Hybrid gels: influence of water and oil phase on textural and rheological properties

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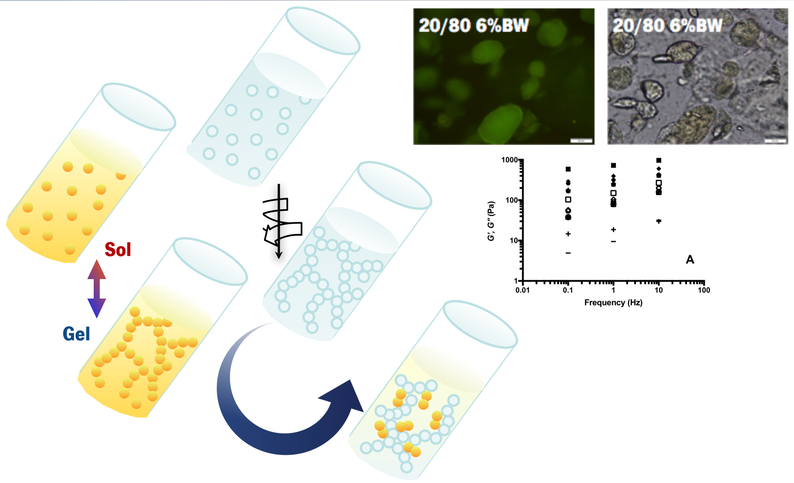
Introduction

The mixture of water-based and oil-based gels provides distinct and unique characteristics to hybrid gels, different textural and rheological properties can be obtained. Hybrid gels remain a very recent topic concerning pharmaceutical and food applications and despite recent studies on the use of hybrid gels for controlled delivery of compounds these structures are still under-studied in regard to their food application possibilities [1, 2]. To improve knowledge and expanding ways to use these systems, it is important to understand their textural and rheological properties. Knowing their micro and nanostructure allows tailoring their properties and thus maximizing their applicability in foodstuffs. We report on how the combination of a beeswax-based oleogel and sodium alginate-based hydrogel influences the gel structural properties. A more disarranged distribution of oleogel particles was observable for the 50:50 ratios of hydrogel and oleogel. X-ray diffraction data unveiled that once polycrystallinity is reached (in hybrid gels) these patterns remain persistent for all tested ratios. Samples with increasing oleogel ratio revealed a firmness decrease and a consequent reduction of spreadability values. Consequently, is observed less adhesivity for these samples, due to a more pronounced disaggregated structure. For all hybrid gels a gel-like behaviour (G´ > G´´) was observed in rheology tests. Results showed that it is possible to modify the hybrid gels' rheological and textural behaviour by a controlled mixture ratio of oleogels and hydrogels. This opens the possibilities of food applications for this kind of systems.

Methods

Oleogel controls were produced with 3 and 6% (w/w) of beeswax using vegetable oil, corresponding to OG3 and OG6, respectively and hydrogel control were produced using 2% (w/w) alginate, named Al). Hybrid gels (HGs) were produced by mixing oleogel and hydrogel fractions in different ratios using a mechanical mixer at 600 RPM during 45 min and 24 h equilibration at ambient temperature before each analyses.

- 5 different ratios of HGs were developed: 1:99; 5:95; 10:90; 20:80 and 50:50.
- Sample firmness, spreadability, and adhesiveness were measured using texture analyser (Stable Microsystems, Surrey, UK) with a conical TTC Spreadability Rig (HDP/SR) attachment.
- Oscillatory rheometry was performed using a Discovery Hybrid Rheometer (DHR) from TA (New Castle, US) at 25 °C with Stainless steel cone-plate geometry of 60 mm, with an angle of 2.006° and truncation of 64 µm was used.
- Scans from 5.0º to 50º (2θ) were performed with X-Ray Diffractometer X Pert PRO MRD system from PanAnalytical with a Cu source, X-ray tube (λ = 1.54056 Å) at 45 kV and 40 mA. The fine calibration offset for 2Theta = -0.0372 deg.



Results

Morphological and textural characterization

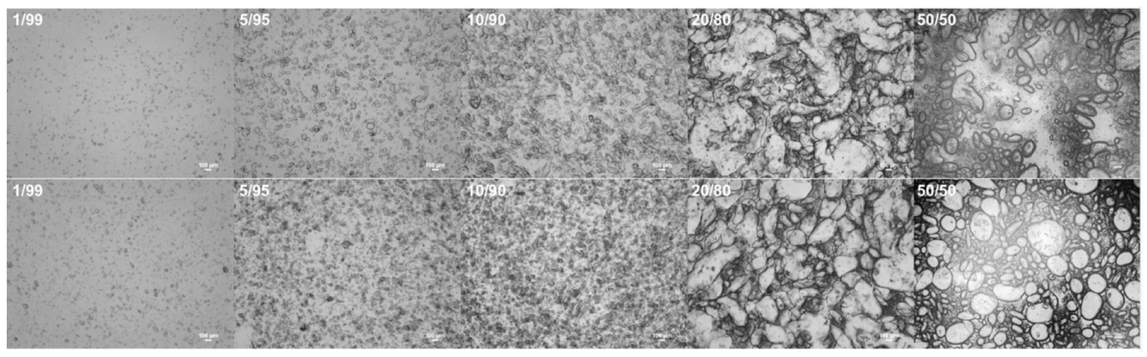


Figure 1 - Micrographs of hybrid gels with increasing concentration of oleogel. Row above presents hybrid gels with oleogels with 3% (w/w) concentration of gelator - HG3 ; Row below presents hybrid gels with oleogels with 6% (w/w) concentration of gelator - HG6. Pictures were taken at a magnification of 15 X.

- A more disarranged distribution of oleogel particles for HG3 50:50 (hybrid gels with OG3); less structural strength, therefore gel flow occurs.
- Shear process of the emulsification is responsible for the introduction of oleogel particles inside the hydrogel matrix, materializing an oil-in-water or oleogel-in-hydrogel structural arrangement.
- HG samples with the same oleogel present differences regarding oleogel particles distribution.
- Alongside with the increasing of oleogel addition to the overall HG concentration, larger particles are identified and this behaviour is potentiated when oleogel ratio is increased.

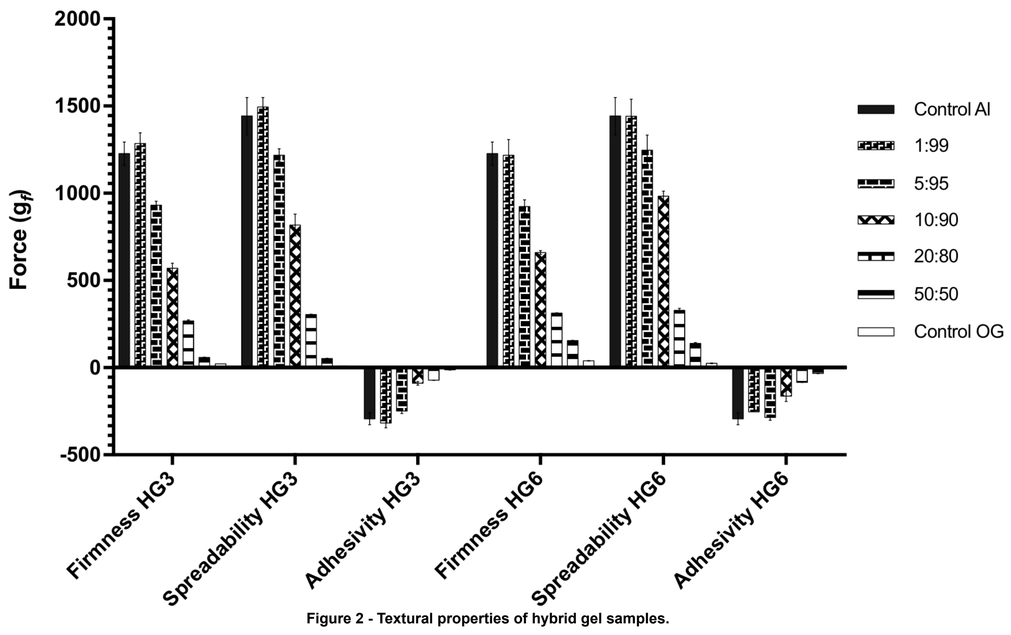


Figure 2 - Textural properties of hybrid gel samples.

- Oleogel influence (HG3 and HG6), significant for HGs after 10:90 ratio (including this one). Suggesting that after oleogel fraction reaches at least 10 % of the total mass of HG's this is the critical point/ratio where varying the gelator concentration starts to affect the final textural properties (firmness, spreadability and adhesiveness).
- Adhesivity profile of HGs is an indication of the cohesiveness of the material.
- Decrease in firmness, and spreadability force values alongside the increase of oleogel fraction in the overall composition of hybrid gels. The more stickiest the sample is, the more negative the value is.

Rheological characterization

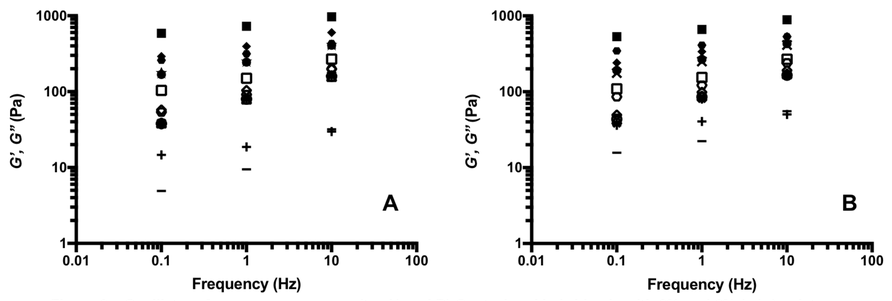


Figure 3 – Oscillatory frequency sweep results: A) and B) Control and hybrid gels with 3% and 6% (w/w) gelator concentration respectively (● 1:99; ▲ 5:95; ♦ 10:90; ■ 20:80; ⬣ 50:50; + control OG; × control Al). *G'* open symbols and *G''* closed symbols.

- Both HG3 and HG6 can be classified as a gel since G' is generally an order of magnitude larger than G'' (below 10 Hz).
- Frequency dependence was little observed for HGs with higher hydrogel fraction, a typical behaviour of elastic networks.

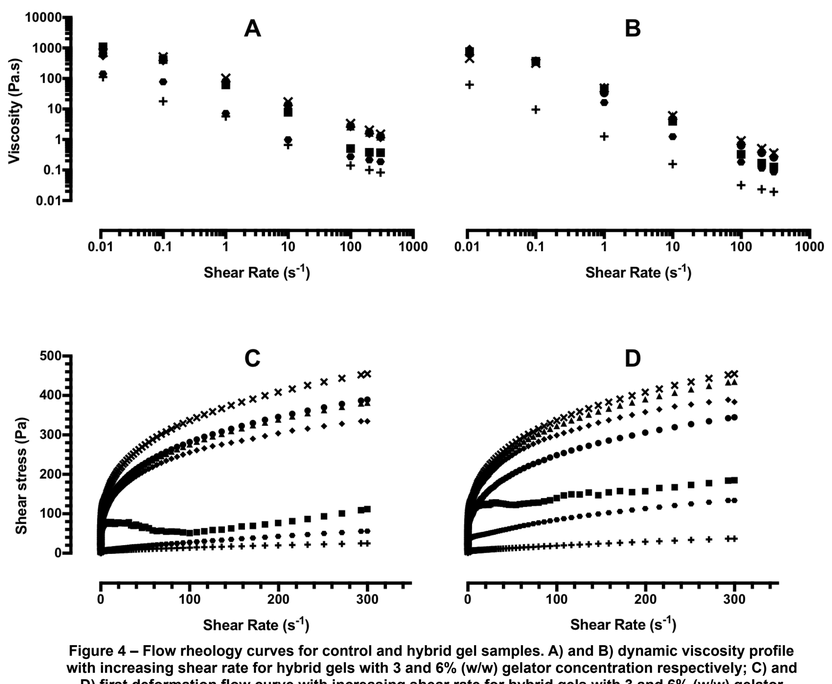


Figure 4 – Flow rheology curves for control and hybrid gel samples. A) and B) dynamic viscosity profile with increasing shear rate for hybrid gels with 3 and 6% (w/w) gelator concentration respectively; C) and D) first deformation flow curve with increasing shear rate for hybrid gels with 3 and 6% (w/w) gelator concentration respectively. (● 1:99; ▲ 5:95; ♦ 10:90; ■ 20:80; ⬣ 50:50+ control OG; × control Al)

- Flow rheology shows the degree of influence of OG6 on HG deformation behaviour.
- OG6 induced more proximity within the viscosity and stress values recorded for each sample ratio in the same shear-rate value.
- HG6 samples (Figure 4B) recorded higher values of viscosity for the same shear-rate.
- Stress overshoot seen for HG3 50:50 in flow rheology (Figure 3D) is not observed for the same HG6 50:50 (Figure 5C).

X-Ray Diffraction

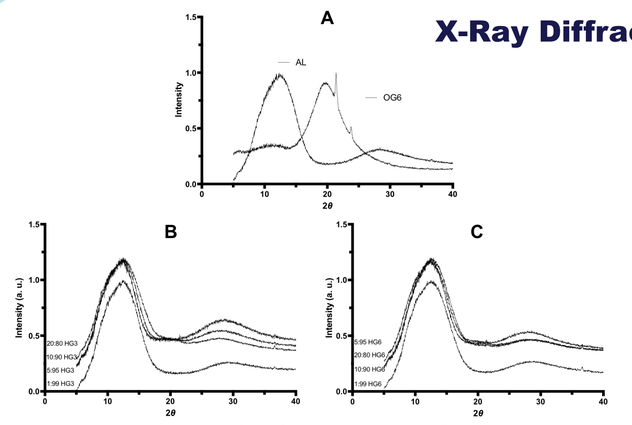


Figure 5 –XRD patterns for A) Control samples; B) and C) hybrid gels with 3 and 6% (w/w) gelator concentration respectively.

- Polycrystallinity is detected for control OG6, in Figure 5A, in wide angle regions with d-spacings in the range of 3.74 to 8.04 Å. HG samples (and Al control) are semi-crystalline in nature with peaks at 12, 28 and 36.
- Reflections present d-spacings ranging in the intervals of d (001) 6.99 – 7.18 Å; d (002) 3.09 – 3.23 Å and d (003) 2.45 – 2.46 Å respectively.

Conclusions

The evidenced tailoring ability is a strength to direct hybrid gels into applications where gel strength and shear capability are crucial parameters. Gel-like behaviour (G´ > G´´) was identified for all HGs. Differences on firmness, spreadability and adhesivity between samples with different oleogel strength (HG3 vs HG6) are minimized by the applied strong shear in HG development, however after increasing the oleogel fraction from 10 % upwards, the registered results are significative different. Crystal polymorphism is changed when HGs are produced and the values gathered in XRD remain consistent with the increase of the fraction of oleogel. Going further, oil polarity can be one of the main variables towards the study of carbon oil phase effect on hybrid gels development and consequent functionality. Also different types of gelling compounds and bioactive incorporation are some of the possibilities regarding hybrid gels applications in the future.

References

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