Food & Function

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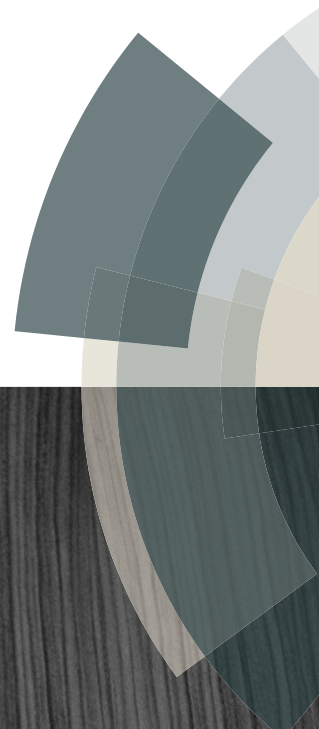
PAPER
Ashok R. Patel *et al.*
Edible applications of shellac oleogels: spreads, chocolate paste and cakes

Edible applications of shellac oleogels: spreads, chocolate paste and cakes†

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We demonstrate three potential edible applications of shellac oleogels as (i) a continuous oil phase for preparation of emulsifier-free, structured w/o emulsions (spreads), (ii) a replacer for oil-binders in chocolate paste formulations and (iii) a shortening alternative for cake preparation. Water-in-oil emulsions with up to 60 wt% water were prepared without the need for an emulsifier by simply using shellac oleogels as the continuous oil phase. The water droplets in these emulsions (size < 40 μm) were stabilized via interfacial and bulk crystallization of shellac. Chocolate paste prepared by complete replacement of an oil-binder and a partial replacement of palm oil (∼27%) with a shellac oleogel, showed no sign of 'oiling-out' when stored at elevated temperature (30 °C) for several weeks. Further, cakes prepared using oleogel-based w/o emulsions (20 wt% water) as a shortening alternative showed comparable functionalities (texture and sensory attributes) to the standard cake.

Introduction

Solid fats are major components in a majority of food products which are used on a daily basis including spreads, whipped creams, chocolates, ice-creams and various bakery products. The functionality and texture of solid fat containing food products are based on the underlying colloidal network of fat crystallites that physically trap oil in this network structure.[1,2] This fat crystal network (composed of saturated fats) is essential for providing structure to the liquid oil and consequently, without saturated fats, these products would not be possible to formulate.[3,4] However, the consumption of excessive amounts of saturated fats is considered highly unhealthy and has been found to show deleterious health effects including negative effects on cholesterol profiles and increase in the incidence of cardiovascular and other related diseases. Due to the increased emergence of such studies, a lot of research effort has been currently focused on seeking alternatives to structure liquid oil without the use of saturated fats.[5] Accordingly, strategies aimed at creating soft matter structures with the functionality of fats,

but with the nutritional profile of liquid oils (i.e. low in saturated fats and high in unsaturated fats), currently represent an important area of research that is highly relevant both from the academic as well as the industry points of view.[6] Of these approaches, oleogelation has been actively explored as an emerging technology geared towards the development of healthier lipid-based food products to control the life style and diet induced disorders such as obesity and cardiovascular diseases.[3,6]

Oleogelation, as the name implies, involves gelation of oil with the help of a single gelator or a synergistic combination of different gelator molecules.[1] Currently, oleogels have been receiving increased attention from researchers working in the food domain as indicated by recent reports on identifying newer food-grade oleogelators.[3,7–10] Recently, some researchers have even demonstrated interesting food applications of oleogelation such as replacement of solid fats and reduction of saturated fats in ice creams,[11,12] cooked frankfurters,[13] sausages and cookies[14] as well as for development of delivery systems of nutraceuticals.[15]

Our group has recently identified shellac (a food-grade resin) as a new structuring agent capable of gelling edible oil at low concentrations.[16] The rheological, thermal and microscopy evaluations further indicated that shellac oleogels could have potential food applications.[17] In the current paper, we demonstrate three different edible applications of these oleogels as (i) a continuous oil phase for preparation of emulsifier-free, structured w/o emulsions (spreads), (ii) a replacer for oil-binders in chocolate paste formulations and (iii) a shortening alternative for cake preparation.

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Results and discussion

Preparation and characterization of structured water-in-oil emulsions (spreads)

Shellac has an excellent oleogelation property which was exploited in our earlier work to make oil gels at concentrations as low as 2 wt%.[16,17] The gelation behaviour was due to the fat-like crystallization shown by shellac in the oil continuous phase when hot dispersions of melted shellac in oil were cooled below its crystallization temperature. This network of shellac crystallites was responsible for the solid fat-like texture of developed oleogels and emulsions. The network of crystallites in the oleogel sample is clearly visible when imaged under polarized light using an optical microscope (PLM) (Fig. 1a). The crystallites were seen to be arranged in a spherulitic morphology as confirmed from the prominent 'Maltese crosses' observed throughout the sample when viewed under cross-polarized light (Fig. 1a, inset). These radiant patterns arise due to the birefringence created from the alignment of crystallites in the lamellae of a spherulite.[18] Due to this extensive network of shellac crystallites, the oleogels also served as a continuous phase to create emulsifier-free, structured w/o emulsions. The PLM image of the emulsion showed tiny water droplets and crystal aggregates dispersed in an oil continuous phase (Fig. 1c). The emulsions were prepared by melting the oleogels followed

by homogenization (at 11 000 rpm) with the water phase (20 wt%) at high temperature and subsequent cooling to 5 °C. The initial formation of these emulsions (with droplet sizes below 40 μm) in the absence of an emulsifier can be attributed to a high level (30 wt%) of surface active wax alcohols (with a chain length of C28–32) that contributes to the surface activity of shellac.[19] Further cooling of hot emulsions below the crystallization temperature of shellac results in crystallization in both the bulk phase as well as at the water–oil interfaces, contributing to the long term stability of emulsions over an extended period of storage (4 months). The presence of fine crystallites at the interface of water droplets was confirmed from confocal microscopy. The presence of opaque dark water droplets dispersed in the continuous oil phase (doped with Nile Red) and the presence of crystallites on the droplet surface under reflective mode are shown in Fig. 1b. The oleogel emulsion was also viewed under a cryo-scanning electron microscope (cryo-SEM) after freeze fracture and sputter-coating. The water droplet physically trapped in a network of crystals as observed under cryo-SEM is shown in Fig. 1d.

The rheological properties of oleogels and emulsions were compared using amplitude sweeps. As seen in Fig. 2, neither the oleogel nor the emulsion showed any definite yield point (a point of permanent deformation) due to a progressive decrease in the elastic (G') and viscous (G'') moduli with the increase in the % strain. This behaviour of an absence of a clearly defined plateau owing to the progressive loss of the resistance of the system to deformation is indicative of fat-like crystal network formation as reported in our previous study.[17] The emulsion prepared using the oleogel as the continuous phase also showed a similar pattern of the LVR (linear viscoelastic region) curve with much lower initial values of G' and G'' and the appearance of a crossover point (which indicates gel to sol transition) at lower values of % strain. The results do indicate the shear sensitive nature of the oleogel and oleogel-based emulsions which could be considered useful for food applications where easier spreading of fat-continuous emulsions is desired.
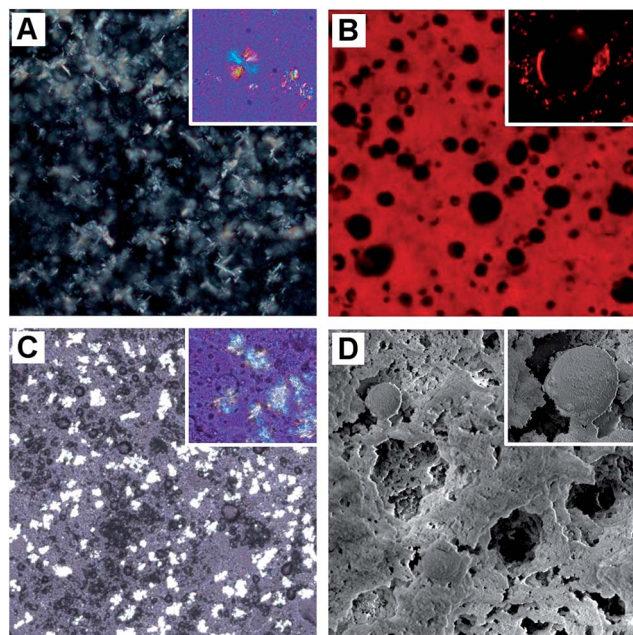

Fig. 1 (A) PLM image of the oleogel prepared using 2 wt% shellac in sunflower oil (image width: 200 μm), inset: spherulite aggregate of shellac crystals (image width: 50 μm); (B) confocal microscopy image of the oleogel emulsion prepared using 20 wt% water and shellac oleogel (2 wt%) as the continuous phase (image width: 200 μm), inset: water droplet covered with fine crystallites of shellac (image width: 25 μm); (C) PLM image of the oleogel emulsion (image width: 200 μm), inset: emulsion droplets and crystal aggregates (image width: 50 μm); (D) cryo-SEM image of the freeze fractured oleogel emulsion (image width: 100 μm), inset: enlarged image of a water droplet (image width: 25 μm).
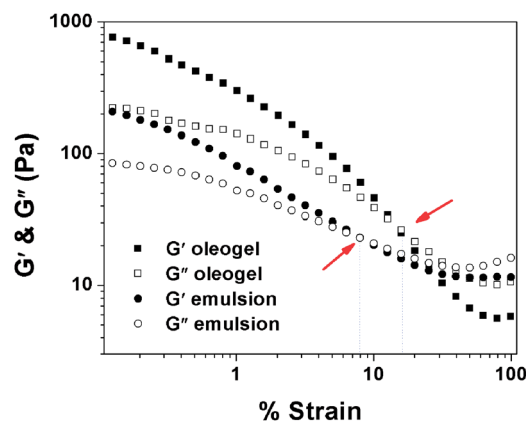

Fig. 2 A comparative graph of G' and G'' versus % strain for 2 wt% shellac oleogel and oleogel-based emulsion prepared using 20 wt% water and shellac oleogel (2 wt%) as the continuous phase. The crossover points are marked with arrows. The measurements were carried out at 5 °C and a frequency of 0.25 Hz.

Typically, the total content of fat in spreads varies from 80 wt% for full-fat spreads (regular margarines) to 60 wt% for reduced-fat and 40 wt% for low-fat spreads. As the fat content is lowered, the emulsification and stabilization become much more challenging because of two main factors: (a) the enhanced viscosity of the emulsion (resulting from the increase in the phase volume of the dispersed water phase) which makes it difficult to achieve finer droplet sizes and (b) the decrease in the crystallisable fat phase (due to the decrease in the fat content) which increases the possibility of higher agglomeration and re-coalescence of dispersed water droplets.[20] Thus, the choice of emulsifier becomes much more critical in formulating emulsions with lower fat content, as is the case with reduced and low-fat spreads. The ability of shellac oleogels to form emulsifier-free, w/o emulsions was further explored by increasing the water phase relative to the fat phase while keeping the concentration of shellac fixed at 5 wt% of the total emulsion. As expected, with the increase in the water phase, the emulsions became more and more difficult to homogenize and at fat contents below 40 wt%, the emulsions formed were unstable and showed phase separation after overnight storage at 5 °C. The increase in the water phase led to an increase in the gel strength of the emulsion as confirmed by the rheological data of amplitude sweeps presented in Fig. 3. The complex modulus, G^* (a measure of the total resistance of a sample to deformation) increased with the decrease in the fat phase (and the corresponding increase in the phase volume of the dispersed water phase). The curves showed similar patterns of a progressive decrease in the modulus with the increase in the % strain and an absence of a definitive critical strain as observed with the oleogel samples. The droplet size measured using diffusive NMR suggested that the size distribution was not influenced by the increase in the water phase with all the emulsions showing a narrow distribution range. There were however, some differences in the volume weighted mean droplet sizes, D33 (Fig. S1†) with values increasing from ~28 μm for 80 wt% fat to ~38 μm for 40 wt% fat.

Preparation and characterization of chocolate pastes

Chocolate pastes are dispersions of cacao powder and sugar particles in oil continuous medium with a considerable proportion of solid fat. Chocolate pastes have interesting rheological properties wherein they behave like a soft solid preventing sedimentation of dispersed particles and separation of liquid oil ('oiling out') and at the same time, displaying a more liquid-like spreading capability (yielding). This viscoelasticity is attributed to the crystallization of solid fats in the oil continuous medium.[21] Accordingly, solid fats (hydrogenated vegetable oils or natural oils with high levels of saturated fatty acids) are used for chocolate paste formulations. In addition, an oil binder (high melting triglyceride based on hydrogenated liquid oil) is incorporated into the recipe to prevent 'oiling out' at storage temperatures.

To explore the oil-binding properties of shellac, the potential chocolate applications of the shellac oleogel were evaluated by formulating a chocolate paste (based on the recipe given in Table S1†) by completely replacing the oil binder on a 1 : 1 ratio (Fig. 4). Shellac (1.5 wt%) was added to the chocolate paste in the form of an oleogel which meant that besides complete replacement of the oil binder, palm oil was also partially replaced (~27%) with liquid rapeseed oil. The solid fat content (SFC) profile shown in Fig. 5 clearly shows the difference in the crystallisable fat present in the reference as compared to the oleogel pastes. The solid fat (crystallisable fat) content was understandably lower for the oleogel paste at all studied temperatures due to the decreased content of palm oil (saturated fatty acids ~ 49.8%) which was replaced by liquid rapeseed oil (saturated fatty acids ~ 7.4%). The lower value of SFC at temperatures between 35 and 40 °C also confirms that the oleogel paste is most likely to not have any greasy taste which is usually the case with oleogels prepared using high melting waxes.[17] Further, samples subjected to storage at 30 °C for accelerated stability studies did not show any 'oiling out' even after 4 weeks of storage (Fig. 4b), suggesting that the replacement of the oil binder with shellac did not have any adverse effect on the physical stability of the paste.

The rheological properties of these chocolate pastes were compared using a range of experiments including flow measurements (ICA46 (2000) official method for chocolate
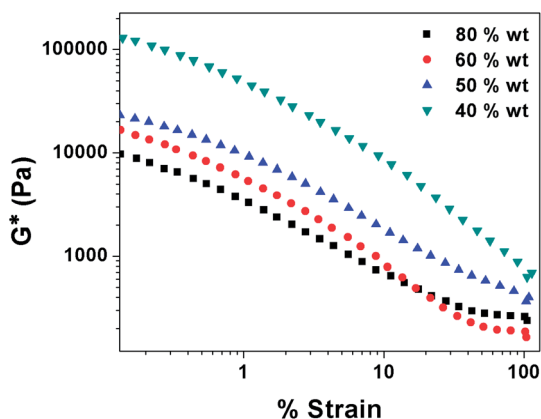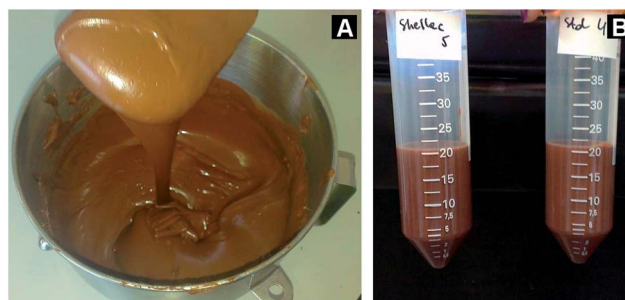

Fig. 3 A comparative graph of the complex modulus *versus* % strain for oleogel-based emulsions prepared at different fat contents ranging from 80–40 wt% while keeping the shellac concentration constant at 5 wt% of the total emulsion. The measurements were carried out at 5 °C and a frequency of 0.25 Hz.

Fig. 4 (A) Photograph of the chocolate paste prepared using the shellac oleogel; (B) pictures of the chocolate paste prepared using the shellac oleogel (on left) and the reference chocolate paste prepared using an oil binder (on right) after 4 weeks of storage at 30 °C. No oiling out was seen in either of the samples.
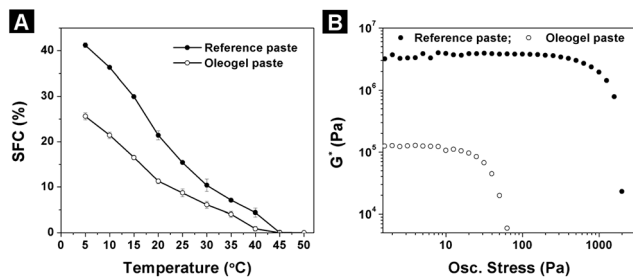
Fig. 5 (A) Solid fat content (SFC) profile of reference and oleogel pastes; (B) data from amplitude sweeps (a plot of complex modulus *versus* oscillatory stress) of reference and oleogel pastes. The measurements were carried out at 20 °C and a frequency of 1 Hz.

rheology)[22,23] and dynamic shear tests (amplitude and frequency sweeps). The values for the Casson yield stress and plastic viscosity were obtained by fitting the data of the upward (increasing shear rate) and downward (decreasing shear rate) flow curves (Fig. S2†) with the Casson model (eqn (1)); the values are tabulated in Table 1.

$$\sqrt{\sigma} = \sqrt{\sigma_{CA}} + \sqrt{\eta_{CA}}\sqrt{\dot{\gamma}} \qquad (1)$$

where σ is the shear stress (Pa), σ_{CA} = Casson yield stress (Pa), η_{CA} = Casson plastic viscosity (Pa s) and $\dot{\gamma}$ = shear rate (s^{-1}). The values of plastic viscosity give an indication of the flow of molten chocolate during processing and also the sensory attributes of finished products.[24,25] A higher plastic viscosity (>5 Pa s) can pose processing problems for certain types of chocolate formulations.[25] In the case of both oleogel as well as reference pastes, the low plastic viscosity values were comparable. On the other hand, the yield stress (minimum stress required for a sample to yield or flow) was relatively higher for the oleogel paste probably due to the higher inter-particulate interactions among dispersed particles (sugar particles) at lower solid fat contents.[26] Thixotropy is defined as the decrease in the apparent viscosity with the increase in time at a constant shear rate.[27] The continuous decrease in the apparent viscosity during shearing followed by a recovery when the flow is discontinued results in a hysteresis loop. Thixotropy can be quantified by measuring the area of this loop or by calculating the difference of shear stress at a specific shear rate (usually 5 or 40 s^{-1}) on the flow curves.[25,28] In the current study, the difference between the shear stress at 5 s^{-1} was calculated to obtain the value of thixotropy. The higher value exhibited by the paste prepared using the oleogel can be attributed to the typical rheological properties of shellac oleogels such as shear sensitivity (higher drop in viscosity with increase in shear owing to the structure breakdown) and partial structure recovery as reported previously.[17]

The dynamic shear tests were also performed to characterize and compare the two paste formulations. The amplitude sweeps clearly showed a vast difference in the LVR regions between the reference paste and the oleogel paste with the value of critical stress being more than 10 fold higher for the reference paste as compared to the oleogel paste (Fig. 5b). The $G*$ values throughout the curve were higher for the reference paste by almost a decade as compared to the oleogel paste. This difference can be correlated with the large difference in the SFC values (Fig. 5a) for the pastes at 20 °C (21.4% for the reference paste as compared to 11.3% for the oleogel paste). The viscoelasticity of the paste was further compared using data from frequency sweeps (Fig. 6); both the G' and G'' were higher for the reference paste as compared to the oleogel paste as expected. In both formulations, the higher values of G' compared to G'' indicate more 'solid-like' behaviour of pastes. However, the patterns of curves were different for the two studied pastes; the G' of the oleogel paste showed a stronger frequency dependence (higher positive slope) which is indicative of a weak gel structure[29] which probably contributes to a comparatively lower plastic viscosity as seen in the flow measurements.

Preparation and characterization of cakes

Cake margarine is a special type of margarine designed for incorporation of a large amount of air and homogenous fat distribution into the batter thus ensuring uniform expansion during baking and a resultant end product with a homogenous crumb structure.[30] In order to obtain this, it is very crucial that the cake margarine has a creamier structure and a desired plasticity. Since, cake margarine is a w/o type emulsion, small β′ crystals of fats in the continuous phase are preferred as they increase the firmness and incorporation of air into the batter at a given solid fat content.[31] However, the amount of cake margarine used for baking applications contributes significantly to the total calories and the fat content (which is sometimes referred to as 'hidden fats') of the end products.
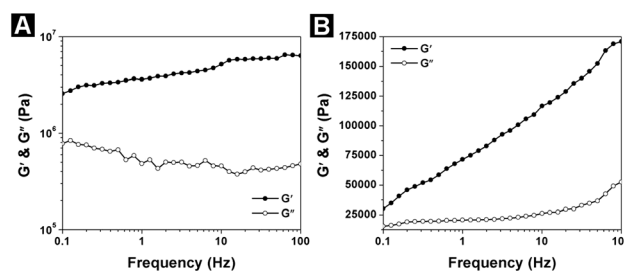

Fig. 6 Frequency sweeps of reference (A) and oleogel (B) pastes.

Table 1 Rheological parameters obtained from flow curves: Casson yield stress for upward and downward curves (↑σ_{CA} and ↓σ_{CA} respectively), Casson viscosity for upward and downward curves (↑η_{CA} and ↓η_{CA} respectively) and thixotropy

	↑σ_{CA} (Pa)	↑η_{CA} (Pa s)	↓σ_{CA} (Pa)	↓η_{CA} (Pa s)	Thixotropy (Pa)
Ref.	9.7 ± 0.7	4.7 ± 0.3	7.4 ± 0.4	4.6 ± 0.4	5.8 ± 0.3
Shellac	14.1 ± 0.8	3.3 ± 0.2	7.6 ± 0.3	3.4 ± 0.3	11.7 ± 0.5

Hydrogenated oils or natural oils high in saturated fats are used as the continuous phase for formulating cake margarines and thus saturated fatty acids constitute a high proportion of hidden fat content in bakery products.[32]

Oleogel-based emulsions where structured liquid oil is used as a continuous phase were evaluated for bakery applications in order to decrease the total saturated fat content in bakery products such as cakes (Fig. 7). The batter and cake properties were studied using rheology and texture analysis. The absence of solid fat crystals in oleogel-based emulsions led to a more runny consistency of shellac oleogel emulsion (SE) batter as compared to the std sample (prepared using cake margarine), confirmed from a 10-fold difference in the G' (~7000 Pa for std as compared to ~700 Pa for SE) and a much lower cross-over point for SE (5% as compared to 80% strain for std) (Fig. 8). The decrease in the firmness of batter also had an influence on the air incorporation resulting in a comparatively higher batter density (0.86 g ml^{-1} of SE compared to 0.73 g ml^{-1} for std). However, in spite of the difference in the consistency and density of the batter, the baked cakes showed mostly comparable texture and sensorial attributes. The TPA curve shown in Fig. 9 was used to calculate textural parameters such as firmness, springiness index, cohesiveness and chewiness (Table 2). Only the springiness index and chewiness were found to be statistically different ($p < 0.05$). Springiness index is defined as the ratio of height the sample springs back to after maximum

Fig. 9 Comparative TPA curves for cakes made using cake margarine and shellac oleogel emulsions.

Table 2 Textural parameters obtained from TPA curves

Parameters	Cake margarine	Shellac emulsion
Firmness (N)	4.05 ± 0.31	3.48 ± 0.23
Cohesiveness	0.69 ± 0.02	0.64 ± 0.01
Adhesiveness (N mm)	$-0.003 \pm 1 \times 10^{-3}$	$-0.004 \pm 1 \times 10^{-3}$
Springiness index[a]	0.43 ± 0.01	0.72 ± 0.01
Chewiness[a]	1.33 ± 0.09	2.23 ± 0.11

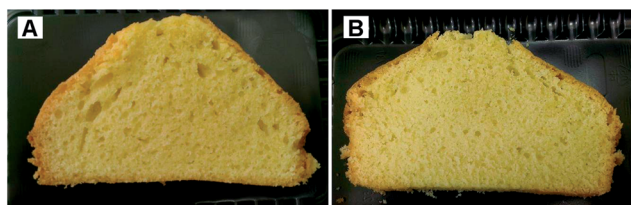[a] The difference is statistically significant ($p < 0.05$).

Fig. 7 (A & B) Photographs of cakes prepared using shellac oleogel emulsions and standard cake margarine as shortenings, respectively.
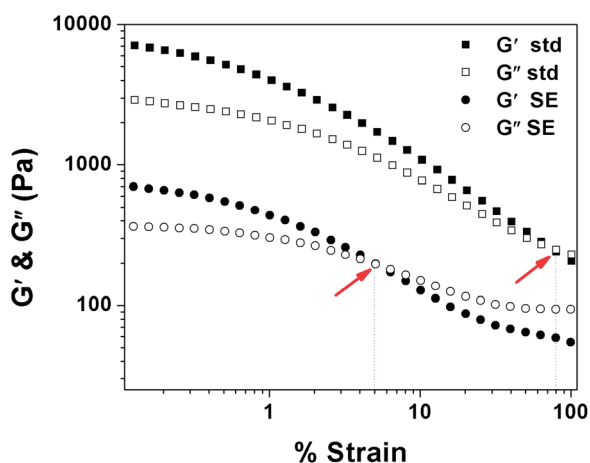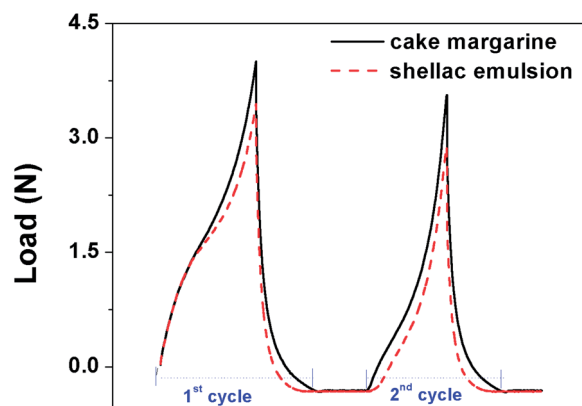

Fig. 8 Comparative graph of G' and G'' versus % strain for batters made using cake margarine (std) and shellac oleogel emulsion (SE) as shortenings. The crossover points are marked with arrows. The measurements were carried out at 20 °C and a frequency of 1 Hz.

deformation and is indicative of the elasticity of the sample.[33] The higher values of springiness index of the SE cake (0.72) compared to the std cake (0.43) can be related to the increased elasticity of the SE cake probably due to the higher level of protein crosslinking in the batter. Usually, cake margarine or conventional shortening has a high amount of fat crystals that forms a barrier and prevents extensive crosslinking in the gluten network thereby shortening the structure of the batter.[34,35] It is understandable because in the case of SE, the structuring comes only from the shellac crystal network (crystallisable fat content is 9.9% compared to 28% for cake margarine at 20 °C, Fig. S3†). The elasticity of the SE cake is also reflected in the higher values of chewiness (Table 2).

Based on the results of the sensorial evaluation (Fig. 10), it was found that the SE cake was comparable to the standard cake for all the studied parameters except for two related parameters of uniformity in cell size and crumbliness ($p < 0.05$). The lower uniformity in cell size or voids for the SE cake is due to the uneven distribution of air in the batter which are not efficiently stabilized due to the lack of solid fat crystals in the batter network. The resultant non-uniformity of these air pockets also makes the cake less coherent and crumbly, leading to the formation of crumbs while handling the cake. However, other properties of cakes such as sponginess and moistness that relate to the mouth feel were comparable suggesting that there is potential for using oleogel-based emulsions as shortening alternatives. Currently, we are evaluating the possibility of adding foam stabilizers (emulsifiers) in order to ensure

increased air incorporation and subsequent stabilization during baking.

Experimental

Materials

Shellac wax, SSB® Cera 2 (acid value: 2–25 mg KOH g^{-1} and saponification value: 40–60 mg KOH g^{-1}), was received as a generous gift sample from SSB Stroever GmbH & Co. KG., Germany. Rapeseed oil, palm oil and standard cake margarine were received as gift samples from Vandemoortele R&D Izegem, Belgium. Sugar (Barry Callebaut, Wieze, Belgium), hazelnut paste (Natra All Crump, Nijverheidsstraat, Belgium), cacao powder (Cargill, Wormer, The Netherlands) and skimmed milk powder (Friesland Campina, Belgium) were received as gift samples. Palsgaard PGPR 4125, Palsgaard AMP 4448, and Palsgaard Oil Binder 01 (fully hydrogenated triglycerides) were generously donated by Palsgaard A/S, Demark. Nile Red was purchased from Sigma Aldrich Inc. (USA). Cake flour, eggs and baking powder were purchased from a local supermarket. Distilled water was used for all the experiments.

Preparation of oleogel-based w/o emulsions

Shellac oleogels were first prepared by dispersing accurately weighed amounts of shellac in rapeseed oil followed by heating these dispersions at a temperature above the melting point of shellac (>85 °C) under mild agitation (200 rpm) using a magnetic stirrer (Model EM3300T, Labotech Inc., Germany). The clear oily dispersions of shellac thus formed were then cooled to room temperature immediately, resulting in the formation of oleogels. To prepare w/o emulsions, the melted shellac oleogels were added to accurately weighed water samples (heated >85 °C) followed by shearing at 11 000 rpm with the help of a high dispersion unit (Ultraturrax® IKA®-Werke GmbH & Co. KG, Germany). The sheared liquid emulsions were then cooled to room temperature to get textured

emulsions. Oleogels and emulsion samples were stored at 5 °C until use for further experiments.

Characterization of oleogel-based w/o emulsions

Microstructure studies. The microstructure of oleogels and emulsions was studied under polarized light using a Leica DM2500 microscope (Leica Microsystems, Belgium). For confocal microscopy, Nile Red was first dissolved in rapeseed oil and this oil was then used for preparing the oleogel and emulsion samples. Samples were imaged using a Nikon A1R confocal microscope (Nikon Instruments Inc., USA). Excitation was performed by means of a 488 nm Ar laser and fluorescence was detected through a 525/50 bandpass filter. Images were acquired and processed with Nikon NIS Elements software. For cryo-SEM, samples of the oleogel and emulsion were placed in the slots of a stub, plunge-frozen in liquid nitrogen and transferred into the cryo-preparation chamber (PP3010T Cryo-SEM Preparation System, Quorum Technologies, UK) where they were freeze-fractured and subsequently sputter-coated with Pt and examined in a JEOL JSM 7100F SEM (JEOL Ltd, Tokyo, Japan).

Rheological measurements. The rheological measurements were carried out on an advanced rheometer AR 2000ex (TA Instruments, USA) equipped with a Peltier system for temperature control. A parallel plate cross-hatched geometry of diameter 40 mm was used and the geometry gap was set at 1000 μm. Amplitude sweeps (strain = 0.01 to 100%) were carried out to determine the linear viscoelastic region of emulsions prepared at different water contents.

Droplet size analysis. Water droplet size analysis of the w/o emulsions was performed by pulsed field gradient nuclear magnetic resonance (pfg-NMR) on a benchtop Maran Ultra spectrometer (Oxford Instruments, UK) operating at a frequency of 23.4 MHz in combination with the Droplet size application (Resonance Instruments Ltd.). Samples were analyzed at 5 °C to minimize inter-droplet water diffusion. To suppress the NMR contribution of the fat phase, pfg-NMR experiments were conducted using an inversion recovery stimulated echo pulse sequence. In the performed experiments, the diffusion time (Δ) was set to 0.2 seconds, the gradient strength was fixed at 1.74 T m^{-1}, while the gradient duration (δ) was varied in 17 steps from 400 to 4500 ms. By measuring the echo attenuation ratio of the NMR signal as a function of the gradient duration, it is possible to determine the hindered diffusion behaviour and hence the droplet size distribution.

Preparation of chocolate pastes

A standard chocolate paste containing a commercial oil binder (Palsgaard Oil Binder 01) at 1.5 wt% was prepared and compared with a paste made using shellac oleogels replacing 100% of oil binder and around 27% of palm oil with rapeseed oil (refer Table S1† for the recipe). The preparation process was as follows: the oil binder in a part of palm oil and shellac oleogel were both melted above 70 °C followed by addition of all other ingredients (except Palsgaard PGPR 4125, Palsgaard AMP 4448 and the remaining fat) and subsequent refining at 50 °C using
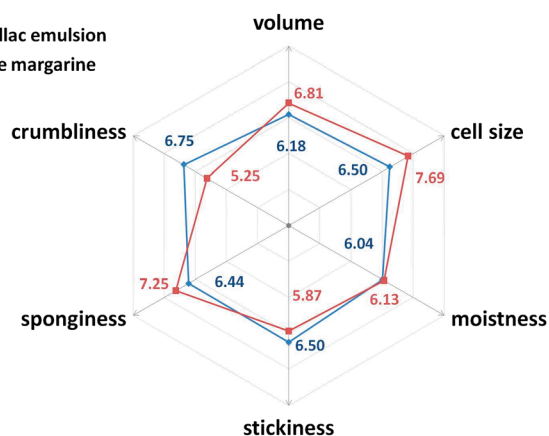

Fig. 10 Comparative sensorial parameters of cakes prepared using shellac emulsions and cake margarine as shortenings. Only the differences in the cell size and crumbliness were found to be statistically significant ($p < 0.05$).

an Exakt 80S 3-roll mil (Exakt Technologies Inc., USA). After refining, the remaining fat, Palsgaard PGPR 4125 and Palsgaard AMP 4448 were mixed with the refined mix for 30 minutes in a commercial mixer (Bowl Lift Stand Mixer, Kitchen Aid, USA). The paste was stored at 18 °C to assist post-crystallization of fat. Some samples were also stored at 30 °C and observed regularly for any oiling-out over a period of storage.

Characterization of chocolate pastes

Rheological measurements. The flow properties of molten chocolate samples were determined using a rheometer equipped with a concentric cylinder system (stator radius = 15 mm and rotor radius = 14 mm and gap of 5920 μm). Chocolate samples were prepared by heating in an oven at 52 °C for an hour. Approximately, 20 grams of chocolate samples were weighed into the cylinder. Measurements were performed in accordance with the ICA46 (2000) official method for chocolate. The temperature of the rheometer was set at 40 °C and regulated using a water bath (Julabo Gmbh, Seelbach, Germany). After a pre-shear period of 15 min at 5 s^{-1}, the shear rate was stepwise raised from 2 s^{-1} to 50 s^{-1} (ramp up) in a 3 min interval, then kept constant for 1 min at 50 s^{-1}, and then decreased stepwise to 2 s^{-1} (ramp down) in 3 min. Shear stresses were recorded and fitted to the Casson model. The mean value and standard deviation of triplicate readings were recorded.

Oscillatory measurements were carried out using parallel plate geometry as mentioned before. Stress sweeps (oscillatory stress = 1 to 5000 Pa) were carried out to determine the linear viscoelastic region and critical stress for standard and shellac pastes. Frequency (0.1 to 100 Hz) sweeps were also done to gain more information on the rheological properties.

Solid fat content. The solid fat content (SFC) was determined using a pfg-NMR (details covered above). The samples (fat extract of the pastes) were first heated above 80 °C to remove the crystal memory followed by an incubation at 0 °C for an hour. The SFC was measured in the range of 5 to 55 °C with intervals of 5 °C. The incubation time at each temperature was 30 minutes; all measurements were conducted on three samples and the results are reported as mean ± SD.

Preparation of cakes

In order to evaluate the potential application of shellac oleogel-based emulsions as a shortening alternative, classic 4/4 sponge cakes were prepared using 300 g wheat flour, 13 g baking powder, 300 g liquid whole egg, 300 g sugar and 300 g standard cake margarine or shellac oleogel emulsion (20 wt% w/o). The cake batter was prepared by mixing these ingredients in a Kitchen Aid® mixer followed by baking at 175 °C for 35 minutes.

Characterization of cake batters

To evaluate the air incorporation and the fat structure in the batter, density measurements and oscillatory rheological measurements were carried out. For density measurements, batter samples filled in glass cylinders with a known volume were accurately weighed in triplicate. For rheology studies, amplitude sweeps (strain = 0.1% to 100%) were conducted using parallel plate geometry.

Characterization of cakes – texture analysis

The baked cakes were subjected to texture profile analysis (TPA) tests on a texture analyser (Instron Model 5942, USA). TPA was carried out by first preparing cubes with a size of 2 cm from the centre of cakes. These cubes were then subjected to a 2 step compression using a cylindrical probe of 6 cm diameter at a speed of 10 mm min^{-1}. In the first cycle, the sample was compressed to 50% of its height (50% strain) followed by the removal of load through an upward movement of the probe. The whole cycle was repeated in step 2. The measured force during these 2 cycles as a function of time was plotted to get a TPA curve. Measurements were done on 10 replicates of each sample. The mean and SD values of each parameter were statistically analysed.

Preliminary sensory analysis. A preliminary sensory analysis was carried out to compare the sensorial properties of these cakes and to evaluate the overall acceptability of shellac emulsions as shortening alternatives. A blind test was carried out on a panel of 20 people where they were asked to compare the two cake samples on properties such as appearance and handling (volume, cell size uniformity and crumbliness) and mouth feel (sponginess, moistness and stickiness) by giving ranks for individual properties from 1–9.

Statistical analysis. Data from texture and sensorial evaluation of cakes were compared using statistical analysis. An unpaired, two-tailed Student T-test was used on the data to establish the statistical significance in the differences observed.

Conclusions

In conclusion, three different edible applications of shellac oleogels were studied to evaluate its role as a stabilizer in emulsifier-free spread formulation, a replacer for oil binder in chocolate pastes and a structurant for shortening alternatives in cake preparation. Due to the presence of surface active components like long chain fatty alcohols in shellac, a fine dispersion of water droplets in melted shellac oleogels was obtained which was further stabilized by bulk and interfacial crystallization of shellac when the emulsions were cooled down. Emulsifier-free emulsions (with up to 60 wt% water) that were stable for over 4 months were successfully prepared. Chocolate paste formulations prepared with 100% replacement of oil binder and ~27% replacement of palm oil did not show any 'oiling out' when stored for over 4 weeks at 30 °C confirming the oil binding properties of shellac. The potential of using shellac oleogel-based emulsion as a shortening alternative was clear from the preliminary bakery trails where cakes with comparable mouth feel to commercial shortening were successfully prepared.

Shellac has a long history of use in foods and has a GRAS status and food additive E number (E904) when used as a coating/glazing agent. Based on the status of shellac and the above-discussed results, it can be concluded that shellac oleogels can be used for some interesting food applications.

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