Instrumental and sensory characterisation of oleogels for cosmetic use

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Introduction

Gel-based cosmetic products could be categorised as either hydrogels, emulgels or oleogels. While a hydrogel contains water as a liquid component, an emulgel contains a thickened oil phase as a part of an emulsion (Almeida et al, 2008). Oleogels are made by entrapping the bulk liquid by an oleogelator to form a complex semisolid structure. In principle, the oleogelgel formation mechanisms could be divided into two groups: self-assembly systems and crystal particles systems (Vintiloiu & Leroux, 2008; Tarun et al., 2011).

Despite having some distinct advantages (e.g. absence of preservatives or surfactants), the use of oleogels in cosmetic products is still sporadic. This may be due to insufficient data on the physico-chemical characteristics of oil/oleogelator combinations, specifically their rheological parameters. In addition, very little is known about sensory differences that those combinations produce.

Aim

The aim of this study was to compare the effects of different types of oleogelators on instrumental and sensory properties of oleogels made with common emollient types: hydrocarbon, synthetic ester and natural oil.

Materials and Methods

Materials

The oils used were chosen to represent three major groups of emollients in cosmetic formulation, i.e. petrochemically-derived (mineral oil), synthetic esters (isopropyl palmitate) and natural triglycerides (sunflower oil). The oleogelators used are presented in Table 1.

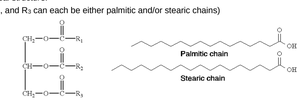
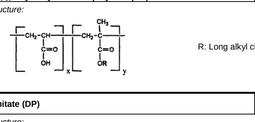
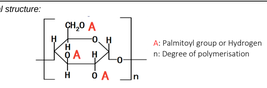
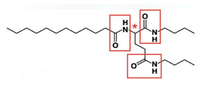
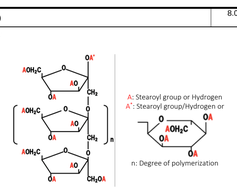
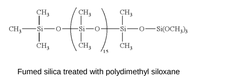
INCI name	Recommended usage level (%)
Palmitic/stearic triglyceride (PST)	2.5 – 10.0
Chemical structure: (R_1, R_2, and R_3 can each be either palmitic and/or stearic chains) 	
Acrylates/C_{10-30} alkyl acrylate crosspolymer (AA)	3.0 – 15.0
Chemical structure:  R: Long alkyl chain	
Dextrin palmitate (DP)	6.0 – 10.0
Chemical structure:  A: Palmitoyl group or Hydrogen n: Degree of polymerisation	
Dibutyl lauroyl glutamide (DLG)	1.0 – 8.0
Chemical structure: 	

Table 1. Chemical structure and usage levels of the oleogelators

Stearoyl inulin (SI)	8.0 – 15.0
Chemical structure:  A: Stearoyl group or Hydrogen A': Stearoyl group/Hydrogen or n: Degree of polymerization	
Silica dimethicone silylate (SDS)	2.0 – 10.0
Chemical structure:  Fumed silica treated with polydimethyl siloxane	
Silica	2.0 – 10.0
Chemical structure: Fumed silica SiO_2	

While AA, DP, SI and DLG are chosen for their stated capability to gel all three types of oils, it was of interest to test a plant-derived triglyceride PST as a representative of the 'natural' oleagelator. In addition, two versions of silica, a hydrophilic and a hydrophobic type, were also added to the list of oleogelators.

The **benchmark** was Ceridal Lipogel (Stiefel GSK, Norway), a moisturiser intended for extremely dry skin, consisting of petrolatum, microcrystalline wax (cera microcristalllina) and cyclopentasiloxane.

Preparation method

Oleogels were produced as single-phase systems, using an overhead mixer. With the exception of silica, all oleogelators had to be heated with respective oils in order to produce a homogeneous oleogel. The cooling process was conducted in a controlled manner, until the sample reached the room temperature. Preliminary formulations were made using the minimum and maximum recommended oleogelator levels (Table 1). Since many were unsuccessful, the concentration levels were altered in order to produce oleogels with acceptable semisolid characteristics.

Physico-chemical characterisation

A rheological 'snapshot test', consisting of dynamic and flow tests, was carried out on all samples using RheoStress RS75 (Haake GmbH, Germany) with a serrated 35mm parallel plate, at 22^0C. The dynamic test used was an oscillatory stress sweep, at a constant frequency of 1Hz, starting from 0.5Pa. A flow test was a shear rate sweep from 10 to 300s^{-1}, performed in a reverse manner in order to avoid instrumental artefacts.

In addition, all samples were assessed for texture parameters using a 'back extrusion' test on the texture analyser TA.XT Plus (Stable Micro Systems, UK), with a 0.5-inch cylinder probe.

Sensory characterisation

Sensory assessment was done on a selected range of samples (Table 2), using a panel of semi-trained participants and a modification of the published sensory method (Meilgaard et al, 2007). The parameters analysed were firmness, cohesiveness, spreadability, absorbency, greasiness and slipperiness. These parameters were clearly defined to the panel during their initial training in sensory terminology and scales, which has provided them with the sensory references to use as comparative points while delivering their judgements. The above sensory parameters were measured on the scale of 0-10, with increments of 0.5.

Results and Discussion

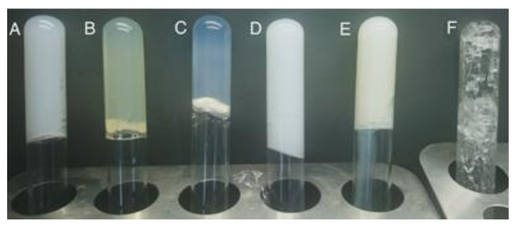


Figure 1. Characteristic examples of oleogels formed with the test materials:
A - mineral oil + 10% SI; B - sunflower oil + 10%DP; C - isopropyl palmitate + 2.75% DLG; D - mineral oil + 9% C10-30 AA; E -sunflower oil + 10% PST, F- mineral oil + 9% silica

Figure 2 presents two sets of results obtained using oscillatory stress sweep. Both show the relationship between the oscillatory stress (x axes), the complex modulus G* (first y axes, known also as the rigidity of the sample) and the phase angle δ (second y axes). The phase angle (lag phase) shows how much the measured deformation lags behind the applied one. At the point of yield stress, G* dramatically decreases, whilst δ increases, usually above 45^0, indicating a transition between predominantly solid to predominantly liquid state. This has clearly seen in example **b** on Figure 2, while example **a** shows the case where the yield point has not been reached during the scope of the run.

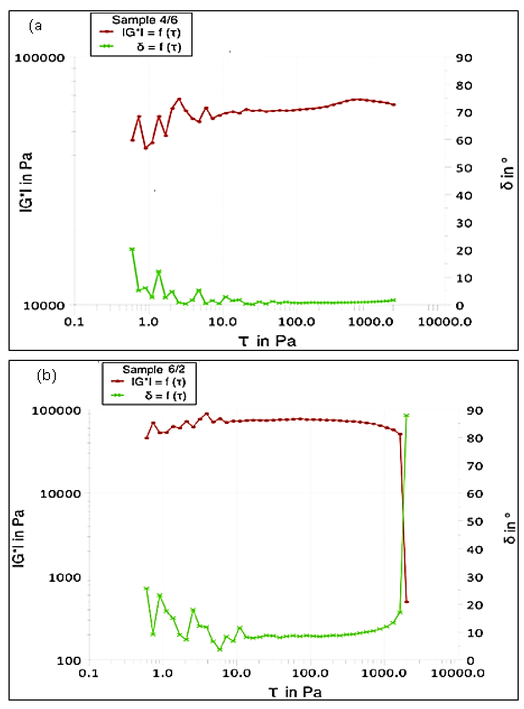


Figure 2. Characteristic oscillatory stress sweep responses, showing changes in the phase angle δ and the complex modulus G* for two oleogels with mineral oil. (a) mineral oil + 9% silica; (b) mineral oil + 2.75% DP

The most informative rheological parameters were found to be: **apparent viscosity** (at 300s-1), **yield stress** (obtained from the flow curve), a **crossover point** between elastic modulus (G') and viscous modulus (G'') and **rigidity** (expressed as complex modulus G*).

A typical texture analysis graph is shown in Figure 3, showing **firmness** and **cohesiveness** as the highest peaks on the immersion and de-immersion curve, respectively. The area under the positive part of the curve measures **consistency** and the area under the negative curve is defined as **index of viscosity**.

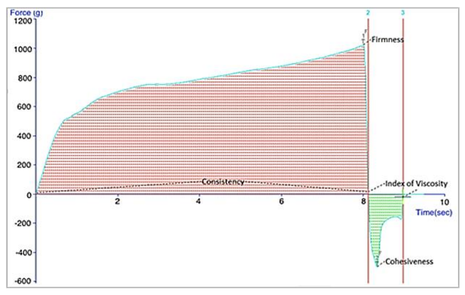


Figure 3. An example of a typical 'back extrusion' plot obtained from the texture analyser for an oleogel

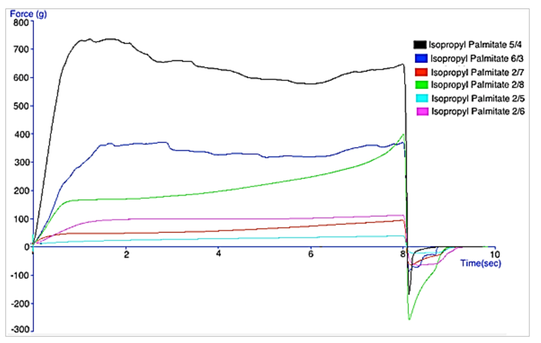


Figure 4. An example of the texture analysis results obtained for the oleogels with isopropyl palmitate and different oleogelators

In the sensory test, sample 024 (9% silica in mineral oil) has shown the highest firmness, but it has scored low in other parameters (Figure 4). This finding corresponds well with the rheology data. Sample 011 (8% SI in isopropyl palmitate) and 023 (2.75% DLG in isopropyl palmitate) have shown similar sensory characteristics, except for their firmness and cohesiveness. The two oleogels made with sunflower oil, 007 (6% DP) and 002 (10% PST) have shown quite different sensory parameters, with 002 being the most similar to the benchmark. Greasiness was found to be the lowest in the case of mineral oil/silica oleogel (024).

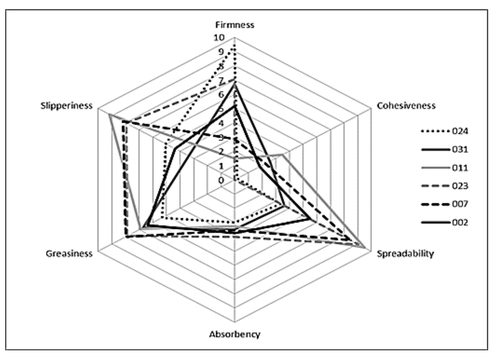


Table 2.
The composition of samples used for sensory testing

Category	A	B	C
Product Code (Reference)	Mineral oil	Isopropyl palmitate	Sunflower oil
024	9% Silica		
031	Benchmark lipogel		
011		8% Stearoyl Inulin	
023		2.75% Dibutyl lauroyl glutamide	
007			6% Dextrin palmitate
002			10% Palmitic/stearic triglyceride

Figure 4. Spider (radial) diagram showing the average sensory scores obtained by a semi-trained panel for the most successful oleogels

Depending on the chemical structure of the oleogelator, the intermolecular forces that can occur in an oleogel system could be hydrogen bonds, π–π stacking or London dispersion forces. The chemistry of the oil phase also contributes to the gelation behaviour and could affect the macroscopic (e.g. opacity and texture) and microscopic (e.g. aggregate size) properties (Tarun et al, 2011). An oleogelator molecule must be insoluble enough for the structure to self-assemble and form a gel, yet it must be relatively soluble to be able to interact with the liquid phase. If the oleogelator is too soluble, a solution will be formed, whereas if the oleogelator is too insoluble, the lack of interaction with the liquid phase will cause precipitation (Tarun et al, 2011; Daniel & Marangoni, 2012). This sensitive balance has not been achieved in a large number of samples investigated in this study, but a small range was found to have appropriate characteristics for cosmetic use.

Conclusion

Five cosmetic oleogelators were dispersed into three standard cosmetic oils: mineral oil, isopropyl palmitate and sunflower oil. Contrary to some literature data, approximately one third of the trial formulations was unsuccessful. Only three oleogelators (dibutyl lauroyl glutamide, dextran palmitate and stearoyl inulin) were able to produce stable structures with all three oils. A naturally-derived palmitic/stearic triglyceride could only produce stable oleogels with chemically similar sunflower oil, while acrylates/C10-30 alkyl acrylate crosspolymer and silica only worked in the hydrocarbon-based mineral oil. It is interesting to note that hydrophobic silica (silica dimethicone silylate) did not produce stable oleogels in this study.

References

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