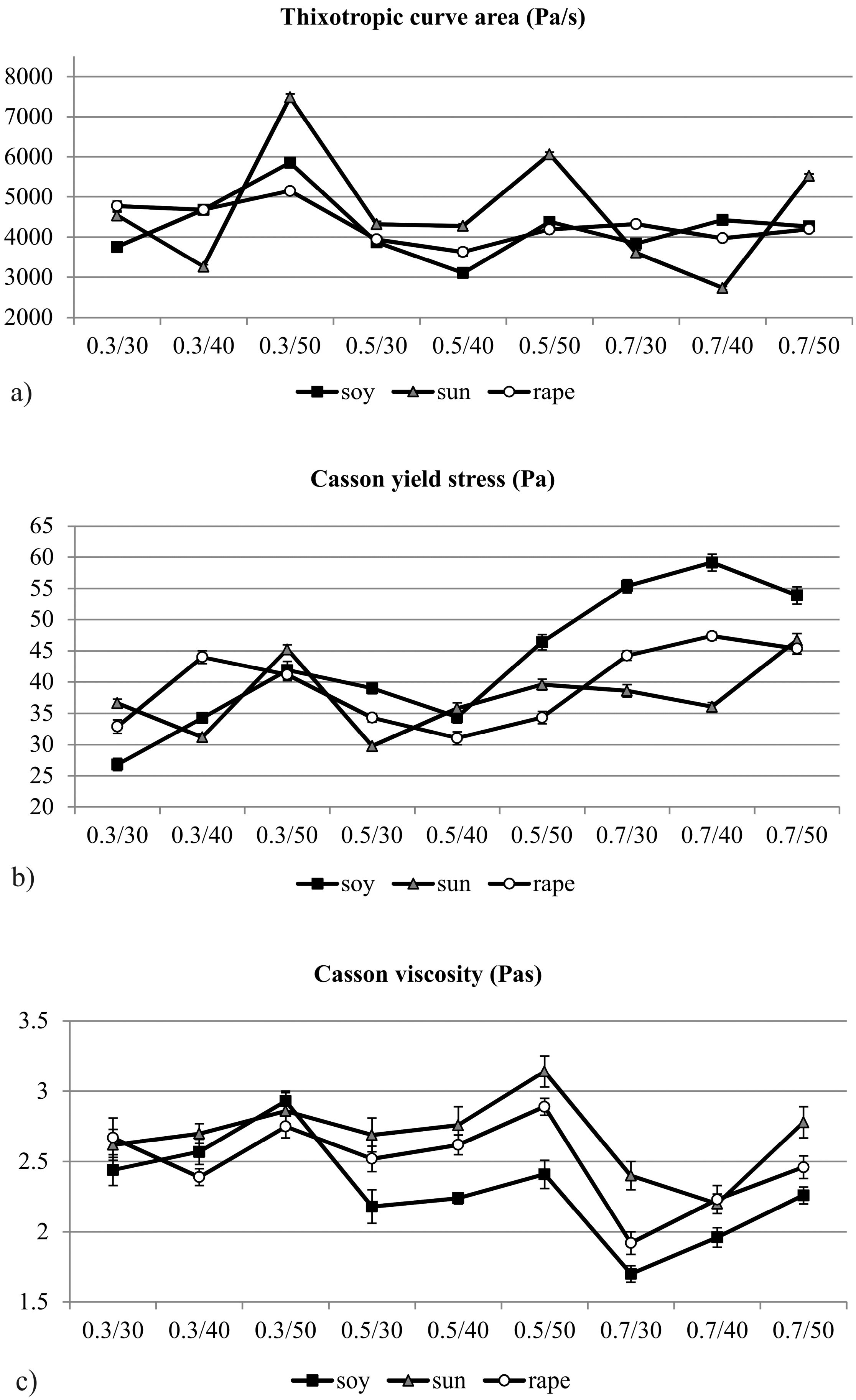
Sample	Yield stress (Pa)	Thixotropic curve area (Pa/s)	Mean value of viscosity at maximum share rate (Pas)	tanδ = G''/G'
Lecithin				
Soy	6.78±1.23^{c}	3737.36±86.24^{b}	13.78±1.57^{b}	nd*
Sunflower	0.80±0.12^{a}	805.32±21.11^{a}	4.97±0.16^{a}	nd*
Rapeseed	3.98±0.96^{b}	3602.54±78.56^{b}	12.13±0.42^{b}	nd*
Fat phase				
$soy_{0.3}$	9.51±0.45^{ab}	5149.56±13.20^{d}	0.62±0.03^{ab}	0.73±0.15
$soy_{0.5}$	7.23±0.71^{c}	4493.12±50.68^{a}	0.61±0.04^{ab}	0.76±0.11
$soy_{0.7}$	8.77±0.30^{ab}	4611.30±12.60^{b}	0.59±0.05^{ab}	0.76±0.10
$sun_{0.3}$	9.52±1.17^{ab}	5437.98±18.53^{e}	0.63±0.02^{a}	0.62±0.17
$sun_{0.5}$	9.33±1.05^{ab}	4922.23±13.06^{c}	0.62±0.02^{b}	0.68±0.13
$sun_{0.7}$	9.87±1.17^{b}	5204.45±16.05^{d}	0.67±0.04^{a}	0.81±0.15
$rape_{0.3}$	7.15±0.76^{c}	5738.15±26.12^{f}	0.68±0.01^{a}	0.67±0.21
$rape_{0.5}$	8.21±0.82^{ac}	4899.69±80.33^{c}	0.69±0.03^{a}	0.88±0.11
$rape_{0.7}$	8.60±0.56^{abc}	5198.47±17.23^{d}	0.64±0.05^{a}	0.83±0.13

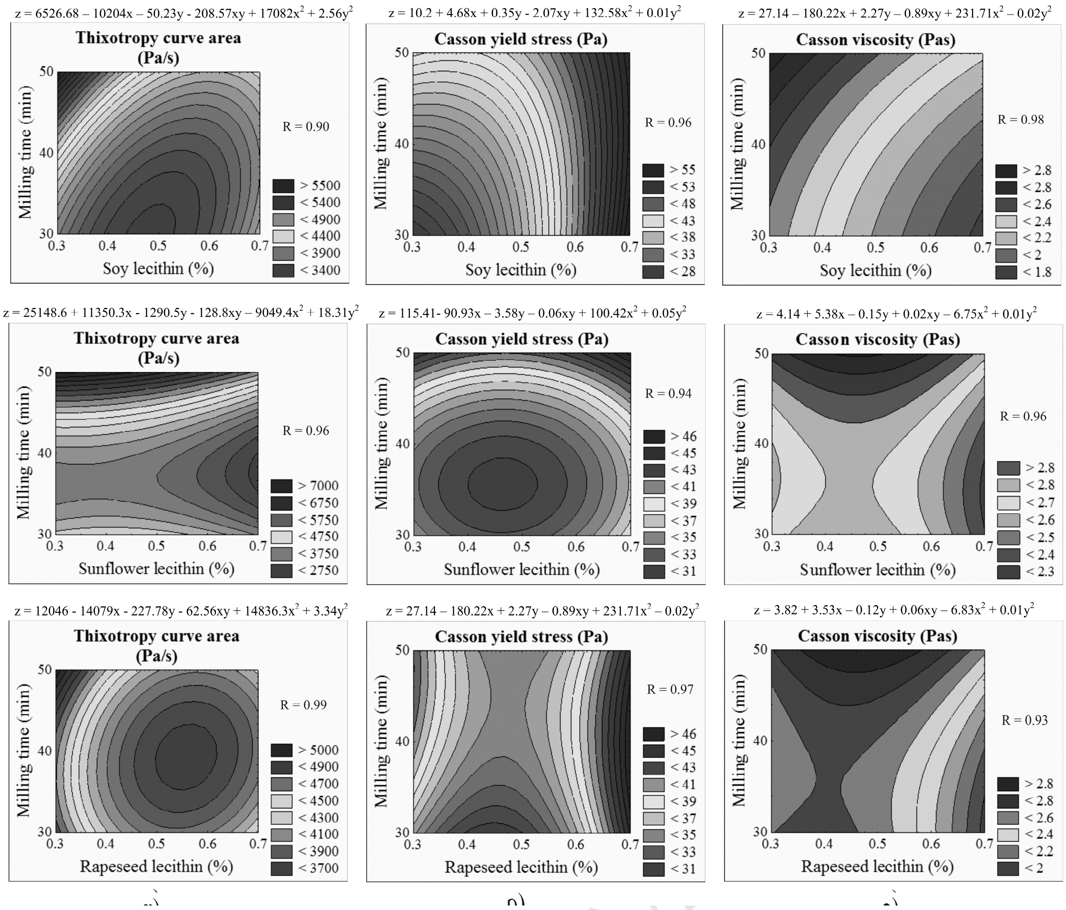
Values are means of three determinations ± standard deviation. Values in the same column with the same letter in superscript are not statistically different ($p<0.05$).

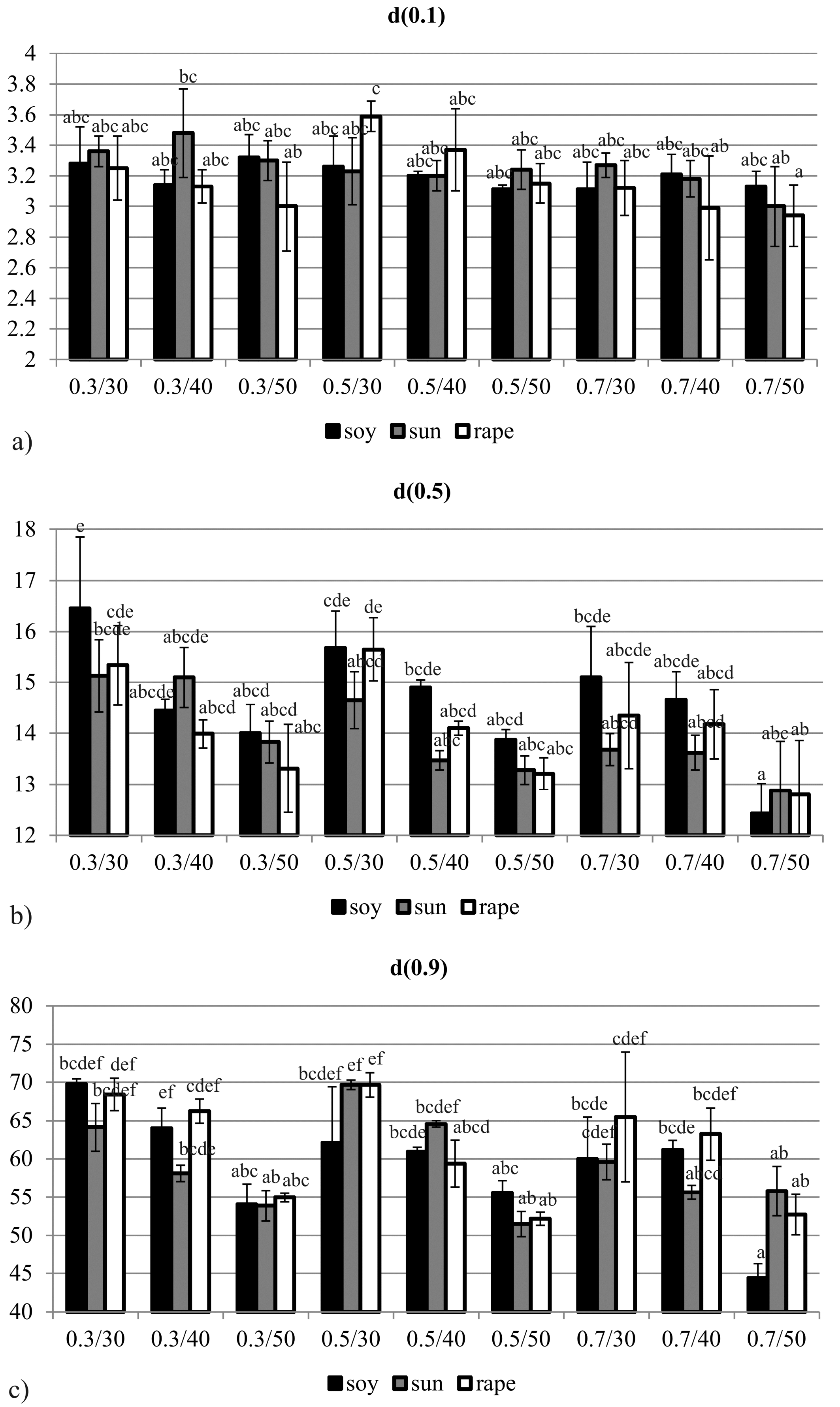
*not determined


Soy lecithin
Sunflower lecithin
Rapeseed lecithin
τ (Pa)
γ (1/s)
a)
soy0.3
soy0.5
soy0.7
b)
sun0.3
sun0.5
sun0.7
c)
rape0.3
rape0.5
rape0.7
d)
soy0.3 - G'
soy0.3 - G"
soy0.5 - G'
soy0.5 - G"
soy0.7 - G'
soy0.7 - G"
G' (Pa), G" (Pa)
f (Hz)
e)
sun0.3 - G'
sun0.3 - G"
sun0.5 - G'
sun0.5 - G"
sun0.7 - G'
sun0.7 - G"
f)
rape0.3 - G'
rape0.3 - G"
rape0.5 - G'
rape0.5 - G"
rape0.7 - G'
rape0.7 - G"
g)


τ (Pa)
γ (1/s)
a)
b)
c)
soy$_{0.3}$30
soy$_{0.3}$40
soy$_{0.3}$50
soy$_{0.5}$30
soy$_{0.5}$40
soy$_{0.5}$50
soy$_{0.7}$30
soy$_{0.7}$40
soy$_{0.7}$50
sun$_{0.3}$30
sun$_{0.3}$40
sun$_{0.3}$50
sun$_{0.5}$30
sun$_{0.5}$40
sun$_{0.5}$50
sun$_{0.7}$30
sun$_{0.7}$40
sun$_{0.7}$50
rape$_{0.3}$30
rape$_{0.3}$40
rape$_{0.3}$50
rape$_{0.5}$30
rape$_{0.5}$40
rape$_{0.5}$50
rape$_{0.7}$30
rape$_{0.7}$40
rape$_{0.7}$50


Thixotropic curve area (Pa/s)
8000
7000
6000
5000
4000
3000
2000
0.3/30 0.3/40 0.3/50 0.5/30 0.5/40 0.5/50 0.7/30 0.7/40 0.7/50
a)
soy sun rape
Casson yield stress (Pa)
65
60
55
50
45
40
35
30
25
20
0.3/30 0.3/40 0.3/50 0.5/30 0.5/40 0.5/50 0.7/30 0.7/40 0.7/50
b)
soy sun rape
Casson viscosity (Pas)
3.5
3
2.5
2
1.5
0.3/30 0.3/40 0.3/50 0.5/30 0.5/40 0.5/50 0.7/30 0.7/40 0.7/50
c)
soy sun rape


z = 6526.68 – 10204x – 50.23y - 208.57xy + 17082x² + 2.56y²
Thixotropy curve area (Pa/s)
R = 0.90
Soy lecithin (%)
z = 10.2 + 4.68x + 0.35y - 2.07xy + 132.58x² + 0.01y²
Casson yield stress (Pa)
R = 0.96
Soy lecithin (%)
z = 27.14 – 180.22x + 2.27y – 0.89xy + 231.71x² – 0.02y²
Casson viscosity (Pas)
R = 0.98
Soy lecithin (%)
z = 25148.6 + 11350.3x - 1290.5y - 128.8xy – 9049.4x² + 18.31y²
Thixotropy curve area (Pa/s)
R = 0.96
Sunflower lecithin (%)
z = 115.41- 90.93x – 3.58y – 0.06xy + 100.42x² + 0.05y²
Casson yield stress (Pa)
R = 0.94
Sunflower lecithin (%)
z – 4.14 + 5.38x – 0.15y + 0.02xy – 6.75x² + 0.01y²
Casson viscosity (Pas)
R = 0.96
Sunflower lecithin (%)
z = 12046 - 14079x - 227.78y - 62.56xy + 14836.3x² + 3.34y²
Thixotropy curve area (Pa/s)
R = 0.99
Rapeseed lecithin (%)
z = 27.14 – 180.22x + 2.27y – 0.89xy + 231.71x² – 0.02y²
Casson yield stress (Pa)
R = 0.97
Rapeseed lecithin (%)
z – 3.82 + 3.53x – 0.12y + 0.06xy – 6.83x² + 0.01y²
Casson viscosity (Pas)
R = 0.93
Rapeseed lecithin (%)
Milling time (min)



Values represent the means of three measurements ± standard deviation.

Values followed by different lower-case letters in the same column are significantly different from each other (p<0.05).

- Utilization of by-products – sunflower and rapeseed lecithin as emulsifiers.
- Different viscosity and phospholipid composition of lecithins.
- Impact on rheological properties of the cream fat phase and final product.
- 0.5% of soy and rapeseed lecithin or 0.7% of sunflower lecithin
- 40-min milling time