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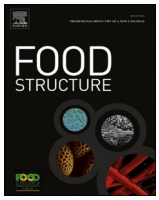

Impact of high-intensity ultrasound on the development of phytosterol-based oleogels

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ABSTRACT

Oil structuration offers an alternative to high saturated fats and has gained significant attention over the past decade. Phytosterols present a promising option as oleogelators due to their low saturated fat content and health benefits. However, they struggle to effectively structure liquid oils at low concentrations. High-Intensity Ultrasound (HIU) has shown potential to enhance oleogels physical properties through cavitation. This study aims to use phytosterols to create oleogels in rapeseed oil, both with and without HIU, and assess their physical properties. Commercial sterols (10 %w/w) were mixed with rapeseed oil. One sample served as a control without HIU, while others were treated with HIU at various amplitudes and durations. After 24 hours at 20°C, samples were analyzed for microscopy, oil binding capacity, melting behavior, polymorphism, hardness, viscosity, and viscoelasticity. HIU produced a single melting peak, reduced crystal size, and decreased oil loss. It also enhanced hardness, viscosity, and viscoelasticity, with significant improvements observed primarily in samples sonicated for longer durations (10 s), regardless of amplitude. The most notable results were from a 10 s pulse treatment (5 s ON/5sOFF/5sON) at 50 % amplitude, which maintained the oleogel stability for 30 days without phase separation. Thus, HIU is a viable, eco-friendly method to enhance phytosterol oleogels physical properties, allowing for effective oil structuration.

1. Introduction

Replacing saturated fat with unsaturated fat or lowering fat content is a current trend of the food industry to improve its nutritional aspects. Using unsaturated oils is a reasonable alternative, however, not a small task, since solid fats provide many desirable attributes: structure, texture, mouthfeel, and flavor (Patel & Dewettinck, 2016).

Oil structuration has been developed for more than a decade and presents a reasonable option to replace high saturated fats. Oleogels are solid-like materials obtained by structuring liquid lipids, usually a mixture of unsaturated oil and a high-melting point oleogelator (<10 %) (Co & Marangoni, 2012). Several components -lipids or not-, such as lecithin (Zhuang et al., 2021), monoglycerides (da Pieve et al., 2010), waxes (Doan et al., 2017), phytosterols (Oliveira et al., 2023), ethylcellulose (Zetzl et al., 2012), and others, can be used as oleogelators

Phytosterols are minor lipid components inherently present in vegetable oils. The most common types of sterol compounds are β-sitosterol, stigmasterol, or campesterol. Single sterols or a mixture of them can be found industrially as a white powder and are obtained mostly during vegetable oil refining (Engel & Schubert, 2005). Phytosterols are an interesting alternative oleogelator because they combine two big nutritional advantages, a low saturation content and the nutraceutical benefits of consuming phytosterols (Matheson et al., 2018). The nutritional benefits of phytosterol-gelled oleogels emulsions have already been evaluated, self-assembled microstructures served as physical barriers that impeded the interaction between lipase and the lipid substrate, resulting in lower lipid digestion. Additionally, this effect was summed to the lipophilic nutraceuticals benefit of phytosterol consumption (Dong et al., 2020).

The use of phytosterols as an ingredient in food products is a challenge because it is insoluble in water and has poor solubility in oil at room temperature (Engel & Schubert, 2005). An alternative is esterification of the phytosterol and/or solubilization at high temperatures (Truong et al., 2019). Appropriate processing is needed to dissolve phytosterols such as heating (temperature above the melting point) under stirring and further cooling. Phytosterol oleogels result in a semi-solid and viscoelastic gel, with a high amount of liquid oil and a high capacity to encapsulate and deliver lipophilic compounds (Ashkar

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& Davidovich-Pinhas, 2024).

Several studies have reported oleogels structure by phytosterols (Bot et al., 2008; Martins et al., 2019). This oleogelator can form stable gels (Bin Sintang et al., 2017; Yang et al., 2017), oleogels emulsions (Ashkar & Davidovich-Pinhas, 2024) and foams (Qiu et al., 2021; Truong et al., 2019). A common agreement among all studies is that phytosterols form a more stable and stronger structure, without a gritty texture and tendency of agglomeration when combined with other oleogelators such as monoglycerides, lecithin, γ-oryzanol, or waxes (Matheson et al., 2017; Truong et al., 2019).

High-intensity ultrasound (HIU) has been evaluated as an interesting alternative to improve the physical properties of oleogels (da Silva & Danthine, 2021; Giacomozzi et al., 2020; Rumayor-Escobar et al., 2023). Indeed HIU, through cavitation changed the interactions between the oleogelator and oil and provided some specific benefits for oleogels such as improving solubility of the oleogelator (Jadhav et al., 2022), reducing phase separation (Jana & Martini, 2014), and reducing the amount of oleogelator needed (Giacomozzi et al., 2020). Moreover, HIU has proved to be an attractive alternative for reducing gritty texture and big crystals that are formed in some low saturated fats (da Silva et al., 2020). No previous study evaluated HIU in oleogels structured with phytosterol, thus the objective of this study was to evaluate the effect of high-intensity ultrasound (HIU) on the phytosterol oleogels physical properties, in order to try to produce stable, smooth, and self-sustainable oleogels using only phytosterols as structuring agent.

2. Material and methods

2.1. Material

Rapeseed oil was acquired from Royale Lacroix (Flémalle, Belgium), and its triacylglycerols composition is 29.3 % triolein (OOO), 22.6 % dioleoyl-linoleoyl glycerol (OOL), 12.1 % dioleoyl- linolenoyl (OOLn, and 6.5 % dioleoyl-palmitate glycerol (POO). The phytosterol CardioAid™ plant sterol was donated from ADM Nutrition (Valencia, Spain). The composition given was a majority of beta-sitosterol (40–58 %), followed by campesterol (20–30 %), and stigmasterol (14–22 %), the melting point range was between 135 and 145°C.

2.2. Methods

2.2.1. Sample preparation

Oleogels (50 mL) were prepared by mixing the rapeseed oil with 10 % of phytosterols (pre-tested determined) at 150 °C/ 30 min in a 100 mL Becker over a heat plate with 300 rpm magnetic stirring. The melted blend was then transferred to a water-cooled crystallization cell (100 mL) that was set at 90°C. The system was then cooled at 1 °C/min under magnetic stirring (150 rpm) until the first crystals appeared T_c= 55.0 ± 1.5 °C. After the first crystals were visualized the sample was either collected without HIU (wo HIU) or with HIU (20 kHz, CPX 750, Cole 115 PA Parmer Instruments, Illinois, USA). Sonication was applied with a 13-mm probe that was placed in the middle of the crystallization cell. Conditions used were: 25 % or 50 % amplitude (in power 25 % and 50 % represent, 17 ± 1 W and 54 ± 1 W, respectively), for 5 s, or 10 s continuous or in 5 s pulse (5 s ON/5 sOFF/5sON). Thus, seven treatments were evaluated, and named as oleogels (1) wo HIU or 0 %, (2) 25 % 5 s, (3) 25 % 5sP, (4) 25 % 10 s, (5) 50 % 5 s, (6) 50 % 5sP, and (7) 50 % 10 s, the coding represents HIU amplitude and duration used on each sample. During crystallization with or without sonication the temperature of the samples was monitored. All conditions showed no significant temperature increase due to sonocrystallization except for sample 50 % 10 s (ΔT = 4.3 ± 0.9 °C). After sonication, samples (50 mL) were placed in 100 mL plastic containers (filling 2.5 cm of the container) and stored in an incubator at 20 ± 0.5 °C for the static cooling step (~0.5 °C/min) and stored for 24 h before further analysis. Oleogels with or without HIU were prepared in triplicate.

2.2.2. Microstructure

The phytosterol oleogels microstructure was evaluated using polarized-light microscopy (PLM, Nikon Eclipse E400, Kanagawa, Japan). The images were obtained with the digital camera (Nikon, DS-Fi2, Tokyo, Japan) coupled to the microscope. Microstructure was evaluated using a 20 × magnification objective after a drop of the crystallized oleogel was placed between a slide and a cover slide at 20 ± 2 °C.

2.2.3. Melting behavior

The melting behavior of the oleogels was evaluated using differential scanning calorimetry (DSC), Q2000 DSC (TA Instruments, New Castle, DE, USA). DSC was calibrated using indium and eicosane and coupled with a refrigeration cooling system (TA Instruments, New Castle, DE, USA). Eight to twelve milligrams of oleogel were weighted in the T-zero hermetic pan, and an empty pan was used as a reference. Oleogels were stabilized at 20°C for 1 min and then heated to 150°C using a 5 °C/min heating rate. The melting curves were investigated using the Universal Analysis Software version 4.2 (TA Instruments, New Castle, DE, USA). The parameters assessed were onset temperature (T_{on}), peak temperature (T_p), end temperature (T_{end}), and enthalpy (ΔH).

2.2.4. Rheology

Viscosity and viscoelasticity of the oleogels were measured using a modular compact rheometer MCR 302 (Rheoplus, Anton Paar, Graz, Austria). A geometry plate plate of 40 mm diameter, 20°C, and 1000 μm gap was used for all measurements. Viscosity was measured using a structured recovery (thixotropy) condition, three-sequence intervals were measured: (1) 2 min shear rate at 1 s^{-1}, (2) 2 min shear rate at 100 s^{-1}, and (3) 2 min shear rate at 1 s^{-1}. The average of the first curve was used as the viscosity (Pa.s) of the sample. Afterward, by comparing the first and third curves the structure recovered (%) was also evaluated. Strain sweeps were evaluated from 0.0008 % to 100 % strain at 1 Hz. The results of viscoelasticity (G' and G") were calculated as an average of the linear viscoelastic region (LVR) using the Rheoplus software (Anton Paar, Graz, Austria). The frequency sweeps were evaluated by variating the angular frequency from 0.1 to 100 rad/s, with a fixed LVR strain of 0.01 %. All samples were analyzed in triplicate for each test.

2.2.5. Texture

Oleogel hardness was measured after 24 h at 20°C, using a Texture Analyzer (TAXT plus, Stable Micro Systems, UK) equipped with a 5 kg load cell placed in a controlled cabinet temperature set at 20 ± 0.05 °C. A 5-mm diameter cylinder probe was used for the penetration test. The probe penetrated 1 mm/s for 10 mm. Hardness was expressed as the maximum force of the first peak (N). Analysis was performed in triplicate.

2.2.6. X-ray diffraction

Polymorphism of the phytosterols oleogels was evaluated by X-ray diffraction at 20°C, using a Bruker D8 Advance Diffractometer (Bruker, Karlsruhe, Germany). A LynxEye detector (Bruker, Germany), with Cu K radiation (= 1.54178 Å, 40 kV, 30 mA) was used. The short and long spacing were evaluated (1–27 °). The step size of the measurements was 0.02 °.

2.2.7. Oil loss

The non-entrapped oil in the oleogel network was evaluated by centrifugation according to da Silva and Danthine (2021). A 5810 R Eppendorf centrifuge was used, for 15 min at 10000 rpm (14869 xg). Approximately 1 g of stabilized oleogel was used. An empty Eppendorf (*wa*), the Eppendorf with oleogel (*wb*), and the Eppendorf after oil leaking (*wc*) were weighted. Calculation of the oil loss was done following Eq. 1. Analysis was performed in quadruplicate.

$$\text{Oil loss} = \left(\frac{wc - wa}{wb - wa}\right) * 100 \quad (1)$$

2.2.8. Statistic

Each process and analytical measurement were performed in replicates as described above. The results were submitted to analysis of variance (ANOVA) using Minitab 18 software. Means were compared using Tukey's test with a significance level of 5 % ($\alpha \leq 0.05$).

3. Results and discussion

3.1. Melting behavior

The phytosterol powder showed a melting point of 136.5 ± 0.05 °C, results similar to this have been observed in the literature (Vaikousi et al., 2007). For this reason, the melting behavior of the oleogels was measured up to 140°C, as shown in Fig. 1. The oleogel without HIU showed two endothermic peaks, one around 95 °C and a second one around 120°C (Fig. 1, black-filled arrows). Similar melting behavior of phytosterols oleogel has also been described in previous studies (Bin Sintang et al., 2020; Vaikousi et al., 2007).

The broadening of the peak and the drop in T_p compared to the pure phytosterol is due to increased amounts of liquid phase. This results in a solubility effect where the solid fraction (10 % of phytosterol) dissolves, thereby resulting in broader endothermic transitions at lower temperatures (Vaikousi et al., 2007). The different endothermic peaks observed for samples without HIU might be due to the different interactions with the rapeseed oil and the different sterols present (β-sitosterol, campesterol, and stigmasterol), followed by the formation of different crystalline structures. Nevertheless, these interaction differences seem to be changed by HIU, since all sonicated samples showed an expressive reduction of this first endothermic peak (~95°C). This result suggests that sonication might have united the different crystals present in these oleogels forming only one crystal unit that melted in one single peak. Multicomponent oleogel crystals have been previously evaluated and the conclusion was that the change from multiple peaks and endothermic peaks to one unique melting peak with a lower T_p is usually indicative of co-crystallization among the crystalline components (Tavernier et al., 2017). Sonication in fats can results in a crystalline matrix with a narrower melting peak, towards a lower temperature suggesting that more pure crystals are formed due to sonication and/or that the molecules in the crystalline matrix are highly organized resulting in a fast melting (Lee et al., 2022). There were no significant differences in the melting enthalpy of the oleogels tested, all conditions tested presented enthalpy around 5.7 ± 1.2 J/g. This result is in agreement with previously sonicated oleogels studied (Da Silva & Danthine 2022a). Although sonication changes the organization of the crystals, and the position and shape of the endothermic peaks, this change in melting behavior is not always followed by significant changes in the melting parameters such as T_{on}, T_p and enthalpy (da Silva et al., 2019)

3.2. Oil loss

The oil loss results can be found in Fig. 2. The control sample without HIU showed 56.2 ± 2.8 % of oil loss after centrifugation, similar to what has been reported for different types of phytosterols when used alone in the same proportion (10 %) on several types of oils (Pang et al., 2024). In general, HIU for only 5 s, regardless of the power level/amplitude used was not able to change this parameter ($p > 0.05$). However, when applied for 10 s, either using pulses or continuous application with both HIU amplitudes, it showed a significant improvement in the oil binding capacity of the oleogel ($p < 0.05$). A lower power level (~17 W, 25 % amplitude) showed the same improvement as a higher (50 % amplitude, ~54 W) only if a 10 s continuous application was used. This result indicates that phytosterols need a longer sonication duration to improve their oil-binding capacity. According to Sharifi et al. (2019), HIU conditions such as power, time, and temperature affect the mechanical properties and oil migration of propolis wax oleogels. The minimum oil loss in this case occurred when the power was 300 W, duration 120 s and sonication was applied at 7.5°C. Da Silva and others (2020) have found that HIU decreased oil migration in fats with low saturation by promoting the crystallization of triacylglycerols with low melting points through sonication. These triacylglycerols typically remain uncrystallized without HIU. Additionally, the increased volume of crystallized material encapsulated more effectively the liquid phase and also prevented oil separation or oiling out by creating a fine network of crystals, which effectively retained the liquid oil within the structure (Jana & Martini, 2014; Sharifi et al., 2019).

When mixed with other oleogelators the phytosterol seems to have a higher oil binding capacity than alone (Martins et al., 2019). The result was attributed to the increase in the mass fraction of the crystalline network in the oleogel system. A higher amount of crystalline structure formed a denser network, more effective in entrapping liquid within the system (Pang et al., 2024). Due to the change observed in the melting behavior, and previous works using HIU, it seems that HIU might also have affected the crystalline structure of the phytosterol-oleogel, as

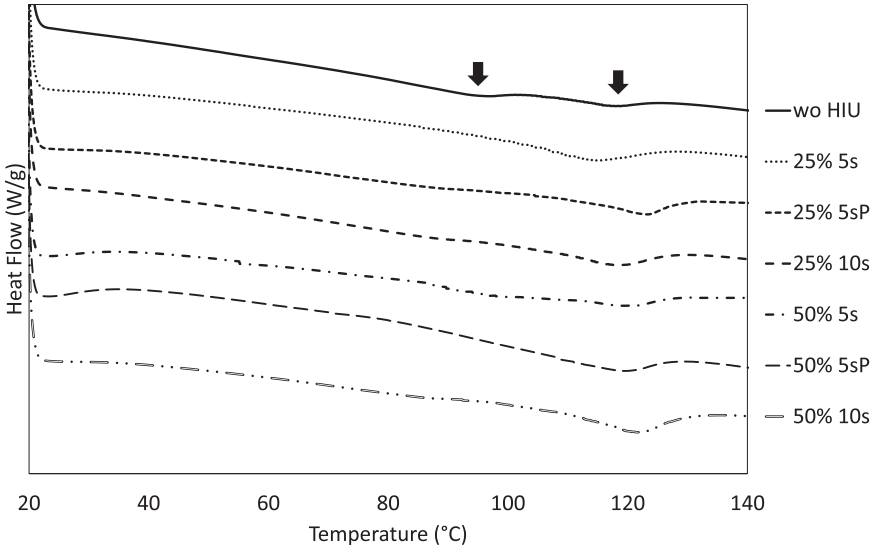

Fig. 1. Melting behavior of the sonicated and non-sonicated (wo HIU) oleogels using different sonication conditions. (Exo up ↑).

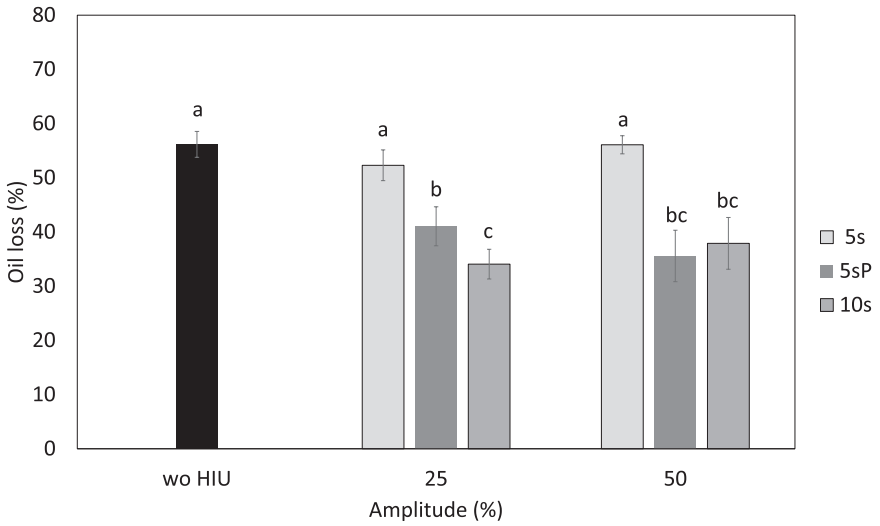

Fig. 2. Oil loss (%) results of the phytosterols oleogels using different High-intensity ultrasound (HIU) conditions. Means with different superscripts are significantly different (α=0.05).

observed in other oleogelators that have been previously described (Giacomozzi et al., 2020).

3.3. Rheology

The rheology results can be found in Fig. 3. Viscoelasticity results obtained in the amplitude sweeps are presented in Fig. 3A and B, as an average of G' and G", of the LVR, respectively. All oleogels presented a G' > G" confirming the gel or elastic behavior of all samples, regardless of the HIU condition tested. The highest G' value (Fig. 3A) was found for samples sonicated for 5sP or 10 s using 50 % amplitude, which were similar to each other ($p > 0.05$). Followed by samples sonicated for a similar time but lower amplitude (25 %). All amplitudes using only 5 s sonication showed lower improvements, however they were still significantly higher than the non-sonicated sample, suggesting that HIU can improve the viscoelasticity of the phytosterols oleogels in all conditions tested.

Similar behavior can be observed for G", and viscosity (Fig. 3C),

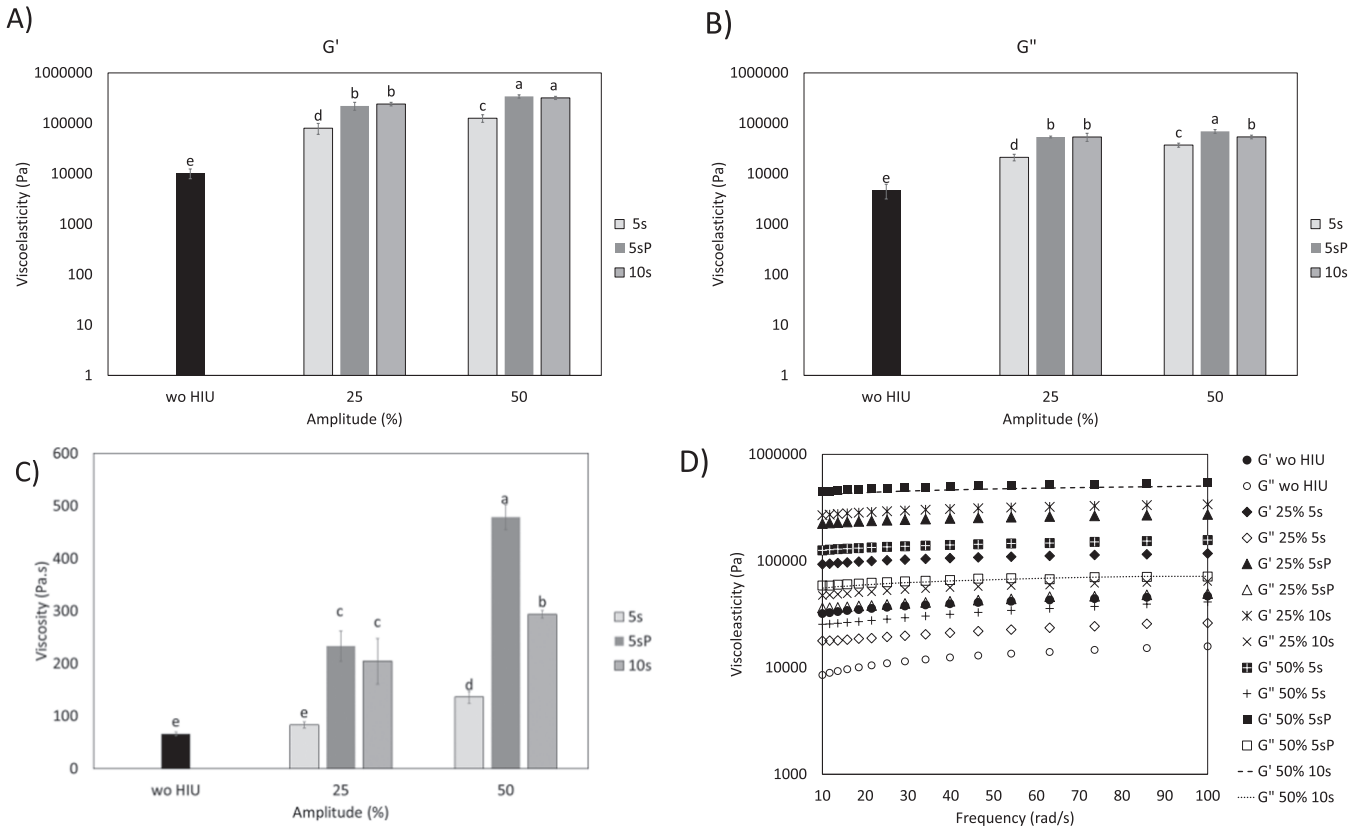

Fig. 3. Rheology results of the sonicated oleogels (A) G' and (B) G" attained by amplitude sweeps, (C) viscosity, (D) G′ and G" obtained by frequency sweeps. Means with different superscript are significantly different (α=0.05). Sonicated samples are followed by the amplitude (25 or 50 %) and duration (5 s, 5 s in pulses or 10 s), and non-sonicated sample is named wo HIU.

however on these results the sonicated sample 50 % 5 sP had the highest value with no similarity with other conditions. Additionally, the 25 % 5 s viscosity was similar to no HIU condition, suggesting that the effect of this treatment might be not enough to improve the phytosterol oleogel significantly in all physical parameters ($p > 0.05$).

The frequency sweeps (Fig. 3D) also showed similar behavior, with G'> >G", and higher G' for samples 50 % 5sP and 50 % 10 s, followed by samples 25 % 10 s and 25 % 5sP, and lower G' for the non-sonicated sample. It seems that at least 10 s of sonication in a higher amplitude (50 %, 54 W), needs to be applied to have a positive effect on rheological behavior. Pulses normally promote the same power, however in a shorter time with reduces the heating promoted by cavitation and gives a break to induce more nucleation before a second sonocrystallization step.

A similar increase was previously observed when phytosterols were mixed with other oleogelators as monoglycerides (Bin Sintang et al., 2017; Yang et al., 2018), or when the concentration of phytosterols is increased (Martins et al., 2019). HIU has also been tested on several others oleogelators such as monoglycerides, lecithin, vegetable waxes, or their combinations. In general, if crystallization conditions (cooling rate, and moment of sonication) are optimized they always show an improvement in rheological properties such as viscosity (da Silva & Danthine, 2021), or elasticity (Giacomozzi et al., 2020).

3.4. Texture

The hardness of the oleogels (Fig. 4) also showed a higher value for sample sonicated for 10 s, either using 25 % or 50 % or either using pulses or not. The highest hardness was around 4 N for sample 50 % 5sP. The lowest hardness (<1 N) was observed for samples only sonicated for 5 s and non-sonicated samples. Confirming that at least 10 s would be necessary for any induction on the physical properties of the oleogels and that using a higher amplitude (50 %) leads to even better results. Sharifi et al. (2019), also observed a higher improvement in hardness with an increase of power and duration, which was attributed to the effect of cavitation on the crystalline structure. However, there is a maximum power that HIU can be applied without compromising the crystalline structure instead of improving it. For multicomponent oleogels this seems to be 50 W for 10 s (da Silva & Danthine, 2021), and for propolis wax 225 W for 120 s (Sharifi et al., 2019).

3.5. Microstructure

Generally, phytosterols oleogels were structured by a network of big needles and fibril (Fig. 5). This fibril-like network has also been previously observed for other phytosterols oleogels (Qiu et al., 2021; Vaikousi et al., 2007; Yang et al., 2017).

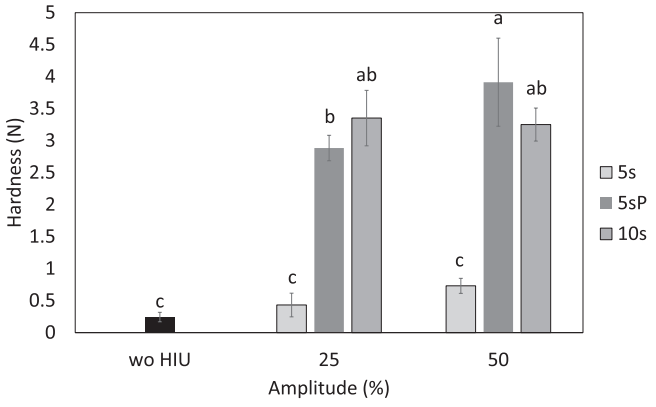

Fig. 4. Hardness (N) results of the phytosterols oleogels using different High-intensity ultrasound (HIU) conditions. Means with different superscript are significantly different (α=0.05).

Sonication of these oleogels using only 5 s seems to reorganize a little the crystal network. As observed in the sample with HIU the crystal network was quite heterogeneous. Increasing the sonication time seemed to homogenize the crystals and change them to less thicker crystals since a finer fibril compact network was formed on samples sonicate for 5sP or 10 s. Additionally, this effect was even more pronounced on samples sonicated using 50 % amplitude.

Although HIU previously changed the size and shape of the crystals in another oleogel system (da Silva & Danthine, 2021; Teodoro da Silva & Danthine, 2022) for phytosterols oleogels HIU affected the interconnections between the crystals and consequently the crystal network since in all samples it was possible to see the big fibrils even after treatment, but they formed a more interconnected network. This might happen because cavitation generated in the presence of few crystals induced secondary crystallization and either broke the primary crystals or avoided their extensive growth due to the higher nucleation rate. Oleogels with a more interconnected crystal network showed higher mechanical properties, as can be observed in hardness, rheology, and oil migration. These features can be important when such oleogels are used in foods thus implying that certain textural behaviors can be mimicked according to the oleogel formulation (Martins et al., 2019).

Although the fibril network can still be observed after sonication, it seems that the connection was stronger when HIU was applied for 25 or 50 % using 5sP or 10 s. A stronger and more connected network of oleogelators has also been observed after the sonication of monoglycerides and hardfats (da Silva & Danthine, 2021). In this study, since a lipid material with a very high melting point was used, it was assumed that sonication would result in the formation of smaller crystals and a more structured network. HIU may have functioned as either (1) an inducer of secondary nucleation, leading to more nuclei and consequently smaller crystal growth, or (2) a mechanism where the induced shear force broke the clusters into smaller needle-like structures. However, these effects are contingent on the specific conditions of oleogelation and HIU testing.

The big-shaped crystals formed on phytosterol oleogels have been previously reported as a negative characteristic. Because sterols crystals tend to grow even bigger, they tend to agglomerate and sediment, and consequently release the liquid oil in a relatively short period (a few hours to days) (Chen et al., 2020; Martins et al., 2019, 2022; Vaikousi et al., 2007). The larger the crystal, the higher the chance of agglomeration, which directly affects the stability and sensory perception of this system (Vaikousi et al., 2007). For this reason, most of the studies have mixed phytosterols with other oleogelators to form stronger and stable crystalline networks. HIU besides changing the network is also able to prevent this agglomeration from happening as observed in Fig. 6. Besides the improvement in the microscopic view, macroscopically these oleogels were visually more structured, and agglomeration didn't occur after 30 days of storage when 50 % for at least 10 s were used. According to Jana and Martini (2014), the small needle-like oleogels treated with HIU possess a large surface area, enhancing their ability to interact with one another. This increased interaction facilitates greater oil entrapment, thereby helping to delay phase separation.

3.6. X-ray

Fig. 7 shows the X-ray patterns obtained for the oleogels with and without sonication. All the oleogels showed the same pattern in the long spacing region, with a main peak corresponding to a distance of 36.8 Å, followed by its higher order reflection peaks. Similar d-spacings have been observed previously for pure phytosterols in powder state (Li et al., 2021). According to literature, phytosterols in liquid oils have been previously described as molecular tubular structures that aggregate to form a three-dimensional network (Bot et al., 2008; Matheson et al., 2017). Additional diffractions outside of the hexagonal geometry (e.g., lamellar or cubic packing in the short spacing (zoom in Fig. 6B)), peaks at 5.4, 4.8, 4.7, 4.65, and 4.6 Å could be observed for all samples. A

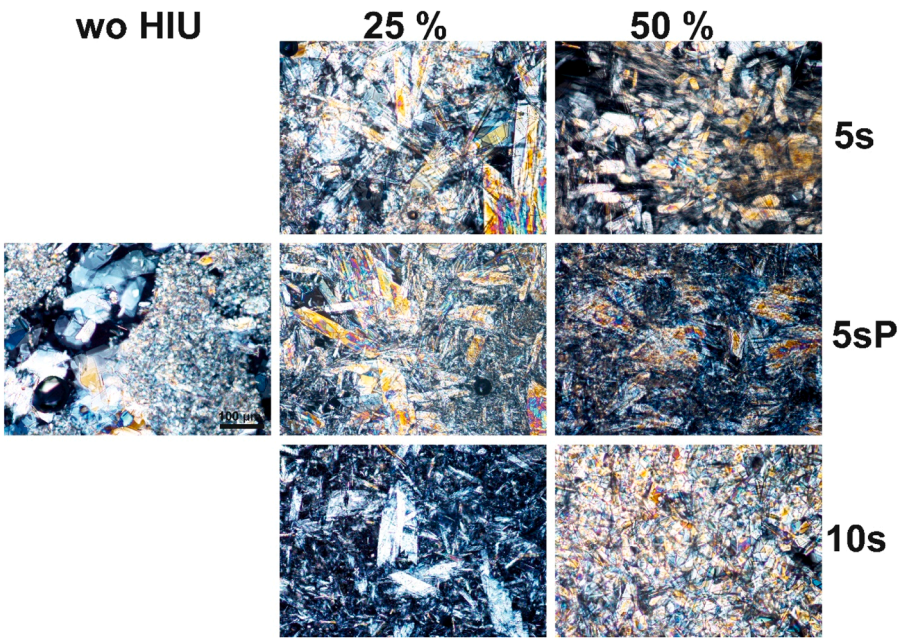

Fig. 5. Microstructure of the phytosterols oleogels with and without High-Intensity Ultrasound (wo HIU) using different HIU conditions, as amplitude (25 or 50 %) and duration (5 s, 5 s in pulses or 10 s).

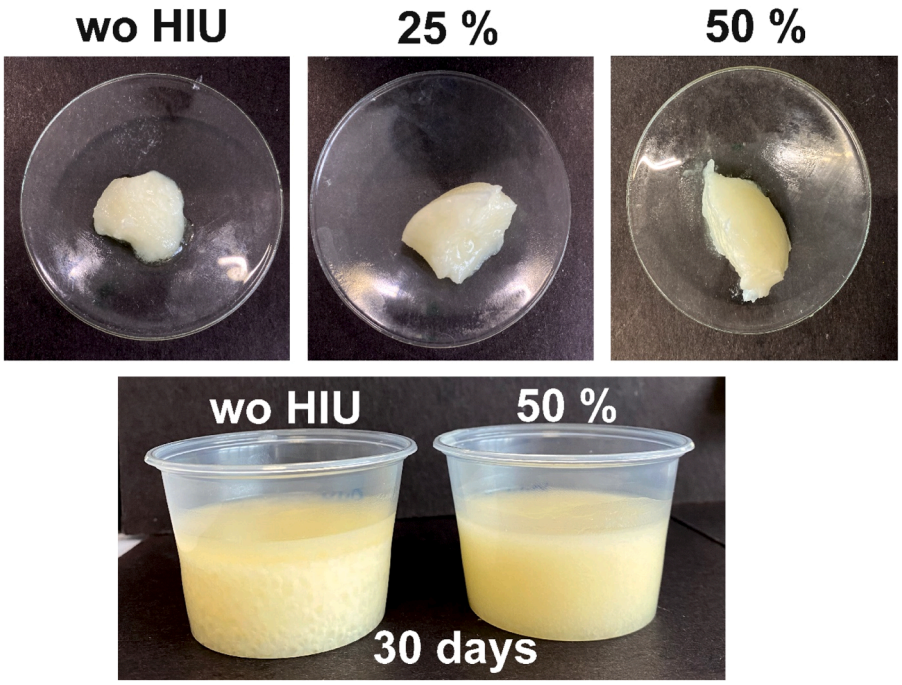

Fig. 6. Visual appearance of the oleogels with and without high-intensity ultrasound (HIU), 24 h and 30 days after oleogel production. HIU in this image was applied for 10 s.

similar pattern was also observed in a previous study (Qiu et al., 2021; Yang et al., 2017).

Interestingly, the use of ultrasounds did not change the packing or the polymorphism of the oleogels, which agrees with what was previously found for other oleogelators (da Silva & Danthine, 2021; Teodoro da Silva & Danthine, 2022).

4. Conclusion

We can conclude that HIU significantly improved phytosterols oleogelation properties and consequently their physical properties by improving phytosterols stability and solubility. To be able to cause some change cavitation HIU must be applied for at least 10 s, continuous on a lower amplitude (25 %) or in pulses with a higher amplitude (50 %). 50 % 5sP is the best condition found among all tested. Moreover, a further investigation regarding the stability of phytosterols on oils after sonication to prevent agglomeration and phase separation over time is worth supplementary investigation.

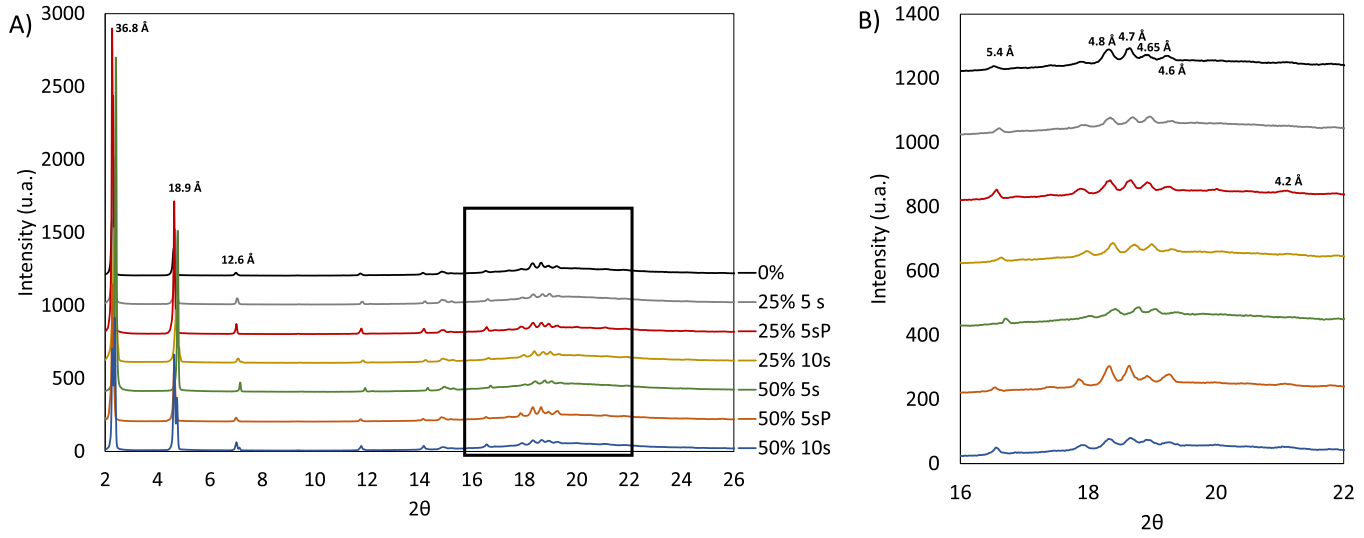

Fig. 7. X-ray diffraction of the phytosterols oleogels with and without high-intensity ultrasound (HIU).

CRediT authorship contribution statement

Sabine Danthine: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision. **Thais Lomonaco Teodoro da Silva:** Writing – review & editing, Writing – original draft, Validation, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of Competing Interest

I have nothing to declare

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Data availability

Data will be made available on request.

References

Ashkar, A., & Davidovich-Pinhas, M. (2024). Development of highly stable phytosterol oleogel particle-based emulsions with improved bioaccessibility of β-carotene. *Food Hydrocolloids, 146*(July 2023). https://doi.org/10.1016/j.foodhyd.2023.109167

Bin Sintang, M. D., Danthine, S., Khalenkow, D., Tavernier, I., Tzompa Sosa, D. A., Julmohammad, N. B., Van de Walle, D., Rimaux, T., Skirtach, A., & Dewettinck, K. (2020). Modulating the crystallization of phytosterols with monoglycerides in the binary mixture systems: Mixing behavior and eutectic formation. *Chemistry and Physics of Lipids, 230*(ember 2019), Article 104912. https://doi.org/10.1016/j.chemphyslip.2020.104912

Bin Sintang, M. D., Rimaux, T., Van de Walle, D., Dewettinck, K., & Patel, A. R. (2017). Oil structuring properties of monoglycerides and phytosterols mixtures. *European Journal of Lipid Science and Technology, 119*(3), 1–14. https://doi.org/10.1002/ejlt.201500517

Bot, A., Adel, R. Den, & Roijers, E. C. (2008). Fibrils of γ-oryzanol + β-sitosterol in edible oil organogels. *Journal of American Oil Chemistry Society, 85*, 1127–1134. https://doi.org/10.1007/s11746-008-1298-7

Chen, X. W., Sun, S. De, Yang, G. L., & Ma, C. G. (2020). Engineering phytosterol-based oleogels for potential application as sustainable petrolatum replacement. *RSC Advances, 10*(1), 244–252. https://doi.org/10.1039/c9ra06950j

Co, E. D., & Marangoni, A. G. (2012). Organogels: An alternative edible oil-structuring method. *Journal of the American Oil Chemists' Society, 89*, 749–780. https://doi.org/10.1007/s11746-012-2049-3

da Pieve, S., Calligaris, S., Co, E., Nicoli, M. C., & Marangoni, A. G. (2010). Shear nanostructuring of monoglyceride organogels. *Food Biophysics, 5*(3), 211–217. https://doi.org/10.1007/s11483-010-9162-3

da Silva, T. L. T., Barrera, D. A., & Martini, S. (2019). Use of high-intensity ultrasound to change the physical properties of oleogels and emulsion gels. *Journal of American Oil Chemistry Society, 96*, 681–691. https://doi.org/10.1002/aocs.12215

da Silva, T. L. T., Cooper, Z., Lee, J., Gibon, V., & Martini, S. (2020). Tailoring crystalline structure using high-intensity ultrasound to reduce oil migration in a low saturated fat. *Journal of American Oil Chemists' Society, 97*, 141–155. https://doi.org/10.1002/aocs.12321

da Silva, T. L. T., & Danthine, S. (2021). Effect of high-intensity ultrasound on the oleogelation and physical properties of high melting point monoglycerides and triglycerides oleogels. *Journal of Food Science, 86*(2), 343–356. https://doi.org/10.1111/1750-3841.15589

Doan, C. D., Tavernier, I., Sintang, M. D. Bin, Danthine, S., Van de Walle, D., Rimaux, T., & Dewettinck, K. (2017). Crystallization and gelation behavior of low- and high melting waxes in rice bran oil: A case-study on berry wax and sunflower wax. *Food Biophysics, 12*(1), 97–108. https://doi.org/10.1007/s11483-016-9467-y

Dong, L., Lv, M., Gao, X., Zhang, L., Rogers, M., Cao, Y., & Lan, Y. (2020). In vitro gastrointestinal digestibility of phytosterol oleogels: Influence of self-assembled microstructures on emulsification efficiency and lipase activity. *Food and Function, 11*(11), 9503–9513. https://doi.org/10.1039/d0fo01642j

Engel, R., & Schubert, H. (2005). Formulation of phytosterols in emulsions for increased dose response in functional foods. *Innovative Food Science and Emerging Technologies, 6*(2), 233–237. https://doi.org/10.1016/j.ifset.2005.01.004

Giacomozzi, A., Palla, C., Carrin, M. E., & Martini, S. (2020). Tailoring physical properties of monoglycerides oleogels using high- intensity ultrasound. *Food Research International, 134*(April), Article 109231. https://doi.org/10.1016/j.foodres.2020.109231

Jadhav, H. B., Pratap, A. P., Gogate, P. R., & Annapure, U. S. (2022). Ultrasound-assisted synthesis of highly stable MCT based oleogel and evaluation of its baking performance. *Applied Food Research, 2*(2), Article 100156. https://doi.org/10.1016/j.afres.2022.100156

Jana, S., & Martini, S. (2014). Effect of high-intensity ultrasound and cooling rate on the crystallization behavior of beeswax in edible oils. *Journal of Agricultural and Food Chemistry, 62*(41), 10192–10202. https://doi.org/10.1021/jf503393h

Lee, J., Willett, S. A., Akoh, C. C., & Martini, S. (2022). Impact of high-intensity ultrasound on physical properties and degree of oxidation of lipase modified menhaden oil with caprylic acid and/or stearic acid. *Journal of the American Oil Chemists' Society, 99*(2), 141–151. https://doi.org/10.1002/aocs.12560

Li, J., Yu, H., Yang, Y., Drummond, C. J., & Conn, C. E. (2021). Effect of crystallization state on the gel properties of oleogels based on β-sitosterol. *Food Biophysics, 16*(1), 48–57. https://doi.org/10.1007/s11483-020-09648-6

Martins, A. J., Cerqueira, F., Vicente, A. A., Cunha, R. L., Pastrana, L. M., & Cerqueira, M. A. (2022). Gelation behavior and stability of multicomponent sterol-based oleogels. *Gels, 8*(1). https://doi.org/10.3390/gels8010037

Martins, A. J., Cerqueira, M. A., Pastrana, L. M., Cunha, R. L., & Vicente, A. A. (2019). Sterol-based oleogels' characterization envisioning food applications. *Journal of the Science of Food and Agriculture, 99*(7), 3318–3325. https://doi.org/10.1002/jsfa.9546

Matheson, A. B., Koutsos, V., Dalkas, G., Euston, S., & Clegg, P. (2017). Microstructure of β-sitosterol:γ-oryzanol edible organogels. *Langmuir, 33*(18), 4537–4542. https://doi.org/10.1021/acs.langmuir.7b00040

Matheson, A., Dalkas, G., Clegg, P. S., & Euston, S. R. (2018). Phytosterol-based edible oleogels: A novel way of replacing saturated fat in food. *Nutrition Bulletin, 43*, 189–194. https://doi.org/10.1111/nbu.12325

Oliveira, S. M., Martins, A. J., Fuciños, P., Cerqueira, M. A., & Pastrana, L. M. (2023). Food additive manufacturing with lipid-based inks: Evaluation of phytosterol-lecithin oleogels. *Journal of Food Engineering, 341*(October 2022). https://doi.org/10.1016/j.jfoodeng.2022.111317

Pang, M., Xu, L., Wang, Y., Liu, L., & Cao, L. (2024). Potential functional oleogels based on phytosterol and diacylglycerol corn oil: Development and physicochemical characterization. *Lwt, 198*(March). https://doi.org/10.1016/j.lwt.2024.115987

Patel, A. R., & Dewettinck, K. (2016). Edible oil structuring: An overview and recent updates. *Food Function, 7*, 20–29. https://doi.org/10.1039/C5FO01006C

Qiu, C., Lei, M., Lee, W. J., Zhang, N., & Wang, Y. (2021). Fabrication and characterization of stable oleofoam based on medium-long chain diacylglycerol and β-sitosterol. *Food Chemistry, 350*(January), Article 129275. https://doi.org/10.1016/j.foodchem.2021.129275

Rumayor-Escobar, A., Peña, M. M. de la, de la Rosa-Millán, J., Arredondo-Ochoa, T., Dibildox-Alvarado, E., & Tejada-Ortigoza, V. (2023). Effect of high intensity ultrasound on soybean and avocado oleogels' structure and stability. *Food Structure, 36*, Article 100315. https://doi.org/10.1016/j.foostr.2023.100315

Sharifi, M., Goli, S. A. H., & Fayaz, G. (2019). Exploitation of high-intensity ultrasound to modify the structure of olive oil organogel containing propolis wax. *International Journal of Food Science and Technology, 54*, 509–515. https://doi.org/10.1111/ijfs.13965

Tavernier, I., Doan, C. D., Van de Walle, D., Danthine, S., Rimaux, T., & Dewettinck, K. (2017). Sequential crystallization of high and low melting waxes to improve oil structuring in wax-based oleogels. *The Royal Society of Chemistry, 7*, 12113–12125. https://doi.org/10.1039/C6RA27650D

Teodoro da Silva, T. L., & Danthine, S. (2022). Influence of sonocrystallization on lipid crystals multicomponent oleogels structuration and physical properties. *Food Research International, 154*, Article 110997. https://doi.org/10.1016/j.foodres.2022.110997

Truong, T., Prakash, S., Bhandari, B., & EU. (2019). Effects of crystallisation of native phytosterols and monoacylglycerols on foaming properties of whipped oleogels. *Food Chemistry, 285*(September 2018), 86–93. https://doi.org/10.1016/j.foodchem.2019.01.134

Vaikousi, H., Lazaridou, A., Biliaderis, C. G., & Zawistowski, J. (2007). Phase transitions, solubility, and crystallization kinetics of phytosterols and phytosterol-oil blends. *Journal of Agricultural and Food Chemistry, 55*, 1790–1798. https://doi.org/10.1021/jf0624289

Yang, D.-X., Chen, X.-W., & Yang, X.-Q. (2018). Phytosterol-based oleogels self-assembled with monoglyceride for controlled volatile release. *Journal of the Science of Food and Agriculture, 98*(2), 582–589. https://doi.org/10.1002/jsfa.8500

Yang, S., Li, G., Saleh, A. S. M., Yang, H., Wang, N., Wang, P., Yue, X., & Xiao, Z. (2017). Functional characteristics of oleogel prepared from sunflower oil with β-sitosterol and stearic acid. *Journal of the American Oil Chemists' Society, 94*(9), 1153–1164. https://doi.org/10.1007/s11746-017-3026-7

Zetzl, A. K., Marangoni, A. G., & Barbut, S. (2012). Mechanical properties of ethylcellulose oleogels and their potential for saturated fat reduction in frankfurters. *Food Function, 3*(3), 327–337. https://doi.org/10.1039/c2fo10202a

Zhuang, X., Gaudino, N., Clark, S., & Acevedo, N. C. (2021). Novel lecithin-based oleogels and oleogel emulsions delay lipid oxidation and extend probiotic bacteria survival. *LWT, 136*(P2), Article 110353. https://doi.org/10.1016/j.lwt.2020.110353