Cellulose ether emulsions as fat source in cocoa creams: thermorheological properties (flow and viscoelasticity)

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ABSTRACT

Flow behaviour and viscoelastic properties at three different temperatures (20, 45 and 70 °C) of cocoa filling creams have been studied. These creams were composed of cocoa, starch, sugar, skimmed milk powder and non-digestible cellulose ether emulsions as fat source. Two types of methylcelluloses, MC, and two types of hydroxypropyl methylcelluloses, HPMC, with different chemical substitution degrees were employed. Results showed important differences in zero shear viscosity and shear thinning character at room temperature, due to the different internal structure revealed by the viscoelastic moduli spectra. Temperature sweeps of storage modulus showed different temperature gelation depending on the chemical substitution of the cellulose ethers. At 45 °C, both MC were already gelified and the behaviour of A4M and MX creams became quite similar, with significant differences respect to HPMC creams. However, once HPMC were also gelled at 70 °C all the creams had analogous characteristics both in flow and viscoelastic behaviour. The knowledge of the thermorheological properties of these cocoa creams could be an interesting and useful tool in industrial filling processes, such as pastry or confectionary, where they could be applied.

Keywords: viscosity, oscillatory measurements, filling creams, hydrocolloids, temperature.

1. Introduction

Filling creams are a major component in many pastry and confectionary products. Their physical properties vary extensively from semisolid to more spreadable and plastic, depending on their specific application. Typical baked fillings usually contain 30-35% fat, although this amount can reach up to 60% when certain properties of spreadability or adhesion are desired (Abboud, 1999; Miele, Di Monaco, Masi, & Cavella, 2015). The fats normally used in this type of products are saturated fats (Idris and Samsuddin, 1993).

The amount of fat used and its characteristics, as well as the composition of ingredients in general, will have a significant influence on the structural properties of the final product. Rheological properties are among the most important physical properties defining the structure of a food system and they contribute to the characterization and control of the texture when different formulations are used (Liu, Xu, & Guo, 2007). Different flow and temperature conditions as well as recipe change (elimination or incorporation of new ingredients) will influence the rheological behaviour (Lončarević et al., 2016; Marcotte, Hoshahili, & Ramaswamy, 2001; Meza, Carboni, & Peralta, 2018; Pichler, Pozderović, & Pavlović, 2012), and thus have a key role in industrial food manufacturing processes. Moreover, due to the correlation between rheological parameters and sensory evaluation of food, rheology can be used as a tool to establish new formulations or improve existing ones.

Generally, filling creams are shear thinning fluids with viscoelastic behaviour typical of weak gels (Tárrega, Ramírez-Sucre, Vélez-Ruiz, & Costell, 2005). Nevertheless, the presence of hydrocolloids and the changes in temperature can influence the rheological behaviour.

Fat overconsumption is associated with obesity and other related diseases (Bray & Popkin, 1998; Chajès et al., 2008; Mozaffarian, 2016; Sun et al., 2007). For this reason, consumer demand low fat foodstuffs with a healthier lipid profile, but with similar physical and sensory properties to those of the conventional product. However, fat reduction is not an easy task for food manufacturers, due to the wide variety of important functionalities exerted by fat, both in structure and sensory properties as well as in technological aspects (Drewnowski, 1992; Drewnowski and Almiron-Roig, 2009; Zoulias, Oreopoulou, & Kounalaki, 2002).

A wide number of strategies have been employed to mimic fat functionality in food items. It is recognized that hydrocolloids are widely used as texture modifiers with the purpose of improving the rheology of food systems (Saha & Bhattacharya, 2010) since they can compensate the loss of structure in reduced-fat food (Meyer, Bayarri, Tárrega, & Costell, 2011; Peng & Yao, 2017). They are used mainly as thickeners and stabilizers in a variety of foods (ADA, 2005; Lucca and Tepper, 1994) and could offer similar eating pleasure as high-fat food, without providing excessive energy (Drewnowski, 1992).

Non digestible emulsions have become a recent strategy for fat reduction. They are partially digested, so the amount of fat bioavailable is reduced. Only the fraction of ingested lipids and lipophilic components which are micellarized will be available for absorption into the blood, the so called “bioaccessible” fraction (Verkempinck et al., 2018). The fat initially present in a food containing a non-digestible emulsion would be the same as in a standard conventional product, but fat bioaccessibility will be lower in the non-digestible emulsion, so problems like obesity, and illnesses related to fat overconsumption will be reduced.

Cellulose ether emulsions have been demonstrated to be effective as not digestible o/w emulsions. Their advantages are: lower fat content than conventional fat, a fat profile rich in unsaturated fatty acids, no *trans* fatty acids and lower fat digestibility (Tarancón, Salvador, & Sanz, 2013, Espert et al., 2017).

Both methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) possess thermal gelation properties (Chen, Kang, & Chen, 2008; Li, 2002; Sanz, Fernández, Salvador, Munoz, & Fiszman, 2005; Sanz, Falomir, & Salvador, 2015).

The effectivity to reduce *in vitro* fat digestion has been associated to the specific cellulose ether employed and their thermal gelation properties. Methylcellulose (MC) with higher molecular mass showed the highest effectivity and hydroxypropyl methylcellulose (HPMC) the lowest (Espert, 2017).

Recently the MC and HPMC emulsions have been applied in a cocoa cream recipe and the *in vitro* fat digestibility and sensory perception investigated. The MC and HPMC emulsions were found effective to reduce the *in vitro* cream fat digestibility (Espert et al., 2019).

Industrial application of the non-digestible cellulose ether emulsions as fat source in cocoa creams also requires knowledge of the creams rheological properties. There are

no previous studies about the rheological properties of cocoa creams made with cellulose ether emulsions.

In this study the thermorheological behaviour (both in flow and linear viscoelasticity) of cocoa filling creams made with different non digestible cellulose ether emulsions as fat source is investigated. The obtained conclusions will be helpful to determine the suitability of each emulsion according to the required cream properties and the specific application, especially when heating processes are applied.

2. Materials and methods

2.1 Preparation of emulsions

Four types of emulsions were prepared using different types of cellulose ethers supplied by The Dow Chemical Co. (USA): methylcelluloses A4M and MX, and hydroxypropyl methylcelluloses F4M and K4M. The percentage of chemical substitution is: A4M (30 g/100 g methoxyl), MX (methoxyl >30 g/100 g), F4M (29 g/100 g methoxyl and 6.8 g/100 g hydroxypropyl) and K4M (22.5 g/100 g methoxyl, 7.7 g/100 g hydroxypropyl). All of them possess the same molecular weight, except for the MX that has higher molecular mass (The Dow Chemical Company, 2002).

The emulsions were composed of 47 g/100 g sunflower oil (Koipe Sol, Deoleo S.A, Madrid, Spain), 51 g/100 g water and the different hydrocolloid (2 g/100 g). After preparation they were stored at room temperature for 24 h before the measurements.

The preparation of the emulsion basically consists of two stages. The cellulose ether was first dispersed in the oil using a Heidolph stirrer at the lowest speed for five min. Then, to obtain an emulsion, water (preferably at a temperature comprised between 1 and 20 °C, depending on the type of ether) was gradually added to the previous dispersion while stirring, obtaining the hydration of the cellulose ether (hydration and viscosity development occurs after cold water addition). Finally, The 200 g mixture was homogenized using an IKA T18 basic homogenizer (Ultra-Turrax, IKA, Germany) (S18N-19G dispersion tool) for 15 s at speed 1 (6500 rpm) and 60 s at speed 4 (17500 rpm) until the emulsion was obtained.

The resulting emulsion is an oil-water emulsion in which the continuous phase is the network formed by the hydrated cellulose and the discontinuous phase is the sunflower oil. It has a weak gel physical consistency and showed a good physical and oxidative

stability at room temperature, for a period of not less than two weeks (Borreani, Espert, Salvador, Sanz, Quiles, & Hernando, 2017; Sanz, Salvador, Fiszman, & Laguna, 2013).

2.2 Preparation of creams

Cocoa creams were prepared using the proportions shown in Table 1. A food processor (TM31 Thermomix, Vorwerk, Wuppertal, Germany) was used to mix the ingredients. At first, starch (CTex 06205, Cargill BV, Netherlands), sugar (Disem, Spain), skimmed powder milk (1 g/100 g fat) (Central Lechera Asturiana, Spain), cocoa powder (Chocolates Valor S.A., Alicante, Spain) and mineral water were mixed at 90 °C for 6 min at speed 2 (200 rpm) in order to enable starch gelatinization. After that, mixture was allowed to cool at room temperature. Then, the hydrocolloid based emulsion or sunflower oil (in case of control cream) were added by mixing in the processor for 6 min at speed 2 without temperature selection to obtain the filling cream. The fat content (23.5 g/100 g) was the same in the hydrocolloid based emulsions and in the control cream, to be able to identify the effect associated to hydrocolloid incorporation. However, although the initial fat content is the same in all the creams, it should be considered that fat bioaccessibility is lower in the hydrocolloid based emulsions creams (Espert et al., 2019).

All the creams were stored at 5 °C for 24 h before the measurements.

2.3 Rheological characterization

Rheological measurements were carried out with a controlled stress rheometer (AR-G2, TA Instruments, Crawley, England) equipped with a Peltier system for temperature control. A serrated plate–plate (40 mm) was used in all the experiments, applying a gap of 1 mm. Exposed surfaces of the samples were covered with Vaseline oil (Panreac, Spain) to avoid dehydration.

Small amplitude oscillation sweeps (SAOS) were performed in order to analyse the viscoelastic properties. To determine the extent of the linear viscoelastic region (LVR) stress sweeps (from 0.1 to 100 Pa in logarithmic distribution, 10 points per decade) were carried out at 1 Hz.

Temperature sweeps were performed from 20 °C to 80 °C at a heating rate of 1 °C/min in order to observe the effect of heating in the cream structure. Storage moduli at a frequency of 1 Hz within the LVR (0.15 % strain) were recorded as a function of temperature.

Flow curves and frequency sweeps were carried out at 20 °C and also in samples previously heated until 45 °C and 70 °C (1 °C/min heating rate from room temperature). Before each assay, an equilibration time sweep (15 min) was conducted at the selected temperature (45 °C and 70 °C).

Frequency sweeps were performed between 0.01 and 10 Hz within the linear region (at 0.5 and 1 Pa, depending on the characteristic of the cream) and both the values of storage modulus (G'), loss modulus (G'') and $\tan \delta$ were recorded. They were fitted to power law equations (Sanz et al, 2017):

$$G' = G'_1 v^{m'} \quad (1)$$

$$G'' = G''_1 v^{m''} \quad (2)$$

where v is the applied frequency (in Hz), G'_1 and G''_1 correspond to the viscoelastic moduli at 1 Hz and the dimensionless parameters m' and m'' give information about the frequency dependence.

Stepped flow curves were performed in control stress mode in the range of 1 to 1000 Pa with a logarithmic distribution of 10 points per decade, setting a time of 30 s per point. The simplified Carreau model was used to describe the flow behaviour of the creams (Tarrega et al, 2012, Mezger, 2014):

$$\eta = \frac{\eta_0}{\left(1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)^2\right)^s} \quad (3)$$

where η_0 (Pa s) is the zero shear viscosity, corresponding to the constant viscosity of the plateau for very low shear rates, $\dot{\gamma}_c$ is the critical shear rate, related to the bend between the plateau and the falling of the flow curve in the range of shear thinning behaviour, and s (dimensionless) informs about the shear thinning character of the sample, as it corresponds to the slope of the straight line in the log-log plot in the second region (Mezger, 2014).

In order to ensure reproducibility, all the measurements were repeated at least three times, with samples prepared in different days and performed 24 h after formulation of the different creams. A fresh sample was loaded for each measurement. In

measurements at 20 °C samples were allowed to rest for 15 min (to stabilise and temper the sample) before the measurements.

Experimental values of flow curves and oscillatory frequency sweeps were fitted to mathematical expressions using the program KaleidaGraph 4.0 (Synergy Software).

2.4 Statistical analysis

All the rheological data for triplicate creams measurements were subjected to analysis of variance (ANOVA). To determine the significant differences between the samples, the Tukey test was used (XLStat 2010 (Addinsoft, Barcelona, Spain)). A significance level of $p < 0.05$ was applied.

3. Results and discussion

Representative flow curves of the different creams at 20 °C are shown in Fig.1. All the cocoa creams studied showed shear thinning behaviour, as viscosity highly decreased when increasing shear rate. Also a constant plateau for very low shear rates was observed in all cases. The experimental data were satisfactorially fitted ($r > 0.995$) to simplified Carreau model (3). The fits correspond to the continuous lines in Fig. 1 and the mean values of the parameters obtained when fitting the triplicated flow curves are shown in Table 2.

The creams containing HPMC emulsions (K4M and F4M) presented similar flow behaviour and they were not really different from the cream containing the methylcellulose A4M (no significant differences are shown). However, the MX cream was quite different for the other three tested, as the zero shear viscosity (η_0) was even one order of magnitude higher and it had a stronger shear thinning behaviour (highest s index). Intermediate flow behaviour corresponded to the control starch based cream.

In practice, zero shear viscosity is related with the consistency of the semisolid product in the recipient. These differences are seen in the image in Fig. 2 where three levels of consistency in spoon are shown: The MX cream, with the highest η_0 and the thickest consistency; the control, with an intermediate consistency; and the F4M cream, with the lowest η_0 and the thinnest appearance. However, since the creams presented different shear thinning behaviour, as indicated by the s index, the differences in viscosity for high shear rates were reduced. Viscosity values at 100 1/s were ranging between 5.8 and

7.8 Pa s for the cocoa cream containing cellulose ethers and they were not significant differences between the two MC. Hence, the behaviour of all the creams at spreadable velocities became more similar.

These differences are even more clearly visualized when analyzing viscosity as a function of shear stress. The range of shear stresses at which viscosity is constant is greater for MX cream and control than for the other three creams studied, and they have a more abrupt fall of viscosity.

In order to study viscoelastic behaviour of the creams, frequency sweeps were performed. The mechanical spectra obtained (viscoelastic moduli as a function of frequency) at 20 °C is plotted in Fig. 3. All the spectra were satisfactorily fitted ($r > 0.995$) to the empirical equations (1) and (2) and the mean values of the parameters obtained for the three replicates measured are shown in Table 2.

The predominance of the storage modulus (G') over the loss modulus (G'') in the whole range of frequencies studied indicates that all creams presented a gel-like behaviour, with an internal three-dimensional network (Mezger, 2014; Sanz et al., 2015, 2017; Tárrega et al., 2012), due to the presence of the cellulose-based semisolid emulsion, as well as the presence of starch, which also gives them consistency, especially in the case of control cream without emulsion.

The results showed two groups of creams with different viscoelastic behaviour (Fig. 3), corroborated by the results obtained when analysing statistical differences in $\tan \delta$ (G''/G') at 1 Hz. The spectra of MX creams turned to be quite similar to the control starch based cream. Both creams have the same frequency dependence (as reveals ANOVA in Table 2), although MX creams were firmer and with a stronger elastic character.

On the other hand, the rest of the cocoa creams had different dynamic spectra, with higher frequency dependence of both moduli (m' were about twice the corresponding to the previous group).

These results indicated that the second group presented a weaker internal structure (with higher values of $\tan \delta$) which is in accordance with the flow behaviour previously analysed. The strongest internal structure of MX cream lead to a higher consistence at rest (η_0), a stronger shear thinning behaviour and a greater value for the stress necessary to decrease viscosity (resistance to flow). On the other hand, A4M cream, despite being a methylcellulose like MX cream, showed a closer behaviour to the hydroxypropyl

methylcellulose creams. This difference among A4M and MX can be associated to the highest methoxil level and the highest molecular mass of MX.

The evolution of the linear viscoelastic functions with temperature in the range 20 to 80 °C is presented in Fig. 4. The thermal gelation ability of MC and HPMC can be observed in the corresponding creams. Three different kind of behaviour are clearly observed, regarding to the control cream, the MC and the HPMC creams. As previously reported (Sanz et al., 2015), the increase in methoxyl content in cellulose ether reduced the temperature required to observe an increase in elasticity, so creams with methylcellulose emulsion (MX and A4M) showed a lower gelation temperature than the HPMC creams, being the lowest temperature found in MX because its higher methoxyl content. At low temperatures cellulose ethers have a great capacity of water retention, but after heating a release of water will occur forming strong bonds with internal chains, resulting in very stable gel structures. The higher molecular mass and the higher methoxyl substitution increase cellulose hydrophobicity, resulting in greater intermolecular association since the hydrophobic groups are closer. On the other hand, the presence of hydroxypropyl substitutions produced an increase in the gelation temperature, which depended on the substitution degree. The increase in G' values, related to cellulose ether gelation, took place at the highest temperature for the K4M cream.

To investigate how the thermal gelation properties of the cellulose ether emulsions affect their flow and viscoelastic properties, flow curves and SAOS tests were performed at 45 and 70 °C. The obtained flow curves were fitted to Carreau simplified model (3) and the mechanical spectra to power law equations (1) and (2). The mean values obtained for the parameters of the curve fits are shown in Table 2.

The differences showed at room temperature (20 °C) both in flow and viscoelastic moduli (G' and G'') between the two MC creams almost disappeared at 45 °C when both MC are completely gelled. The loss tangent (G''/G') of both creams were about 0.1 (corresponding to loss angles of approx. 5 degrees) and a slight frequency dependent is observed, what confirms the existence of a strong internal network (Fig.5). A4M cream highly increased viscosity from 20 to 45 °C approaching MX values (Table 2) and the mechanical spectra (G' and G'') became similar to the corresponding to MX cream (see values of $\tan \delta$ in Fig. 5). The temperature increase also had influence in MX creams, enhancing their viscosity and firmness (G'), but the effect was not so significant.

On the other hand, results for both HPMC showed that these celluloses were not significantly affected by temperature when changing from 20 to 45 °C. F4M creams at 45 °C were a bit more viscous than the creams at room temperature, but K4M creams did not present changes neither in viscosity nor in viscoelasticity (Table 2). These creams containing HPMC emulsions needed higher temperatures to gelify. At 70 °C the changes in viscosity and structure are clear, as zero shear viscosity increased one order of magnitude and loss tangent values (Fig.5) dropped to 0.15 (loss angles of 10 degrees approx.). The differences detected at 45 °C disappeared at 70 °C, since both HPMC creams had a close rheological behaviour when they were gelled, with similar flow curves and loss tangent values (Fig. 5).

Regarding to the control starch based creams, parameters in Table 2 show that they did not present significant changes with temperature in both flow and viscoelastic behaviour, only a slight decrease in viscosity and in dynamic moduli was produced.

When comparing all the cocoa creams at high temperatures, it stands out that MC creams became the most viscous ones and also the creams with a strongest internal network. When HPMC were gelled the cocoa creams behaviour approached the control cream rheological behaviour.

Moreover, the shear thinning behaviour increased when the celluloses gelify, so the viscosity drop with shear rate was more abrupt. As a consequence, the viscosity values for high velocities are similar to the ones corresponding to room temperature, although the consistency at the recipient was much greater.

Conclusions

A thermorheological characterization of cellulose emulsion based cocoa creams was carried out. Temperature sweeps of storage modulus showed different temperature gelation depending on the chemical substitution in cellulose ethers.

Significant differences existed in zero shear viscosity and shear thinning character at room temperature, due to the different internal structure revealed by the viscoelastic moduli spectra. MX cream was clearly different to the rest of the cellulose creams, with a similar behaviour to the control starch based cream. The large differences detected in consistency at the recipient were reduced at spreadable velocities.

At 45 °C, both MC were already gelified and the behaviour of A4M and MX creams became quite similar, with significant differences respect to HPMC creams. However,

once HPMC were also gelled at 70 °C all the creams had analogous characteristics both in flow and viscoelastic behaviour.

Both chemical substitution and temperature are key factors to consider in cellulose ether creams for establishing the most suitable formulation, especially when heating processes are applied. The studied creams could be an alternative to conventional full fat products and they may provide different options according to the desired characteristics and the application process.

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TABLES

Table 1. Composition of the studied cocoa creams.

Ingredients	g/100 g	
	Control	Emulsion based creams
Starch	4	2.25
Cocoa powder	2.5	2.5
Skimmed milk powder	5	5
Sugar	10	10
Water	55	30.25
Emulsion	-	50
Sunflower oil	23.5	-

Table 2. Mean values of the parameters obtained from flow curves fits to Carreau model (3) and power law equations (1,2) fits for mechanical spectra for the different creams, at the three temperatures studied.

			Flow curves			Mechanical spectra			
	Sample	T (°C)	η_0 (Pa s)	$\dot{\gamma}_c$ (1/s)	s	G'(Pa)	m'	G''(Pa)	m''
MC emulsions	MX	20	253496 ^{Ba}	0.0005 ^{Bbc}	0.423 ^{Ba}	743 ^{Aa}	0.090 ^{Ab}	130 ^{Bd}	0.154 ^{Ac}
		45	419620 ^A	0.0009 ^A	0.480 ^A	1568 ^B	0.021 ^B	123 ^B	0.005 ^B
	A4M	20	16323 ^{Bc}	0.0011 ^{Aa}	0.330 ^{Bc}	524 ^{Bb}	0.268 ^{Aa}	216 ^{Aa}	0.201 ^{Abc}
		45	405533 ^A	0.0013 ^A	0.483 ^A	1394 ^A	0.063 ^B	148 ^A	0.105 ^B
HPMC emulsions	F4M	20	11093 ^{Bc}	0.0009 ^{Aab}	0.320 ^{Ccd}	351 ^{Bd}	0.271 ^{Aa}	150 ^{Ac}	0.220 ^{Aab}
		45	43992 ^B	0.0004 ^A	0.383 ^B	377 ^B	0.186 ^B	134 ^A	0.254 ^A
		70	180066 ^A	0.0007 ^A	0.453 ^A	819 ^A	0.100 ^C	130 ^A	0.105 ^B
	K4M	20	9863 ^{Bc}	0.0006 ^{Aabc}	0.307 ^{Cd}	351 ^{Bd}	0.293 ^{Aa}	173 ^{Ab}	0.273 ^{Aa}
		45	15508 ^B	0.0004 ^A	0.343 ^B	380 ^B	0.267 ^A	168 ^A	0.285 ^A
		70	104547 ^A	0.0007 ^A	0.433 ^A	592 ^A	0.070 ^B	90 ^B	0.067 ^B
		Starch based	Control	20	94260 ^{Ab}	0.0003 ^{Ac}	0.390 ^{Ab}	426 ^{Ac}	0.114 ^{Ab}
45	88806 ^A			0.0002 ^A	0.400 ^A	322 ^A	0.119 ^A	68 ^A	0.187 ^A
70	86730 ^A			0.0002 ^A	0.410 ^A	306 ^A	0.086 ^A	51 ^A	0.209 ^A

^{ABCD} For each sample, values in the same column with the same letter are not statistically different with temperature (p<0.05) according to Tukey's test.

^{abcd} For the same temperature (20 °C), values in the same column with the same letter are not statistically different (p<0.05) according to Tukey's test.

Figure legends

Figure 1. Flow curves for the different cocoa creams studied at 20°C: ▼ A4M, ▲ MX, ■ F4M, ◆ K4M, ● Control.

Figure 2. Consistency at the recipient of the cocoa creams.

Figure 3. Storage modulus (G' : filled symbols) and loss modulus (G'' : open symbols) as a function of oscillation frequency for the different cocoa creams studied at 20 °C.

▼ A4M, ▲ MX, ■ F4M, ◆ K4M, ● Control.

Figure 4. Temperature sweeps (1 K/min) for the storage modulus (G') corresponding to the cocoa creams studied: ▼ A4M, ▲ MX, ■ F4M, ◆ K4M, ● Control.

Figure 5. Loss tangent (G''/G') as a function of frequency for the cocoa creams at different temperatures: ▼ A4M, ▲ MX, ■ F4M, ◆ K4M. Closed symbols: 20°C, Open symbols: 45°C, +, ×: 70°C.

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