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Nano-hydroxyapatite Pickering emulsions as edible mayonnaise-like food sauce templates: A novel approach for food design

Maria Eduarda Relvas [a,b], Larissa C. Ghirro [c,d], Isabel M. Martins [a,b], Jose Carlos B. Lopes [a,b], Madalena M. Dias [a,b], Maria Filomena Barreiro [c,d,**], Andreia Ribeiro [a,b,*]

[a] *Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[b] *ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[c] *Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*

[d] *Laboratório Associado para a Sustentabilidade e Tecnologia Em Regiões de Montanha (SusTEC), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*

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ABSTRACT

Pickering emulsions have the potential to enhance product stability and provide opportunities to create functional solutions that align with labelling requirements. The present work aims to develop Pickering emulsions stabilised by nano-hydroxyapatite (n-HAp) particles to replace traditional mayonnaises. The study addresses the effect of n-HAp solid particle concentration (5–15 wt%) and oil-water ratio (50:50, 60:40, 70:30, and 80:20, *v/v*) on emulsion stability, rheological properties, and oxidative stability. The results indicate that the produced Pickering emulsions have good stability for the tested period of 90 days, except for the 80:20 o/w emulsion that undergone a prompt quick phase separation. The Pickering emulsions produced with higher n-HAp concentration or oil content have a semi-solid structure, rendering them desirable options for replicating the texture of traditional mayonnaises. Regarding oxidative stability, the Pickering emulsions showed considerably improved stability compared to commercial mayonnaises (~13 times higher), suggesting higher resistance to peroxidation and a longer shelf-life.

1. Introduction

Emulsification technology is widely used across industries, particularly in food processing. Various food products, including dressings, sauces, creams, butter, and beverages, rely on emulsions to achieve desired texture and stability (Tan and McClements, 2021). Mayonnaise, appreciated in many countries, is a classic sauce used to condiment different foodstuffs to enhance flavour. It is an oil (65–80%)-in-water emulsion (O/W), with egg yolk (6–20%) acting as a traditional emulsifier (Akcicek et al., 2022; Lu et al., 2021). However, concerns have been raised regarding potential health, safety, and ethics issues (Motta-Romero et al., 2017), which led the food industry to seek solutions for its replacement. Egg yolk has been related to increased total cholesterol content and associated with microbial contamination by *Salmonella enteritidis* (Akcicek et al., 2022; Lu et al., 2021); which led the food industry to seek solutions for its replacement. The use of low-fat egg yolk granules as an emulsifier can be an alternative strategy to produce mayonnaises with lower cholesterol levels (Motta-Romero et al., 2017). Moreover, cruelty-free issues related to intensive animal farming also started to be discussed and vegan products are becoming increasingly sought after. Egg-free mayonnaises have recently been studied using chickpeas, fava beans, and yellow split lentils as analogue protein substitutes (Armaforte et al., 2021); in addition, Ali and EL Said (2020) studied the potential use of Arabic gum as an egg substitute and an antimicrobial and antioxidant agent in the development of vegan mayonnaise. In this context, another alternative for low-cholesterol mayonnaise-like products is to explore the use Pickering emulsions produced with non-toxic particles to partially or totally replace egg yolk as stabiliser (Akcicek et al., 2022; Ghirro et al., 2022; Ribeiro et al., 2023). Comparable physical and chemical properties to traditional mayonnaises have be achieved by tuning the Pickering emulsion formulation (Ghirro et al., 2022).

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[*] Corresponding author.

[**] Corresponding author.

E-mail addresses: barreiro@ipb.pt (M.F. Barreiro), asribeiro@fe.up.pt (A. Ribeiro).

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Pickering emulsions are particle-stabilised emulsions and are typically categorised by their strong resistance to coalescence (Øye et al., 2023; Ribeiro et al., 2023; Tan and McClements, 2021). These emulsions offer several advantages, including lipid oxidation retardation, digestion modulation, and active compounds encapsulation (Tan and McClements, 2021). In addition, Pickering emulsions appearance, rheological properties, and lack of surfactants (Li et al., 2022), have gathered widespread interest at both academic and industrial levels, particularly in the food industry.

The development of egg-yolk-free mayonnaise sauces through Pickering emulsions is currently raising high interest, with several studies addressing this approach. Akcicek et al. (2022) used gum nanoparticles to produce Pickering emulsions for egg yolk-free vegan mayonnaise, with and without olive pomace extract-loading, showing comparable stability to control commercial samples. Additionally, the olive pomace extract-loaded Pickering emulsions presented improved oxidation stability compared to the unloaded ones. Lu et al. (2021) reported the use of apple pomace particles as emulsion-stabilising agents to develop cholesterol-free mayonnaise. Except for colour, the authors reported identical properties to traditional mayonnaises, namely physical stability and rheological behaviour. Ghirro et al. (2022) used curcumin-based solid dispersion particles, with the final products presenting a yellow hue. Other studies explored the use of wheat gluten and chitosan particles, reinforcing the interest in the potential of Pickering emulsions to develop these types of products (Hosseini and Rajaei, 2020; Liu et al., 2018). From this point of view, the production of Pickering emulsions with neutral colours, namely white emulsions, can be advantageous in tuning the emulsion colour by adding natural colourants or natural extracts rich in active compounds. This can reflect an attractive approach for conferring functionality and fortification by incorporating natural bioactive compounds.

While many studies focus on organic particles as Pickering stabilisers, inorganic particles are also viable alternatives and, in some cases, with differentiated distinct advantages (Binks et al., 2017; Kim et al., 2023; Ribeiro et al., 2022a). When applied as emulsion stabilisers, inorganic particles introduce advantages since they are less prone to degradation by environmental stresses, mainly temperature and ionic strength, enabling emulsion structural integrity for extended periods (Ribeiro et al., 2022b). Silica is the most studied inorganic material (Griffith and Daigle, 2018; Tikekar et al., 2013), followed by calcium carbonate (Binks et al., 2017; Huang et al., 2019), and, recently, hydroxyapatite (HAp; $Ca_{10}(PO_4)_6(OH)_2$) (Ribeiro et al., 2022a; Song et al., 2018). HAp particles were applied to produce Pickering emulsions as Freud's emulsions replacers in snake venom treatment (Rodríguez et al., 2019) and in the development of scaffolds for anti-inflammatory drug (ibuprofen) release (Hu et al., 2014). HAp is a biocompatible inorganic material used in biomedical and biotechnological applications. Food-grade HAp is emerging as a commercial product (nanoXIM-Food, www.fluidinova.com), and its application in the food area has received significant attention (Ribeiro et al., 2022a). In addition, the biological safety of HAp has been reported in previous works of Ramis et al. (2018) and Epple (2018). Stable O/W Pickering emulsions and vitamin E-loaded Pickering emulsions were produced for incorporation in food matrices, adding new insights into food functionalisation (Ribeiro et al., 2022a). Calcium-rich inorganic particles, such as HAp, can be a source of calcium since, at low pH, this material is dissolved into its original counterparts (calcium and phosphate ions), as observed in the stomach during digestion (Epple, 2018). In the previous work of Ribeiro et al. (2022a), HAp Pickering emulsions showed different behaviour throughout the gastrointestinal tract digestion, namely in the stomach where HAp dissolution occurred. HAp can be used to increase the calcium ions in the intestine for absorption, which can positively impact bone and tooth maintenance, muscle contraction, blood clotting and cardiovascular system functioning (Li et al., 2018). Thus, HAp is a promising ingredient to be used in Pickering emulsions stabilisation since it can function as a source of calcium, bringing innovation to product development and increasing human well-being.

The growing demand for safe and healthy food products leads to research investment in developing new processes and products to satisfy consumers' concerns. In this context, the present work aims to develop oil-in-water (O/W) Pickering emulsions stabilised by HAp particles to achieve a formulation identical to the traditional mayonnaises. The effect of oil-water ratio (50:50, 60:40; 70:30 and 80:20, *v/v*) and HAp concentration (5–15 wt%) on emulsion stability, rheological properties, and oxidative stability over a storage period of 90 days was evaluated. To the best of the authors knowledge, this is the first study addressing the use of HAp particles to produce O/W emulsions mimicking the properties of commercial mayonnaises. Given the chemical composition and structure of HAp, this material is promising in the development of disruptive products that can work as calcium sources. Additionally, their typical white colour renders these Pickering emulsions ideal for serving as a base product for modulating the final colour and bioactivity by adding natural colourants or extracts, becoming more attractive to consumers. HAp Pickering emulsions with properties similar to traditional mayonnaises are a promising strategy for developing products with differentiated functionalities.

2. Experimental methods

2.1. Materials

Fluidinova S.A (www.fluidinova.com) supplied the HAp aqueous paste (nanoXIM-Care paste). According to the technical information provided by Fluidinova, nanoXim-Care paste is composed by 15.5 ± 0.5 (wt.%) of HAp nanoparticles with typical particle size <50 nm in a rod-like shape, 4.5 ± 0.5 (wt.%) KCl, and water content ≤ 81.0 (wt.%). This paste has a similar composition to nanoXIM-FoodPaste, the food grade HAp paste also commercialised by Fluidinova. Sunflower oil and two kinds of commercial mayonnaises (traditional and light recipes) were purchased from a local market. Fluorescent dyes, Nile Red and Nile Blue A, and isopropyl alcohol (99.7%) were obtained from Sigma-Aldrich and Riedel-de Haen, respectively. Distilled water, treated in a Milli-Q water purification system (TGI Pure Water Systems, Greenville, SC, USA), was used. All other chemicals were of analytical grade.

2.2. Pickering emulsions preparation

The Pickering emulsions were produced in batch mode using a rotor-stator homogeniser (Miccra RT D-9, Mulheim, Germany), following the methodology previously developed by Ribeiro et al. (2022c). The production process is divided into two steps. In the first step n-HAp particles were dispersed in distilled water to the desired concentration (5–15 % wt.) using the rotor-stator homogeniser at 11000 rpm for 1 min. The second step pertains to the emulsion production; briefly, the sunflower oil was continuously fed into the previously prepared n-HAp aqueous dispersion using a peristaltic pump at 240 rpm (43 mL/min) at a constant emulsification rate (11000 rpm) using a rotor-stator homogeniser at room temperature. The n-HAp concentrations reported in this study refer to the aqueous phase, which was kept constant (200 mL). The oil phase volume was adjusted to reach the required oil-water ratio. This results in a homogenisation time (and thus energy input) proportional to the oil volume to be dispersed into the fixed water volume. The final Pickering emulsion volume for each ratio is presented in Table 1. After production, the emulsions were kept in a dry place at room temperature. A photographic record of the Pickering emulsions' appearance was carried out using a Nikon Camera. The produced Pickering emulsions were named according to the used formulation, indicating the oil-water ratio and n-HAp content, as shown in Table 1.

2.3. n-HAp Pickering emulsions characterisation

After production, all Pickering emulsions were characterised using

Table 1
Produced Pickering emulsions according to their formulation in terms of oil-water ratio, n-HAp content, and total emulsion volume for each ratio.

Sample name	Oil-water ratio (*v/v*)	n-HAp content (% wt.)[a]	Total emulsion volume (mL)
50:50–5%	50:50	5	400
60:40–5%	60:40	5	500
70:30–5%	70:30	5	667
80:20–5%	80:20	5	1000
60:40–10%	60:40	10	500
60:40–15%	60:40	15	500

[a] n-HAp content based on the aqueous phase.

different techniques. These include the drop test to check the type of formed emulsion, colourimeter analysis to access colour attributes, optical microscopy and confocal laser scanning microscopy to inspect morphology, and diffraction particle size analyser for droplet size determination. Oxidative stability was also evaluated using a Rancimat equipment, and the rheologic behaviour was evaluated using a rheometer. In addition, the produced samples were compared with commercial mayonnaises as benchmarks.

2.3.1. Emulsion type, macroscopic stability, and colour properties

The conventional emulsion drop test was used to classify the prepared emulsions as O/W or W/O type. This test evaluates the behaviour of the emulsion in contact with the two phases used (sunflower oil and water). If the emulsion droplets quickly disperse in water but remain agglomerated in the oil phase, it is an O/W emulsion; otherwise, it is a W/O emulsion. For this test, 2–3 emulsion drops were added to the water and oil phases, stirred gently, and then visually inspected. The test was carried out immediately after production and after 7 and 90 days of storage.

Digital photographs of all Pickering emulsions were taken post-production and periodically during storage to register their physical stability. A Nikon Camera was used, and the macroscopic stability, namely phase separation, was inspected throughout the storage duration.

Colour analysis was measured using a colourimeter model CR-400 (Konica Minolta Sensing Inc., Japan) equipped with an accessory container to hold the liquid samples. The colour space values (L*, a* and b*) were determined using an 8 mm diaphragm aperture. The L* value indicates the brightness of the sample; the a* coordinate represents the variation from green when negative (-a*) to red when positive (+a*); and the b* coordinate represents the variation from blue when negative (-b*) to yellow when positive (+b*).

2.3.2. Optical microscopy and confocal laser scanning microscopy

Optical microscopy (OM) was used to examine droplet morphology and monitor the Pickering emulsions' stability after production and during storage. The sample was poured in a glass microscope slide, and the observation was performed using a Carl Zeiss Axiotech 100 HD optical microscope Zeiss Instruments, Jena, Germany) fitted with a digital camera (AxioCam 105 colour) for image acquisition and processing with Zen software (2.3 blue edition).

Confocal laser scanning microscopy (CLSM) was used to examine the morphology of the emulsion in finer detail and to confirm the role of n-HAp particles as Pickering stabilisers. The Pickering emulsions were stained with Nile red and Nile blue fluorescent dyes at 0.1% *w/v* in isopropyl alcohol, and the microscope analyses were done using a Leica TCS-SP5 AOBS (Leica Microsystems Inc. Heidelberg, Germany). An argon laser at 488 nm and 633 nm excites Nile red and Nile blue, respectively. This technique enables the observation of n-HAp and oil separately, making it possible to check the effective coverage of the oil droplets by the n-HAp particles.

2.3.3. Droplet size analysis

The droplet sizes of the Pickering emulsions right after production, and at 7 and 90 days of storage, were determined using a laser diffraction particle size analyser (Beckman Coulter LS230, California). Each emulsion was dispersed in an aqueous medium before obtaining the volume distributions. The average size was determined from the acquired volume distributions and presented as the average diameter in volume, $d_{4,3}$. This data complements the microscopy analyses since an increase in the droplet size can indicate coalescence phenomena. The data is expressed as average ± SD.

2.3.4. Oxidative stability studies

The oxidative stability of both n-HAp Pickering emulsions and commercial mayonnaises was assessed using a Rancimat model 743 equipment (Metrohm, Herisau, Switzerland). According to the technical data sheet of the equipment, Rancimat can be used for studying the oxidative stability of oils, fats, and foods containing oils. A conductivity method was applied for this evaluation. Initially, 6 g of the emulsion sample were weighed into the equipment cell, where a dry, clean, and filtered air stream was bubbled at a flow rate of 20 L/h and a temperature of 121 °C. Each measurement was conducted in duplicate. The oxidative stability of the samples was determined as the induction period. To define this period, the software associated with the Rancimat equipment uses the curve obtained from the conductivity measurements. The induction period is determined as the time between the beginning of the recording and the intersection point of the tangents to the conductivity curve. The results provide valuable insights concerning the stability properties of the product, which are crucial for determining shelf-life and their suitability for food applications.

2.3.5. Rheological properties

Rheological studies were conducted to understand the effect of the n-HAp concentration and of the oil-water ratio on the viscous and viscoelastic behaviour of the Pickering emulsions. These measurements were carried out after 7 days of storage. The rheological behaviour of commercial mayonnaises was also studied. An Anton Paar rheometer (Anton Paar, GmbH, Austria) with a parallel plate was used, and the rheological measurements were performed at 20 °C using a gap interval of 0.5 mm. The viscosity measurements of the Pickering emulsions and commercial mayonnaises were conducted as a function of the shear rate in the range 0.1–1000 1/s. Before frequency sweep, the linear viscoelastic region (LVE) was determined by amplitude sweep tests at fixed 0.05 % strain. The dynamic frequency sweep tests of storage modulus (G') and loss modulus (G'') were conducted within the LVE region from 0.3 to 100 rad/s.

2.3.6. Nutritional and energy value

The nutritional and energy values of the Pickering emulsions were estimated considering the following assumptions: (i) sunflower oil content is the main contributor to the nutritional composition, and (ii) other components, such as water and Pickering particles, were considered to have a negligible impact. Thus, the total energy of n-HAp Pickering emulsions was determined according to the European Parliament and Council Regulation No. 1169:

$$\text{Energy (kcal)} = 4 \times \text{carbohydrate (g)} + 9 \times \text{fat (g)} + 4 \times \text{protein(g)}$$

The nutritional information of the reference mayonnaise was used for comparison.

3. Results and discussion

3.1. n-HAp Pickering emulsions production

Pickering emulsions stabilised by n-HAp were produced with different contents of solid particles (5–15%) and oil-water ratios (50:50, 60:40, 70:30 and 80:20, *v/v*). For 15 wt% the original n-HAp paste was used. The other concentrations (5 and 10 wt%) were obtained by dilution. According to previous studies of the group, the lower used concentration was 5 wt% (Ribeiro et al., 2022c). The role of n-HAp particles in O/W emulsion stability was assessed to check their Pickering potential to stabilise emulsions with oil-water ratios over 50:50. The emulsion stability is an important parameter to study since it determines the potential for product application and shelf-life.

3.1.1. *Oil-water ratio effect*

The effect of the oil-water ratio on the emulsion stability was evaluated for oil-water ratios - 50:50, 60:40, 70:30, and 80:20 - at a fixed n-HAp concentration of 5 wt%, water basis. All Pickering emulsions exhibited an O/W type by the drop test independently of the oil content (see supplementary material – Fig. S1).

The n-HAp particle wettability can influence the emulsion type. Wettability refers to the ability of solid particles to be wetted by the emulsion phases (oil and water) and is related to the contact angle. The solid particles with contact angle values below 90° are preferentially wetted by water (hydrophilic characteristics) and, therefore, suitable for forming O/W emulsions. In contrast, when the contact angle values above 90°, the particles are preferentially wetted by oil (hydrophobic characteristics), forming W/O emulsions (Low et al., 2020; Ribeiro et al., 2023). Previous work reported n-HAp particles to have predominant hydrophilic characteristics (contact angle ~20°) (Ribeiro et al., 2022e), giving rise to O/W emulsions.

Fig. 1 shows the emulsions OM images right after production, the droplet size distributions evolution along the 90-day storage period (sampled at 0, 7 and 90 days), and photos of the emulsions taken after 90 days of storage.

Visual inspection of the OM images shows that the produced Pickering emulsions have a high number of well-defined droplets. Moreover, dense emulsions with tightly packed droplets were observed for the whole range of tested oil-water ratios. Table 2 summarises the effects of the oil-water ratio and storage time on the mean droplet size. An

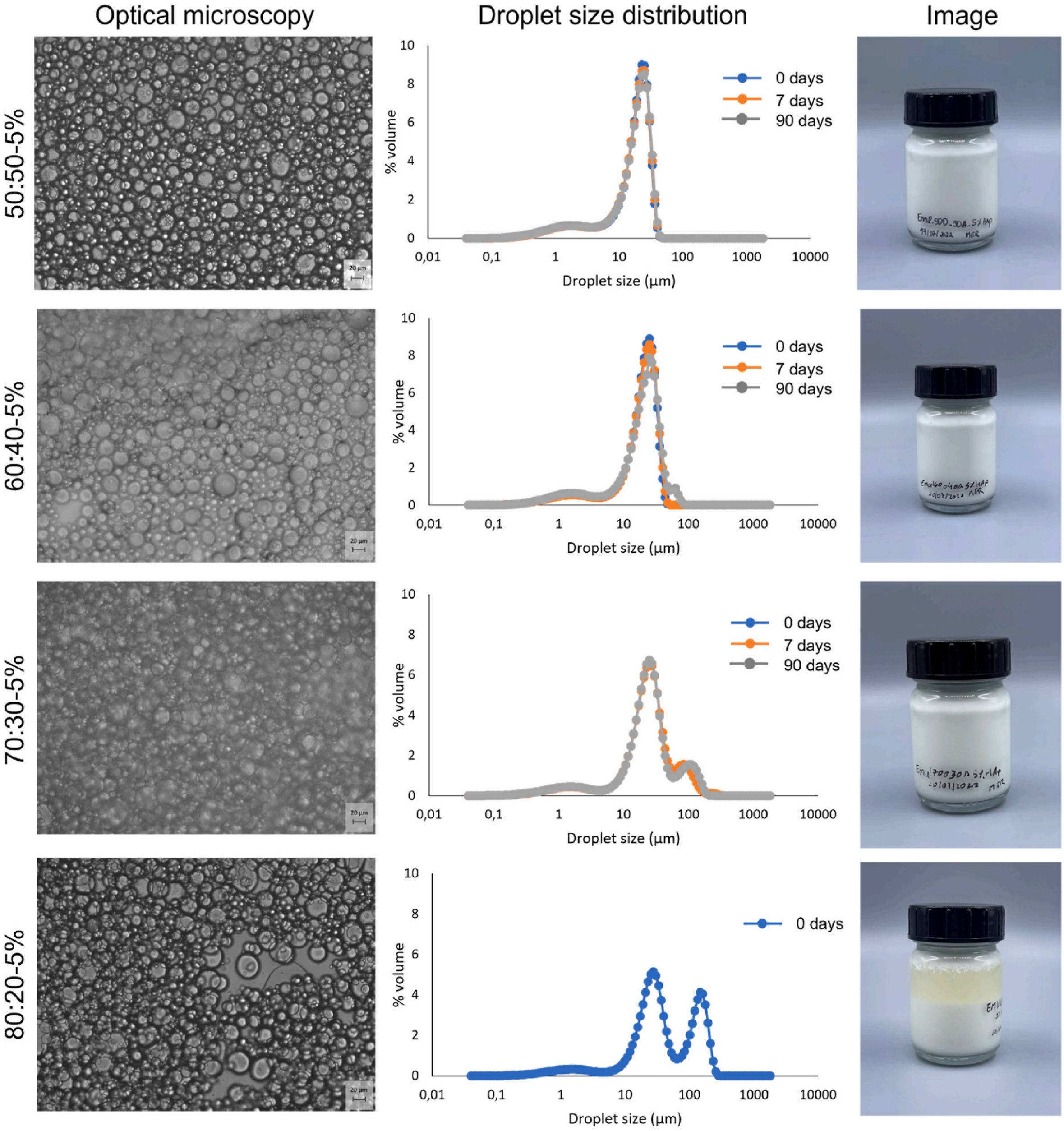

Fig. 1. Optical microscopy images (after production, t0), droplet size distribution (at storage times of 0, 7 and 90 days) and photo registration for the samples after 90 days for Pickering emulsions as a function of the oil ratio and at fixed n-HAp concentration (5 wt%). All optical images were taken with a magnification of 20x.

Table 2
Effect of the oil-water ratio on Pickering emulsion droplet size (D[4,3]) after production and over 7 and 90 days storage time. Values represented as average droplet size ± SD (μm).

Sample	0 days	7 days	90 days
50:50–5%	18.61 ± 0.04	18.73 ± 0.07	18.77 ± 0.05
60:40 5%	20.17 ± 0.12	20.60 ± 0.02	24.43 ± 0.25
70:30 5%	35.99 ± 2.07	35.02 ± 1.04	38.81 ± 0.78
80:20 5%	77.10 ± 10.94	nd	nd

nd – not determined due to the emulsion phase separation.

increase in the oil-water ratio leads to an increase in the mean droplet size. This behaviour has been previously reported for n-HAp Pickering emulsions with an oil-water ratio lower than 50:50 (Ribeiro et al., 2022c). Kim et al. (2023) encountered identical behaviour in Pickering emulsions stabilised by silica particles, where the mean droplet size increased from 638 μm to 1331 μm as the oil volume fraction increased from 75 to 85.

Regarding the effect of storage time, a nearly constant droplet size was observed for the emulsion produced with lower oil-water ratio, the 50:50–5% emulsion, and just a slight increase in mean droplet size was observed for the formulations with oil-water ratios of 60:40 and 70:30, most noticeably after 90 days. This effect is also accompanied by slight variations in the droplet size distribution (Fig. 1, middle column). However, these changes do not generally affect the emulsion's stability since macroscopic homogeneity is still observed after 90 days, particularly concerning creaming formation, which was absent for all samples (Fig. 1, right column). The only observed instability was related to the 80:20–5% sample, for which oil separation was detected at the top of the emulsion after 90 days. Although the OM image shows an emulsion with spherical droplet morphology, the droplet size distribution obtained right after emulsification indicated the presence of a group with a larger droplet sizes, suggesting that the system is susceptible to coalescence. This result is corroborated by the oil separation that occurred after a few days, which is why the follow-up of this sample was not conducted.

The Pickering emulsions were stored at room temperature in a transparent glass vial, as shown in the photo registration in Fig. 1. After 90 days of storage, long-term storage stability was observed for the samples produced with oil-water ratios from 50:50 to 70:30. For these emulsions, no phase separation was observed, indicating that n-HAp particles are irreversibly adsorbed at the oil surface, preventing destabilisation. However, oil separation was observed for the Pickering emulsion produced with 80:20 oil-water ratio, which can be explained by the lack of solid particles to stabilise this oil content.

3.1.2. n-HAp concentration effect

The effect of n-HAp concentration on Pickering emulsion stability was also evaluated, by varying the n-HAp solid particle concentration from 5 to 15 wt% at a fixed oil-water ratio of 60:40. The stability was examined during 90 days at room temperature (sampling at 0, 7 and 90 days). The drop test also confirmed that all the produced emulsions were of O/W type.

Fig. 2 shows the optical images of the n-HAp Pickering emulsions immediately after production, the droplet size distribution evolution over storage time, and the Pickering emulsion's photo registration after 90 days. In the optical microscopy images, right after production, all

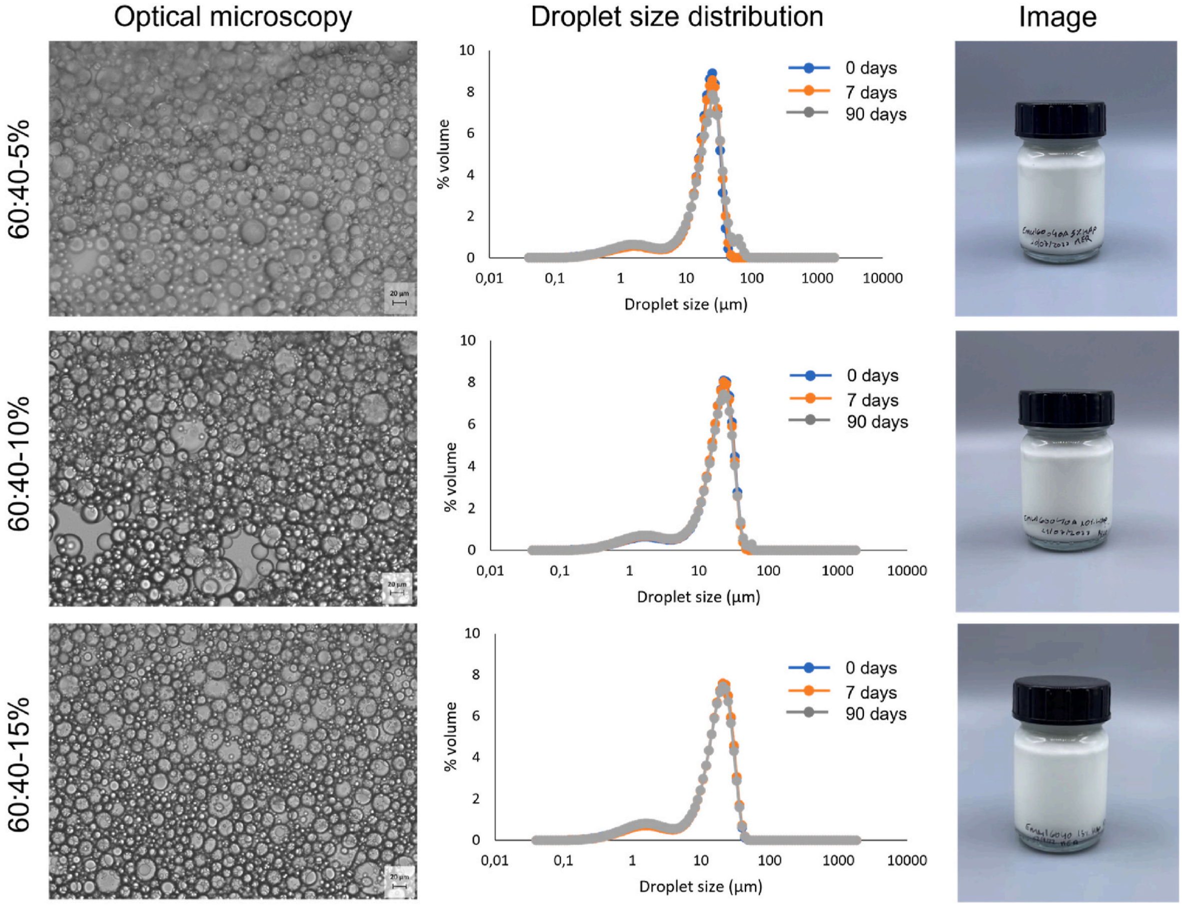

Fig. 2. Optical microscopy images (after production, t0), droplet size distribution (at the storage times of 0, 7 and 90 days) and photo registration for the samples after 90 days for Pickering emulsions as a function of the n-HAp concentration and at fixed oil-water ratio (60:40). All optical images were taken with a magnification of 20x.

Pickering emulsions are characterised by a spherical shape and individualised droplets. Macroscopically, all the analysed Pickering emulsions were homogeneous, with no evidence of phase separation after 90 days of storage at room temperature, as can be observed by the photo registration.

Table 3 presents the mean droplet size of Pickering emulsions over storage time as a function of n-HAp concentration. The data shows that the mean droplet size decreases as the n-HAp content increases. The 60:40–10% and 60:40–15% Pickering emulsions maintained its mean droplet size after 90 days of storage. However, the Pickering emulsion stabilised with 5 wt% of n-HAp particles revealed a slight increase in size also reflected in its size distribution. These results agree with others reported in the literature on the influence of solid particle concentration on emulsion mean droplet size. For example, Kim et al. (2023) developed high internal phase Pickering emulsions stabilised by silica particles and reported a small decrease in the droplet diameter as the silica content increased. Liu et al. (2018) and Wang et al. (2020) also reported the same behaviour dealing with the stabilisation of emulsions with high levels of the oil phase and wheat gluten and starch-based solid particles, respectively.

In this work, the n-HAp Pickering emulsions revealed stability for the analysed period of 90 days, indicating that solid particles maintained their role as a stabiliser. Overall, the stability of the n-HAp Pickering emulsions can be mainly attributed to (i) irreversible adsorption of n-HAp particles at the oil interface and (ii) limited free movement of droplets due to the emulsion network structure (McClements, 2016; Ribeiro et al., 2022c).

3.1.3. n-HAp role on Pickering emulsions stabilisation

Drawing from the above-discussed results for Pickering emulsion stability, optical analyses, and mean droplet diameter, Fig. 3 presents a schematic representation evidencing the role of n-HAp content in Pickering emulsion stabilisation For a fixed n-HAp content, the availability of particles to stabilise the surface of the oil droplets is a limiting factor. As the oil-water ratio increases from 50:50 to 70:30, a reduction in the number of particles in suspension is noted. For the 80:20 emulsion, the scarcity of particles prevents complete coverage of the oil particles (dashed line around the oil droplets in Fig. 3), and the emulsion becomes unstable, corroborated by the observed phase separation as discussed in section 3.1.1. Conversely, at a fixed oil-water ratio, as the n-HAp content increases, more particles become available to stabilise the oil droplets. Consequently, some of these particles remain in suspension and contribute to the stability of the Pickering emulsion by acting as a thickening agent, increasing the emulsion viscosity (Ribeiro et al., 2022c).

Typically, n-HAp Pickering emulsions exhibit a positive zeta potential (higher than 30 mV) (Ribeiro et al., 2022a, 2022b), which can be attributed to the presence of the n-HAp particles (34 mV) at the oil-water interface and in suspension in the continuous phase. The strong zeta potential of the n-HAp Pickering emulsions enables the maintenance of the electrostatic repulsion between droplets, thereby preventing oil coalescence and allowing their stability for longer periods of time (Ribeiro et al., 2022b). Electrostatic interactions play a crucial role in Pickering emulsion stability; however, the ones observed with n-HAp particles are different from the ones observed in egg yolk or egg analogues mayonnaise. When egg yolk is used, the stabilisation is ensured by the naturally presented phospholipids (lecithin), which act as a conventional emulsifier holding hydrophobic and hydrophilic regions. The hydrophilic head is protonated at acid pH, enhancing the affinity with the water phase (Shen et al., 2020). Concerning mayonnaise-like foods containing egg yolk and egg analogues, the electrostatic interactions depend on the used compounds (Huang et al., 2021; Lu et al., 2022; Mao et al., 2023). Previous studies highlighted the electrostatic interactions between kappa-carrageenan/yolk protein (Huang et al., 2021) and chickpea flour and soy isolate proteins/kappa-carrageenan (Lu et al., 2022), showing that the type of interactions significantly affects the macroscopic properties of plant-based egg products. The kappa-carrageenan bounds with the positive charge groups of yolk proteins interfering with the thermal gelation process.

Table 3
Effect of the n-HAp concentration on Pickering emulsion droplet size (D[4,3]) after production and over 7 and 90 days storage time. Values represented as average droplet size ± SD (μm).

Sample	0 days	7 days	90 days
60:40–5%	20.17 ± 0.12	20.60 ± 0.02	24.43 ± 0.25
60:40–10%	19.11 ± 0.03	18.79 ± 0.08	19.61 ± 0.03
60:40–15%	17.32 ± 0.03	17.46 ± 0.01	17.46 ± 0.99

3.2. Interfacial structure of n-HAp Pickering emulsions

The effective role of the n-HAp particles on Pickering emulsion stabilisation was assessed using confocal laser scanning microscopy (CLSM). For this test, a sample of the Pickering emulsion was stained with Nile blue to label the n-HAp particles and Nile red to label the oil phase. Fig. 4 shows the CLSM images for the Pickering emulsions with 7 and 90 days. The 80:20–5% emulsion was not evaluated since it presented instability. In the CLSM images, the red fluorescence corresponds to the localisation of the n-HAp particles, while the green fluorescence indicates the oil droplets. In the overlapped images (3rd and 4th column, 7 days and 90 days, respectively), both n-HAp particles and the sunflower oil phase can be perceived. From the n-HAp images, it clear that the solid particles tend to form a well-defined halo, and in the overlaid images, this n-HAp halo surrounds the oil droplets. This result corroborates the presence of n-HAp particles at the oil droplet surface, indicating the formation of the interfacial layer, avoiding emulsion coalescence. These images also show how the oil and n-HAp content affect the droplet organisation. As the oil-water ratio increases from 50:50 to 70:30, the n-HAp Pickering droplets tend to be closer. This effect can be related to the high oil content that promotes the formation of a higher number of droplets and the development of a more viscous system, preventing droplets' mobility, as suggested by the confocal image of the 70:30–5% sample. The increase in the n-HAp particle content from 5 to 15 wt% also seems to promote the formation of an emulsion with droplets packed closely. This combination of events generates a particle-particle network, creating a tight structure at the oil interface of the Pickering emulsion droplets (Tan and McClements, 2021).

After 90 days of storage, it is perceptible that the n-HAp particles remained at the boundary of the oil droplets, ensuring emulsion stability.

3.3. n-HAp Pickering emulsions versus commercial mayonnaises

The rheological properties of the produced n-HAp Pickering emulsions were evaluated and compared with commercial mayonnaise formulations (traditional and light recipes). Afterwards, the most similar n-HAp Pickering emulsions in terms of rheological properties with commercialised products were chosen to study and compare the colour attributes, oxidative stability and nutritional value. These parameters are important in view of the product's acceptability.

3.3.1. Rheological properties

All the produced Pickering emulsions were characterised in order to evaluate the impact of emulsion formulation (solid particles content 5–15 wt% and oil-water ratio from 50:50 to 70:30) on apparent viscosity and viscoelastic properties. Fig. 5 shows the apparent viscosity versus shear rate curves, storage modulus (G′) and loss modulus (G″) versus frequency curves for the n-HAp Pickering emulsions and commercial mayonnaises (traditional and light).

The steady shear flow curves presented in Fig. 5A show that the

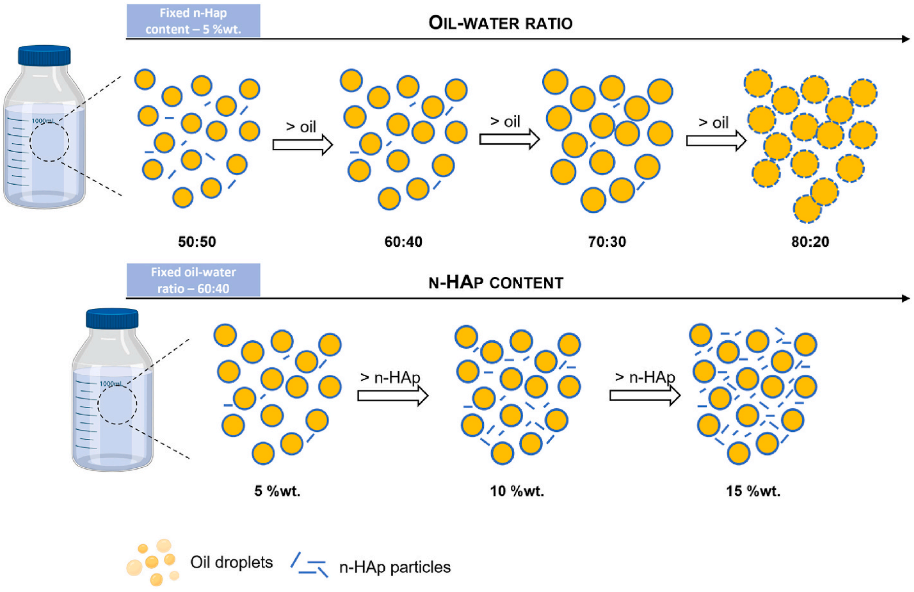

Fig. 3. Schematic representation of Pickering emulsions showing the effect of oil-water ratio, n-HAp content, and the electrostatic repulsions between n-HAp particles in suspension and at the oil surface.

apparent viscosity of the n-HAp Pickering emulsions is affected by the oil content, with higher viscosities observed for higher oil ratios. The amount of n-HAp particles (fixed 60:40 oil-water ratio) has a smaller impact on apparent viscosity, since just a modest increase of viscosity with concentration is observed. Ren et al. (2021) observed that stabilising Pickering emulsions with mixtures of proteins and κ-carrageenan resulted in an increase in apparent viscosity as the concentration of solid particles increased, primarily attributed to the higher content of κ-carrageenan. Motta-Romero et al. (2017) studied options to produce low-cholesterol emulsifier with low-fat egg yolk granules to apply in mayonnaise production; the results showed that higher viscosity of mayonnaise with granules may be attributed to a thicker protein shell with higher degree of protein aggregation. Another observation for Fig. 5A is that the apparent viscosity of all samples decreases with the applied shear rate, suggesting pseudoplastic fluid properties. This behaviour was also reported by other authors that evaluated the viscosity properties of the Pickering emulsions stabilised by apple pomace solid particles (Lu et al., 2021), pea protein isolate (Li et al., 2022), zein/pectin composite (Jiang et al., 2019), and tea water insoluble proteins/ƙ-carrageenan mixtures (Ren et al., 2021). This behaviour can be related to the arrangement of the oil droplets in the emulsion system. The application of a certain shear tension breaks the large droplet clusters into smaller ones, leading to a deformation of the internal Pickering emulsion structure and to a decrease in the viscosity as the shear rate increases (Lu et al., 2021).

The formation of gel-like structures was evaluated from the dynamic oscillatory measurements. Fig. 5C shows the moduli G′ and G″ as a function of frequency. For all measurements, the value of G′ is higher than G″, and both moduli demonstrate weak frequency dependency in the tested frequency range. This result supports the predominantly solid-like structure of the n-HAp Pickering emulsions. Similar behaviour was also achieved for Pickering emulsions stabilised by insoluble proteins/ƙ-carrageenan mixtures (G’>G″), which was related to the formation of network structure in Pickering emulsions (Ren et al., 2021).

Based on this rheological study, the 60:40–15% and 70:30–5% Pickering emulsions were selected due to their similarity to the commercial formulations in terms of apparent viscosity and oscillatory analyses; Fig. 5B and D shows the comparison between these Pickering emulsions (blue and green lines) and the commercial mayonnaises (grey and black lines). While the apparent viscosity of the 60:40–15% and 70:30–5% Pickering emulsions is comparable to each other and to the commercial mayonnaises, slight lower value for the Picketing emulsions is observed. However, the Pickering emulsions show higher G′ and G″ values than commercial mayonnaises. The apparent viscosity of commercial mayonnaises is usually controlled by adding polysaccharides (such as modified starch) as thickeners. No thickening agent was applied in the case of the produced n-HAp emulsions, highlighting the n-HAp Pickering emulsions as an interesting option from the formulation and consumer point of views; they have fewer additives and identical properties.

Fig. 6 shows the visual appearance of the most promising n-HAp Pickering emulsions, namely the ones produced with 60:40–15% and 70-30-5%, as well as commercial mayonnaises (traditional and light recipes). These images highlight the solid-like structure of the developed Pickering emulsions and commercial formulations, as evidenced by their ability to maintain their respective shapes with no structure deformation when placed on a smooth surface. This feature can be attributed to the semi-solid structure of the Pickering emulsions resulting from the three-dimensional network structures that prevent the free movement of droplets (Lu et al., 2021; Ribeiro et al., 2022c).

Considering that 60:40–15% and 70:30–5% Pickering emulsions allow the development of a similar system to commercial formulations, the colour attributes, oxidative stability and nutritional values of these Pickering emulsions were studied and compared to the commercial formulations.

3.3.2. *Colour properties*

The 60:40–5% and 70:30–15% Pickering emulsions (at 7 and 90 days storage) and the commercial mayonnaises were analysed using a colourimeter and the results are summarized in Table 4. The colour properties, including the lightness (L*), greenness-redness (a*) and blueness-yellowness (b*) are represented qualitatively as they are expressed in relative units. The n-HAp Pickering emulsions present a similar hue regardless of its composition. The brightness (L*) refers to the ability of the system to scatter the light and is a crucial factor in determining the appearance and acceptability of mayonnaise-like sauces (Carcelli et al., 2020). The Pickering emulsions presented L* values ranging from 80.54 to 80.88 for the 60:40–5% and 70:30–15% samples, respectively. Values close to 80 indicate that the Pickering emulsions present high brightness. Additionally, a small increase in the L* value can be observed as the n-HAp particle concentration increases, which indicates the particles' influence on the emulsion's colour. Moreover, the L* value of the

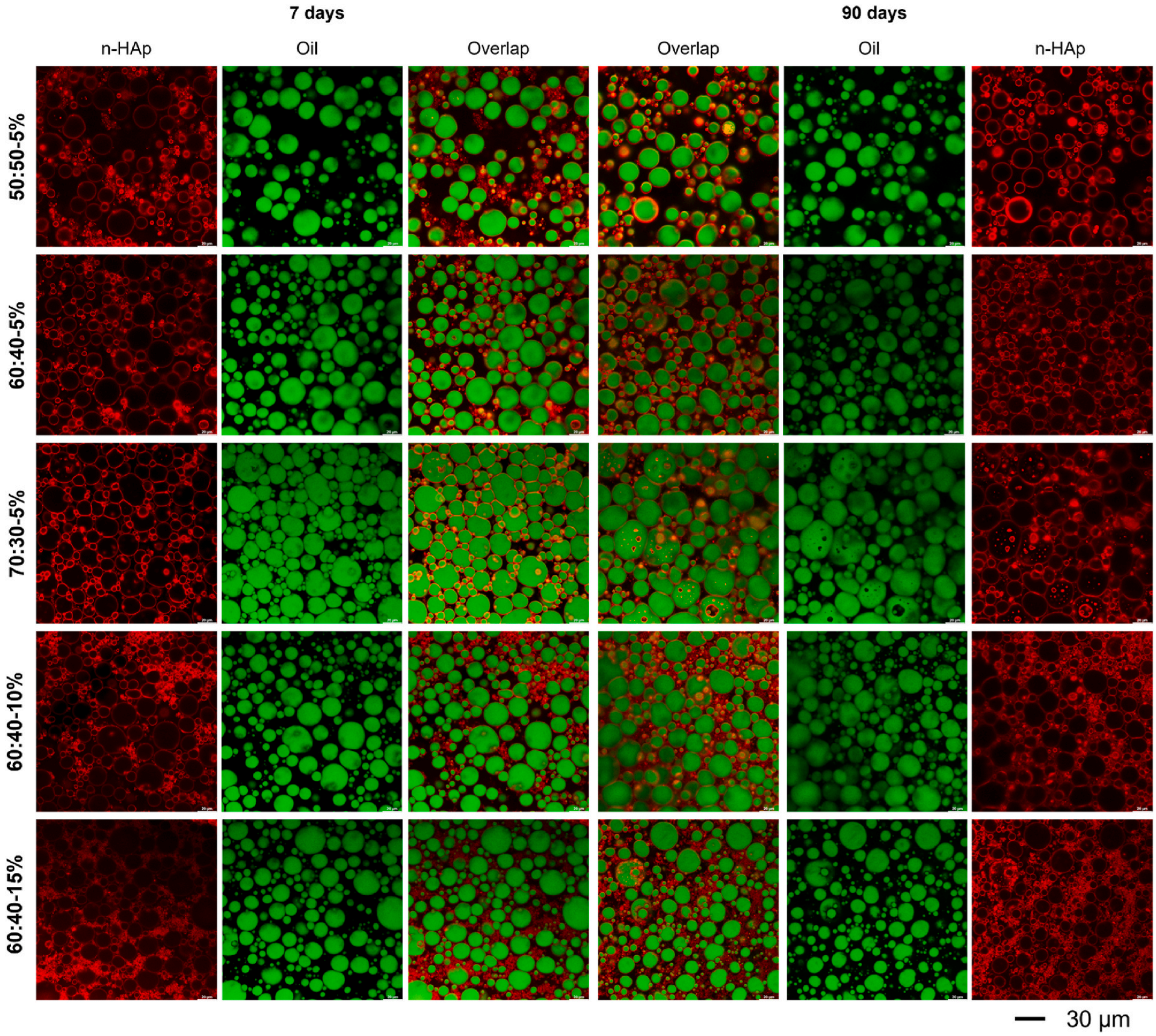

Fig. 4. Confocal laser scanning microscopy (CLSM) images of the Pickering emulsions produced with different n-HAp concentrations (5–15 %, water basis) and the oil content (50–70%) over storage time of 7 and 90 days. n-HAp particles and oil phase were stained with Nile red and Nile blue, respectively. All images were taken with a magnification of 40x without zoom.

n-HAp Pickering emulsions is similar to one of the tested conventional formulations, namely light mayonnaise (79.04). Regarding the blueness-yellowness (b*) parameter, conventional mayonnaise is yellow due to the influence of egg yolk, oil and other ingredients such as mustard. Compared with the tested Pickering emulsions, where the oil is the only common yellow source, there is a significant difference between the +b* values relative to the commercial mayonnaises. However, it is observed that the increase in the oil ratio increases the +b* values. The low, near 0, values of a* values that there was no significant effect provided by green (-a*) or red (+a*). Although very small, after 90 days, n-HAp emulsions showed a slight decrease in all analysed parameters.

Corroborating the colour analyses, Fig. 6 clearly shows the colour differences between the n-HAp Pickering emulsions and the commercial mayonnaises; the effect of egg yolk and/or other additives is evident in the yellowing of the commercial product. As expected, new formulations for yolk-free or low-fat mayonnaise products present colour characteristics that differ from the conventional ones since different ingredients are used. Products with different characteristics can also be found in the literature. In the work conducted by Lu et al. (2021), the novel mayonnaise-based products have a light brown colour. In another study dealing with a surfactant-free mayonnaise produced with curcumin particles, a yellowish colour was obtained (Ghirro et al., 2022). Thus, the detected colour difference among the reported emulsions mainly depends on the solid particles' colour. In the case of the produced Pickering n-HAp emulsions, the white colour can be seen as an advantage, allowing colour tunning according to the intended final application. Thus, natural extracts, natural colourants or condiments can be added to control the final colour, and to introduce functionalities, helping to develop products meeting consumer expectations.

3.3.3. Oxidative stability and nutritional properties

The oxidative stability of the selected n-HAp Pickering emulsions (60:40–15% and 70:30–5%) and commercial mayonnaises (traditional and light) was evaluated using the Rancimat method; results are shown in Table 5. The oxidation stability was measured 7 days after the Pickering emulsion production. Table 5 shows that the induction period times of the n-HAp Pickering emulsions were 4.47 h for 60:40–15% and 3.15 h for 70:30–5%. These Pickering emulsions evidenced a significant improvement in the oxidation induction time compared with both commercial mayonnaises, for which a maximum of 0.35 h was obtained. In contrast to commercial emulsions, stabilised by egg yolk, n-HAp Pickering emulsions form a physical interface layer involving the oil, which tends to be more robust and effective against degradation and separation of pro-oxidant compounds present in the aqueous phase.

The interfacial layer plays an important role in protecting the emulsion, as it separates the unsaturated fatty acids in the oil phase from

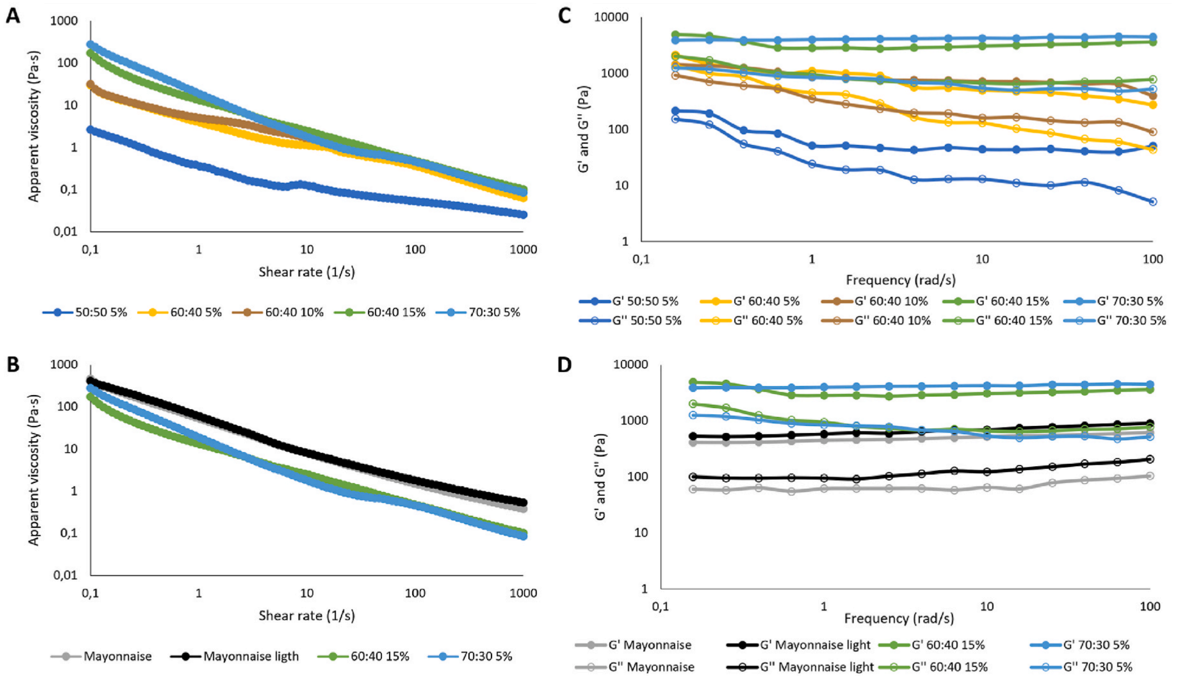

Fig. 5. Apparent viscosity versus shear rate and G' (storage modulus) and G'' (loss modulus) versus frequency curves of the n-HAp Pickering emulsions (A and C), and comparison between most promising n-HAp Pickering emulsions formulations with commercial mayonnaises (B and D).

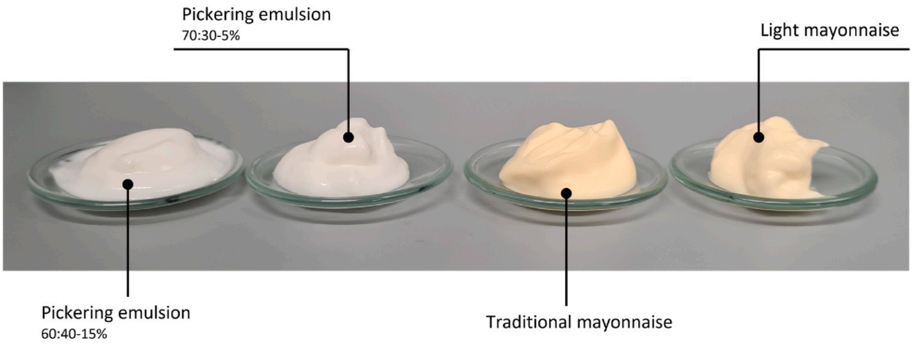

Fig. 6. Visual appearance of the 60:40–15% and 70:30–5% n-HAp Pickering emulsions and commercial mayonnaises (traditional and light).

Table 4
Colour analysis of n-HAp Pickering emulsions (t7 and t90 days) and commercial mayonnaises (traditional and light).

	7 days			90 days		
	L*	a*	b*	L*	a*	b*
60:40–15%	80.88 ± 0.16	−0.83 ± 0.03	1.37 ± 0.16	79.51 ± 0.01	−0.65 ± 0.01	0.92 ± 0.01
70:30–5%	80.54 ± 0.08	−0.95 ± 0.03	2.85 ± 0.04	79.25 ± 0.01	−0.90 ± 0.01	2.15 ± 0.01
Traditional mayonnaise	77.90 ± 0.04	−2.90 ± 0.03	16.88 ± 0.02	nd	nd	nd
Light mayonnaise	79.04 ± 0.05	−1.47 ± 0.01	15.37 ± 0.01	nd	nd	nd

nd – not determined.

Table 5
Oxidative stability from induction period values of the n-HAp Pickering emulsions and commercial mayonnaises (traditional and light). Results are presented as mean ± SD.

Sample	Induction period (h)
60:40–15%	4.47 ± 0.35
70:30–5%	3.15 ± 0.05
Traditional mayonnaise	0.35 ± 0.02
Light mayonnaise	1.35 ± 0.02

potential oxidants such as oxygen and transition metal ions present in the water phase (Keramat et al., 2022). Thus, the physical properties of the interfacial layer can influence the diffusion of pro-oxidants, free radicals, and oxygen (McClements, 2016). Additionally, increasing the apparent viscosity of Pickering emulsions can reduce the oxygen diffusion rate, oil droplet collision, and mobility of pro-oxidant compounds in the continuous phase. The results obtained for n-HAp Pickering emulsions suggest an effective coverage of the oil droplets with n-HAp particles that hinder oxygen permeability through the oil/water interface. Consequently, the oil phase remains more protected from oxidation.

The enhancementof Pickering emulsions' oxidative stability with increasing particle concentration was discussed by Akcicek et al. (2022). They reported an increase of the induction period from 4.05 to 4.85 h when rocket and chia seed gum nanoparticle concentration increased from 0.5 to 1.5 %wt.; however, the induction period was lower when compared to commercial mayonnaises.

The nutritional value and the total energy of the n-HAp Pickering emulsions were estimated considering the composition of the emulsion formulation in terms of oil content; water and n-HAp particles contribution was considered negligible. The estimated values were compared to those of commercial mayonnaises and are summarized in Table 6. The selected n-HAp Pickering emulsions have reduced fat content (55.4 and 64.4 g/100 g in 60:40–15% and 70:30–5%, respectively) compared to the traditional mayonnaise (66 g/100 g) and higher fat content in comparison to the light mayonnaise version (26 g/100 g). Nevertheless, it should be mentioned that commercial recipes, mainly light mayonnaises, also contain carbohydrates (7.3 g/100 g). In light mayonnaises, carbohydrates are commonly added to compensate for reducing fat content (oil phase) and to tune the textural and sensory characteristics. Regarding product energy, the Pickering emulsions have reduced caloric values (498 kcal in 60:40–15% and 581 kcal in 70:30–5%) compared to the traditional mayonnaise (611 kcal) and higher caloric values in comparison to the light mayonnaise version (266 kcal).

Effectively, when comparing the 60:40–15% and 70:30–5% Pickering emulsions to the traditional mayonnaise, it is possible to conclude that the Pickering emulsion formulations have lower fat content, is carbohydrate-free and less caloric, which are important parameters to consider in the development of new products. In this context, the n-HAp Pickering emulsions hold promising potential, offering consumers a more nutritionally balanced and equally attractive product.

Table 6
Estimated nutritional values of the n-HAp Pickering emulsions compared to the nutritional values of the commercial mayonnaises (traditional and light).

	Traditional mayonnaise	Light mayonnaise	60:40–15%	70:30–5%
Energy (kcal)	611	266	498	581
Fat (g/100 g)	66	26	55.4	64.4
Carbohydrate (g/100 g)	3.7	7.3	0	0
Sugars (g/100 g)	2.5	2.5	0	0
Fibre (g/100 g)	0	0	0	0
Proteins (g/100 g)	0.6	0.6	0	0

4. Conclusions

Hydroxyapatite (HAp), a calcium phosphate, is proposesd in this work as a Pickering stabiliser to develop promising and disruptive food formulations mimicking mayonnaise sauces. The effect of production parameters, including n-HAp particles concentration and oil content, was evaluated targeting stable systems. Different formulations were produced, varying the oil-water ratio from 50:50 to 80:20 at a fixed n-HAp concentration of 5 wt%, and varying the n-HAp concentration from 5 to 15 wt% at a fixed oil-water ratio of 60:40. The drop test assay indicated that all produced Pickering emulsions were O/W type regardless of oil and n-HAp content. The evaluated droplet size distributions confirm a clear relationship between the used formulation and the obtained mean droplet size. Namely, the n-HAp concentration increase led to a decrease in the mean droplet size, and the oil content increase led to a slightly higher mean droplet size. Considering the evaluated storage period of 90 days, destabilisation (phase separation) was only observed for the sample with the highest oil content (80:20–5%). Slight destabilisations at the microscopic level were observed for the 60:40–5% and 70:30–5% formulations, where a slight increase in the mean droplet size was observed. However, this increase was not sufficient to cause phase separation under macroscopic observation. The evaluation by optical and confocal microscopy confirmed spherical droplets' formation and n-HAp particles surrounding the oil core. Additionally, the presence of the n-HAp particles around the oil droplet was confirmed by confocal microscopy, even after 90 days of storage.

The developed n-HAp Pickering emulsions offer promising solutions as mayonnaise-like food sauce alternatives with the advantages of being low-fat, eggless and carbohydrate-free compared to commercial mayonnaises. The n-HAp Pickering emulsions enable the production of systems with identical rheological properties and better oxidative stability over commercial mayonnaises. The n-HAp particles form an interfacial layer that hinders oxygen permeability retarding the lipid oxidation rates. The white colour of the n-HAp Pickering emulsion formulations can be seen as an advantage, enabling colour and functionality tunning by using natural colourants, extracts, or condiments, which increases consumer attractiveness.

Overall, Pickering emulsion-based products can be tailored for various viscosities, textures, and functionalities, demonstrating the versatility of this approach. In this context, this work is a step forward in disruptive product development by replacing surfactants with low-fat, eggless, and carbohydrate-free products.

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CRediT authorship contribution statement

Maria Eduarda Relvas: Investigation. **Larissa C. Ghirro:** Investigation. **Isabel M. Martins:** Writing – review & editing, Supervision. **Jose Carlos B. Lopes:** Conceptualization. **Madalena M. Dias:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Maria Filomena Barreiro:** Writing – review & editing, Resources. **Andreia Ribeiro:** Writing – original draft, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jfoodeng.2024.112181.

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