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Clustering of oil droplets in o/w emulsions enhances perception of oil-related sensory attributes

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ABSTRACT

The sensory perception of o/w emulsions is determined by their structure and physicochemical properties. The aims of this study were (a) to determine the influence of oil droplet clustering in o/w emulsions on sensory perception and (b) to link their sensory attributes to rheological, tribological and structural properties. Clustered emulsions were prepared by combining o/w emulsions stabilised by different sets of emulsifiers: (a) positively-charged gelatine and negatively-charged whey protein (WPI), and (b) positively-charged gelatine and negatively-charged diacetyl tartaric acid ester of mono- and diglycerides (DATEM). Oil droplet clusters ranging in diameter from 1 to 50 µm were obtained. The difference in charge density between gelatine- and DATEM-stabilised oil droplets was higher than that between gelatine- and WPI-stabilised droplets. This difference allowed to alter the interaction strength within oil droplet clusters. The sensory perception of clustered emulsions was quantified using the Rate-All-That-Apply (RATA) methodology with untrained subjects (n = 83). Participants assessed o/w emulsions varying in cluster size (1 µm–50 µm), cluster strength (tuned by changing the emulsifier-pairs), and single droplet emulsions with and without adjusted viscosity, as well as a reference emulsion with large single droplets (comparable in size to emulsions with large clusters). Creaminess and thickness intensities were significantly higher for clustered o/w emulsions compared to that of single droplet o/w emulsions with the same oil content and similar oil droplet/cluster size. With increasing cluster size, creaminess and thickness intensities increased significantly for hetero-aggregated clusters with weak interactions (gelatine-whey protein). When cluster interactions were stronger (gelatine-DATEM), creaminess intensity increased to a lesser extent and grittiness intensity increased considerably. Thickness and creaminess were strongly correlated to the rheological (e.g. consistency) and tribological properties (e.g. fiction coefficient at 10 mm/s) of o/w emulsions with clustered oil droplets. Grittiness and fattiness were strongly correlated to the tribological properties (slope of mixed regime) of o/w emulsions and their interactions with saliva. We conclude that clustering of oil droplets in o/w emulsions by hetero-aggregation allows to enhance the sensory perception of fat-related attributes by tuning rheological and tribological properties, and provides an effective method to structure liquid foods to obtain specific sensory properties.

1. Introduction

Reduction of fat content in foods while maintaining desired sensory properties, such as creaminess, remains a challenge. The sensory perception of o/w emulsions is largely determined by the rheological and tribological properties, which are influenced by oil volume fraction and oil droplet size. With increasing oil volume fraction, the viscosity of o/w emulsions increases and the perception of fat-related sensory attributes is enhanced (Chojnicka, Sala, de Kruif, & van de Velde, 2009; Lett, Norton, & Yeomans, 2016). Not only the oil volume fraction, but also the oil droplet size determines the sensory properties of emulsions. Decreasing the oil droplet size at constant oil volume fraction has been shown to increase creaminess (Lett et al., 2016), possibly as a consequence of an increase in viscosity (Pal, 2011). The sensory perception of o/w emulsions is also related to several other physical characteristics such as flow behaviour and lubrication properties (Kim, Gohtani, &

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Yamano, 1996; Lett et al., 2016; Starov & Zhdanov, 2003). The rheological properties of o/w emulsions are mostly related to thickness and creaminess perception, while the lubrication properties have been shown to be related to attributes such as melting, fattiness and creaminess (Akhtar, Stenzel, Murray, & Dickinson, 2005; de Wijk, Janssen, & Prinz, 2011; Izutsu & Wani, 1985).

Besides oil volume fraction and oil droplet size, the clustering of oil droplets in o/w emulsions has been demonstrated to affect the rheological properties of emulsions (Dalgleish, 2006). Clustering can be the result of different attractive interactions between oil droplets. Several studies have shown that oil droplets in o/w emulsions can be clustered by use of electrostatic interactions, also referred to as hetero-aggregation (Fuhrmann, Sala, Stieger, & Scholten, 2019; Mao & McClements, 2011, 2012; 2013a; 2013b). Hetero-aggregation allows clustering of oil droplets in o/w emulsions in a controlled manner. To obtain hetero-aggregated oil droplets, two emulsions stabilised with oppositely charged emulsifiers are combined. Due to electrostatic attraction between the emulsifier-stabilised oil droplets, clusters are formed when repulsive interactions are overcome. Several emulsifier combinations for hetero-aggregates have been described, including β-lactoglobulin and lactoferrin (Iqbal, Hameed, Baloch, & McClements, 2013; Mao & McClements, 2011, 2012), whey protein isolate and modified starch (Mao & McClements, 2013b), and whey protein isolate and saponins (Maier, Oechsle, & Weiss, 2015; Maier, Zeeb, & Weiss, 2014). Recently, it was shown that cluster size and cluster strength of hetero-aggregated oil droplets in o/w emulsions can be controlled using gelatine in combination with whey protein or DATEM (Fuhrmann et al., 2019). Several studies have demonstrated that emulsion viscosity increases largely as a result of oil droplet clustering (Mao & McClements, 2012; 2013a). The main reason for the increase in viscosity by clustering of oil droplets is an increase in effective volume fraction of the dispersed oil droplets (Tadros, 1996, 2004). When oil droplets are clustered, water is enclosed within the clusters, which effectively increases the volume fraction of the dispersed phase. Such an effect may be compared to the incorporation of water droplets into w/o/w emulsions, where water droplets are emulsified and dispersed in the oil phase and thereby the volume fraction of the oil phase increases. For w/o/w emulsions, the increased volume fraction of the dispersed phase has a positive influence on sensory perception of fat-related attributes (Oppermann, Piqueras-Fiszman, de Graaf, Scholten, & Stieger, 2016; Oppermann, Renssen, Schuch, Stieger, & Scholten, 2015; Oppermann, Verkaaik, Stieger, & Scholten, 2017). Double emulsions can therefore be used as a strategy for fat reduction while maintaining sensory perception of fat-related attributes such as creaminess.

Structural changes of emulsions occurring during oral processing can influence sensory perception, especially the perception of attributes perceived at later stages of the consumption process (Vingerhoeds, Blijdenstein, Zoet, & van Aken, 2005). During oral processing, saliva is incorporated into the emulsion, which introduces salivary proteins, enzymes and salts. Interactions between saliva and emulsion droplets can lead to changes in the emulsion structure. O/w emulsions stabilised with whey protein isolate have been observed to flocculate upon mixing with saliva due to electrostatic interactions between positively-charged whey proteins and negatively-charged mucins (Chojnicka et al., 2009; Scholten, 2017; Silletti, Vingerhoeds, Norde, & van Aken, 2007). These structural changes during oral processing influence both rheological and tribological properties of the emulsions and can influence sensory properties.

To the best of our knowledge, the sensory perception and tribological properties of o/w emulsions with clustered oil droplets have not been studied yet. The aims of this study were (a) to determine the influence of oil droplet clustering in o/w emulsions on sensory perception and (b) to link their sensory attributes to rheological, tribological and structural properties. We hypothesised that creaminess and thickness perception of o/w emulsions is enhanced by clustering of oil droplets and that the degree of enhancement is related to cluster size and strength. Additionally, we hypothesised that the interactions between saliva and hetero-aggregated oil droplets influence the structure and sensory properties of clustered o/w emulsions by interfering with the electrostatic interactions between oil droplets.

2. Materials and methods

2.1. Materials

Whey protein isolate (BiPRO WPI) was obtained from Davisco (Lot # JE 062-3-420, USA). Diacetyl tartaric acid ester of mono- and diglycerides (DATEM) was kindly provided by CP Kelco (USA). Gelatine Type 250 PS 30 was obtained from Rousselot (Lot #1207647, The Netherlands). Citric acid (p.a.) and sodium hydroxide (p.a.) were obtained from Sigma Aldrich (Steinheim, Germany). Sunflower oil (Reddy, The Netherlands), vanilla aroma (Dr Oetker, Germany) and sugar (Giro, The Netherlands) were purchased from a local retailer. All ingredients used were food grade.

2.2. Preparation of o/w emulsions

The composition of all studied o/w emulsions together with droplet size, critical strain and zeta potential is shown in Table 1, and a schematic overview of o/w emulsions can be found in Fig. 1. Further information to flow behaviour and tribological properties can be found in Table 3. O/w emulsions with clustered oil droplets were prepared using hetero-aggregation by combining oppositely-charged o/w emulsions. Emulsions differed mainly in cluster size (small, medium, large) and cluster strength (weakly and strongly interacting clusters). As reference, o/w emulsions with individual oil droplets of the size of the large oil droplet clusters were prepared. Another reference sample consisted of an o/w emulsion with the same viscosity of the emulsion containing large oil droplet clusters. The viscosity of the reference emulsion was adjusted by addition of xanthan as thickening agent. In total, 13 emulsions were prepared (Table 1).

2.2.1. Preparation of single droplet o/w emulsions

First, aqueous solutions of the different emulsifiers were prepared. Whey protein isolate (6.4 mg/mL aqueous solution) was dissolved in a 7.5 mM citric acid solution. The solution was stirred for 2 h at room temperature, after which the pH was set to 7 with 1 M NaOH. For gelatine solutions, gelatine (20 mg/mL aqueous phase) was added to the citric acid solution and heated at 80 °C for 30 min whilst stirring to hydrate and dissolve the gelatine. The pH was then adjusted to 5 or 7 using 1 M NaOH/1 M HCl. DATEM was dissolved in the oil phase (4 mg/mL oil) due to its limited solubility in water. The solution was heated at 80 °C for 10 min. Both gelatine and DATEM solutions were cooled to 40 °C before further processing.

To prepare single droplet o/w emulsions, the aqueous phase and the oil phase were mixed slowly, while pre-emulsifying with a rotor-stator homogeniser (Ultra-Turrax T25, IKA, Germany) at 8000 rpm for 3 min. A stock emulsion with a total oil volume fraction of 0.4 was obtained. Subsequently, the pre-emulsions were homogenised in a 2-stage homogeniser (PandaPlus, Niro Soavi, Parma, Italy) at 50 bar and 250 bar for 2 cycles. The emulsions were diluted using the corresponding aqueous solution to obtain a final oil volume fraction of 0.2. Emulsions with larger droplet sizes (GW01_large) were emulsified with a rotor-stator homogeniser (Ultra-Turrax T25, IKA, Germany) at 8000 rpm for 5 min and not further processed. To obtain reference emulsions with adjusted viscosity (GW01_Xan and GD01_Xan), stock emulsions (volume fraction oil 0.4) were diluted with xanthan solutions (0.6% (w/v) in citric acid solution pH 5/7) to obtain a final xanthan concentration of 0.3% (w/v emulsion) and a final oil volume fraction of 0.2. After the preparation of emulsions, 0.63% (w/v) sugar and 0.018% (w/v) vanilla aroma were added to all emulsions. The emulsions were stored for a maximum of 1 week at 4 °C before physical measurements

Table 1
Composition of the o/w emulsions. All emulsions had an oil volume fraction of 0.2. The aqueous phase of all o/w emulsions contained 0.63% sugar (w/v), 0.018% (w/v) vanilla aroma and 7.5 mM citric acid/NaOH solution. WPI: whey protein isolate, DATEM: diacetyl tartaric acid ester of mono- and diglycerides.

Samples		**Emulsion composition**					**Emulsion mixtures**			**Emulsion characteristics**		
O/w emulsion	Sample code	Gelatine	DATEM	WPI	Xanthan	pH	Gelatine-stabilised emulsion	DATEM-stabilised emulsion	WPI-stabilised emulsion	Zeta Potential	Critical Strain	Size
		%(w/v)	*%(w/v)*	*%(w/v)*	*(% w/v)*		*(%)*	*(%)*	*(%)*	*(mV)*	*(%)*	*(μm)*
DATEM single droplet	GD 01	0	0.12	0	0	5	0	100	0	−60 ± 1	–	1.9 ± 0.6
Gelatine single droplet (pH 5)	GD 10	0.6	0	0	0	5	100	0	0	+10 ± 1	–	2.6 ± 0.1
Gelatine-DATEM cluster (small)	GD 19	0.06	0.11	0	0	5	10	90	0	–	–	5.6 ± 0.6
Gelatine-DATEM cluster (medium)	GD 37	0.18	0.08	0	0	5	30	70	0	–	–	10.8 ± 0.9
Gelatine-DATEM cluster (large)	GD 55	0.3	0.06	0	0	5	50	50	0	−1 ± 8	4.1 ± 0.8	37.6 ± 1.7
WPI single droplet	GW 01	0	0	0.19	0	7	0	0	100	+7 ± 2	–	2.1 ± 0.5
Gelatine single droplet (pH 7)	GW 10	0.6	0	0	0	7	100	0	0	−45 ± 3	–	1.9 ± 0.3
Gelatine-WPI cluster (small)	GW 19	0.06	0	0.17	0	7	10	0	90	–	–	7.9 ± 0.3
Gelatine-WPI cluster (medium)	GW 37	0.18	0	0.13	0	7	30	0	70	–		14.8 ± 0.7
Gelatine-WPI cluster (large)	GW 55	0.3	0	0.1	0	7	50	0	50	−9 ± 2	1.8 ± 0.6	47.7 ± 1.4
Reference: Iso-viscous GD55	GD01_Xan	0	0.12	0	0.3	5	0	100	0	–	–	1.9 ± 0.6
Reference: Iso-viscous GW55	GW01_Xan	0	0	0.19	0.3	7	0	0	100	–	–	2.1 ± 0.5
Reference: Iso-size GW55	GW01_large	0	0	0.19	0	7	0	0	100	–	–	40.9 ± 9.5

were performed. The emulsions used for sensory tests were prepared 24 h before providing the samples to participants.

2.2.2. Preparation of o/w emulsions with clustered oil droplets

Hetero-aggregated o/w emulsions were prepared by combining two single droplet o/w emulsions at different volume ratios (v/v). After combining the two single droplet o/w emulsions, the hetero-aggregated o/w emulsions were slowly stirred and subsequently stored for 24 h at 4 °C before further use. The pH of the emulsions did not change upon mixing. Upon storage for 3 days at room temperature, clustered emulsions with large clusters (GW55, GD55) and emulsions with large droplets (GW01_large) showed creaming behaviour. All other clustered emulsions and single droplet emulsions did not display creaming. Creaming was reversible by careful re-dispersion, by manually shaking.

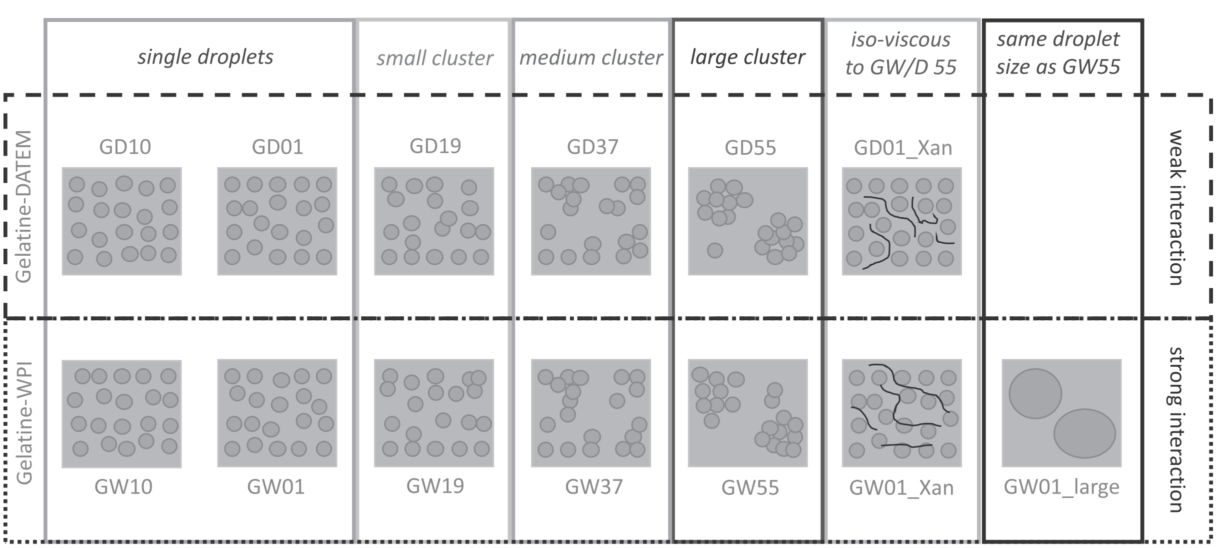

Fig. 1. Schematic overview of the o/w emulsions prepared. G, D and W indicate the emulsifiers used (gelatine, DATEM and whey protein isolate), Xan indicates the thickener used (xanthan). Numbers indicate mixing ratio of oppositely-charged o/w emulsions, i.e. GD55 refers to 50% gelatine-stabilised emulsion mixed with 50% DATEM-stabilised emulsion and GD10 refers to 100% gelatine and 0% DATEM (see Table 1 for composition).

None of the single droplet and clustered emulsions showed coalescence. The mixing ratios of the oppositely-charged single droplet emulsions can be found in Table 1.

All samples were coded with a 2-letter-2-digit code. GD refers to emulsions stabilised with gelatine and/or DATEM, whereas GW refers to emulsions stabilised with gelatine and/or whey proteins. Numbers indicate the mixing ratio between the two oppositely-charged single droplet emulsions. For example, the code GD55 refers to an emulsion consisting of 50% (w/v) gelatine-stabilised emulsion mixed with 50% (w/v) DATEM-stabilised emulsion, while GD01 denotes an emulsion consisting of 100% (w/v) DATEM-stabilised emulsion.

2.3. Determination of oil droplet cluster size

Static light scattering (Mastersizer 2000S; Malvern Instruments, Ltd., Worceshire, UK) was used to quantify the particle size distribution of single droplet o/w emulsions. The refractive index of the dispersed phase (sunflower oil) was set at 1.47 and that of the continuous water phase at 1.33. Three measurements were done per aliquot. Due to the shear forces applied during the measurement, the particle size distribution of o/w emulsions with clustered oil droplets could not be obtained with the Mastersizer, since oil droplet clusters broke up during the measurement.

For o/w emulsions with clustered oil droplets, the effective size was determined by light microscopy. The emulsions were diluted with an aqueous solution of the same pH to separate clusters on a microscope slide. The slide was covered with a coverslip. From each slide, 6 images in predefined positions were taken using an optical light microscope (Axioskop 2 plus, Carl Zeiss AG, Germany) equipped with a camera (Axiocam ERc 5S, Carl Zeiss AG, Germany) and Visio imaging software. The images were analysed for particle area using ImageJ/Fiji. From the particle area, an effective cluster diameter, referred to as effective diameter, was calculated assuming a spherical shape for the clusters. The brightness was adjusted automatically. A threshold was used to define a minimum size of 0.1 μm to remove background noise.

2.4. Zeta potential

The zeta potential was determined using a Zetasizer Nano ZS series (Malvern Instruments, Worcestershire, UK). Single and clustered emulsions were diluted at least 100× with the corresponding aqueous phase (without emulsifier). Each emulsion was measured in triplicate at 20 °C.

2.5. Rheological characterisation of o/w emulsions

Rheological tests were conducted with an Anton Paar 302 Rheometer (MCR 302, Anton Paar GmbH, Graz, Austria) using a concentric cylinder cup geometry (sandblasted CC17). Gap size was set at 0.02 mm. Flow curves were determined by measuring viscosity at an increasing shear rate from 1 to 100 s^{-1} in a time period of 10 min at 22 °C. Measurements were performed in triplicates with newly prepared emulsions to obtain averaged values. Flow curves were fitted in a shear rate range from 1 to 100 s^{-1} to the Ostwald-de Waele power-law model (Ostwald, 1925):

$$\eta = K * \dot{\gamma}^{n-1} \quad (1)$$

In this model, η represents viscosity (Pa·s), $\dot{\gamma}$ (s^{-1}) shear rate, K flow consistency index (Pa·s^n) and n flow index, which indicates the magnitude of the shear thinning behaviour ($0 < n < 1$). Additionally, the apparent viscosity at a shear rate of 50 s^{-1} is reported.

To estimate the interaction strength of clustered emulsions, the critical strain and the stress at the critical strain were determined. To obtain the critical strain and the stress at critical strain, oscillatory tests were performed using a parallel plate geometry with a diameter of 50 mm. The gap height was set to 1 mm. A strain sweep was conducted at a frequency of 10 rad/s (1.59 Hz) and strain increased from 0.01% to 100% at 22 °C. The storage modulus G′ and the loss modulus G″ were determined. Critical strain and stress at critical strain were defined as the strain and the stress at which the storage modulus G' deviated by 5% from the values found in the linear viscoelastic regime.

2.6. Tribological characterisation of o/w emulsions

An Anton Paar Rheometer (MCR 302, Anton Paar GmbH, Graz, Austria) equipped with a tribological setup (T-PTD 200-SN81766963) was used to measure tribological properties. The selected geometry was a glass ball-on-three PDMS-pins setup (PDMS pins (r = 2.8 mm), glass ball (d = 12.6 mm)). 600 μL of emulsion was loaded into the cell and a normal force of 1 N was applied. The rotational speed was increased from 0.1 rpm to 1000 rpm (equivalent to 0.47 mm/s to 470 mm/s) for run 1 and 3, and was decreased from 1000 rpm to 0.1 rpm for run 2 and 4 in 300 s each. Torque and normal force were recorded and friction coefficients, μ, calculated. The temperature was kept at 22 °C. All measurements were performed in triplicate with new batches. Between each set of measurement, the pins were renewed to avoid wear of the tribo-pair. During the first run, the PDMS pins were still adjusting to their final position, and the results were not taken into account. Only the third run was used for further analyses, in which the speed was increased over time. From 3 individual measurements of the 3rd run, the friction coefficient, μ, was taken as a function of speed. An overview of frictional parameters extracted from the Stribeck curves is depicted in Fig. 3. Three friction coefficients were extracted from different sections of the curves: the average friction coefficient in the boundary regime (μ_{bound}), and the friction coefficients at 10 mm/s ($\mu_{10\,mm/s}$) and 80 mm/s ($\mu_{80\,mm/s}$). Additionally, a power-law model was used to determine the exponent b, which was used to characterise changes in friction coefficient with speed in the mixed lubrication regime (slope of curve in mixed regime) as

$$\mu \sim speed^b \quad (2)$$

2.7. Saliva addition to o/w emulsions

To partly mimic in-mouth conditions, human saliva was added to the emulsions. Human saliva was collected from 10 participants and pooled together as described in literature (Silletti et al., 2007). Saliva was collected in cooled plastic tubes (Greiner centrifuge tubes 15 mL, Merck, US) from volunteers (n = 10), after rinsing their mouth with water. Saliva was centrifuged at 10,000 g for 30 min at cooled conditions to remove debris and reduce air content (Beckmann, Avanti TM J-25 I, JA-21, Beckman Coulter B.V. Mijdrecht, The Netherlands). The supernatant was collected. Emulsions and saliva were combined in a 1:1 ratio, based on the ratio commonly used in literature (Laguna, Farrell, Bryant, Morina, & Sarkar, 2017; Vingerhoeds et al., 2005), in an Eppendorf tube and carefully mixed for 1 min by repeatedly turning the tube upside down. The temperature during mixing was not controlled. The pH after mixing was not further adjusted. To characterise the effect of saliva addition on the physical properties of emulsions, particle and cluster size, rheological and tribological properties were determined as described above.

2.8. Sensory evaluation of o/w emulsions

Thirteen o/w emulsions (Fig. 1) were evaluated by an untrained panel (n = 83 participants; 62 female, 21 male; mean age 23.5 ± 3.8 years, age range 19–38 years) using the Rate-All-That-Apply methodology (RATA) (Meyners, Jaeger, & Ares, 2015). Participants were recruited from the Wageningen University & Research campus. Participants were asked to confirm the absence of intolerance towards the ingredients present in the emulsions and received financial compensation upon completion of the study. Participants received a digital copy

Table 2
Overview of sensory terms and definition used for RATA evaluation of all emulsions by n = 83 subjects. Definitions were taken from Oppermann, de Graaf, et al. (2017) and Oppermann, Verkaaik, et al. (2017); van Aken et al. (2011) and Benjamins et al. (2009) and adjusted where required.

Sensory attributes with descriptions	
Mouth-feel	***After-feel***
Thick Intensity of thickness of the product in the mouth after taking a bite/sip. This attribute is perceived by moving the tongue up and down against the palate. This moving up and down is especially important for more thick products. If a product is very thin it immediately spreads throughout the mouth. From water to yoghurt thickness	**Creamy** Degree to which a product leaves a soft creamy after-feel after swallowing. It is related to the creamy/soft mouthfeel sensation but is less intense.
Airy Degree to which a product is airy. The product feels light on the tongue and is a bit foamy. It takes little effort to take it apart. This taking apart is done with the tongue. Whipped egg white is very airy (maximum score) and is not coherent; it takes little effort to take it apart. Airy is perceived between the tongue and the palate.	**Fat** The degree to which a product leaves a fatty feeling in the mouth. This is a typical coating in the mouth. It can be felt on the teeth and palate by moving the tongue alongside them.
Grainy Degree to which a product contains grains. This attribute can be judged by rubbing the tongue against the palate. Air bubbles as granules as semolina pudding	**Burning** Intensity of the burning feeling after swallowing a spicy or sour product. Burning, prickling after-feel at the back of the throat
Creamy The intensity of the creaminess/softness. This is a soft, full feeling in the mouth, which is also thick-soft and supple. The product is not rough and not dry. It leaves a soft, fatty feeling and is often in combination with fat. It is perceived in the whole mouth and gives a velvety feeling in the whole mouth. Flows through the mouth; velvety; warm; soft	**Astringent** The intensity of astringency after swallowing or expectorating the product. It is the tart or rough feeling in the mouth that remains after eating for example spinach, whine, or rhubarb. The feeling is perceived in the whole mouth. Contracting after-feel
Sticky Intensity of stickiness. This is a sticky feeling that can be perceived with tongue and palate. An example of a really sticky product is the caramel of a Mars candy bar. It is perceived between the teeth during a chew movement. The degree to which a product comes loose from different parts of the mouth determines the intensity of stickiness. Sticky but you get strands in the mouth	**Coating** The degree to which a product leaves a feeling in the whole mouth. It can be felt on the teeth and the palate.
Heterogeneity Intensity of the feeling of heterogeneity. This is the feeling you get from a product that is both thin and thick at the same time. The feeling can also be cloudy or flake-like. It occurs if a product does not melt evenly after putting it into the mouth. Sometimes it takes a while before it can be perceived. The feeling is perceived in the whole mouth.	**Grainy** Feeling like particles remain in mouth, can be smaller or bigger. Like small salt particles, bubbles, semolina.
Fatty Intensity of fatty feeling in the mouth. It gives a smooth feeling and a coating on the palate. At first it is perceived on the inside of the edge between teeth and gums and later it is also perceived on the outside. Fatty layer that stays in the mouth	**Lingering** A feeling that sample or the perception of the sample stays long in mouth
Watery Consisting of containing water, Thin, weak texture, opposite of viscous, lacking body	
Astringent Intensity of astringent or rough feeling in the mouth. A chalky, rough feeling in the mouth (especially on the teeth) like eating nuts or spinach. It can be perceived in the following places: at the front of the palate (border gum and teeth), at the back of the throat, at the back of the tongue, and at the cheeks.	
Sour Intensity of sour flavour	
Vanilla Intensity of vanilla flavour. Taste of vanilla	
Oil flavour Intensity of oily, fatty flavour. Taste of salad oil or fat	
Sweet Intensity of sweet flavour. Sweet taste	

of the sensory terms and their explanations before participation. An overview of the attributes and explanations can be found in Table 2. Subjects gave written informed consent prior to the study.

The emulsions were presented in two sessions of 60 min in randomised order. 20 mL of each emulsion was served in yellow 25 mL plastic cups labelled with a random 3-digit code. Participants rated the emulsions on 20 attributes (Table 2). The attributes for the RATA, as well as the explanations, were selected from several previous studies using emulsions (Benjamins, Vingerhoeds, Zoet, de Hoog, & van Aken, 2009; Oppermann, de Graaf, et al., 2017; van Aken, Vingerhoeds, & de Wijk, 2011). The RATA assessment was performed in two parts. First, "mouth-feel" attributes were assessed. Subjects were instructed to spit out the emulsions at the moment they would usually swallow them. After spitting out the emulsions, attributes were selected and scored. Then, participants evaluated the "after-feel" attributes. Subjects were instructed to take a sip of the emulsion and swallow, wait for 10 s and then assess the attributes. The time was indicated using a stopwatch integrated into the digital questionnaire. Between tasting of two samples, participants had a 2 min break and were asked to rinse their mouth with water and eat white bread. Intensity ratings were done using a 9-point scale with anchors "weak" and "strong" and the possibility to choose "not applicable". Data was collected using tablets with a questionnaire made in EyeQuestion (Version 4.11.3).

2.9. Statistical data analysis

Statistical analysis of the RATA data was done following the procedure described previously (Ares et al., 2014; Meyners et al., 2015; Oppermann, de Graaf, et al., 2017). RATA data were considered as continuous intensity scores with "not applicable" being evaluated as 0 (Meyners et al., 2015). A two-way ANOVA was carried out. Significance levels were described using Tukey's Honest Significant Difference Test (HSD) at 95% confidence level. Significance levels for physical parameters (cluster size, friction coefficients) were calculated in a similar manner. Principal component analysis, correlation analysis based on a Spearman's rank correlation and cluster analysis (k-means) were

Table 3

Physical properties of the o/w emulsions (oil volume fraction 0.2) before (a) and after addition of saliva (b). Addition of saliva refers to o/w emulsions mixed with saliva in a 1:1 ratio. For oil droplet size and friction properties, values with the same superscript letter (Tukey-HSD test) are not significantly different at $p < 0.05$. F and p-values provided indicate the variation within one variable. Indications of significant differences between variables before and after addition of saliva are given as (ns) ($p > 0.05$), *($p < 0.05$),**($p < 0.01$) or ***($p < 0.001$).

O/w emulsion	Sample code	Effect. cluster size	Consistency	Flow index	μ_{bound}	$\mu_{10\,mm/s}$	$\mu_{80\,mm/s}$	b
		(μm)	*K ()Pa·s^n*	*n (−)*	*(−)*	*(−)*	*(−)*	*exponent (/mm/s)*
		F = 149.5 p < 0.001			*F = 40.3 p < 0.001*	*F = 2.3 p > 0.05*	*F = 10.8 p < 0.001*	
Single droplet emulsions								
WPI	GW 01	2.1 ± 0.5^{a}	0.002	0.92	0.31 ± 0.01^{ade}	0.35 ± 0.04^{a}	0.23 ± 0.02^{bc}	−0.34
Gelatine (pH 7)	GW 10	1.9 ± 0.3^{a}	0.005	0.96	0.41 ± 0.02^{b}	0.31 ± 0.04^{a}	0.24 ± 0.05^{bc}	−0.2
Equi-viscos control (to GW55)	GW01_Xan	2.1 ± 0.5^{a}	1.68	0.22	0.36 ± 0.02^{bde}	0.26 ± 0.01^{a}	0.17 ± 0.01^{acd}	−0.24
Equi-sized control (to GW55)	GW01_large	40.9 ± 9.5^{de}	0.003	0.92	0.43 ± 0.01^{b}	0.43 ± 0.09^{a}	0.22 ± 0.05^{bcd}	−0.41
DATEM	GD 01	1.9 ± 0.6^{a}	0.002	0.94	0.31 ± 0.01^{ade}	0.25 ± 0.04^{a}	0.17 ± 0.01^{acd}	−0.16
Gelatine (pH 5)	GD 10	2.6 ± 0.1^{a}	0.01	0.88	0.41 ± 0.03^{b}	0.32 ± 0.04^{a}	0.26 ± 0.02^{b}	−0.25
Equi-viscos control (to GD55)	GD01_Xan	1.9 ± 0.6^{a}	2.004	0.22	0.24 ± 0.01^{a}	0.20 ± 0.01^{a}	0.11 ± 0.01^{a}	−0.17
Gelatine-DATEM clustered emulsions ("strong clusters")								
Small cluster	GD 19	5.6 ± 0.6^{ab}	0.033	0.56				
Medium cluster	GD 37	10.8 ± 0.9^{bc}	1.31	0.07	0.56 ± 0.04^{c}	0.25 ± 0.25^{a}	0.12 ± 0.01^{a}	−0.55
Large cluster	GD 55	37.6 ± 1.7^{d}	2.8	0.07	0.37 ± 0.04^{bd}	0.17 ± 0.01^{a}	0.20 ± 0.01^{bcd}	−0.54
Gelatine-WPI clustered emulsions ("weak clusters")								
Small cluster	GW 19	7.9 ± 0.3^{ab}	0.013	0.69				
Medium cluster	GW 37	14.8 ± 0.7^{c}	0.178	0.51	0.29 ± 0.03^{ae}	0.22 ± 0.10^{a}	0.15 ± 0.03^{ad}	−0.54
Large cluster	GW 55	47.7 ± 1.4^{e}	1	0.31	0.28 ± 0.02^{a}	0.19 ± 0.01^{a}	0.17 ± 0.01^{acd}	−0.27

O/w emulsion	Sample	Effect. cluster size	Consistency	Flow index	μ_{bound}	$\mu_{10\,mm/s}$	$\mu_{80\,mm/s}$	b
	code	*(μm)*	*K ()Pa·s^n*	*n (−)*	*(−)*	*(−)*	*(−)*	*exponent (/mm/s)*
		F = 33.8 p < 0.01			*F = 10.6 p < 0.001*	*F = 2.1 p > 0.05*	*F = 4.7 p < 0.01*	
Single droplet emulsions								
WPI	GW 01	$1.3 \pm 0.3^{b*}$	0.01	0.99	$0.41 \pm 0.01^{bcde**}$	$0.38 \pm 0.07^{a(ns)}$	$0.27 \pm 0.07^{ab(ns)}$	−0.16
Gelatine (pH 7)	GW 10	$25.1 \pm 9.9^{cd**}$	0.251	0.38	$0.31 \pm 0.01^{a**}$	$0.30 \pm 0.04^{a(ns)}$	$0.22 \pm 0.02^{ab(ns)}$	−0.14
Equi-viscos control (to GW55)	GW01_Xan	$2.5 \pm 0.6^{ab(ns)}$	0.26	0.43	$0.34 \pm 0.02^{ac(ns)}$	$0.34 \pm 0.02^{a*}$	$0.19 \pm 0.03^{b(ns)}$	−0.21
Equi-sized control (to GW55)	GW01_large	$48.7 \pm 8.4^{e(ns)}$	0.003	0.94	$0.34 \pm 0.01^{ac**}$	$0.35 \pm 0.17^{a(ns)}$	$0.23 \pm 0.10^{ab(ns)}$	−0.56
DATEM	GD 01	$1.2 \pm 0.1^{b(ns)}$	0.18	0.7	$0.31 \pm 0.01^{a(ns)}$	$0.31 \pm 0.05^{a(ns)}$	$0.24 \pm 0.03^{ab*}$	−0.13
Gelatine (pH 5)	GD 10	$25.7 \pm 8.2^{cd**}$	0.173	0.42	$0.35 \pm 0.02^{abc*}$	$0.35 \pm 0.04^{a(ns)}$	$0.24 \pm 0.01^{ab(ns)}$	−0.19
Equi-viscos control (to GD55)	GD01_Xan	$2.0 \pm 0.4^{ab**}$	0.25	0.44	$0.37 \pm 0.01^{abcd**}$	$0.37 \pm 0.08^{a*}$	$0.23 \pm 0.04^{ab**}$	−0.43
Gelatine-DATEM clustered emulsions								
Small cluster	GD 19	$5.6 \pm 2.8^{ab(ns)}$	0.03	0.48				
Medium cluster	GD 37	$14.5 \pm 3.9^{ac(ns)}$	0.09	0.43	$0.45 \pm 0.07^{de(ns)}$	$0.43 \pm 0.02^{a(ns)}$	$0.39 \pm 0.01^{a**}$	−0.7
Large cluster	GD 55	$36.3 \pm 7.5^{de(ns)}$	0.09	0.44	$0.44 \pm 0.03^{bde*}$	$0.43 \pm 0.13^{a*}$	$0.36 \pm 0.01^{ab***}$	−0.61
Gelatine-WPI clustered emulsions								
Small cluster	GW 19	$7.5 \pm 2.8^{ab(ns)}$	0.022	0.5				
Medium cluster	GW 37	$7.5 \pm 2.4^{ab**}$	0.061	0.76	$0.37 \pm 0.02^{abcd*}$	$0.50 \pm 0.15^{a*}$	$0.40 \pm 0.15^{a*}$	−0.19
Large cluster	GW 55	$23.7 \pm 5.2^{cd**}$	0.02	0.88	$0.49 \pm 0.06^{e**}$	$0.53 \pm 0.05^{a**}$	$0.36 \pm 0.02^{ab**}$	−0.82

performed. For these calculations, R Studio (Version 1.0.143) was used with the additional packages SensoMineR, factoextra, corrplot, multcomp, ggplot2, multcompView and agricolae and FactoMineR.

3. Results and discussion

3.1. Emulsion characteristics

Table 3 gives an overview of effective oil droplet cluster size, rheological and tribological properties of all o/w emulsions with (b) and without (a) added saliva. The effect of saliva addition on effective oil droplet cluster size, rheological and tribological properties of the o/w emulsions is discussed in section 3.3. Hetero-aggregated emulsions varied in cluster size from 10 µm (small) to 50 µm (large). As expected, cluster size was controlled by the mixing ratio of oppositely charged single o/w emulsions. The largest cluster size was obtained by mixing equal amounts of oppositely charged single emulsions (GD55 and GW55). Cluster size was found to be around 47 µm for GW55 and about 40 µm for GD55. Smaller clusters were formed for unequal mixing ratios of oppositely charged emulsions (GD19, GD37, GW19 and GW37), as an excess in droplets of one charge limits cluster growth (Fuhrmann et al., 2019). All single droplet emulsions (GD01, GD10, GW01 and GW10) including emulsions with an adjusted viscosity (GW01_Xan and GD01_Xan), had oil droplet sizes around 1–2 µm, with the exception of GW01_large, which had an oil droplet size of 41 µm. In Fig. 2, we show exemplarily micrographs of non-clustered and clustered emulsions.

Typical flow curves of single droplet and clustered o/w emulsions together with the fits of the Ostwald-de Waele power law model are shown in Fig. 4. Most single droplet emulsions (GD01, GD10, GW10 and GW01, GW01_large) showed flow indices n of around 1, thus exhibited Newtonian flow behaviour. Single droplet gelatine-stabilised emulsions at pH 5 (GD10) showed weak shear-thinning behaviour (n = 0.86).

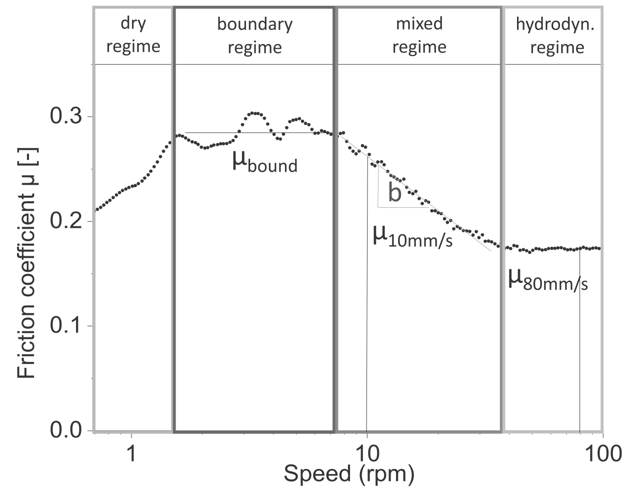

Fig. 3. Friction coefficient as a function of speed for an o/w emulsion with an illustration of the extracted tribological parameters: average friction coefficient in the boundary regime (μ_{bound}), friction coefficients at 10 mm/s ($\mu_{10\,mm/s}$) and 80 mm/s ($\mu_{80\,mm/s}$) and exponent b (slope of curve in mixed lubrication regime).

Highly clustered emulsions displayed flow index values $0 < n < 0.21$, indicating strong shear-thinning behaviour. The effect of droplet clustering was also seen in the consistency K. For single droplet emulsions (GD10, GD01, GW01, GW10), K was in the range of 0.001–0.01 Pa·s^n. For emulsions with large clusters (GD55, GW55), K was 1.0 and 2.8 Pa·s^n. K increased by three orders of magnitude for these clustered emulsions compared to that of the single droplet emulsions, which is mainly related to the increase in effective volume fraction caused by oil droplet clustering. As mentioned above, clustered emulsions entrap

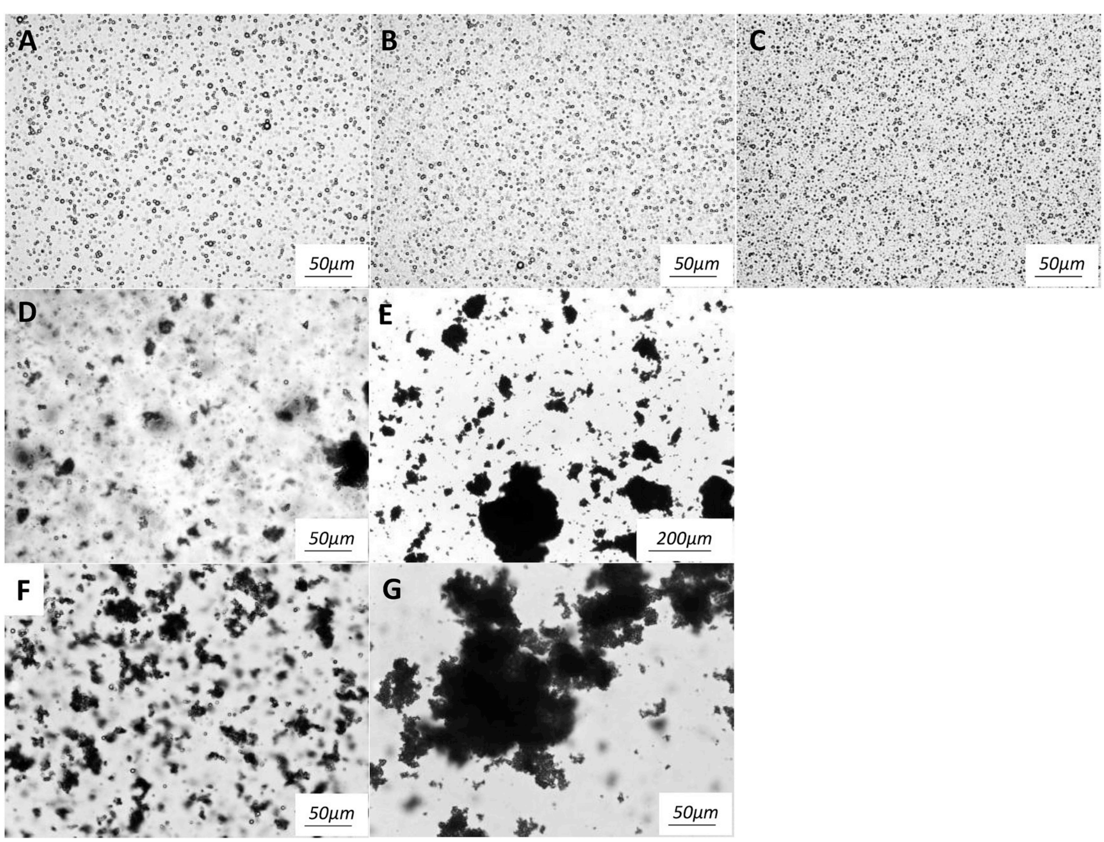

Fig. 2. Micrographs of single droplet emulsions varying in emulsifier (A: gelatine at pH 7, B: WPI, C: DATEM) and clustered emulsions (D: GD small, E: GD large, F:GW small, G:GW large). Scale bars show for images A-D and F-G 50 µm, for image E 200 µm.

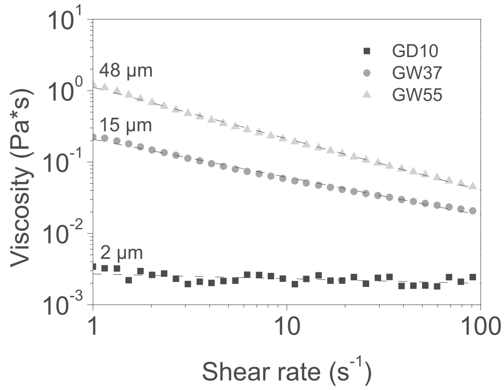

Fig. 4. Typical flow curves of single droplet o/w emulsion (GD10), hetero-aggregated clustered o/w emulsions with medium cluster size (GW37) and hetero-aggregated clustered o/w emulsions with large cluster size (GW55) as a function of shear rate in a range from 1 to 100 s^{-1}. Dashed lines show the best fits to the Ostwald-de Waele power law model. The total oil volume fraction was 0.2 for all emulsions.

water between droplets, which causes a decrease in free aqueous bulk phase (Mao & McClements, 2013a; van Aken, Oliver, & Scholten, 2015). These findings are in line with the results shown in the studies by Mao and McClements (2012, 2013a). The viscosity values of hetero-aggregated emulsions in our study were higher than those reported for hetero-aggregated clustered emulsions consisting of modified starch-/whey-stabilised clusters (Mao & McClements, 2013a), but comparable to those of clustered emulsions stabilised by proteins (Mao & McClements, 2012).

Also the interaction strength of clustered emulsions was assessed by determining the critical strain upon oscillatory deformation (Table 1). The critical strain of single droplet emulsions and smaller clusters could not be determined, as the loss modulus of emulsions with small clusters was higher than the storage modulus. The critical strain was around 2% for GW55 and 4% for GD55. The stronger electrostatic attraction within clusters stabilised with gelatine and DATEM (GD) thus led to a 2× higher critical strain compared to clusters with gelatine and WPI (GW) due to differences in charge density of the emulsifiers. The assessment of the zeta-potential (Table 1) showed that DATEM-stabilised emulsions were, as expected, negatively charged, with a zeta potential of around −60 mV. WPI-stabilised emulsions displayed a negative charge of −45 mV at pH 7. Gelatine (pI around 8–9) showed a slightly positive charge of +10 mV at pH 5 and of +7 mV at pH 7. The difference in zeta potential for gelatine-DATEM emulsions at a pH of 5 was, therefore, around 70 mV and for gelatine-WPI emulsions around 50 mV, at pH 7. The gelatine-DATEM combination, hence, provided stronger electrostatic attraction between oil droplets, and higher cluster strength.

Table 3 (a) gives an overview of the tribological properties of all o/w emulsions. The friction coefficient of single droplet emulsions stabilised by DATEM was lower than that of single droplet emulsions stabilised by gelatine. As the oil droplet size was similar for both emulsions, the difference in friction coefficient was related to the different emulsifiers used. Due to the higher hydrophobicity of DATEM compared to that of gelatine, oil droplets stabilised with DATEM had a higher affinity for the hydrophobic PDMS surface, thus could form a film on the surface more easily and consequently improve lubrication. Furthermore, DATEM-stabilised droplets coalesced more than gelatine-stabilised droplets as observed by the occurrence of oil patches on the emulsion surface after the tribological measurement (data not shown).

The thickened emulsion (GD01_Xan) showed improved lubrication properties (μ_{bound}, $\mu_{10\,mm/s}$ and $\mu_{80\,mm/s}$), with friction coefficients between 0.11 and 0.24, compared to single droplet emulsions stabilised with DATEM (GD01), with friction coefficients between 0.17 and 0.31. This is in line with observations made by Chojnicka-Paszun and de Jongh (2014), who suggested that xanthan might mask surface roughness and improve lubrication. Clustered emulsions prepared with gelatine and DATEM (GD55) showed a relatively high friction coefficient of μ_{bound} = 0.37 in the boundary regime, a sharp drop at intermediate speeds ($\mu_{10\,mm/s}$ = 0.17) and an increase in the friction coefficient at higher speeds ($\mu_{10\,mm/s}$ = 0.20). In the low-speed regime, the lubrication behaviour of the emulsions with strongly bound clusters (GD55) was dominated by the tribological properties of the gelatine emulsion. With increasing speed, the friction coefficient of clustered emulsions (GD55) decreased more strongly than that of homogeneous gelatine-stabilised emulsions (GD10). This behaviour might possibly be related to a higher affinity to coalescence and film formation of DATEM-stabilised droplets, as the emulsion droplets are closer to each other within clustered samples than in non-clustered samples. For large clusters consisting of gelatine and WPI (GW55), all friction parameters (μ_{bound}, $\mu_{10\,mm/s}$ and $\mu_{80\,mm/s}$) were below the values of single droplet emulsions. $\mu_{10\,mm/s}$ decreased from above 0.3 for single droplet emulsions (GW01 and GW10) to 0.19 for clustered emulsions. By clustering, the effective volume fraction of oil droplets increased, which seemed to improve the lubrication properties of the emulsions. Clustering decreases the distance between droplets in the emulsion, and as such, coalescence and accompanying film formation might occur more easily. Higher interaction strength might also explain the higher μ_{bound}, observed for large GD clusters (GD55), compared to weakly bound clusters (GW55). Higher interaction strength between the droplets increases the stiffness of the clusters. Less deformable, thus stiffer clusters may spread less easily on the surface of the tribo-pair. This effect of droplet stiffness has been previously observed in double w/o/w emulsions (Oppermann, de Graaf, et al., 2017).

Homogeneous emulsions with large droplets (GW01_large; $\mu_{10\,mm/s}$ = 0.43) had higher friction coefficients than homogeneous emulsions with smaller droplets (GW01; $\mu_{10\,mm/s}$ = 0.35). This is in agreement with previous studies on single droplet o/w emulsions with varying droplet size (Dresselhuis et al., 2007).

To summarise, the viscosity of hetero-aggregated clustered o/w emulsions strongly increased compared to that of single droplet o/w emulsions with the same oil volume fraction due to an increase in effective volume fraction. The friction coefficient of hetero-aggregated clustered o/w emulsions with strongly interacting clusters was higher in the boundary and the beginning of the mixed regime than that of emulsions with weakly interacting clusters. The friction coefficients in the boundary regime (μ_{bound}) and at higher speeds ($\mu_{80\,mm/s}$) depended on the emulsifier type, and thus cluster strength.

3.2. Sensory perception of single droplet and hetero-aggregated clustered o/w emulsions

Table 4 shows the mean intensity scores of RATA ratings for mouthfeel (4a) and after-feel attributes (4b). Both cluster size and cluster strength significantly influenced thickness intensity. Emulsions with large clusters (GW55, GD55) were perceived significantly thicker than single droplet emulsions (GD01, GD10, GW01, GW10). Weakly bound clusters (GW55) were perceived significantly less thick then strongly bound clusters (GD55). The increase in thickness is in agreement with the increase in viscosity of o/w emulsions upon clustering.

Similar to thickness, creaminess intensity was significantly higher for clustered emulsions than for single droplet emulsions (GD01, GD10, GW10, and GW01). Creaminess intensity of clustered emulsions ranged between 3.7 and 5.4, whereas single droplet emulsions had intensities of around 3.0. For strongly bound clusters (GD19, GD37, GD55), creaminess intensities of 3.8, 4.0 and 4.4 were found, and thus increased with cluster size. For weakly bound clusters (GW19, GW37 and GW55), creaminess intensities of 3.7, 4.7 and 5.4 were observed. Single droplet emulsions thickened with xanthan (GD01_Xan, GW01_Xan) had comparable thickness and creaminess intensities as emulsions with large clusters (GD55, GW55). Weakly bound clusters (GW) were

Table 4

(a) Mean RATA ratings of (a) mouth-feel attributes (n = 83 subjects) and (b) after-feel attributes with standard error (SE) for the studied emulsions. Means with the same superscript letter (Tukey-HSD test) are not significantly different at $p < 0.05$. F and p-values provided indicate the variation within one attribute.

Mouthfeel attributes	Airy	Astringent	Creamy	Fatty	Grainy	Heterogeneity	Sour	Sticky	Sunflower oil	Sweetness	Thick	Vanilla	Water
	$F = 12.5$ $p < 0.001$	$F = 10.0$ $p < 0.001$	$F = 47.8$ $p < 0.001$	$F = 21.5$ $p < 0.001$	$F = 45.8$ $p < 0.001$	$F = 3.3$ $p < 0.001$	$F = 60.8$ $p < 0.001$	$F = 20.7$ $p < 0.001$	$F = 4.7$ $p < 0.001$	$F = 8.2$ $p < 0.001$	$F = 77.6$ $p < 0.001$	$F = 6.8$ $p < 0.001$	$F = 51.1$ $p < 0.001$
GD01_Xan	2.6 ± 0.2^{d}	2.7 ± 0.3^{abc}	5.7 ± 0.2^{a}	5.4 ± 0.2^{a}	1.2 ± 0.2^{d}	3.1 ± 0.3^{bc}	4.7 ± 0.3^{ab}	3.5 ± 0.3^{a}	3.4 ± 0.3^{a}	2.1 ± 0.2^{b}	5.7 ± 0.2^{ab}	2.0 ± 0.2^{a}	2.8 ± 0.2^{e}
GD_01	2.9 ± 0.3^{cd}	2.9 ± 0.3^{ab}	2.7 ± 0.2^{fg}	3.0 ± 0.2^{f}	1.2 ± 0.2^{d}	3.3 ± 0.3^{abc}	5.4 ± 0.3^{a}	1.6 ± 0.2^{f}	2.6 ± 0.3^{bc}	2.0 ± 0.2^{b}	2.2 ± 0.2^{f}	2.1 ± 0.2^{a}	6.0 ± 0.2^{a}
GD_10	2.4 ± 0.2^{d}	3.0 ± 0.3^{ab}	3.2 ± 0.2^{efg}	3.3 ± 0.2^{ef}	1.0 ± 0.1^{d}	3.2 ± 0.3^{abc}	4.9 ± 0.3^{ab}	1.6 ± 0.2^{f}	3.0 ± 0.2^{abc}	2.1 ± 0.2^{b}	2.4 ± 0.2^{f}	2.5 ± 0.2^{a}	5.9 ± 0.2^{a}
GD_19	3.6 ± 0.3^{bc}	3.0 ± 0.3^{ab}	3.8 ± 0.2^{cde}	3.9 ± 0.2^{cdef}	2.8 ± 0.3^{c}	4.3 ± 0.3^{a}	4.8 ± 0.3^{ab}	2.2 ± 0.2^{cdef}	2.9 ± 0.2^{abc}	2.0 ± 0.2^{b}	3.4 ± 0.2^{de}	2.0 ± 0.2^{a}	4.8 ± 0.2^{bc}
GD_37	4.2 ± 0.3^{b}	3.0 ± 0.3^{a}	4.0 ± 0.2^{cde}	4.1 ± 0.3^{bcde}	3.8 ± 0.4^{b}	3.8 ± 0.3^{abc}	4.1 ± 0.3^{b}	2.4 ± 0.3^{cde}	2.8 ± 0.3^{abc}	2.2 ± 0.2^{ab}	4.1 ± 0.3^{cd}	2.0 ± 0.2^{a}	4.4 ± 0.3^{cd}
GD_55	5.1 ± 0.3^{a}	3.0 ± 0.2^{ab}	4.4 ± 0.3^{cd}	4.8 ± 0.2^{ab}	5.0 ± 0.3^{a}	4.2 ± 0.3^{ab}	4.1 ± 0.3^{b}	3.1 ± 0.3^{ab}	2.9 ± 0.2^{abc}	2.2 ± 0.2^{ab}	5.8 ± 0.3^{a}	2.1 ± 0.2^{a}	3.0 ± 0.2^{e}
GW_01	2.9 ± 0.3^{cd}	1.8 ± 0.2^{d}	3.7 ± 0.2^{de}	3.8 ± 0.2^{def}	1.0 ± 0.1^{d}	2.9 ± 0.3^{c}	1.8 ± 0.2^{c}	1.9 ± 0.2^{ef}	3.0 ± 0.2^{ab}	2.9 ± 0.2^{a}	2.4 ± 0.2^{f}	2.5 ± 0.2^{a}	5.9 ± 0.3^{a}
GW_10	2.8 ± 0.3^{cd}	1.8 ± 0.2^{d}	3.6 ± 0.2^{def}	3.7 ± 0.2^{def}	1.0 ± 0.2^{d}	3.4 ± 0.3^{abc}	1.7 ± 0.2^{c}	1.7 ± 0.2^{ef}	2.2 ± 0.2^{c}	2.5 ± 0.2^{ab}	3.0 ± 0.2^{ef}	2.2 ± 0.2^{a}	5.5 ± 0.3^{ab}
GW_19	2.7 ± 0.3^{cd}	2.2 ± 0.3^{bcd}	3.7 ± 0.2^{de}	3.9 ± 0.2^{cdef}	1.0 ± 0.2^{d}	3.2 ± 0.3^{abc}	1.9 ± 0.2^{c}	1.7 ± 0.2^{ef}	3.0 ± 0.2^{abc}	2.6 ± 0.2^{ab}	2.7 ± 0.2^{ef}	2.5 ± 0.2^{a}	5.8 ± 0.3^{ab}
GW_37	3.3 ± 0.2^{bcd}	2.1 ± 0.2^{cd}	4.7 ± 0.2^{bc}	4.3 ± 0.2^{bcd}	1.3 ± 0.2^{d}	3.2 ± 0.3^{bc}	1.9 ± 0.2^{c}	2.7 ± 0.3^{bcd}	3.0 ± 0.3^{ab}	2.4 ± 0.2^{ab}	4.2 ± 0.2^{cd}	2.1 ± 0.2^{a}	4.1 ± 0.2^{cd}
GW_55	3.3 ± 0.2^{bcd}	2.1 ± 0.2^{cd}	5.4 ± 0.2^{ab}	4.7 ± 0.2^{abc}	1.3 ± 0.2^{d}	3.2 ± 0.3^{bc}	1.8 ± 0.2^{c}	2.8 ± 0.2^{abc}	2.9 ± 0.2^{abc}	2.5 ± 0.2^{ab}	4.9 ± 0.2^{bc}	2.3 ± 0.2^{a}	3.7 ± 0.2^{de}
GW01_large	2.8 ± 0.3^{cd}	1.9 ± 0.2^{d}	2.6 ± 0.2^{g}	4.1 ± 0.2^{bcde}	1.4 ± 0.2^{d}	3.3 ± 0.3^{abc}	1.4 ± 0.2^{c}	2.0 ± 0.2^{def}	3.2 ± 0.2^{ab}	2.4 ± 0.2^{ab}	2.2 ± 0.2^{f}	2.3 ± 0.2^{a}	6.2 ± 0.3^{a}
GW01_Xan	2.6 ± 0.2^{d}	1.9 ± 0.2^{cd}	5.5 ± 0.2^{ab}	5.3 ± 0.2^{a}	1.3 ± 0.2^{d}	2.9 ± 0.3^{c}	1.6 ± 0.2^{c}	2.9 ± 0.2^{abc}	3.4 ± 0.3^{a}	2.2 ± 0.2^{ab}	5.2 ± 0.2^{ab}	2.2 ± 0.2^{a}	3.1 ± 0.2^{e}

Afterfeel attributes	Astringent	Burning	Coating	Creamy	Fatty	Grainy	Lingering
	$F = 6.8$ $p < 0.001$	$F = 7.1$ $p < 0.001$	$F = 9.6$ $p < 0.001$	$F = 38.7$ $p < 0.001$	$F = 16.5$ $p < 0.001$	$F = 19.6$ $p < 0.001$	$F = 6.1$ $p < 0.001$
GD01_Xan	3.0 ± 0.3^{abc}	1.9 ± 0.3^{abcde}	4.8 ± 0.2^{a}	5.5 ± 0.2^{a}	5.6 ± 0.2^{a}	1.2 ± 0.2^{d}	4.8 ± 0.3^{a}
GD_01	3.3 ± 0.3^{ab}	2.4 ± 0.3^{a}	3.5 ± 0.2^{cd}	3.6 ± 0.2^{de}	4.1 ± 0.3^{cd}	1.3 ± 0.2^{d}	4.2 ± 0.3^{ab}
GD_10	3.4 ± 0.3^{a}	2.1 ± 0.3^{abcd}	3.7 ± 0.2^{bcd}	3.4 ± 0.3^{ef}	3.7 ± 0.2^{cd}	1.2 ± 0.2^{d}	4.4 ± 0.3^{ab}
GD_19	3.1 ± 0.2^{abc}	2.2 ± 0.3^{ab}	3.7 ± 0.2^{cd}	3.8 ± 0.2^{de}	4.4 ± 0.2^{bcd}	2.2 ± 0.3^{bc}	4.1 ± 0.2^{ab}
GD_37	3.0 ± 0.3^{abc}	2.1 ± 0.2^{abc}	3.9 ± 0.3^{bc}	4.0 ± 0.3^{cde}	4.0 ± 0.3^{cd}	2.7 ± 0.3^{b}	4.1 ± 0.3^{ab}
GD_55	3.1 ± 0.3^{abc}	2.1 ± 0.3^{abc}	4.2 ± 0.3^{abc}	4.4 ± 0.3^{bcd}	4.4 ± 0.3^{bcd}	3.6 ± 0.3^{a}	4.2 ± 0.3^{ab}
GW_01	2.7 ± 0.3^{abcd}	1.4 ± 0.2^{bcdef}	3.7 ± 0.2^{bcd}	4.0 ± 0.3^{cde}	4.2 ± 0.3^{bcd}	1.1 ± 0.2^{d}	3.8 ± 0.3^{b}
GW_10	2.5 ± 0.2^{bcd}	1.3 ± 0.2^{cdef}	3.6 ± 0.3^{cd}	3.8 ± 0.2^{de}	3.6 ± 0.3^{d}	1.2 ± 0.2^{d}	4.0 ± 0.3^{ab}
GW_19	2.6 ± 0.3^{abcd}	1.5 ± 0.2^{bcdef}	3.7 ± 0.2^{bcd}	3.9 ± 0.2^{cde}	4.2 ± 0.3^{bcd}	1.3 ± 0.2^{d}	3.7 ± 0.3^{bc}
GW_37	2.8 ± 0.2^{abc}	1.9 ± 0.2^{abcdef}	4.3 ± 0.2^{abc}	4.8 ± 0.3^{abc}	4.5 ± 0.3^{bc}	1.3 ± 0.2^{d}	4.2 ± 0.2^{ab}
GW_55	2.8 ± 0.2^{abc}	1.3 ± 0.2^{def}	4.3 ± 0.2^{abc}	5.0 ± 0.2^{ab}	5.1 ± 0.2^{ab}	1.5 ± 0.2^{cd}	4.2 ± 0.3^{ab}
GW01_large	1.9 ± 0.2^{d}	1.1 ± 0.2^{f}	2.9 ± 0.2^{d}	2.6 ± 0.2^{f}	3.5 ± 0.3^{d}	1.1 ± 0.2^{d}	2.9 ± 0.2^{c}
GW01_Xan	2.3 ± 0.2^{cd}	1.24 ± 0.2^{ef}	4.6 ± 0.3^{ab}	5.5 ± 0.2^{a}	5.6 ± 0.2^{a}	1.3 ± 0.2^{d}	4.6 ± 0.3^{ab}

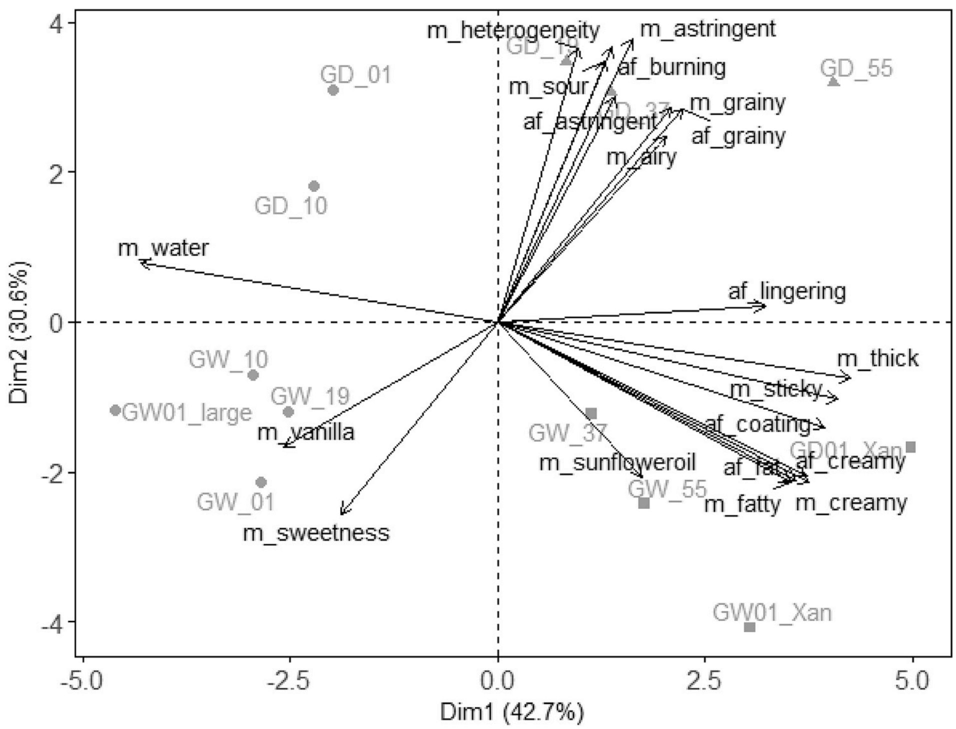

Fig. 5. PCA bi-plot of RATA ratings (n = 83 subjects) of the studied emulsions. Groups of o/w emulsions are indicated by different colours (red, green and blue) and symbol types (triangle, circle, square). The central point of each group is displayed as a large symbol (red dot, green triangle, blue square). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

perceived significantly creamier than strongly bound clusters (GD). This demonstrates that creaminess cannot be explained fully by thickness and viscosity of o/w emulsions, but also cluster strength and cluster structure need to be taken into account.

Besides creaminess and thickness, cluster strength also effected graininess perception. For strongly bound clustered o/w emulsions (GD), graininess significantly increased with increasing cluster size. Clusters (GD) ranging from 5 to 40 μm (GD19, GD37, GD55) increased in graininess intensity from 2.8 for small clusters (GD19) to 5.0 for large clusters (GD55). This increase in graininess intensity was not observed for weakly bound clustered o/w emulsions (GW). For all weakly bound clustered emulsions (GW19, GW37, GW55), graininess intensity was not significantly different from that for single droplet o/w emulsions (GW01, GW10). This suggests that cluster size seems to be less important for graininess perception, but cluster interaction strength of oil droplets seems to be the main driver for graininess perception in these emulsions.

Fig. 5 shows the PCA of the sensory perception of all o/w emulsions. The first two principal components explain more than 73% of the variation in the data and two main descriptive axes were found. The horizontal axis separates emulsions mainly from watery to thick. The vertical axis separates emulsions mainly from grainy and astringent to sweet and vanilla. A hierarchical cluster analysis shows the presence of three cluster families, which are highlighted in Fig. 5 by different colours (red, green and blue). These cluster families are well separated in the PCA. On the left side, the homogenous single droplet o/w emulsions are grouped (red). These emulsions are mainly described by a watery mouth-feel. Emulsions with single droplets but increased droplet size (GW01_large, 41 μm) are also located in this cluster. Emulsions with large, weakly bound clusters (GW37, GW55) are part of a separate cluster (blue) and are mainly related to thick, coating and creamy descriptors. With increasing cluster size, so moving from GW01 and GW10 towards GW55, both thick and creamy mouth-feel increase significantly. This shows that oil droplet clustering leads to an enhancement of these fat-related attributes. In the same group (blue), emulsions thickened with xanthan (GW01_Xan, GD01_Xan) are present. Clearly separated from those emulsions are the gelatine-DATEM (GD) emulsions with strongly bound clusters, which form the third group in the PCA (green) in the upper right quadrant. While also for these emulsions thickness increased and wateriness decreased, they were mainly perceived as grainy, astringent and sour. This is most likely related to the structure of the clusters, as well as the properties of the emulsifier (inherent sour taste of DATEM). While both GW and GD clusters had a comparable size, the interaction strength among oil droplets within the cluster differed. This might have led to a different behaviour in the mouth during oral processing eliciting different sensations. For example, for weakly bound GW clustered emulsions, oil droplet clusters might fall apart due to interactions with saliva, or because of the applied shear during consumption. This may lead to a decrease in viscosity during consumption. However, even though viscosity decreased, creaminess did not.

Clusters that may stay intact in the mouth, like for example those present in GD55 (strongly bound), may be so large and stiff that they might be sensed as a particle and consequently the emulsion was perceived as grainy. Also, the interaction with saliva and the negatively charged mucins therein can contribute to graininess perception. The various emulsifiers interact differently with saliva. Gelatine is positively charged in these emulsions, thus in combination with negatively charged salivary mucins, electrostatic attraction between gelatine-covered droplets and mucins occurs (see section 3.3). Thus, clusters may fall apart upon the addition of saliva, due to competition with negatively charged, DATEM-stabilised droplets. However, saliva could also assist in the aggregation of non-clustered droplets. DATEM and whey protein, on the other hand, are negatively charged in the emulsions and the repulsion between the clusters and the mucins may result in depletion interactions. Both flow and friction behaviour can be strongly changed by the interaction of the emulsions with saliva during consumption and might help to understand the perception of the clustered systems.

To conclude, oil droplet cluster size and cluster strength are the two main physical parameters that separate the hetero-aggregated clustered o/w emulsions over the sensory space. Clustering of oil droplets in o/w emulsion not only alters the rheological and tribological properties, but also the sensory perception of o/w emulsion and can be used to enhance perception of fat related sensory attributes. This finding suggests that the incorporation of aqueous phase inside the oil droplet cluster leading to an increased oil volume fraction has an effect on sensory perception comparable to the incorporation of water droplets into w/o/w emulsions. For hetero-aggregated o/w emulsions with oil droplet clusters as well as for w/o/w emulsions, the increased volume fraction of the dispersed phase has a positive influence on sensory perception of fat-related attributes (Oppermann et al., 2016; Oppermann et al., 2015; Oppermann, Verkaaik, et al., 2017).

3.3. Effect of saliva addition on rheological and tribological properties of single droplet and clustered o/w emulsions

Table 3 provides an overview of oil droplet and cluster size, rheological and tribological properties of single droplet and clustered o/w emulsions mixed with human saliva in a 1:1 ratio. It can be argued that this mixing ratio might lead to an overestimation of the *in vivo* effect of saliva on the emulsions. However, the described experiments were meant as an investigations on the effect of saliva on the properties of the emulsions. Under realistic drinking conditions, the oral residence time of liquid emulsions is likely to be < 5s per sip, and the emulsion:saliva mixing ratio is probably shifted towards more emulsion and less saliva. For the gelatine-stabilised emulsions (GD10, GW10), the droplet size increased from 1 to 2 μm to > 25 μm upon mixing with saliva. This increase in droplet size was most likely due to flocculation of positively charged gelatine-stabilised droplets with negatively charged salivary proteins (mucins). Negatively charged emulsions emulsified with DATEM or whey protein (GD01, GW01) showed no changes in droplet size upon mixing with saliva.

Because flocculation occurred upon mixing with saliva for emulsions with positively-charged droplets (GD10, GW10), the viscosity of these emulsions increased. For GD10, consistency K increased from 0.01 to 0.17 $Pa.s^n$; for GW10, K increased from 0.005 to 0.25 $Pa.s^n$. For both emulsions, the flow index n decreased from 0.88 (GD10) and 0.96 (GW10) to roughly 0.40 upon mixing with saliva, indicating the emulsions became strongly shear thinning. Consistency K of negatively charged single droplet emulsions stabilised with whey (GW01) increased from 0.002 to 0.01 $Pa.s^n$, which is consistent with the limited change in droplet size. However, for the DATEM-stabilised single droplet emulsion GD01, K increased largely from 0.002 to 0.18 $Pa.s^n$, even though droplet size did not change. The increase in viscosity might be caused by depletion or repulsive interactions hindering flow at low shear rates as DATEM-stabilised droplets have a higher charge density than WPI-stabilised droplets.

Emulsions GD55 and GW55 with large clusters showed reduction in effective cluster size upon addition of saliva from around 40 μm to 25–36 μm. Cluster size decreased slightly, as the negatively charged proteins present in saliva likely interacted with gelatine covered droplets, inhibiting binding among oil droplets and thereby (re-)formation of clusters. Although effective cluster size was reduced only slightly, the viscosity of the emulsions decreased considerably. K of GD55 decreased from 2.80 to 0.09 $Pa.s^n$, while GW55 decreased from 1 to 0.02 $Pa.s^n$. This decrease in viscosity was accompanied by a decrease in cluster strength. Emulsions with large gelatine-DATEM clusters showed a reduction of critical strain from about 4.1 to 0.25% upon addition of saliva, and a similar trend was seen in gelatine-WPI emulsions. We suggest that these changes in viscosity and cluster strength are indicative of both the dilution of the emulsions with saliva and changes in the cluster properties (e.g. cluster structure and competition for electrostatic interactions between salivary proteins and droplets). Emulsions thickened with xanthan (GD01_Xan, GW01_Xan) did not show changes in droplet size upon mixing with saliva. This is linked to the negative charge of the droplets, which does not allow electrostatic attraction and subsequent droplet flocculation. For these emulsions, K decreased from 1.9 to 0.25 $Pa.s^n$ for GD01_Xan and from 2 to 0.26 $Pa.s^n$ for GW01_Xan. Emulsions diluted with water in a 1:1 ratio showed a comparable reduction in K to about 0.25 $Pa{\cdot}s^n$, suggesting that the reduction can be attributed to dilution.

In addition, the friction behaviour was affected by addition of saliva. The friction coefficient of positively charged, gelatine-stabilised emulsions (GD10, GW10) decreased slightly in the boundary regime (μ_{bound}), but did not change in the intermediate and high-speed regime ($\mu_{10\,mm/s}$, $\mu_{80\,mm/s}$). This is in contrast with the changes in droplet size. Upon addition of saliva, droplet size increased strongly due to flocculation. Clustering was previously seen to decrease friction. Apparently, saliva is able to increase friction. Also in the case of negatively charged non-clustered emulsions (GD01, GW01) saliva seemed to increase friction. For these emulsions, an overall increase in friction coefficient was observed upon addition of saliva (Table 3), whereas the cluster size remained constant. Laguna and co-workers (Laguna et al., 2017) reported a comparable observation of the effect of saliva on friction. They showed that addition of artificial saliva to skimmed milk increased the friction coefficient. This increase in friction was ascribed to the adherence of the saliva proteins to surfaces of the tribo-pair. Dresselhuis et al. (2007) suggested that proteins in saliva might act as additional components in the bulk and adhere to either surfaces of the tribo-pair, and consequently increase friction. This is in line with our findings. Negatively charged salivary proteins are not expected to interact with negatively charged emulsion droplets, but may adhere to the surfaces of the tribo-pair and increase friction.

In the case of clustered emulsions, the friction coefficients showed an overall increase with addition of saliva. This may be related to changes in the cluster properties. However, a conclusive explanation of the interplay among emulsion properties, saliva, and friction cannot be provided. Further research on the relation between saliva, aggregation and lubrication behaviour of emulsions needs to be performed.

To conclude, addition of saliva changes droplet size, rheological and tribological properties of both non-clustered and clustered emulsions. Positively charged single droplet emulsions tend to flocculate and thereby viscosity increases, whereas negatively charged single droplet emulsions tend to be less affected by saliva addition. For clustered emulsions, mixing with saliva reduces viscosity, which is mainly related to a dilution effect. Friction coefficients generally increase for clustered emulsions.

3.4. Correlations between sensory perception and physical characteristics of hetero-aggregated clustered o/w emulsions

To investigate how sensory attributes are related to emulsion characteristics, correlations between physical parameters describing physical changes upon saliva addition and RATA scores were determined (Table 5). Only mouthfeel attributes related to fat perception during oral processing are presented. We see similar trends for afterfeel, but we focus the discussion on mouthfeel attributes. Physical parameters that were not correlated to sensory attributes are not dealt with. First, correlations of sensory data with physical descriptors of the o/w emulsions are discussed and, subsequently, correlations of the sensory data with physical descriptors of emulsions containing saliva (saliva addition is indicated in the table with a "(+)"). As expected, thickness correlated strongly with consistency K. This is in line with several previous studies showing that perceived thickness is highly viscosity dependent (Akhtar et al., 2005; Camacho, Dop, de Graaf, & Stieger, 2015; Christensen & Casper, 1987; van Aken et al., 2011). Most fat-related attributes were strongly correlated to both rheological (viscosity, flow index and consistency) and tribological parameters. When friction decreased ($\mu_{80\,mm/s}$ and $\mu_{10\,mm/s}$), creaminess and fattiness increased which is in agreement with literature (Chojnicka-Paszun, de Jongh, & de Kruif, 2012; de Wijk et al., 2011; de Wijk & Prinz, 2005; van Aken et al., 2011).

When taking into account the changes in the physical characteristics of the emulsions upon addition of saliva, some of the correlations between sensory attributes and rheological properties of emulsions disappeared. Consistency K and thickness did not correlate anymore when emulsions were mixed with saliva. Instead, as a result of saliva addition,

Table 5
Overview of correlations between sensory attributes (mouthfeel) (white) and physical parameters of o/w emulsions (light grey). Category names containing (+) (dark grey) represent o/w emulsions mixed with saliva. Correlation coefficient and p-values are shown ($p < 0.05$ "*",$p < 0.01$ "**", $p < 0.001$ "***"). Boxes without numbers were not significantly ($p > 0.05$) correlated.

	Airy	Sour	Sweet	Astringent	Thick	Grainy	Creamy	Fatty	Watery	Sticky	Effect. cluster size	Viscosity (at 50/s)
b-exponent (+)						−0.74 *		−0.61 *		−0.64 **	−0.69 *	
$\mu_{80\,mm/s}$ (+)	0.80 **											
$\mu_{10\,mm/s}$ (+)	0.69 *										0.59 *	
Viscosity (at 50/s) (+)												
Flow index n (+)												
Consistency K (+)											0.77 **	
Effect. cluster size (+)											−0.68 *	
b-exponent												
$\mu_{80\,mm/s}$							−0.70 *	−0.68 *		−0.65 *		−0.63 *
$\mu_{10\,mm/s}$					−0.78 **		−0.67 *	−0.61**	0.79 **	−0.66 *		−0.8 **
Flow index n				−0.61 *	−0.77 **	−0.62 *	−0.68 *	−0.77 **	0.76 **	−0.79 **		−0.82 *
Consistency K					0.91 ***		0.77 **	0.85 **	−0.92 ***	0.87 *		0.97 ***
Viscosity (at 50/s)					0.91 ***		0.83 **	0.84 **	−0.95 **	0.85 *		
Effect. cluster size	0.68 *					0.72 **						
Sticky					0.91 **		0.85 **	0.99 ***	−0.88 **			
Watery					−0.98 ***		−0.92 **	−0.87 **				
Fatty					0.89 **		0.88 **					
Creamy					0.9 **							
Grainy	0.61 *											
Thick												
Astringent		0.75 **	−0.76 **									
Sweet		−0.76 **										
Sour												
Airy												

	Flow index n	$\mu_{10\,mm/s}$	$\mu_{80\,mm/s}$	b-factor	Effect. cluster size (+)	Consistency K (+)	Flow index n (+)	Viscosity (at 50/s) (+)	$\mu_{10\,mm/s}$ (+)	$\mu_{80\,mm/s}$ (+)	b-factor (+)
b-exponent (+)	0.76**								−0.62 *		
$\mu_{80\,mm/s}$ (+)									0.84 *		
$\mu_{10\,mm/s}$ (+)		−0.61 *									
Viscosity (at 50/s) (+)						0.84 **	−0.62 *				
Flow index n (+)						−0.78 **					
Consistency K (+)											
Effect. cluster size (+)											
b-exponent											
$\mu_{80\,mm/s}$	0.64 *	0.61 *									
$\mu_{10\,mm/s}$	0.65 *										
Flow index n											
Consistency K											
Viscosity (at 50/s)											
Effect. cluster size											
Sticky											
Watery											
Fatty											
Creamy											
Grainy											
Thick											
Astringent											
Sweet											
Sour											
Airy											

the tribological parameter describing the slope of the mixed regime (b exponent) correlated with certain sensory attributes (graininess, fattiness and stickiness) suggested to be associated with later stages of oral processing (de Wijk et al., 2011). The exponent b represents changes in friction coefficient of emulsions with increasing speed in the mixed regime. The lower the exponent b, the larger the changes in the emulsions, which might be related to a higher affinity to form a film and faster formation of an oil film. Therefore, the emulsions might be perceived as more fatty. If emulsions can form a film more easily by droplet coalescence, as is especially the case for DATEM-stabilised emulsions, lubrication is improved.

In conclusion, rheological properties correlate strongly with thickness and creaminess, which are considerably enhanced by clustering. Friction properties correlate with fattiness, graininess and stickiness, especially when saliva addition is taken into account. Creaminess was found to correlate to tribological properties in the absence of saliva. This provides clear indications that oral processing has to be taken into account when relating physical measurements to sensory perception, especially in different stages of the consumption.

4. Conclusions

Hetero-aggregation of oil droplets strongly influences physical, rheological and tribological properties of o/w emulsions. Due to an increase in effective volume fraction, viscosity increases strongly by oil droplet clustering. Due to an increase in viscosity, clustered o/w emulsions are perceived as thicker and creamier compared to o/w emulsions with single oil droplets. These attributes are enhanced with increasing cluster size. The strength of the clusters affects sensory properties. Emulsions with weakly bound clusters (gelatine-whey protein) are perceived as creamy, whereas emulsions with strongly bound clusters (gelatine-DATEM) are perceived as grainy, even though cluster size is similar. Strongly bound clusters show a steeper decrease of the friction coefficient in the mixed regime. Lubrication behaviour of hetero-aggregated clustered o/w emulsions thus depends on cluster size and strength. Upon clustering, emulsions become better lubricants than single droplet emulsions. Without saliva addition, thickness and creaminess perception correlate well with rheological and tribological properties of o/w emulsions. In contrast, with saliva addition, graininess and fattiness perception are stronger related to tribological properties suggesting that oral processing and the accompanying changes in emulsion structure as a result of mixing with saliva are important contributors to sensory perception. We conclude that clustering of oil droplets in o/w emulsions can be used as a tool to control the sensory perception of emulsions and enhance the perception of fat-related attributes.

Conflicts of interest

The authors have declared that no competing interests exist.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodhyd.2019.105215.

Appendix

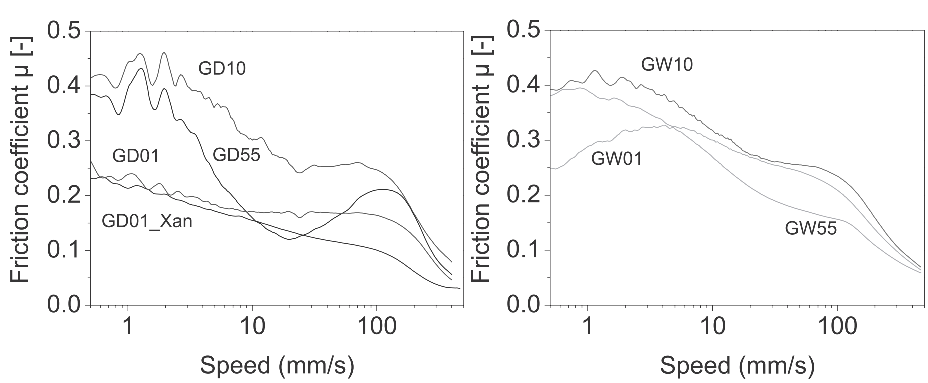

Fig. A.1. shows examples of Stribeck curves of single droplet emulsions (GD01, GD10, GW01, GW10, and GD01_Xan) and clustered emulsions (GD55 and GW55).

Figure A.1 Friction coefficient as a function of speed for single droplet and clustered o/w emulsions for (left) gelatine-DATEM and (right) gelatine-WPI clustered emulsions. (left) The red top line shows a homogeneous gelatine stabilised emulsion (pH 5, GD10), the green line shows a homogeneous DATEM stabilised emulsion (GD01), the blue line shows a highly clustered gelatine-DATEM emulsion (GD55), the black line shows a homogeneous DATEM stabilised emulsion containing 0.3% Xanthan (GD01_Xan). The blue line shows a homogeneous gelatine stabilised emulsion (pH7, GW10), the green line shows a highly clustered gelatine-WPI emulsion (GW55), and the red line shows whey protein isolate stabilised emulsion (GW01). Curves are obtained from averaging 3 measurements.

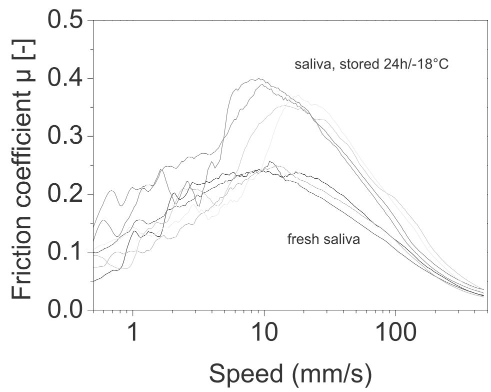

Fig. A.2. shows exemplary Stribeck curves of fresh saliva and saliva stored for 24 h at −18 °C.

Figure A.2 Friction coefficient as a function of speed for fresh saliva and saliva stored for 24 h at −18 °C. Curves are obtained from averaging 3 measurements.

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