Development and Characterization of HPMC-Based Oleogels for Fish Oil Oxidation Protection

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Fishing produces a significant volume of discards (the portion of a fishing catch that is thrown back into the sea, dead or alive, because it's unwanted due to size, species, market value, or quota restrictions) that have little-to-no market value. Consequently, the European Commission promotes strategies aimed at reducing the waste of fishery biomass through their valorization. Fish oil extracted from discards and fish processing side streams is rich in omega-3 fatty acids, which are associated with well-known cardiovascular benefits. However, its high degree of unsaturation makes fish oil very susceptible to oxidation, which poses a major challenge for its stabilization and use. To overcome this problem, hydroxypropyl methylcellulose (HPMC)-based oleogels are a promising approach to structure and protect liquid oils from external factors by immobilizing them within a solid matrix, offering a high nutritional value alternative to conventional animal solid fats. In this context, the present work focuses on the development of fish oil oleogels as a strategy to improve oil stability and functionality. This approach enables applications in food, nutraceutical, and pharmaceutical sectors while promoting waste reduction, value creation, and sustainability in the fisheries sector.

METHODOLOGY:

Preparation of emulsions. Atlantic mackerel (*Scomber scombrus*) fish oil was supplied by IIM-CSIC for oleogel elaboration. The fish oil was thawed and centrifuged at 13,500 rpm for 120 min to eliminate residues. Oil in water emulsions (O/W, 40/60 w/w) were prepared adding high viscosity HPMC (2,600-5,600 cP, 2.0% in H_2O at 20ºC), which was pre-hydrated for at least 48 h in advance to achieve 2.5% w/w in the final emulsion. Right before emulsification, in some cases, gallic acid was added at 0.1 or 0.2% w/w (referred to the oil). Both HPMC and gallic acid were purchased from Sigma-Aldrich (St. Louis, MO, USA). Pre-hydrated HPMC, fish oil and gallic acid solution (when used) were added on a beaker to be emulsified using an oscillatory stirrer (P-Selecta, Rotaterm, Spain) at 120 rpm, followed by homogenization in a high-energy dispersion unit (Ultraturrax T-25 IKA, Germany) at 13,500 rpm for 6 min (Patel et al, 2014).

Drying. Emulsions were air dried at 80 ºC and 10% rh in a convective dryer (Angelantoni, Challenge 250, Italy) until constant weight using different thicknesses: 60 and 100 µm with the use of a baker applicator (Industrial physics, New Albany, Indiana, USA). The dried solid was homogenized using the high-energy dispersion unit at 9,500 rpm until a homogenous paste was obtained, then placed in plastic cuvettes and left to rest overnight at 4°C.

Oleogels characterization. Texture, oil binding capacity (OBC), rheology and oxidation degree of the oleogels were analyzed. Texture profile analysis (TPA) was performed in a texture analyzer TA.XTPlus (Stable Micro System) with a cylindrical probe of 25 mm diameter and using for the test a speed of 1mm/s and a threshold strength of 0.1 N. For OBC, 1 g of oleogel was introduced in an Eppendorf and centrifuged (HW12, Lan technic, Spain) at 13,500 rpm for 25 min (Saavedra *et al*, 2024). The rheology was analyzed in a shear-controlled stress rheometer (Anton Paar Physica, MCR 301, Austria) employing plate-plate geometry (50 mm diameter and 1 mm od gap) determining the linear viscoelastic region and frequency sweeps from 0.1 to 100 Hz. Primary and secondary oxidation was determined following UNE-EN ISO 3960:2017 and UNE-EN ISO 6885:2006 methods, respectively.

RESULTS AND DISCUSSION

TPA results are shown in Figure 1. Oleogel hardness, Figure 1(a), decreased at increasing initial thickness (longer drying time) employed in drying step. The presence of gallic acid lowered it to less than a third of the value independently of initial thickness. The OBC values (≈97%) achieved (Figure 1(b)) were consistent with other reported data (Saavedra *et al*, 2024, Lama *et al*, 2025). The presence of gallic acid significantly reduced the OBC values up to a range from 86 to 62%. The rheological characterization of the oleogels is shown in Figure 2. The strain sweep (Figure 2 (a)) was performed to determine the LVR and a strain of 0.1% was selected to perform the frequency sweeps, Figure 2 (b). All systems are well structured gels with $G' > G''$. Regarding the effect of initial emulsion thickness used in drying, thick samples showed both moduli higher, particularly G'', indicating a less solid oleogel. An increase in gallic acid concentration significantly disrupts the HPMC network, resulting in lower G' and G'' values, being this result in agreement with texture results. The oxidation degree is shown in Figure 3 (a (primary), b (secondary) and c (total)), where each oleogel is compared with fresh oil (red). It is noteworthy that samples dried at the larger thickness exhibited high oxidation. In contrast, the thin-layer dried systems without antioxidants showed a significant reduction in oxidation.

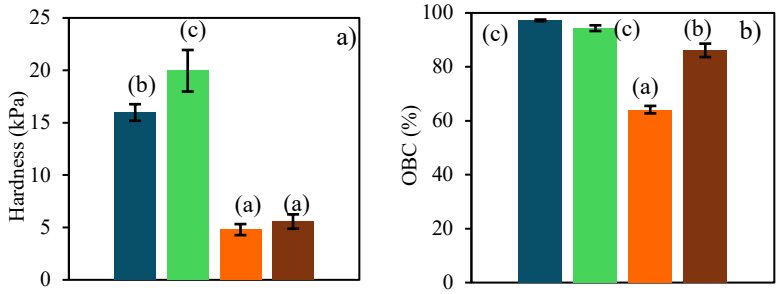

Figure 1.(a) Hardness and (b) OBC of the studied oleogels. Dark blue is 0.1cm dried oleogel, green is 60µm dried oleogel, orange is 0.2% gallic acid and maroon is 0.1% gallic acid.

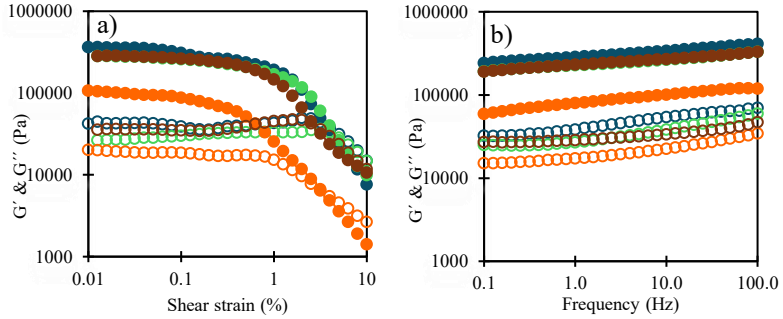

Figure 2. a) Strain sweep and b) Frequency sweep for oleogels. The filled and hollow icons correspond to elastic modulus (G´) and viscous modulus (G´´). Dark blue is 0.1cm dried oleogel, green is 60µm dried oleogel, orange is 0.2% gallic acid and maroon is 0.1% gallic acid.

High gallic acid concentration promoted unexpectedly oleogel oxidation. This result can be attributed to the low oil binding capacity (OBC), leaving a larger fraction of oil exposed to air. Conversely, the system containing 0.1% wt gallic acid was able to preserve the initial oxidation values of the fresh oil.

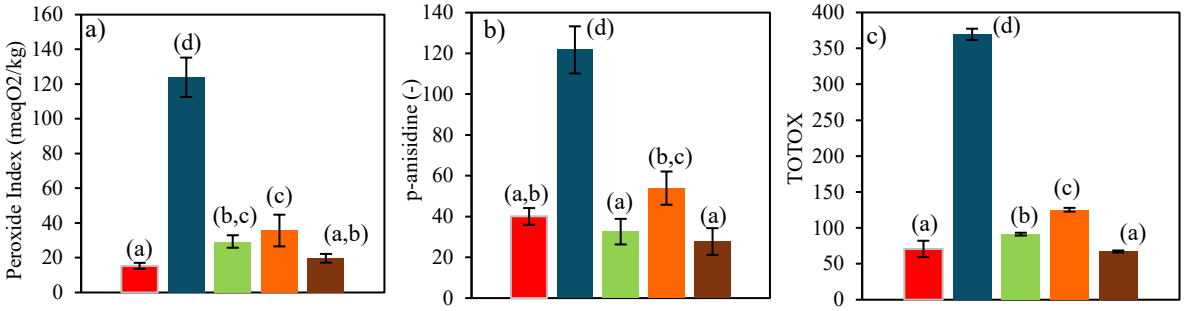

Figure 3. Primary (a), secondary (b) and total oxidation value. From left to right: fresh oil, 0.1cm dried oleogel, 60µm dried oleogel, 0.2% gallic acid and 0.1% gallic acid.

In summary, the results indicate that oleogels dried in thin layers exhibit improved textural and rheological properties, while high gallic acid content disrupt the HPMC network and reduce OBC. Oxidation revealed that high thickness and high antioxidant content lead to increased oxidation due to weak oil structuration. In contrast, the oleogel containing 0.1% w/w gallic acid effectively preserved the initial oxidation state of fresh oil, maintaining adequate oil binding and viscoelastic integrity. These oleogels enable the sustainable valorization of fishery discards into functional ingredients for different applications, supporting fat replacement, bioactive delivery, and circular economy benefits for the fisheries sector.

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REFERENCES:

- Patel, Ashok R.; Cludts, Nick; Bin Sintang, Mohd Dona; Lewille, Benny; Lesaffer, Ans; Dewettinck, Koen. Polysaccharide-based oleogels prepared with an emulsion-templated approach. *Food & Function*, 2014, 5(5), 934–941.

-Saavedra, M.Y.; Montes, L.; Franco, D.; Franco-Uría, A.; Moreira, R. Drying kinetics modeling of hot air drying of emulsion. templated oleogels employing hydroxypropyl methylcellulose as structuring agent. *Food Biosci*. 2024, 59, 103912

-Lama, M.; Franco-Uría, A.; Moreira, R. Characterization of Rapeseed Oil Oleogels Produced by the Emulsion Template Method Using Hydroxypropyl Methylcellulose and the Drying Kinetics of the Emulsions. Foods 2025, 14, 2908.