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# Critical Factors to Obtain Stable High Internal Phase (HIP) Gel-in-Oil Emulsions

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### Synopsis

The interest of the high internal phase (HIP) gel-in-oil concept for the development of emulsions with original aesthetic qualities was highlighted some years ago. Manufactured using a sustainable cold process, these emulsions were characterized by a fresh skin contact and triggered similar emollience to classical emulsions and cream gels with half the oil concentration. However, the factors governing the emulsion structure have not been thoroughly clarified. Composition factors (i.e., the essential structural materials and concentration of the internal gel phase) and the preparation procedure (i.e., emulsification mode and agitation procedure) have been investigated on a standard HIP gel-in-oil emulsion. Their influence on the creation, structure, and stability of gel-in-oil emulsions was determined by conventional observations, stability tests, and rheology experiments, from low to high shear conditions (rotational controlled stress/strain rheometer). Limitations and critical factors such as characteristics of the gel phase and a required dose of emulsifier were highlighted. An emulsification mixing procedure with medium shear using an anchor provided the best results. In addition, conventional conductivity monitoring combined with rheology experiments detected early indicators of the risk of destabilization soon after manufacturing. Precise recommendations to obtain stable HIP gel-in-oil emulsions, characterized by highly stable elastic structure, could be defined.

## INTRODUCTION

### HIGH INTERNAL PHASE EMULSIONS: OVERVIEW AND RECENT CONTEXT

High internal phase emulsions (HIPEs) are rare formulations containing a volume of the dispersed phase exceeding the close packing limit of spheres, above around 74%,[1] stabilized by surfactants or amphiphilic solid particles (high internal phase Pickering emulsions: HIPPEs) or combining both materials.

In recent years, HIPPEs, including water-in-oil (W/O), have been used as templates to manufacture a wide spectrum of functional porous materials based on cellulose, polyurethane, silica, polystyrene–acrylate copolymers, polystyrene composites, polymethyl

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methacrylate, etc.[2] W/O HIPEs and HIPPEs in particular were used in the food and pharmaceutical sectors as a matrix for the encapsulation of hydrophilic active ingredients that are fragile or have perceived obstacles to their use (e.g., protection of probiotics during their travel through the gastrointestinal tract[3] or beta carotene improving the taste of bitter or astringent substances,[4] reducing the irritant effect of active ingredients,[5] etc.). Formulations for encapsulation purposes included waxy components (e.g., beeswax) in the oily phases and required hot manufacturing processes. Their use as vehicles for controlled-release and targeted delivery has also been described.[6] In addition, the texture of W/O HIPEs and HIPPEs was also highlighted as a solution to reduce trans–fatty acid or saturated fat content for healthier food products.[7]

Contrary to HIPEs with a water continuous phase, W/O types are known to be difficult to generate and stabilize without using a large quantity of surfactants, which explains why additional strategies using both structuration of the oily phase with waxes or oil gelators (oleogels) and structuration of the water phase using hydrogels (e.g., gellan, flaxseed gum, carrageenan, konjac glucomannan, and blends of polysaccharides) were developed, sometimes also combined with the Pickering approach.[8,9] In the food sector, extensive research has been carried out using glyceryl and polyglyceryl fatty acid esters as emulsifiers in combination with different stabilization strategies (crystallized oily phase, water-in-oleogel, gel [i.e., hydrogel]-in-gel [i.e., oleogel]).[8,10,11,12] The manufacturing process generally involved high intensity homogenization using rotor/stator devices and required stepwise addition of the dispersed phase.[3,8,9,12] Homogenization was also reported as necessary in studies dedicated to cosmetic applications.[13]

Few publications have dealt with cosmetic applications of W/O HIPEs in the last 5 years, but there have been recent patent filings disclosing skin care applications. A first patent claimed to maximize the fresh feeling while stating the importance of the emulsifier's nature and content to combine this first fresh sensation with a stable formula.[14] A mass proportion between 70% and 99% of the dispersed phase compared to the continuous phase was also reported as necessary for the achievement of high internal phase (HIP) W/O emulsion. The addition of the internal water phase was performed little by little using a dispersing mixer for the preparation. Two other patent disclosures mentioned W/O HIPEs able to stabilize pigments in the internal phase for makeup purposes, requiring precise manufacturing procedures.[15,16]

## HIP GEL-IN-OIL BACKGROUND AND PURPOSE OF THE STUDY

Based on the similar principle of high concentration in dispersed phase, the HIP gel-in-oil concept consists of a high concentration of closely packed gel droplets dispersed within a liquid continuous oil phase (Figure 1). To solve known stability issues of W/O HIPEs and avoid high concentration of surfactants,[8] a tailored non-ionic emulsifying system was developed to withstand a large amount of internal gel phase, combining a small surfactant molecule and a large polymeric surfactant structure.[17] The small molecule quickly migrates to the oil–water interface and helps to create the oil continuous form, while the large molecule ensures stability over time. The gel-in-oil creation is also based on rheology modifiers, giving a gel with a suitable rheology profile (i.e., shear thinning, nonthixotropic, with a moderate elastic character). As for a conventional W/O emulsion, an antifreeze agent such as glycerin or a glycol derivative was found to improve the gel-in-oil stability at cold

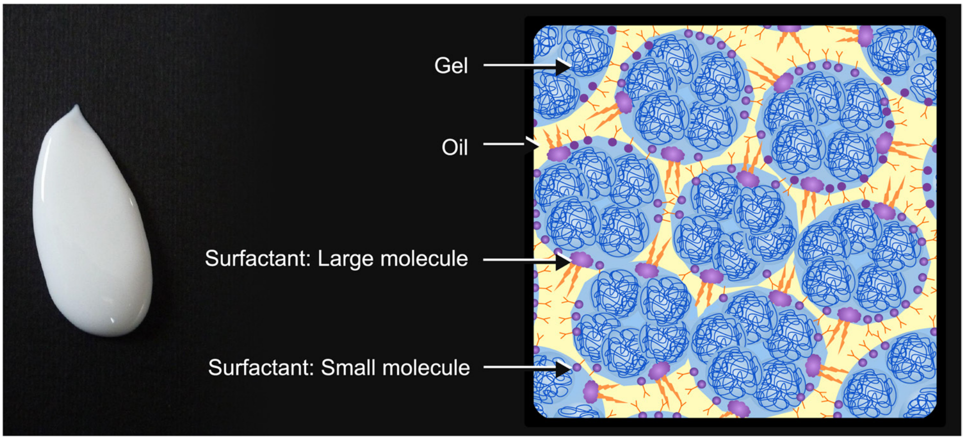

**Figure 1.** Gel-in-oil macroscopic appearance and structure representation.

temperatures, but conversely to water-in-oil, water-in-silicone, and conventional HIP W/O emulsions,[13] the addition of salts was not required.

The interest of the HIP gel-in-oil concept for the development of cosmetic emulsions with original aesthetics was highlighted some years ago.[18] First of all, it provides an attractive smooth and mirrored gloss appearance for the end user, with an unexpected contrasting sensory profile starting with a first fresh sensation evolving to a cushion-comfortable finish. As a result, the gel-in-oil emulsion is able to impart a similar emollience to conventional cream gel, oil-in-water (O/W), and W/O formulations with a reduced oil concentration[19] and provides an inherent water resistance character. The texture of gel-in-oil emulsion alone (without any olfactory, packaging, or brand environment) was demonstrated to arouse positive emotions in consumers.[20]

From the formulator's point of view, the concept takes advantage of high compatibility with active ingredients,[21] including those rich in electrolytes. Gel-in-oils also withstand the incorporation of a high quantity of solvents, sometimes required to solubilize these active ingredients (e.g., glycols, ethanol, etc.). The manufacturing process, cold and using low mixing energy, is industrially advantageous, saving time and increasing sustainability by reducing carbon emissions.[17]

Despite these advantages, the factors affecting the emulsion structure and behavior have not been thoroughly clarified, thus limiting the use of the concept. As is known for other inverse emulsions, it is difficult to predict the long-term stability of gel-in-oil without waiting for three months, even using accelerated tests (storage at 45°C and freeze–thaw cycles in particular). Due to high concentration of the dispersed phase, gel-in-oils mainly provide compact textures, which make them difficult to prepare and diminish the relevance of accelerated tests based on centrifugal force (such as the LUMiFuge® device from Germany) or based on multiple light-scattering analyses (such as the Turbiscan® LAB device from France).

The objective was therefore to study rigorously the factors affecting the emulsion structure, stability, and behavior under stress for a better understanding of the limitations of the formulation. First, details of the manufacturing process needed to be investigated using a simple formula to confirm the recommendations: preparation mode (i.e., direct or indirect) and agitation type (i.e., mixing, homogenization). Key composition factors were also scrutinized: impact of gel viscosity by increasing the doses of a suitable rheology modifier; emulsifier level; ratio between the internal aqueous phase and the external oily phase; and nature of the oil. This work also aimed to find an appropriate test to check quickly that the formulation is optimized without waiting for the conventional stability tests. With this in mind, flow and oscillatory rheology experiments were explored to test the structure and resistance of gel-in-oils.

## MATERIALS AND METHODS

### INGREDIENTS AND COMPOSITION OF THE FORMULATION BASE

Formulation experiments were carried out by changing one parameter at a time. A formula base with a reduced number of ingredients was chosen to facilitate analysis of the impact of changes (Table I).

Ingredients were weighed using an ML 1602 precision balance (Mettler Toledo GmbH, Greifensee, Switzerland) to prepare 300 g of each formulation.

### CHARACTERIZATION AND STABILITY OF FORMULATIONS

*Viscosity measurement.* The viscosity of the samples was measured using a Brookfield LVDVI+™ viscometer using an appropriate spindle and speed 6 (Brookfield Engineering Laboratories Inc., Middleboro, MA, USA). Measurements were taken one day after manufacturing (D1), after 7 days (D7), after 1 month (M1), and after 3 months (M3).

*Microscopic observations.* The stable formulations were observed using an optical microscope Meiji® MT-9300 (Meiji Techno Co., Ltd., Saitama, Japan) with a magnification of ×400, one week after manufacturing (D7), and images were captured by an attached charge-coupled device camera GR500W (Shanghai Goldroom Im/Export Trade Co., Ltd., Shanghai, China).

**Table I**

Formulation Base With Fixed Ingredients and Variables Studied

| Phase | Ingredient | % (w/w) |
|---|---|---|
| Gel | Demineralized water | Up to 100 |
| phase | Hydroxyethyl acrylate/sodium acryloyldimethyl taurate copolymer[a] | 0.6/0.7/0.8/1/1.2 |
| | Xylitylglucoside and anhydroxylitol and xylitol[b] | 3.00 |
| | Phenoxyethanol and ethylhexylglycerin[c] | 0.80 |
| Oily | Octyldodecanol and octyldodecyl xyloside and PEG-30 dipolyhydroxystearate[d] | 0.50/1/1.5/2/2.5/3 |
| phase | Caprylic/capric triglyceride[e] | 3/5/8/13/18/23/28 |

[a] Polyelectrolyte rheology modifier (Seppic, La Garenne Colombes, France).

[b] Moisturizing active ingredient playing here the role of antifreeze agent (Seppic, La Garenne Colombes, France): fixed ingredient in all the trials.

[c] Preservative (Thor Specialty Chemical Co., Ltd., Zhenjiang, China): fixed ingredient in all the trials.

[d] Liquid emulsifying system (Seppic, La Garenne Colombes, France).

[e] Oil (Croda International Plc, Goole, United Kingdom).

*Conductivity measurement.* Conductivity measurements were carried out at room temperature at D1, D7, M1, and M3 using a SevenMulti™ dual pH/conductivity meter (Mettler Toledo GmbH, Greifensee, Switzerland).

*Stability monitoring.* The appearance of the formulations was checked after storage at D1, D7, M1, and M3 in different temperature conditions: room temperature; at 45°C using a BD 400 incubator (Binder GmbH, Tuttlingen, Germany); in −5°C to 40°C freeze–thaw cycles using an MIR-154 Cooled Incubator (SANYO Electric Co., Ltd., Osaka, Japan), at −18°C in a BCD-232ESN refrigerator/freezer (Electrolux, Senlis, France).

### RHEOLOGY EXPERIMENTS

Experiments were conducted at around 20°C, D7 after manufacturing, using a rotational controlled stress/strain Discovery Hybrid Rheometer DHR-2® (Waters—TA Instruments, New Castle, DE, USA). In accordance with the thin particle size of the trials, an anodized aluminum cone with a diameter of 40 mm, and forming an angle of 2° with the plate, was selected for all tests.

Oscillatory frequency sweeps from 0.1 to 100 rad/s were carried out with an anti-evaporation cap within the linear viscoelastic domain. Viscoelasticity was then analyzed to evaluate the level of structuration of the gel-in-oil and its resistance or any change occurring in the structure during the experiment (frequency expressed in Hz in the Figures according to international units). Evolution of storage modulus (G’) and calculation of mean G’/G” (i.e., loss modulus) ratio were followed to easily compare the formulations. The higher the value of mean G’ and relative G’/G” ratio, the greater the elasticity and the stronger the structure of the formulation.

The samples were also subjected to a shear rate ramp ranging from 0 to 1,200 $s^{-1}$ for 120 seconds (up and down ramp; steady state flow protocol) to determine the global flow profile and yield stress. Curve analysis was performed using the Herschel–Bulkley mathematical model to extract yield stress and rate index. Rate index, which varies from values close to zero for a strong shear-thinning profile to one for Newtonian behavior, was used as an additional indicator to supplement the curves. The purpose of this experiment was to subject the formulations to greater stress that can be representative of real stressing situations such as pouring, stirring, mixing, pumping,[22,23,24] etc.

## IMPACT OF MANUFACTURING PROCEDURE: VARIATIONS AND RESULTS

### VARIATIONS ON MANUFACTURING PROCEDURE

Some parts of the manufacturing process remained fixed for all the trials, according to conclusions of previous work.[17] The gel phase was prepared by dispersing the rheology modifier (a) in water using a serrated disc stirrer between 500 and 1,000 rpm (IKA Eurostar 60 digital stirrer, IKA® Works, Guangzhou, China). The antifreeze agent (b) and preservative (c) were added, and stirring continued until a smooth gel texture was obtained. The oily phase was prepared by addition of the emulsifier (d) to the oil and manual stirring for a few seconds with a spatula. Then one phase was introduced into the other, added in one shot.

For practical considerations, due to the high volume of the gel phase, gel-in-oil emulsions were made by an indirect mode (i.e., adding oily phase to gel phase). The direct emulsification mode had not been attempted in previous studies. Previous work also demonstrated that high shear was not required for emulsification, and mixing using a planetary agitation device, such as an anchor or scraper, to gradually wrap the gel with the oil was recommended.[17] This work therefore aimed to investigate the influence of the emulsification mode (i.e., direct or indirect) and to confirm the most suitable mixing procedure on the selected formulation base.

*Direct emulsification mode.* Addition of gel phase to oily phase.

*Indirect emulsification mode.* Addition of oily phase to gel phase.

*Emulsification mixing procedure.* Three devices, involving low to high shear, were tested.

- Stirring with an anchor at 75 rpm for 1 minute, followed by 9 minutes at 300 rpm (IKA Eurostar 60 digital stirrer, IKA® Works, Guangzhou, China).
- Mixing with a serrated disc stirrer between 500 and 1,000 rpm for 10 minutes (IKA Eurostar 60 digital stirrer, IKA® Works, Guangzhou, China).
- Homogenization with a rotor/stator turbine using a Silverson® L4RT high-shear mixer at 4,000 rpm for 4 minutes (Silverson, East Longmeadow, MA, USA).

## RESULTS

All the formulations were stable under the various temperature conditions at 3 months. However, the high conductivity of the formulations obtained with serrated disc mixing and rotor/stator homogenization indicated that defective cream gels with continuous aqueous phase were obtained in these conditions instead of gel-in-oil emulsions. The result was the same with indirect and direct emulsification mode (Table II). As anticipated, gel-in-oil emulsion was characterized with a conductivity value close to zero.[13,14] This outcome

**Table II**

Effect of Variations of the Manufacturing Procedure on a Fixed Formula Containing: Water 85.40%, Rheology Modifier 0.80%, Emulsifier 2.00%, Oil 8.00%, Internal Gel Phase 90% (W/W %)

| Emulsification mode | Indirect | Indirect | Indirect | Direct | Direct | Direct |
|---|---|---|---|---|---|---|
| Agitation | Anchor | Serrated disc | Rotor/stator | Anchor | Serrated disc | Rotor/stator |
| Conductivity D1/M1 (μm/cm) | 0 | ≅453 | ≅441 | 0 | ≅440 | ≅453 |
| Formula type | Gel-in-oil | Cream gel | Cream gel | Gel-in-oil | Cream gel | Cream gel |
| Viscosity D1 (mPa·s) | ≅104,500 | ≅19,600 | ≅20,300 | ≅99,800 | ≅20,500 | ≅19,100 |
| Stability | Stable | Stable | Stable | Stable | Stable | Stable |
| Rheology data | | NT(g) | NT(g) | | NT(g) | NT(g) |
| Mean G' (Pa) | 430 | | | 411 | | |
| Mean G'/G" | 6.7 | | | 6.4 | | |
| Yield stress (Pa) | 30.5 | | | 31 | | |
| Rate index | 0.46 | | | 0.44 | | |

[g] NT: Not tested.

[h] w/w: Weight/weight

confirmed that stirring with low energy, such as with an anchor, is the most effective manufacturing method to obtain gel-in-oil emulsions, irrespective of the emulsification mode. Gel-in-oil emulsions were also characterized by a higher viscosity than defective cream gels with the same composition. This finding was consistent with HIP content and compressed droplets.[1] Despite low mixing energy, gel-in-oil emulsions contained thin internal droplets. As shown in the microscopic appearance in Figure 2, internal gel droplet size was around 1 µm, with a few bigger particles of 2–2.5 µm. The microscopic appearance was identical for indirect and direct emulsification mode.

The rheological profiles of gel-in-oil emulsions obtained with indirect and direct emulsification mode were similar (Table II). Frequency sweep curves (Figure 3) showed that both trials have a strong stable elastic structure with very close G'/G" ratios. Shear behavior was also identical for the two procedures (Figure 4). Analysis of the curves between 0 and 500 $s^{-1}$ indicated a similar yield stress and a medium shear-thinning behavior as signaled by a rate index close to 0.5 (Figure 4, Table II). A change in the slope of the curve was observed, indicating that the acceptable deformation of the product had exceeded above 600 $s^{-1}$. This observation was not linked to visible side effects on the edges of the geometry. Deeper investigation was required in the subsequent experiments to understand if it was a measurement artifact or if it could be related to a characteristic of the product itself.

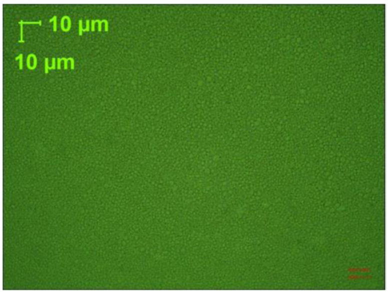

**Figure 2.** Typical microscopic appearance of gel-in-oil emulsion prepared by indirect mode and stirring using an anchor device.

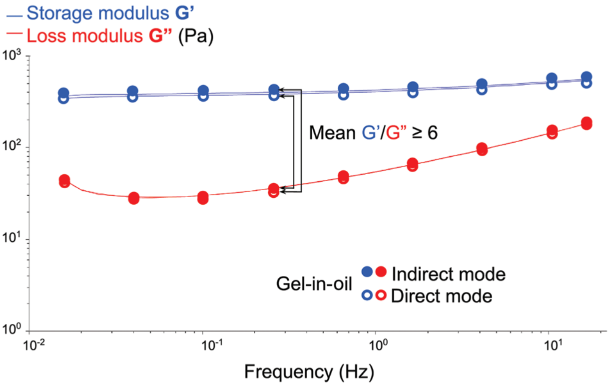

**Figure 3.** Viscoelasticity of gel-in-oil emulsions at different frequencies according to indirect or direct emulsification mode.

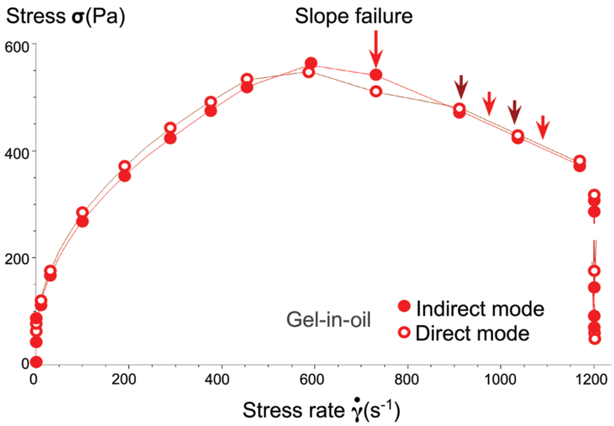

**Figure 4.** Flow profile of gel-in-oil emulsions according to indirect or direct emulsification mode.

These results determined the process for the rest of the study. As the emulsification mode had no impact, the indirect emulsification mode was kept for greater convenience (especially with a view to larger-scale production), followed by mixing with an anchor stirrer. Earlier preparation steps remained unchanged.

## EFFECT OF FORMULATION COMPOSITION: VARIATIONS AND RESULTS

### GEL VISCOSITY

The formulation trials and results in Table III showed that formulations F4, F5, and F6, containing 0.8%, 1%, and 1.2% of rheology modifier respectively, which is associated with a viscosity of the internal aqueous gel greater than or equal to 18,000 mPa·s, provided gel-in-oil emulsions in accordance with the absence of conductivity. These formulations

**Table III**

Variations of Rheology Modifier Concentration and Resulting Effect of Internal Gel Phase Viscosity on a Fixed Formula Containing: Emulsifier 2.00%, Oil 8.00% (w/w %)

| | F1 | F2 | F3 | F4 | F5 | F6 |
|---|---|---|---|---|---|---|
| (a) Dose (w/w %) | 00.40 | 00.60 | 00.70 | 00.80 | 01.00 | 01.20 |
| Gel phase (w/w %) | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 | 90.00 |
| Gel viscosity (mPa·s) | 240 | 2,800 | 8,400 | 18,000 | 42,400 | 64,800 |
| Conductivity D1/M1 (µm/cm) | ≅225 | ≅227 | ≅87 | 0 | 0 | 0 |
| Formula type | Cream gel | Cream gel | Cream gel | Gel-in-oil | Gel-in-oil | Gel-in-oil |
| Viscosity D1 (mPa·s) | ≅500 | ≅3,575 | ≅7,975 | ≅42,700 | ≅68,900 | ≅89,400 |
| Stability | Two phases D7 at 45°C −5°C–40°C | Stable | Stable | Stable | Stable | Stable |
| Rheology data | NT[g] | | | | | |
| Mean G' (Pa) | | 30 | 69 | 397 | 559 | 753 |
| Mean G'/G" | | 3.2 | 2.8 | 6.1 | 6.7 | 7.3 |
| Yield stress (Pa) | | 2 | 8 | 29 | 37 | 31 |
| Rate index | | 0.55 | 0.66 | 0.44 | 0.42 | 0.38 |

[g] NT: Not tested due to instability.

were stable over time, and no differences were observed in their microscopic appearance, similar to Figure 2. Formulations F1, F2, and F3, with aqueous gel viscosity lower than 18,000 mPa·s, were defective cream gels as indicated by high conductivity values. This shows that a minimum viscosity of the internal phase was required to create gel-in-oil emulsions.

Oscillatory experiments revealed that gel-in-oil emulsions were characterized by a stronger elastic structure than defective cream gels, as illustrated by a higher storage modulus value (G') and G'/G" ratios more than doubled (Figure 5 and Table III). The viscoelastic character of gel-in-oil emulsions was also stable to frequency variations. Once the minimum viscosity threshold was reached, the continued increase in gel viscosity had a smaller effect on the elastic character, which nevertheless continued to rise slightly.

Analysis of gel-in-oil emulsion flow profiles (between 0 and 400 $s^{-1}$) showed a lower rate index than defective cream gels, indicating a stronger shear-thinning character (Table III). Higher yield stress was also found, in line with higher viscosity and a more structured/elastic internal organization. The shear-thinning character tended to increase with the increasing viscosity of the internal gel phase and the resulting build-up of the texture of the gel-in-oil emulsions, which explained why gel-in-oil emulsions were still easy to spread on skin, even for very compact textures.[20]

A phenomenon identical to that already observed in the previous flow curves of gel-in-oil emulsions was noticed: a change in the slope of the curves, above around 400 $s^{-1}$ in this case (Figure 6). A careful observation of the device during experiments confirmed the absence of potential sources of error such as visible edge effects (e.g., ejection or digging of the product). In addition, torque was monitored to check that it did not decrease over time.[25] Observation of the product's appearance at the end of the experiment, on the plate of the rheometer, indicated a relationship between the composition of the product and the phenomenon that could be understood as a destructuration, or localized mini-fractures, for F4, extending to a complete breakdown of the formulation for the defective cream gel F3 when submitted to strong shear conditions (Figure 7). The resistance of the structure of gel-in-oil emulsions to high shear was strengthened with the rise of gel viscosity as shown by

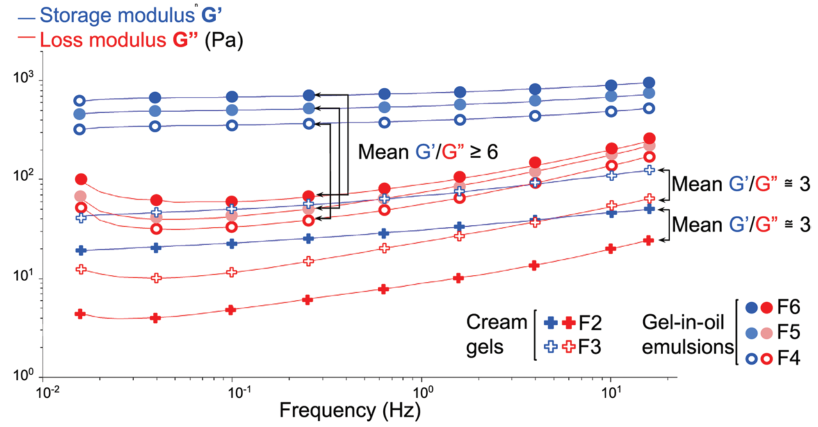

**Figure 5.** Viscoelasticity of formulations at different frequencies according to rheology modifier dosage and resulting internal gel phase viscosity.

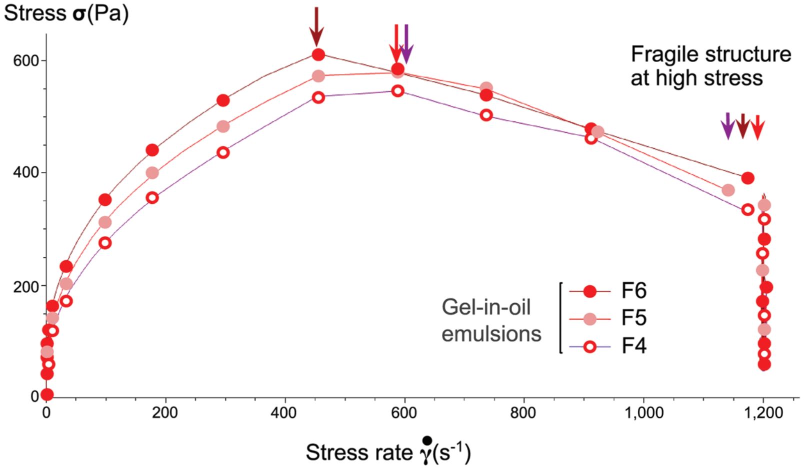

**Figure 6.** Flow profile of gel-in-oil emulsions according to viscosity of internal gel phase.

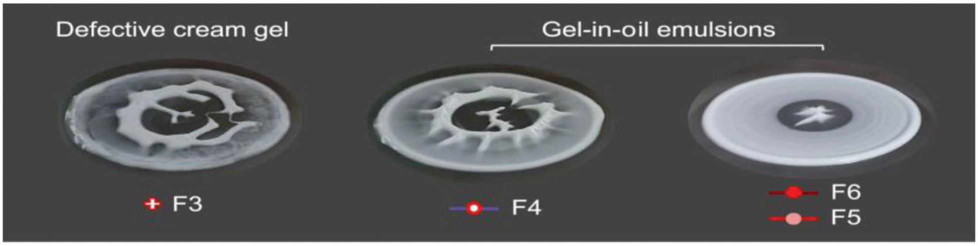

**Figure 7.** Appearance of formulations at the end of the flow experiment.

the more homogeneous appearance of F5 and F6 at the end of the experiments (Figure 7). This improvement between F4 and F5/F6, concomitant with the increasing viscosity of the emulsion, also suggested that the phenomenon was linked to a modification in the structure of the product under stress. A sliding artifact effect due only to contact issues with the device should have strengthened with the increasing viscosity of the formulation. Interestingly, this weakness of the structure was not detected with conventional stability monitoring at 1 month.

### EMULSIFIER DOSAGE

For this part, a slightly greater amount of rheology modifier (a), 1%, was chosen for the best conditions to determine the lowest efficient emulsifier dose. The formulation variations and results in Table IV showed that F7 with 0.5% emulsifier (d) was a defective, unstable cream gel in accordance with its high conductivity value. F8 with 1% emulsifier (d) evolved from a gel-in-oil emulsion at D1 to a defective exuded cream gel after 1 month of storage at 45°C and −18°C. F9 with 1.5% emulsifier (d) showed very little oil exudation after 3 months of storage at −18°C. F10, F11, and F12, with 2%, 2.5%, and 3% emulsifier (d) respectively, were stable gel-in-oil emulsions. This shows that a dose of emulsifier (d) above

**Table IV**
Effect of Emulsifier Concentration on a Fixed Formula Containing: Rheology Modifier 1.00%, Oil 8.00% (w/w %)

| | F7 | F8 | F9 | F10 | F11 | F12 |
|---|---|---|---|---|---|---|
| (d) Dose (w/w %) | 00.50 | 01.00 | 01.50 | 02.00 | 02.50 | 03.00 |
| Gel phase (w/w %) | 91.50 | 91.00 | 90.50 | 90.00 | 89.50 | 89.00 |
| Conductivity D1/ M1 (µm/cm) | 0/330 | 0/>20 | 0/4 | 0 | 0 | 0 |
| Formula type | Cream gel | Gel-in-oil to cream gel | Gel-in-oil | Gel-in-oil | Gel-in-oil | Gel-in-oil |
| Viscosity D1 (mPa·s) | ≅78,100 | ≅150,000 | ≅115,500 | ≅113,500 | ≅98,500 | ≅92,500 |
| Stability | Two phases at −18°C | Exudation at 45°C/−18°C | Exudation at −18°C | Stable | Stable | Stable |
| Rheology data | | | | | | |
| Mean G' (Pa) | 387 | 463 | 640 | 604 | 467 | 396 |
| Mean G'/G" | 2.4 | 2.1 | 6.6 | 7.2 | 5.5 | 4 |
| Yield stress (Pa) | 3 | 35 | 87 | 95 | 77 | 57 |
| Rate index | 0.35 | 0.40 | 0.51 | 0.47 | 0.62 | 0.62 |

1.5% was required to create optimized gel-in-oil emulsions. As expected, the concentration of the emulsifier also affected the emulsion particle size[10] with a thin appearance from 2% and even thinner from 2.5% (Figure 8). The viscosity of gel-in-oil emulsions decreased when the emulsifier dosage increased from 1% to 3%. The reason could be that for HIP emulsions the viscosity is driven by the internal phase concentration and droplet packing.[17]

Oscillatory experiments indicated a weak elastic structure, especially at low frequencies, for F7 and F8 (Figure 9A), with loss modulus values (G") close to storage modulus (G'). These characteristics were consistent with the poor stability of the formulations. A strong and stable elastic structure was built as soon as the emulsifier dosage reached 1.5% (Figure 9B). Once 1.5% emulsifier was attained, the increase in emulsifier concentration had a smaller effect on the elastic character as represented on the curves. Decreasing mean values of G' and G'/G" ratio (Table IV), in line with a decline in yield stress, between 2% and 3% emulsifier was assumed to be caused by a concomitant decreasing concentration of the internal gel phase and droplet packing.

As with variations of the rheology modifier, weaknesses in the gel-in-oil structures were observed under shear, with improvements as the dose of emulsifier (d) increased (Figure 10). F8 was strongly affected above 400 $s^{-1}$, and disturbance in the formula texture could be seen on Figure 11 at the end of the experiment. F9 showed a weak structure above 500 $s^{-1}$ but a more homogeneous texture at the end of the experiment. These results, obtained 7 days after manufacturing, were consistent with the destabilization of these two gel-in-oil emulsions over time, after 1 month for F8 and 3 months for F9 (Table IV). The gel-in-oil

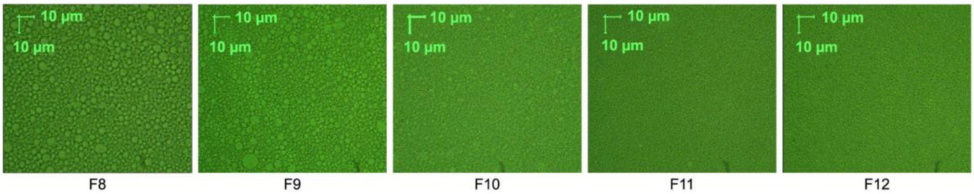

**Figure 8.** Microscopic appearance of gel-in-oil emulsions according to emulsifier concentration.

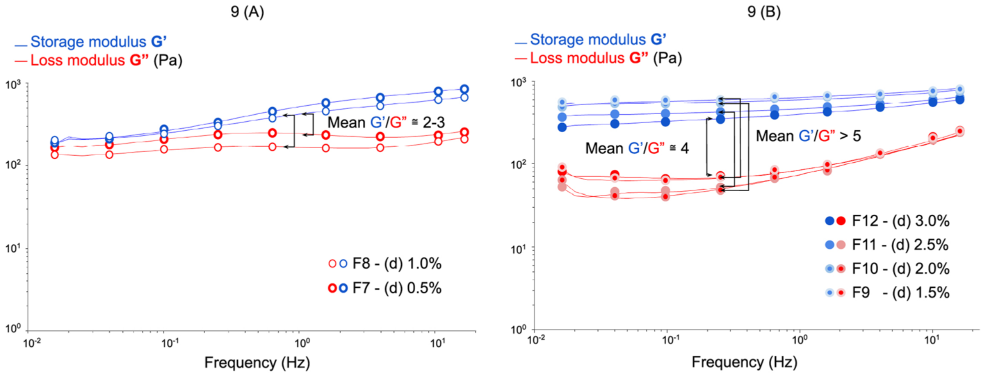

**Figure 9.** Viscoelasticity of formulations at different frequencies (A, B) according to emulsifier dosage.

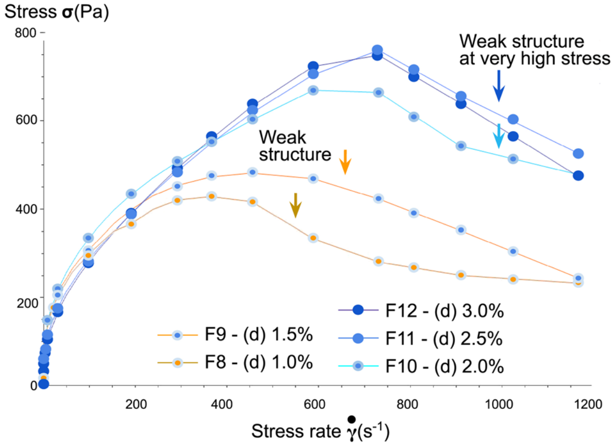

**Figure 10.** Flow profile of gel-in-oil emulsions according to emulsifier (d) dosage.

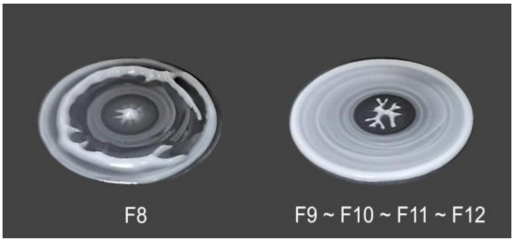

**Figure 11.** Appearance of formulations at the end of the flow experiment.

emulsion structure was strengthened, and its shear resistance was improved from 2% emulsifier (d): F10, F11, and F12 (Figure 10), in line with long-term stability (Table IV). A relative sensitivity to very high stress persisted.

Based on the mathematical analysis, performed in the range where the structures were stable, it is apparent that the two highest doses of emulsifier led to gel-in-oil emulsions

(F11, F12) with a lower shear-thinning behavior as indicated by their rate index superior to 0.5 (Table IV). The relevance of the comparison may be questioned, however, because the model was applied to different shear rate ranges. This mathematical analysis was consequently not considered in the conclusions.

### INTERNAL GEL PHASE/EXTERNAL OILY PHASE RATIO

Variations of the oil/internal gel phase concentration and the results in Table V demonstrated that with 0.8% rheology modifier (a) and 2% emulsifier (d), only an internal gel phase concentration from 80% to 90% provided stable gel-in-oil emulsions (F16, F17, F18) with no differences in the microscopic appearance: all thin and similar to Figure 2. For 93% and 95% gel phase, F14 and F13 respectively, defective cream gels with high conductivity were obtained. Increasing the rheology modifier from 0.8% to 1% helped to obtain a gel-in-oil emulsion with 93% aqueous phase, F15, showing that the parameters do not act independently. Below 80% aqueous phase, gel-in-oils destabilized at D7 at 45°C. For 75% aqueous phase, increasing the dose of polymer from 0.8% (F19) to 1.2% (F20) or emulsifier from 2% (F19) to 3% (F21) does not help to improve the stability of the formulation.

This shows that a concentration of aqueous internal phase less than or equal to 75% or above 93% was not suitable to create stable gel-in-oil emulsions. Variations of the internal gel phase concentration had a strong effect on the viscosity of gel-in-oil emulsions: the higher the concentration and droplet packing, the higher the viscosity.[12]

The concentration of the internal gel phase has a strong effect on the elastic structure of gel-in-oil emulsions. Although increasing the rheology modifier from 0.8% to 1% helped to obtain a gel-in-oil emulsion with 93% aqueous phase stable at 3 months, F15, the mean G'/G" ratio showed a low elastic structure (Table V) with a crossover between storage modulus G' and loss modulus G" at low frequencies and a change to the predominant viscous character (G" > G'; Figure 12), suggesting a risk of destabilization in the long term. The relative elastic character was higher for 90% and 85% of aqueous phase and decreased for 80% (Table V, Figure 12), although the value of the storage modulus increased with the gel proportion.

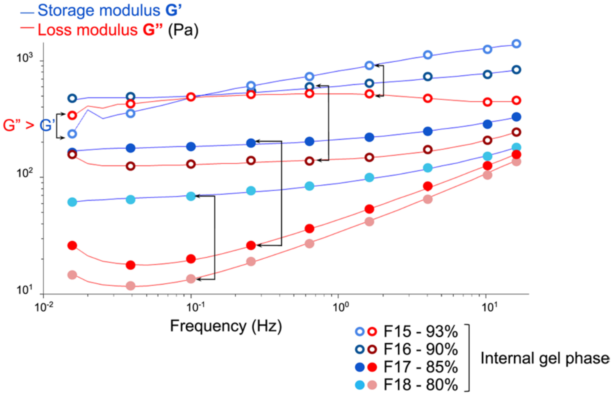

**Figure 12.** Flow profile of gel-in-oil emulsions according to internal gel phase concentration.

**Table V**

Effect of Variations of Oil Dosage (e) and Resulting Variations of Internal Gel Phase Concentration on a Fixed Formula Containing, Rheology Modifier (a) 0.80% or 1.00%, Emulsifier (d) 2.00% or 3.00% (w/w %)

| | F13 | F14 | F15 | F16 | F17 | F18 | F19 | F20 | F21 | F22 |
|---|---|---|---|---|---|---|---|---|---|---|
| (e) Dose (w/w %) | 03.00 | 5.00 | 5.00 | 8.00 | 13.00 | 18.00 | 23.00 | 23.00 | 23.00 | 28.00 |
| (a) Dose (w/w %) | 00.80 | 00.80 | 01.00 | 00.80 | 00.80 | 00.80 | 00.80 | 01.20 | 00.80 | 00.80 |
| (d) Dose (w/w %) | 02.00 | 02.00 | 02.00 | 02.00 | 02.00 | 02.00 | 02.00 | 02.00 | 03.00 | 02.00 |
| Gel phase (w/w %) | 95% | 93% | 93% | 90% | 85% | 80% | 75% | 75% | 74% | 70% |
| Conductivity D1 (μm/cm) | 502 | 504 | 230 | 0 | 0 | 0 | 0 | 0 | 0 | 0.1 |
| Formula type | Cream gel | Cream gel | Gel-in-oil | Gel-in-oil | Gel-in-oil | Gel-in-oil | Gel-in-oil | Gel-in-oil | Gel-in-oil | Gel-in-oil |
| Viscosity D1 (mPa·s) | ≅18,600 | ≅14,200 | ≅221,000 | ≅130,000 | ≅30,100 | ≅15,700 | ≅4,300 | ≅5,400 | ≅3,400 | ≅1,000 |
| Stability | Stable | Stable | Stable | Stable | Stable | Stable | Two phases at 45°C/−18°C −5°C–40°C | Two phases at 45°C/−18°C −5°C–40°C | Two phases at 45°C/−18°C −5°C–40°C | Two phases at RT[h]/45°C/−18°C −5°C–40°C |
| Rheology data | NT(g) | NT(g) | | | | | NT(g) | NT(g) | NT(g) | NT(g) |
| Mean G' (Pa) | | | 715 | 596 | 216 | 94 | | | | |
| Mean G'/G" | | | 1.6 | 3.9 | 4.2 | 2.3 | | | | |

[g] NT: Not Tested.

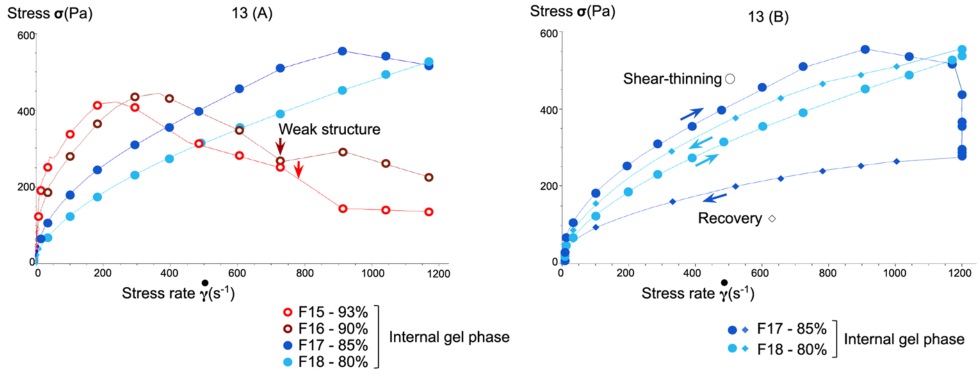

**Figure 13.** Flow profile of gel-in-oil emulsions (A, B) according to internal gel phase concentration.

Internal phase concentration was also decisive in obtaining an optimized resistance of the structure of gel-in-oil emulsions when subjected to high-stress conditions (Figure 13A). From gel phase concentration greater or equal to 90% (F16, F15), the structure of gel-in-oil emulsions was not able to withstand high shear. Conversely, for 80% and 85%, the structure was not affected by shear and exhibited a typical shear-thinning behavior. Furthermore, as shown in Figure 13B, F17 and F18 were able to recover their initial state when the shear was stopped: immediately for F18, and in a slightly delayed manner for F17, exhibiting thixotropic behavior. This means that the decrease in relative elastic character seen during the oscillatory experiments between 85% and 80% of the internal gel phase had no relationship to the structure's resistance at higher stress.

## DISCUSSION

The first aim of this study was to determine the factors affecting the creation and stability of HIP gel-in-oil emulsions. The results demonstrated the importance of both the manufacturing process and composition factors. Gel-in-oil emulsions were easily manufactured in one step, at room temperature, by one-shot addition of one phase onto the other (both indirect/oil-in-gel and direct/gel-in-oil emulsification modes are suitable). One-shot addition simplified the procedure compared to the stepwise addition of the major phase recommended in previous publications.[6,8,9,11] The mixing procedure for emulsification was found to be critical for the creation of gel-in-oil emulsion: on the basis of the almost optimal composition tested, agitation using a low-shear planetary device, such as an anchor or a scraper, was the most effective. This finding also differed from previous publications on W/O HIPEs describing high-shear homogenization procedures from 3,500 rpm to 12,000 rpm.[3,8,10,11,13,27] In addition, HIPEs manufactured in a one-step process were reported to contain relatively large droplets, with size decreasing with increasing homogenization time and intensity,[12] generally around 20 µm or more,[8,14] to around 10 µm (10), and around 5 µm after a required homogenization in an example containing the same emulsifier (d).[13] On the contrary, the gel-in-oil emulsions studied contained small internal droplets, around 1 to 2 µm, without the need for high-shear preparation. An optimized droplet size was reached from above 2% to 2.5% of emulsifier (d) without the interaction of other parameters, which was also in line with a dosage greater than 1.5% required to achieve long-term stability. The study pointed out critical requirements of the internal gel phase to create gel-in-oil emulsions: a viscosity greater than or equal to 18,000–20,000 mPa·s achieved with a suitable rheology modifier and a maximum gel phase concentration of 90–93% depending on the rheology modifier dose. A restricted range starting from 80% of internal gel phase led to stable formulations after 3 months of storage (Figure 14). As expected from the principle of HIPEs, the viscosity and texture consistency of gel-in-oils were found to be connected mostly with the internal gel phase concentration.[12] In addition, it could be noted that the final viscosity of the gel-in-oil emulsion did not help to predict the stability of the formulation, as evidenced in Table V.

The effect of the nature of the oil on gel-in-oil emulsions was also investigated while keeping a dose of 8% combined with a fixed dose of rheology modifier (a) 0.8% and emulsifier (d) 2%. Eight oils were tested: mineral oil (Hangzhou Refinery China, Zhejiang, China), dimethicone (Dow Corning, Midland, MI, USA), C15–19 alkane (Seppic, La Garenne Colombes, France), squalane (Aprinnova, Emeryville, MA, USA), caprylic/capric triglyceride (Croda, Cowick, United Kingdom), cetearyl ethylhexanoate (Seppic, La Garenne Colombes, France), coco-caprylate/caprate (Seppic, La Garenne Colombes, France), and sweet almond oil (Vantage Specialty Chemicals®, Deerfield, MI, USA). All assays resulted in gel-in-oil emulsions after production (data not shown), demonstrating that the nature of the oil was not a critical parameter. Most gel-in-oil emulsions were stable after 3 months, except the ones with dimethicone, C15–19 alkane, and sweet almond oil, suggesting that combinations of silicone and plant oil with ester could be tried to optimize the stability. Additional rheology experiments will need to be carried out to evaluate the effect of nature of the oil on gel-in-oil viscoelasticity and behavior when subjected to a higher shear ramp. This data might help to optimize oil combinations.

The second objective of the study was to find a tool to check soon after manufacture that the gel-in-oil structure was optimized and, ultimately, to be able to anticipate instability issues that often occurred 3 months after manufacture. Rheology, in particular oscillatory experiments coupled with frequency or temperature sweeps, is a well-known technique to test the robustness of the internal structure of a formulation. Correlations with formulation stability were demonstrated on regular O/W and W/O emulsions.[27,28–31] The flow profile is also useful to understand and predict the behavior of the product in use, such as pouring

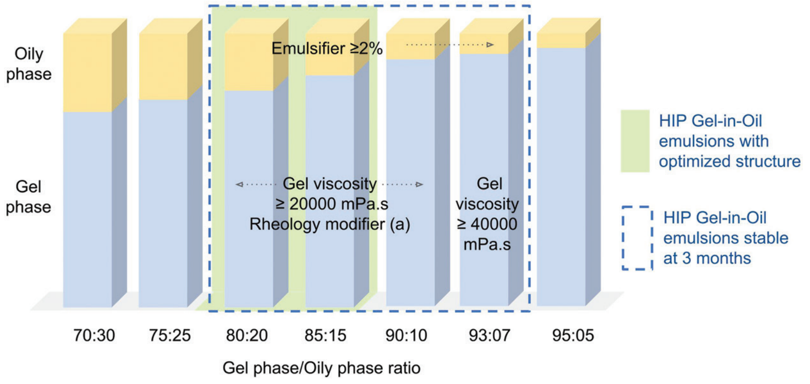

**Figure 14.** Summary of influence of the different composition factors and contribution of rheology to conventional stability monitoring.

out of packaging, spreadability, etc.[32–35] but can also contribute to analyzing the stability of the formula, especially based on evaluations of yield stress and thixotropy (i.e., time for a sheared product to recover its initial configuration).[36,37] Predominant elastic character was much reported in previous publications as a characteristic of HIPEs,[3,8,10,11,26] but a clear relationship with the stability of the emulsion was not shown. Oscillatory experiments carried out in the different parts of this work demonstrated that stable gel-in-oil emulsions were characterized by an elastic structure, stable to frequency sweep. Unstable gel-in-oil emulsions or gel-in-oil evolving to cream gels during aging due to insufficient dose of emulsifiers (F7 and F8) could be detected by a very weak elastic structure at low frequencies. However, F9 showing delayed exudation after 3 months of storage is a counterexample as weaknesses in its structure were not detected by this sole measurement. Defective cream gels, obtained when the gel phase viscosity was too low, were also differentiated by a significantly weaker structure than gel-in-oil emulsions. However, because the relative elastic character (G'/G") was also shown to be closely connected to the internal gel phase concentration, it seemed complicated to predict instability issues on the basis of this parameter alone. Shear-thinning behavior was also reported as a characteristic of HIPEs, without any relationship to the stability of the formulation.[3,25] In the case of the gel-in-oil emulsion base studied, tracking the risk of breakage on the flow curve at high shear helped to set the conditions to obtain the most stable structures. The most suitable ratio between external oily phase and internal gel phase, revealed as decisive, was determined to be from 20:80 to 15:85 W/W in the formula studied. The optimum concentration of emulsifiers was refined to greater than or equal to 2% (Figure 14). The essential role of internal gel phase concentration could explain why weaknesses of the structures were observed when studying the impact of emulsification mode, gel viscosity, and emulsifier dosage. The gel internal phase concentration was arbitrarily chosen around 90% in these trials. It would be interesting to supplement the trials with ratios 20:80 and 15:85 to confirm the low viscosity limit.

Thus, a combination of the two types of rheology experiment (application of a low oscillatory stress at different frequencies and shear rate ramp) detected early signs of structural weakness, 7 days after manufacturing, for inappropriate compositions. This approach helped to anticipate instability issues occurring after 1 or 3 months of storage with conventional stability monitoring and can support the development of customized HIP gel-in-oil emulsions.

## CONCLUSION

The study, combining conventional characterization methodology and rheology experiments, helped to better understand the influence of the different factors on the structure and behavior of HIP gel-in-oil emulsions under stress. Rheology experiments highlighted a strong and highly elastic structure reflecting the organization of the HIP for optimized formulations. Relationships among conductivity, rheology profiles (behavior under stress and elastic character), and formulation stability were clearly observed. In addition, rheology measurements can detect early signs of weakness of the structure under stress without the need to wait for long-term stability, and can support formula development in a more general context than the formulation base studied. The knowledge acquired can also remove the legitimate uncertainty of formulators in the face of an unusual formulation concept.

Precise recommendations to obtain an optimized HIP gel-in-oil emulsion could be established, concerning both the composition (minimum viscosity of the internal gel phase and associated dose of rheology modifier; minimum concentration of emulsifier; ratio between the two phases) and the preparation of the formulation. A mixing procedure with medium shear using planetary devices, such as an anchor, during emulsification was essential for the creation of the HIP formula.

The HIP gel-in-oil concept opens up formulation prospects thanks to its sustainable cold manufacturing process, aesthetics with fresh first contact, and proven benefits for skin applications.

## ACKNOWLEDGMENTS

### AUTHOR CONTRIBUTIONS

***Liming Sun:*** conceptualization, methodology, investigation, validation, formal analysis, data curation, writing—original draft, review and editing; **Carla Perez:** conceptualization, supervision, project administration, review; **Alicia Roso:** conceptualization, formal analysis, writing—original draft, review and editing, visualization.

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