



Contents lists available at ScienceDirect

# Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: [www.elsevier.com/locate/colsurfa](http://www.elsevier.com/locate/colsurfa)

## Advancing Pickering emulsions with natural-based solid dispersion particles: Particle screening and design of pectin-based emulsions

Stephany C. de Rezende<sup>a,b,c</sup>, Arantzazu Santamaria-Echart<sup>a,\*</sup>, Andreia Ribeiro<sup>b,c</sup>,  
Madalena M. Dias<sup>b,c</sup>, Maria Filomena Barreiro<sup>a,\*</sup>

<sup>a</sup> CIMO, LA SusTEC, Instituto Politécnico de Bragança, Campus de Santa Apolónia, Bragança 5300-253, Portugal

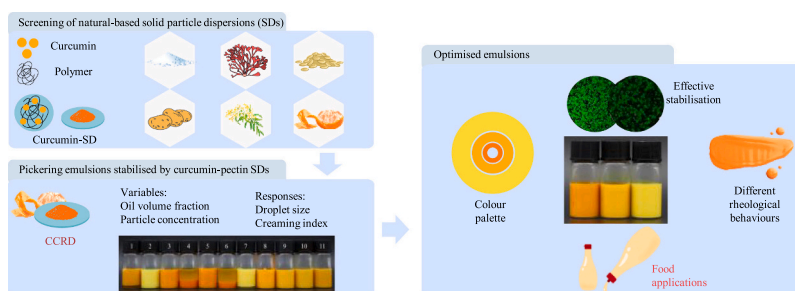
<sup>b</sup> Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM), Department of Chemical Engineering, Faculty of Engineering University of Porto, Rua Dr. Roberto Frias, Porto 4200-465, Portugal

<sup>c</sup> Associate Laboratory in Chemical Engineering (ALICE), Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias, Porto 4200-465, Portugal

### HIGHLIGHTS

- Optimised Pickering emulsions with pectin-curcumin SD particles.
- Stability achieved by balancing oil fraction and SD concentration.
- Predictive models resulted in higher CI and D[4,3] than experimental.
- Rheological analysis confirmed distinct emulsion behaviours.
- Emulsions presented significant potential for food sauces.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

#### Keywords:

Pickering emulsions  
Solid dispersion  
Pectin-curcumin particles  
Stability optimisation  
Natural colouring applications  
Food products

### ABSTRACT

Given the evolving trends in consumption, Pickering emulsions are emerging as a promising solution for functional and healthier foods, highlighting the need to diversify particle stabilisers. This study assessed the potential of curcumin-based solid dispersions (SDs) prepared with natural polymers (pectin, maltodextrin, Arabic gum, potato starch, and k-carrageenan) as Pickering stabilisers. Among these, pectin-curcumin SDs (contact angle =  $48.0 \pm 3.6^\circ$ ) demonstrated effective emulsion stabilisation, as confirmed by confocal microscopy. The impact of oil volume fraction ( $\phi = 0.20\text{--}0.70$ ) and SD concentration (1.0–5.0 % wt.) on emulsion stability was evaluated. An intermediate  $\phi$  (0.45) consistently minimised creaming index (CI = 0–16.67 %) and droplet size ( $D[4,3] = 2.53\text{--}4.12 \mu\text{m}$ ). Complete reduction of creaming (CI = 0 %) was achieved at high SD concentration with low  $\phi$  or low SD concentration with high  $\phi$ , leading to improved stability. The three produced optimised formulations exhibited distinct colour properties ( $L^* = 64.06\text{--}72.00$ ,  $a^* = -11.09\text{--}12.50$ ,  $b^* = 55.10\text{--}60.70$ ), with hues ranging from yellow to orange, highlighting their potential for natural colouring applications. Rheological behaviour varied from gel-like ( $G' > G''$ ) to viscoelastic ( $G' = G''$ ), broadening their potential in food formulations. Higher SD concentrations with lower/intermediate  $\phi$  produced structured, gel-like emulsions suitable for sauces or spreads. In contrast, lower SD concentrations with higher  $\phi$  yielded fluid emulsions for dressings or beverages. These findings highlight the feasibility of SD-based Pickering emulsions for designing stable ( $\geq 30$  days), visually appealing, and texturally versatile food products.

\* Corresponding authors.

E-mail addresses: [asantamaria@ipb.pt](mailto:asantamaria@ipb.pt) (A. Santamaria-Echart), [barreiro@ipb.pt](mailto:barreiro@ipb.pt) (M.F. Barreiro).

<https://doi.org/10.1016/j.colsurfa.2025.137003>

Received 27 February 2025; Received in revised form 8 April 2025; Accepted 20 April 2025

Available online 21 April 2025

0927-7757/© 2025 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

## 1. Introduction

Pickering emulsions are stabilised by solid particles, which form a protective layer at the oil-water interface, preventing coalescence and enhancing stability. This distinctive mechanism provides advantages over conventional emulsions stabilised by molecular surfactants, including enhanced stability, precise control of droplet size distribution, and the added benefits of natural edible particles [1,2]. In the food industry, particularly in developing innovative products aligned with current consumption trends, Pickering emulsions are an attractive solution to cover the demand for natural and functional products [3].

The successful production of Pickering emulsions relies on solid particles with specific characteristics, including size, morphology, and wettability. Particles with contact angles ( $\theta$ ) below  $90^\circ$  are said to be hydrophilic and suitable to form oil-in-water (O/W) emulsions. In comparison, those with values greater than  $90^\circ$  are hydrophobic and adequate to prepare water-in-oil (W/O) emulsions [4]. The particles should ideally exhibit partial wettability by both the oil and water phases, enabling them to adsorb at the interface and form a dense monolayer. This layer stabilises the emulsion by lowering interfacial tension and preventing droplet coalescence [5]. In addition, the formulation's particle concentration and  $\phi$  are crucial factors contributing to Pickering emulsions' stability and improved rheological properties [6,7].

Recent developments focused on synthesising food-grade particles as Pickering stabilisers are mainly based on proteins and polysaccharides. Protein examples include sources such as gelatine [8], whey protein [9], and several plant-based proteins (e.g., soybean, pea, mung bean, chia seed, and chickpea) processed as microgel particles [10–12]. Among polysaccharides, cellulose [13], modified starch [14] and chitosan [15] are the most studied examples. Polysaccharides and proteins combination, e.g., though complexation, were also explored to offer synergistic effects capable of providing a complex interfacial layer that enhances emulsion stability [16]. For example, ovotransferrin-gum Arabic [17], tea residue protein-xanthan gum [18] and zein-pectin [19,20] are among the studied combinations. While previous studies have demonstrated the successful use of protein-polysaccharide complexes and chemically modified polysaccharides for Pickering stabilisation [21–25], these approaches often require additional processing steps to tailor wettability, such as enzymatic treatments, complexation, or chemical modification [16,26]. In contrast, SD technology provides a simpler and more controlled method, enabling precise modulation of wettability, based on the fact that a hydrophobic compound is molecularly dispersed in a hydrophilic polymer matrix.

In a recent study by our group, k-carrageenan-curcumin SD particles have been successfully applied as Pickering stabilisers, resulting in Pickering emulsions with interesting technological properties to produce food sauce analogues [27]. This study presented a novel strategy in which SDs demonstrated their effectiveness in modulating the wettability of hydrophilic polymers, overcoming the typical limitations of natural counterparts that often restrict their practical application across various technological fields, e.g., packaging applications [28]. Expanding the use of these particles in Pickering emulsion production by testing additional natural-based SDs is highly promising, particularly in the food sector.

Unlike traditional methods, SD offers a more straightforward and efficient process for particle wettability design. SD also leads to the formation of particles of controlled size, potentiating their role as effective Pickering stabilisers and providing additional functional benefits derived from the introduced active compounds. Traditionally, by uniformly distributing a hydrophobic active compound within a hydrophilic polymeric matrix in SDs, the crystallinity of the active ingredient is modified, enhancing its solubility and bioavailability [29]. From a complementary perspective, the dispersion of the hydrophobic compound into the polymeric hydrophilic matrix decreases its water compatibility, helping to modulate particle wettability.

This study assesses the potential of natural-based SDs as Pickering stabilisers, formulated using maltodextrin (MD), Arabic gum (AG), potato starch (PS), and pectin (PC) as hydrophilic polymers, and curcumin as the hydrophobic active compound that modulates wettability. For benchmarking purposes, polyvinylpyrrolidone (PVP) and k-carrageenan (KC), previously studied in earlier research [27], were used as synthetic and natural reference materials. After an initial screening, the most suitable SDs were selected for an in-depth study to optimise a Pickering emulsion formulation, focusing on their potential for food products. A design of experiments (Central Composite Rotatable Design, CCRD  $2^2$ ) was used for the optimisation. The effect of the oil volume fraction ( $\phi$ ) and the particle concentration on the Pickering emulsions' stability, expressed as the creaming index (CI) and the mean droplet diameter (D [4,31]), was optimised. In addition, morphology was checked by optical microscopy and long-term stability was analysed for 30 days. The most promising emulsions were characterised by their stability, colour parameters ( $L^*$ ,  $a^*$  and  $b^*$ ), rheological properties, and confocal analysis. The developed emulsions can add value for applications such as dressings, beverages, and nutraceutical delivery systems, providing stability, texture, and curcumin health benefits.

## 2. Materials and methods

### 2.1. Materials

The SD particles were produced using curcumin (65 % purity) obtained from Sigma-Aldrich (Saint Louis, MO, USA), k-carrageenan (KC) from Acros Organics (Geel, Belgium), maltodextrin (MD, dextrose equivalent of 18) kindly donated by Cargill (Wayzata, MN, USA), Arabic gum (AG) from Fisher Scientific UK (Loughborough, England), pectin (PC, 74 % galacturonic acid) from citrus peel, from Sigma-Aldrich, and potato starch (PS) from Panreac Quimica S.L.U (Barcelona, Spain). Polyvinylpyrrolidone (PVP, molecular weight of 40,000 g/mol) was acquired from Sigma-Aldrich (Saint Louis, MO, USA). The emulsifier polysorbate 80 (Tween 80) was provided by Panreac Quimica S.L.U (Barcelona, Spain). Ethanol absolute (99.8 %) was purchased from Honeywell (Seelze, Germany). The oil used to prepare the emulsions was Miglyol 812, purchased from Acofarma (Barcelona, Spain). The used water was distilled water.

### 2.2. Production of curcumin-SD particles

Curcumin-SDs were prepared based on the formulations developed in the group's previous work without pH adjustments [30]. Briefly, 0.4 g of polymer (MD, AG, PS, PC, PVP or KC) and 0.06 g of Tween 80 (15 % wt., polymer-basis) were dissolved in 100 mL of water, and 0.06 g of curcumin (15 % wt., polymer-basis) was dissolved in 50 mL of ethanol. The solutions were combined and sonicated (Qsonica Q500, 500 W, Newtown, CT, USA – 70 % amplitude, 14 kHz) for 10 minutes (30 s on/10 s off). Ethanol was removed via rotary evaporation (Büchi R-114, Flawil, Switzerland using  $40^\circ\text{C}$  and 175 mbar), and the mixture frozen at  $-20^\circ\text{C}$  (LG, model GSL325PVCV, Amstelveen, Netherlands) before freeze-drying at  $-106^\circ\text{C}$  (CoolSafe 110–4, Scanvac, Vassingerød, Lyngø, Denmark). The obtained dry solid powder was stored in a desiccator to prevent moisture absorption and shielded from light until further characterisation. The samples were coded as C-P, where C refers to curcumin, and P refers to the defined polymer sigla. For example, C-PVP refers to the curcumin-PVP SD particles.

### 2.3. Characterisation of curcumin-SD particles

The produced curcumin-SD particles (C-MD, C-AG, C-PS, C-PC, C-PVP, and C-KC) were characterised concerning wettability. Water-in-air contact angles were determined using an optical contact angle device (OCA15 Plus, Dataphysics, Filderstadt, Germany). The SDs were dried in an oven at  $50^\circ\text{C}$  for 24 hours, followed by the preparation of pellets

**Table 1**

Design and experimental matrix of the Central Composite Rotatable Design (CCRD) for emulsions' optimisation.

Design matrix		Experimental matrix		
$x_1$	$x_2$	Runs	Oil volume fraction ( $\phi$ )	SD particle concentration (% wt.)
-1	-1	1	0.27	1.58
1	-1	2	0.63	1.58
-1	1	3	0.27	4.42
1	1	4	0.63	4.42
-1.41	0	5	0.20	3.00
1.41	0	6	0.70	3.00
0	-1.41	7	0.45	0.99
0	1.41	8	0.45	5.01
0	0	9	0.45	3.00
0	0	10	0.45	3.00
0	0	11	0.45	3.00

approximately 13 mm in diameter and 1 mm in thickness using a 15 T manual hydraulic press (GS15011, Specac Ltd., United Kingdom). Contact angle measurements were performed by depositing a 4  $\mu$ L sessile drop of distilled water onto the pellet surface with a high-precision injector. The droplet was recorded for 60 seconds using a high-speed video camera attached to the equipment. Contact angle values were acquired by fitting the profile data to the Laplace-Young equation, automatically computed by the software One Attens. The measurements were performed in triplicate using independent pellets. The results were presented as average contact angles from 10 to 50 seconds  $\pm$  standard deviation, with accompanying images captured 30 seconds after water drops were deposited onto the surface.

#### 2.4. Pickering potential of curcumin-SD particles

To first inspect the ability of the particles to stabilise the emulsions, the six curcumin-SD samples (C-MD, C-AG, C-PS, C-PC, C-PVP, and C-KC) were used to produce Pickering emulsions according to the methodology described by Ghirro et al. (2022), with some modifications. In brief, the  $\phi$  was 0.5, and a fixed concentration of particles (1.2 % wt., total emulsion-basis) was used. The SDs were dispersed in distilled water, after which the oil (Miglyol 812) was slowly added using a peristaltic pump at 3500 rpm (ISM596B, Ismatec SA, Opfikon, Switzerland) under constant stirring (500 rpm) using a stirring plate (RET basic IKAMAG® safety control, VWR, Radnor, PA, USA) to produce a pre-emulsion. This pre-emulsion was emulsified using an Ultra-Turrax homogeniser (Unidrive X1000 Homogenizer Drive from CAT Scientific, Staufen, Germany) at 13500 rpm for 7 minutes.

One week after preparation, the emulsions were inspected visually and by microscopy to check for signs of instability. The apparatus used was a Nikon Eclipse 50i microscope (Tokyo, Japan) equipped with Nikon Digital and NIS-Elements Documentation software. An aliquot of the sample was placed on a slide and gently covered with a coverslip for the analysis. The most promising SDs were chosen to proceed with the development of an optimised emulsion, for which an experimental design strategy was used.

#### 2.5. Optimisation of curcumin-SD particle-based Pickering emulsions

##### 2.5.1. Optimisation procedure

For the optimisation, a CCRD 2<sup>2</sup> with star points was employed, consisting of 11 experimental runs. The design included 3 replicated central points to assess process reproducibility and 4 axial points to extend the experimental range. The independent variables included  $\phi$  ( $x_1$ , v/v) particle concentration ( $x_2$ , % wt.). The CI (%) and the D[4,3] ( $\mu$ m) were defined as the responses. The design and experimental matrix are shown in Table 1. Data were analysed, and the effects were considered significant when  $p \leq 0.05$ .

The experimental results were analysed, and the response surface plots were generated using the Protimiza Experimental Design software (<http://experimental-design.protimiza.com.br>). Model adequacy was evaluated using the coefficient of determination ( $R^2$ ) and the analysis of variance (ANOVA) (F-test) (CCRD 2<sup>2</sup> at a 5 % significance level ( $p \leq 0.05$ )). Tukey's test was performed to compare the differences among the mean values of CI and D[4,3].

Validation tests were conducted, and the predicted values were compared to assess the accuracy of the experimental design model's predictions. Three emulsion formulations were selected for the validation tests, including optimised systems chosen based on the CCRD 2<sup>2</sup> response results (CI and D[4,3]). The emulsions were produced in triplicate, characterised (CI and D[4,3]), and the results are presented as average  $\pm$  standard deviation.

##### 2.5.2. Production and characterisation of the experimental runs

The general procedure for the emulsion preparation followed the description provided in Section 2.4 for Pickering potential evaluation with the adjusted  $\phi$  and particle concentration. According to the defined responses, the CI and mean droplet diameter, expressed as the Brouckere mean diameter (D[4,3]), were determined. Morphology (optical microscopy) was also evaluated, following the methodology described in Section 2.4. To inspect long-term stability, all characterisations were performed at 1, 15, and 30 days for emulsions stored at 25 °C.

The CI was evaluated by pouring 10 mL in 20 mL clear glass vials and calculated using Eq. (1), in which  $H_s$  and  $H_t$  represent the serum layer and total emulsion height, respectively, expressed in cm.

$$CI(\%) = \frac{H_s}{H_t} \times 100 \quad (1)$$

The D[4,3] values were determined by laser diffraction using a DLS Mastersizer 3000 equipped with a Hydro MV unit, Malvern Instruments (Worcestershire, United Kingdom). The refractive indexes used for the oil and water were 1.45 and 1.33, respectively. The particle absorption index was 0.10. Results were determined by averaging 5 consecutive measurements for each sample at room temperature using distilled water as the dispersant medium.

#### 2.6. Colour, interfacial structure, and rheology of the optimised emulsions

The colour parameters were determined using a Konica Minolta Sensing Inc. CR-400 colourimeter (Sakai-ku, Japan). The measurements ( $L^*$ ,  $a^*$ , and  $b^*$  in CIELAB space) were conducted in triplicate, and the results were expressed as the average  $\pm$  standard deviation. RGB colour was generated using a free online converter [31].

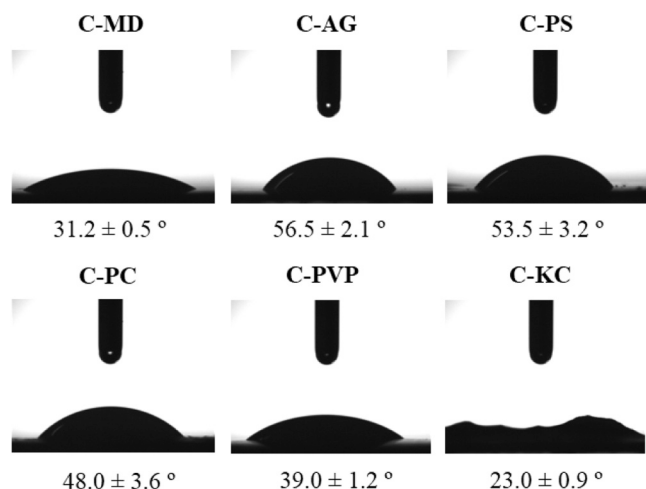
The total colour difference, represented by  $\Delta E$  values, was calculated according to Eq. (2).

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

Where  $\Delta L^*$ ,  $\Delta a^*$ , and  $\Delta b^*$  represent the differences between the colour parameters of the emulsions at time 1 and times 15 and 30 days.

Confocal microscopy was employed to examine the interfacial structure of the Pickering emulsions. In this process, the inherent fluorescence of curcumin (488 nm, green fluorescence) and Nile red (488 nm, green fluorescence), utilised to stain the oil phase (0.1 % wt/vol), was captured. The equipment used was a Leica TCS-SP5 AOBs (Leica Microsystems Inc., Heidelberg, Germany), recording digital images and processing them using LasX software.

The rheological behaviour of the emulsions was analysed using an Anton Paar rheometer (Anton Paar, GmbH, Austria) fitted with a parallel plate, operating at 25 °C. The viscosity of the Pickering emulsions was determined as a function of the shear rate over a range from 0 to 1000 1/s. The frequency sweep was conducted over a range from 0.1 to 100 rad/s, with all measurements taken within the specified linear viscoelastic region (LVE) at a strain of 0.1 %. The data are presented in terms of the



**Fig. 1.** Water-in-air contact angles for curcumin-SD particles produced with different natural polymers (MD-maltodextrin, AG-alginate, PS-starch, PC-pectin, PVP-polyvinyl pyrrolidone, KC- k-carrageenan).

storage modulus ( $G'$ ) and loss modulus ( $G''$ ) as frequency functions.

### 3. Results and discussion

#### 3.1. Curcumin-SD particles wettability

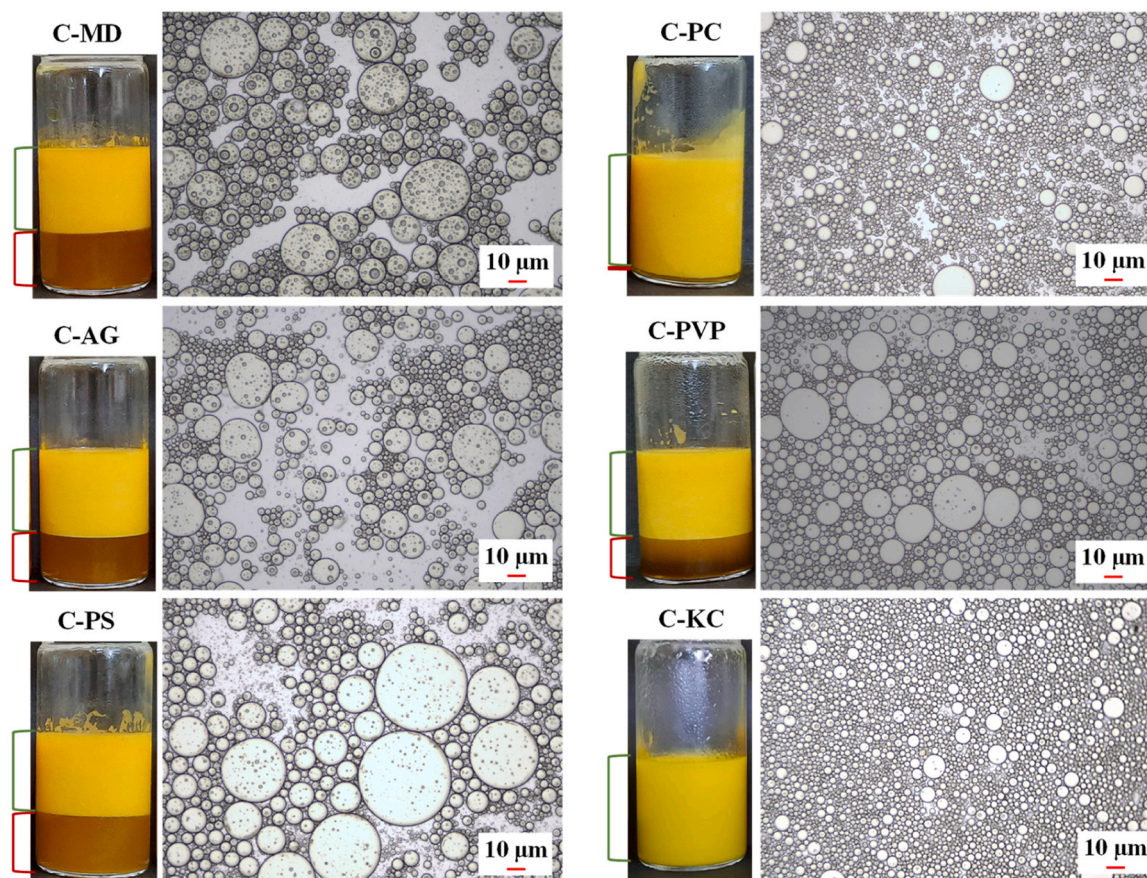
Particle wettability is an essential factor impacting the ability of the particles to act as Pickering stabilisers and to form O/W or W/O

emulsions. It can be accessed by measuring the contact angle ( $\theta$ ). Hydrophilic particles exhibit low air-in-water contact angles ( $\theta < 90^{\circ}$ ), indicating they are more compatible with the aqueous phase, tending to form O/W emulsions. Hydrophobic particles exhibit high air-in-water contact angles ( $\theta > 90^{\circ}$ ), being more compatible with the oil phase, resulting in W/O emulsions [6]. Fig. 1 illustrates the water-in-air contact angles of the produced SD particles, including the benchmarks (C-PVC and C-KC) and the photographic record captured 30 seconds after water droplets were applied to the pellet surface. The tested samples showed wettability values between 23 and  $56.5^{\circ}$ , suggesting a tendency to stabilise O/W interfaces. C-KC revealed rapid water absorption, marking it the most hydrophilic among the tested samples.

#### 3.2. Evaluation of Pickering potential of curcumin-SD particles

SD particles' Pickering potential was tested. Fig. 2 shows images of the produced emulsions and the corresponding morphology analysed by optical microscopy one week after production. Emulsions with smaller droplet sizes are typically associated with superior stability. Among the tested SD particles, C-KC gave rise to emulsions with no phase separation, as expected according to previous work [27]. This was followed by C-PC, which produced emulsions with only slight signs of phase separation, nearly imperceptible to the naked eye. Consequently, both emulsions exhibited a more uniform droplet morphology with smaller sizes.

Based on these findings, C-PC particles were selected to produce an optimised emulsion using a design-of-experiments approach. This decision was further motivated by pectin's versatile role in food applications. Pectin, a natural polysaccharide, is widely used in food products for its functionality and clean-label appeal. It is a gelling agent,



**Fig. 2.** Photographic registration and optical microscopy of the emulsions produced with different SD particles (MD-maltodextrin, AG-alginate, PS-starch, PC-pectin, PVP-polyvinylpyrrolidone, KC- k-carrageenan). The green-marked phase corresponds to the emulsified phase, while the red-marked represents the serum phase.

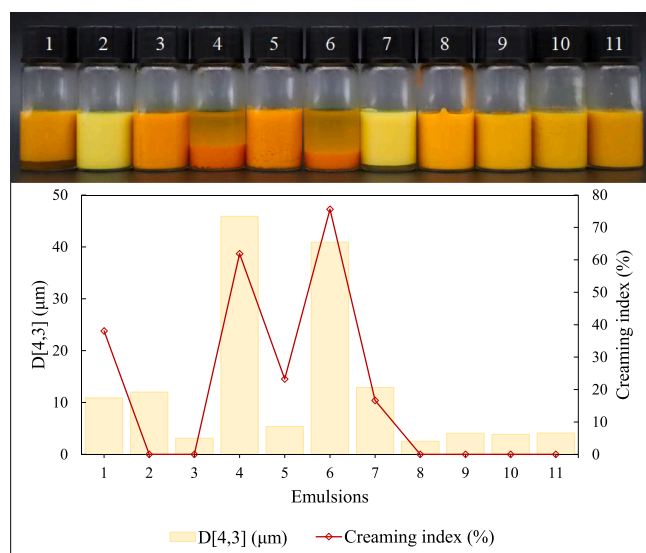


Fig. 3. The visual appearance of the produced emulsions at time 1 day and the experimental results of the D[4,3] ( $\mu\text{m}$ ) and creaming index (%) for the 11 runs defined by the Central Composite Rotatable Design  $2^2$ .

thickener, and stabiliser in products like jams, jellies, and dairy alternatives [32].

The superior performance of pectin in stabilising Pickering emulsions can be attributed to its molecular structure and associated interfacial properties. Pectin features a backbone of  $\alpha$ -(1 $\rightarrow$ 4)-linked D-galacturonic acid units with varying degrees of methoxylation, influencing its amphiphilicity [33]. The presence of hydrophobic methyl ester groups and hydrophilic carboxyl groups facilitates adsorption at the oil-water interface, forming a stabilising layer that reduces coalescence and phase separation [34]. Moreover, pectin can form viscoelastic networks in the continuous phase, which enhances emulsion stability [35].

In addition to its intrinsic emulsifying properties, pectin's interaction with curcumin positively contributes to SDs stabilisation capacity. Pectin is known to interact with polyphenolic compounds through hydrogen bonding, enabling a facilitated entrapment of curcumin in SDs [36]. This phenomenon could promote a more structured and cohesive interfacial layer formed by the SDs, reinforcing the stability of the Pickering emulsion. These interactions may also influence the stability of curcumin, offering additional functional benefits [30].

Pectin has attracted significant interest in Pickering emulsions as a stabiliser due to its biocompatibility and ability to form stable colloidal systems. However, its predominantly hydrophilic nature poses difficulties in achieving the necessary surface wettability balance for proper emulsion stabilisation. Different strategies have been studied to overcome this constraint, often by complexation with other biopolymers to modify wettability and stabilising capacity [1]. These complexes, though effective, come with drawbacks like formulation complexity, sensitivity to pH and ionic strength, and the need for chemical or enzymatic cross-linking to avoid more complex chemistry, which can conflict with clean-label requirements [37]. In this context, the SD particles can offer advantages to overcome these limitations.

### 3.3. Development of optimised pectin-based Pickering emulsions

The particle concentration and  $\phi$  are crucial parameters when optimising a Pickering emulsion.  $\phi$  can influence droplet size, stability and rheological behaviour. Some studies suggest that increased  $\phi$  can result in larger droplets due to reduced interfacial area or increased coalescence [38]. However, other studies indicate that this might lead to the formation of smaller droplets, possibly due to increased viscous forces

during homogenisation, which could promote the breakdown of larger droplets into smaller ones. [39]. Particle concentration is another factor affecting the Pickering emulsions' stability, similar to molecular surfactants in traditional emulsions. Droplets may coalesce at low particle concentration regimes, leading to larger sizes, while higher concentrations prevent coalescence, stabilising the emulsion [5]. Therefore, this work employed a design of experiments, namely a CCRD  $2^2$ , to understand the effect of both factors on stability when the proposed novel pectin-based SDs are used. Stability was checked by determining CI, which indicates instability at the macroscopic level, and the D[4,3] value, which reveals early signs of instability at the microscopic level [40]. CI, as an indicator of destabilisation, reflects the extent of instability and provides insight into emulsions' long-term stability and shelf-life. Ideally, a value close to zero should be obtained. Fig. 3 presents the experimental results of the runs used in the CCRD  $2^2$  experimental design (day 1). The corresponding optical microscopy images are shown in Fig. 4, with the results corroborating the observed trend for D [4,3]. The analysis was also conducted at 15 and 30-day intervals (Figures S4 and S5, Supplementary Material), showing minimal variation with time.

The central points (9–11) yielded similar results, corroborating the reproducibility of the experiments. CI values of zero were achieved in four formulations, including the central points (2, 3, 8, and 9–11), demonstrating the SDs' ability to produce stable emulsions. Higher CI values correspond to higher D[4,3] values, as in formulations 4 and 6. The experimental results obtained at 15 and 30 days were comparable to those at day 1 (Figure S1; Supplementary Material). This condition was selected for the regression analysis (Table 2). The results indicated that  $\phi$  had a significant effect on both responses (CI and D[4,3] at  $p \leq 0.05$ ), while particle concentration did not have a significant effect. The combined effect of both factors ( $\phi$  and particle concentration) was statistically significant, suggesting a positive influence on the final properties of the emulsions.

The experimental results regarding CI and D[4,3] were analysed, and predictive models were developed. An ANOVA was conducted to evaluate the significance of the factors, with p-values computed to assess the statistical significance of the effects. A suitable correlation was observed between the observed and predicted values, according to the obtained  $R^2$  values of 88.3 and 91.0 % for both factors. Table 3 displays the ANOVA results of the estimated regression models. The regression proved to be statistically significant ( $F_{\text{calculated}} > F_{\text{table}}$ ), indicating its suitability for predictive purposes within the evaluated parameters range [41].

The mathematical models for CI and D[4,3] were obtained by considering the statistically significant factors ( $p \leq 0.05$ ). The Eqs. 3 and 4 show the re-parameterized models for CI and D[4,3].

$$y_1 \text{ (CI, \%)} = 3.01 + 12.33 x_1 + 22.81 x_1^2 + 25 x_1 x_2 \quad (3)$$

$$y_2 \text{ (D[4,3], } \mu\text{m)} = 6.36 + 11.77 x_1 + 9.46 x_1^2 + 10.42 x_1 x_2 \quad (4)$$

The response curves assembled from the models are shown in Fig. 5, while Table S1 summarises the detailed predicted and experimental values along with the corresponding relative errors. The response curves for the times 15 and 30 are presented in Figures S2 and S3, confirming the consistency of the results over time. The intermediary  $\phi$  value (0.45) resulted in a low CI value, regardless of the used SD particle concentration. However, the interdependency of both factors was observed at low and high  $\phi$  values, leading to a reduction in CI at both high and low particle concentrations. The same pattern was observed for the D[4,3] curves, where a stronger correlation was observed when low  $\phi$  values were combined with high SD particle concentrations, leading to decreased D[4,3] values. Other reported works indicate that the oil phase volume and particle concentration significantly influence the droplet size distribution [42]. This effect was also observed for formulation 8, where SD particle concentration was at the maximum, leading to the lowest D[4,3] (2.53  $\mu\text{m}$ ). For a fixed  $\phi$ , increasing the

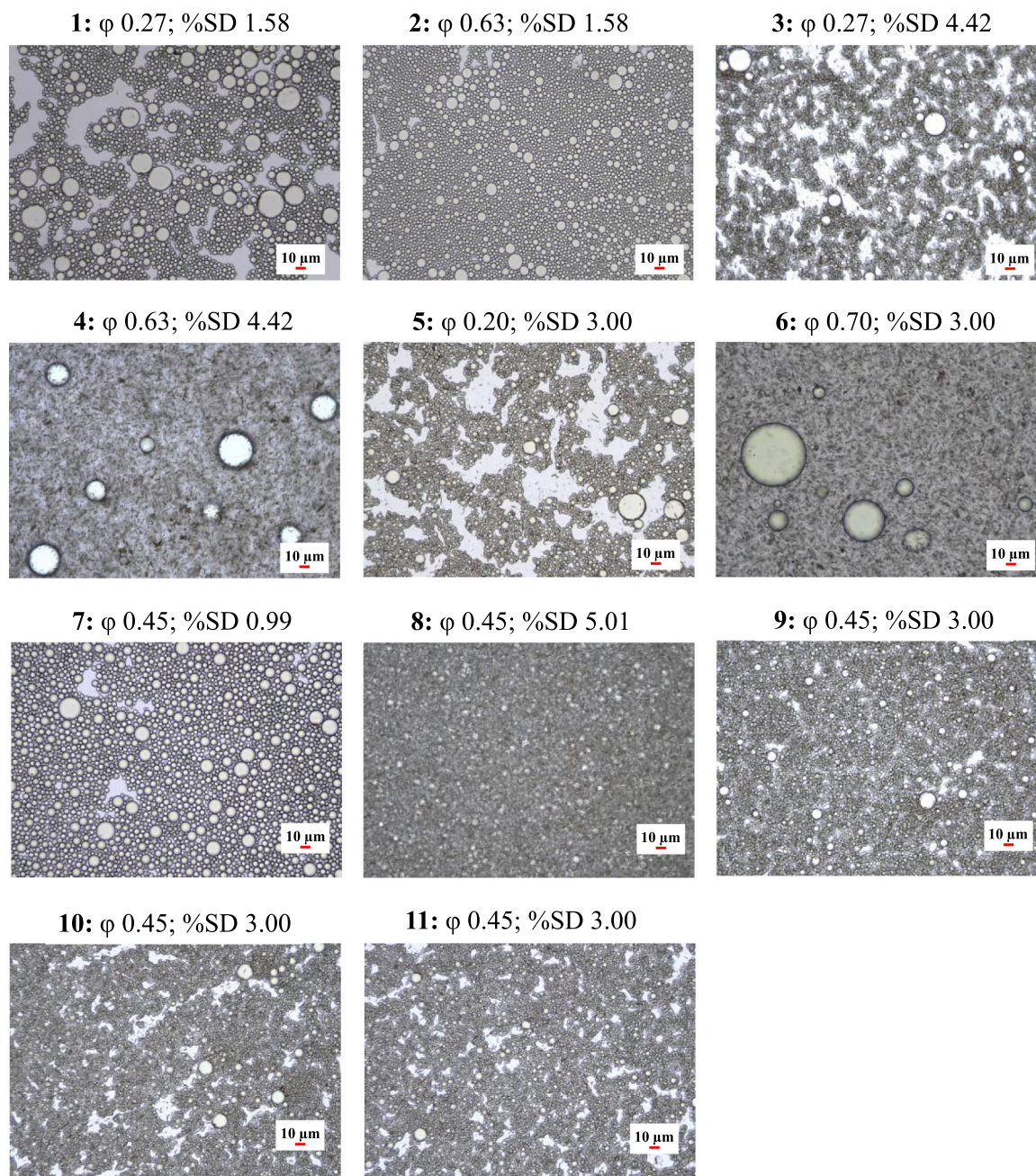


Fig. 4. Optical microscopy of the produced emulsions for the 11 runs defined by the Central Composite Rotatable Design  $2^2$ .

Table 2

Regression coefficients, standard errors, t-values, and p-values for Creaming index (CI, %) and mean particle size (D[4,3],  $\mu\text{m}$ ) responses based on Central Composite Rotatable Design (CCRD  $2^2$ ) results.

Factor	CI (%)				D[4,3] ( $\mu\text{m}$ )			
	Regression coefficient	Standard error	t (5)	p-value	Regression coefficient	Standard error	t (5)	p-value
Mean	0.00	6.46	0.00	1.000	4.01	3.88	1.03	0.349
$x_1$ (L)	12.23	3.96	3.09	0.027 *	11.77	2.38	4.95	0.004 *
$x_1$ (Q)	23.75	4.71	5.04	0.004 *	10.20	2.83	3.60	0.016 *
$x_2$ (L)	0.03	3.96	0.01	0.994	1.43	2.38	0.60	0.573
$x_2$ (Q)	3.20	4.71	0.68	0.528	2.49	2.83	0.88	0.419
$x_1 \cdot x_2$	25.00	5.60	4.47	0.007 *	10.42	3.36	3.10	0.027 *

(L): Linear terms; (Q): quadratic terms; \*Significant factors ( $p \leq 0.05$ );  $x_1$ : Oil volume fraction ( $\phi$ );  $x_2$ : SD particle concentration. CI ( $R^2$ : 91.76 %; adjusted  $R^2$ : 91.00 %); D[4,3] ( $R^2$ : 90.47 %; adjusted  $R^2$ : 88.30 %).

**Table 3**

Analysis of Variance (ANOVA) (Percentage of the explained variance ( $R^2$ ),  $F_{\text{calculated}}$  and  $F_{\text{table}}$  values) for the creaming index (CI, %) and D[4,3] ( $\mu\text{m}$ ) responses.

CI (%) $R^2 = 91.0\%$						
Sources of variation	SS	df	QM	Fcal	Ftab	p-value
Regression	6911.4	3	2303.8	23.6	4.4	0.00049
Residues	683.9	7	97.7	-	-	-
Lack of fit	683.9	5	136.8	Infinity	19.3	NaN
Pure error	0.0	2	0.0	-	-	-
Total	7595.2	10	-	-	-	-
D[4,3] ( $\mu\text{m}$ ) $R^2 = 88.3\%$						
Sources of variation	SS	df	QM	Fcal	Ftab	p-value
Regression	2096.2	3	698.7	17.6	4.4	0.00122
Residues	277.7	7	39.7	-	-	-
Lack of fit	277.6	5	55.5	2248.1	19.3	0.00044
Pure error	0.0	2	0.0	-	-	-
Total	2373.9	10	-	-	-	-

SS: Sum of squares; df: degrees of freedom; QM: quadratic means; NaN: Not a number (an undefined or unrepresentable value). P-value  $\leq 0.05$ .

concentration of the particles enables the formation of smaller droplet sizes, as the particles can cover a larger surface area [43,44].

As can be observed in Figure S1, Formulations 3 and 8 exhibited a slight destabilisation, characterised by increased CI, although D[4,3] values remained relatively unchanged. Additionally, the central points (9–11) and formulation 2 remained stable throughout the 30-day storage period, demonstrating the efficacy of C-PC particles in

stabilising emulsions.

After analysing the results, particularly the surface response profiles, three formulations (predicted as stable) were selected to proceed with the model's validation. Validation experiments were conducted to confirm the observed results in the response surfaces. The three formulations chosen to perform the validation tests, including low, medium, and high  $\phi$ , and SD particle concentrations, are represented in Table 4.

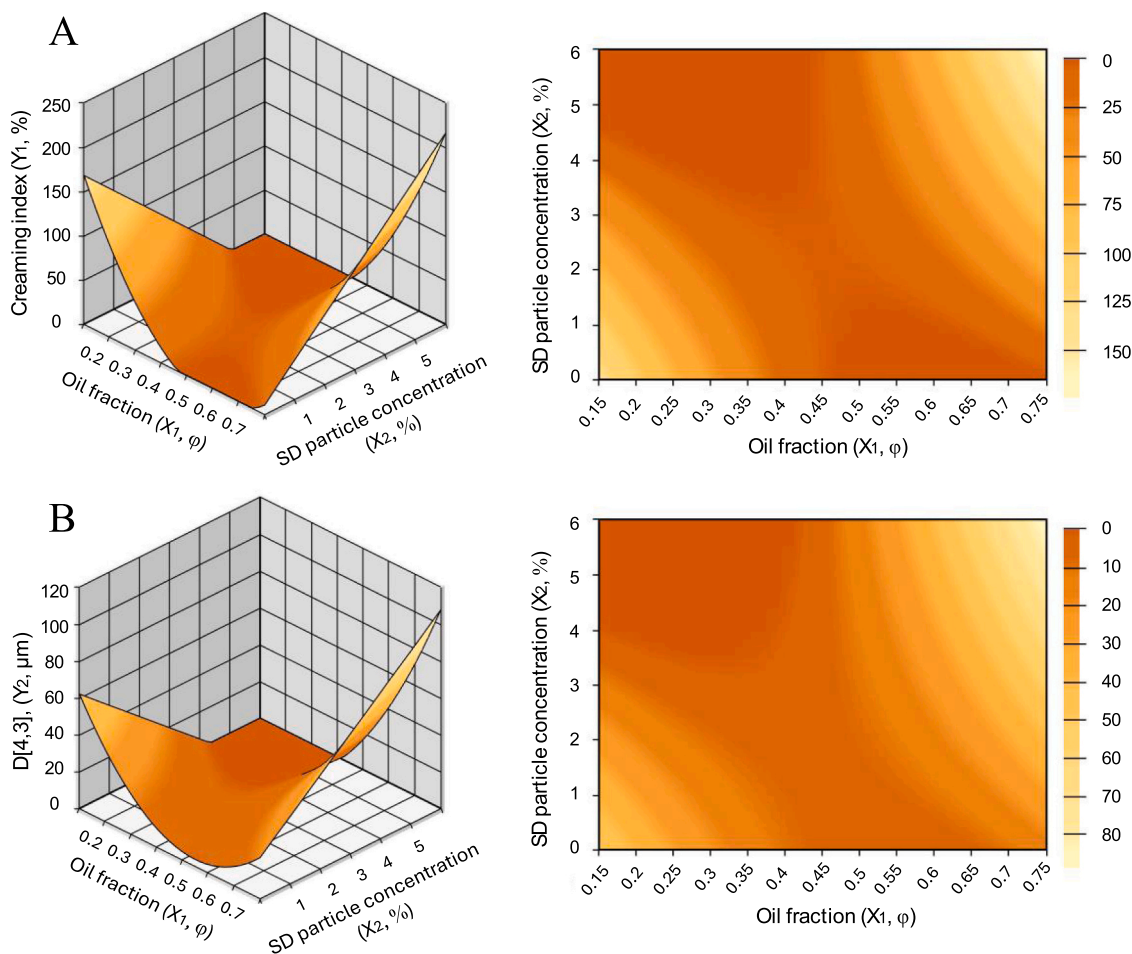
Table 5 presents the predictive and experimentally obtained values and their respective relative errors, although not all were calculated due to mathematical constraints. The models generally yielded higher values than the experimental results for both responses (CI and D[4,3]), suggesting that the actual experimental conditions led to more stable emulsions than those predicted by the models. Overall, formulation V1 emerged as the most robust over the storage time, presenting the lowest D[4,3] values.

The morphology of the optimised emulsions was analysed using optical microscopy (Fig. 6), supporting the experimentally obtained D[4,3] results. The emulsions exhibited tiny spherical droplets uniformly

**Table 4**

Formulations used to validate the Central Composite Rotatable Design (CCRD).

Runs	Oil volume fraction ( $\phi$ )	SD particle concentration (% wt.)
V1	0.30	4.50
V2	0.45	3.00
V3	0.60	1.55

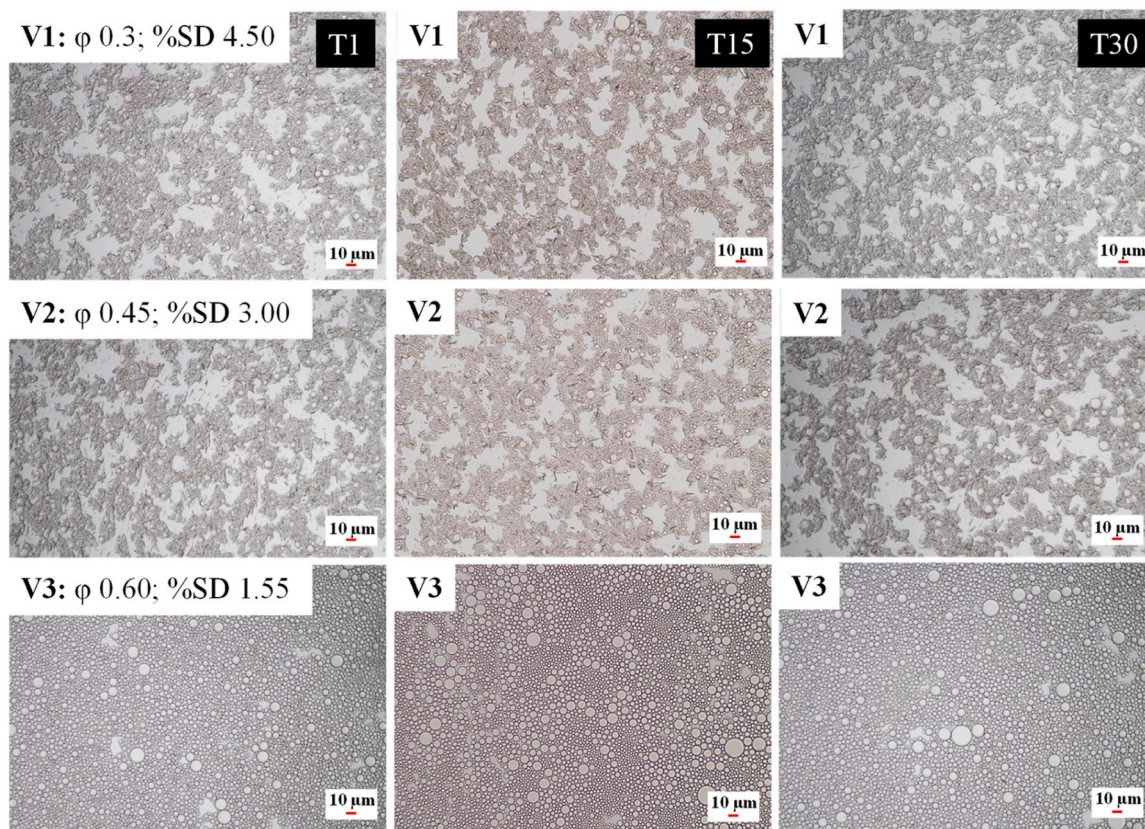


**Fig. 5.** Response surfaces and contour plots for creaming index (%) (A) and D[4,3] ( $\mu\text{m}$ ) (B) as a function of oil volume fraction ( $\phi$ ) and SD particle concentration (% wt.).

**Table 5**Experimental versus predicted values for the model validation runs for the response variables creaming index (CI, %) and droplet size (D[4,3],  $\mu\text{m}$ ).

Time 1						
Runs	CI (%)			D [4,3] ( $\mu\text{m}$ )		
	Experimental	Predicted	Re	Experimental	Predicted	Re
V1	0.00 $\pm$ 0.00	0.00	-	3.45 $\pm$ 0.75	0.00	-
V2	0.00 $\pm$ 0.00	3.15	-	4.45 $\pm$ 0.42	6.10	-37.07
V3	0.00 $\pm$ 0.00	7.62	-	8.64 $\pm$ 0.27	13.62	-57.64
Time 15						
Runs	CI (%)			D [4,3] ( $\mu\text{m}$ )		
	Experimental	Predicted	Re	Experimental	Predicted	Re
V1	0.00 $\pm$ 0.00	0.00	-	4.06 $\pm$ 0.35	0.00	-
V2	1.45 $\pm$ 2.51	6.18	-326.21	5.17 $\pm$ 0.21	6.32	-22.24
V3	0.00 $\pm$ 0.00	6.29	-	8.75 $\pm$ 0.34	14.81	-69.26
Time 30						
Runs	CI (%)			D [4,3] ( $\mu\text{m}$ )		
	Experimental	Predicted	Re	Experimental	Predicted	Re
V1	0.00 $\pm$ 0.00	3.40	-	3.70 $\pm$ 0.12	0.00	-
V2	1.45 $\pm$ 2.51	11.02	-660.00	4.67 $\pm$ 0.61	9.65	-106.64
V3	0.00 $\pm$ 0.00	9.43	-	12.73 $\pm$ 4.07	14.91	-17.12

Results are expressed as average  $\pm$  standard deviation. Relative error, Re (%) =  $[(\text{Experimental} - \text{Predicted})/\text{Experimental}] * 100$ . Some Re values were impossible to calculate once the experimental or predicted values were zero.

**Fig. 6.** Optical microscopy of the optimised formulations (V1, V2 and V3) along the 30 storage days (T1, T15 and T30).

distributed, particularly in the cases of V1 and V2. It was noted that the number of larger droplets increased after 30 days for emulsion V3, as confirmed by D[4,3] (8.75  $\mu\text{m}$  at time 15 and 12.73  $\mu\text{m}$  at time 30). Furthermore, the droplet arrangement varied among the formulations, suggesting different stabilisation mechanisms. V1, formulated with low  $\phi$  and high SD particle concentration, and V2, with intermediate values, displayed a similar morphology characterised by tiny droplets trapped

in a network-like structure. In contrast, V3 exhibited a typical emulsion morphology with uniformly distributed droplets.

#### 3.4. Colour, interfacial structure and rheological properties of optimised emulsions

Fig. 7 illustrates the visual characteristics of the optimised emulsions



Fig. 7. Visual appearance of the optimised formulations (V1, V2 and V3) at 1, 15 and 30 days.

Table 6

Colour parameters of the optimised formulations (V1, V2 and V3) at 1, 15 and 30 days.

Time 1					
Runs	L*	a*	b*	-	RGB
V1	64.06 ± 0.18	11.34 ± 0.23	60.70 ± 0.14	-	
V2	67.41 ± 0.31	4.26 ± 0.73	60.41 ± 0.46	-	
V3	72.00 ± 0.08	-11.09 ± 0.40	57.86 ± 0.27	-	
Time 15					
Runs	L*	a*	b*	ΔE	RGB
V1	63.72 ± 0.61	10.67 ± 2.63	59.11 ± 2.18	1.75	
V2	67.11 ± 0.96	5.40 ± 0.70	59.33 ± 0.93	1.60	
V3	70.90 ± 2.90	-8.64 ± 3.24	56.54 ± 1.11	2.99	
Time 30					
Runs	L*	a*	b*	ΔE	RGB
V1	64.56 ± 0.42	12.50 ± 0.89	59.38 ± 0.67	1.83	
V2	65.28 ± 0.34	4.03 ± 2.53	55.10 ± 0.76	5.72	
V3	70.56 ± 2.65	-6.84 ± 2.57	55.71 ± 0.75	4.98	

Results are expressed as average ± standard deviation.

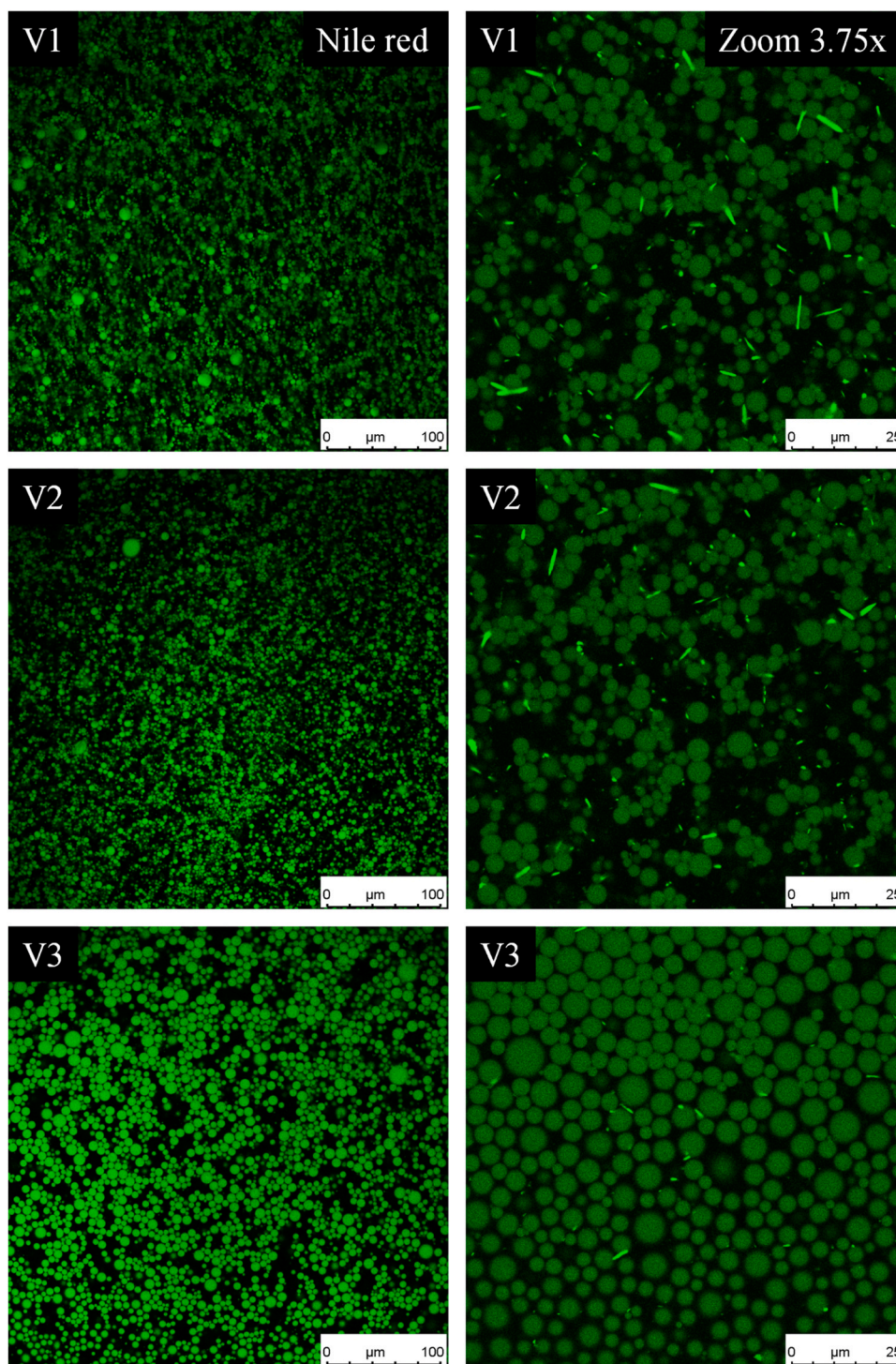
throughout the storage period alongside the associated colour parameters detailed in Table 6. The colour parameters and corresponding  $\Delta E$  during storage were also examined for the CCRD 2<sup>2</sup> 11 runs, with results in Table S2 (Supplementary Material).

Based on the  $\Delta E$  values, emulsion V1 consistently maintained its integral colour throughout the entire storage period. The other two formulations showed low  $\Delta E$  values (lower than 6), suggesting a negligible colour variation over the evaluated period. Their diverse composition led to various orange-yellow hues, making them suitable for developing food products with multiple colours.

Confocal analysis of the optimised emulsions was conducted to assess the SD particles' efficacy as Pickering stabilisers, and the results are presented in Fig. 8. The study was performed using the natural fluorescence of curcumin and the oil phase stained with Nile red, both at 488 nm, which emits green fluorescence. The images corroborated the optical microscopy results and the O/W nature of the emulsions, showing distinct droplet structures for V1 and V2 compared to V3. V1 and V2 showed an intricate network-like structure with smaller, entrapped droplets, while V3 displayed the typical emulsion morphology with larger, uniformly dispersed droplets. These

observations confirmed the smaller droplet sizes of V1 and V2 relative to V3. The natural fluorescence of curcumin-SDs within the stabilising SD particles was evident (images on the right), corroborating their adsorption at the oil/water interface and providing good coverage of the dispersed phase. According to reported data [45], nanonised hydrophilic curcumin, produced using a bottom-up approach through an antisolvent precipitation technique (amorphous form stabilised with protein), becomes dispersed throughout the whole emulsion (dispersed oil phase, continuous water phase, and interface), reducing the interfacial tension while yielding stable O/W emulsions. In contrast, large curcumin crystals (lipophilic) dissolve in the oil or remain in the aqueous continuous phase, resulting in unstable emulsions. In this study, confocal analysis confirmed the successful attachment of the particles at the O/W interface, supported by the stability present in all samples.

The rheological properties of the optimised emulsions were analysed in terms of the viscosity, storage modulus ( $G'$ ) and loss modulus ( $G''$ ), as shown in Fig. 9. The emulsion V1 presented the highest viscosity values, followed by V3 and V2. Certain studies suggest that the viscosity increases as the particle concentration rises [8,46], whereas others associate this effect with increased  $\phi$  [47]. This study's findings supported



**Fig. 8.** Confocal microscopy images of the optimised emulsions (V1, V2 and V3) showing the fluorescence of the oil phase stained with Nile red (left column) and the natural fluorescence of curcumin-SD particles (right column). A zoom of 3.75X was applied to the images on the right column.

this complexity, with formulations V1 (high particle concentration and low  $\phi$ ) and V3 (low particle concentration and high  $\phi$ ) exhibiting high viscosities. These results evidenced the direct impact of the particle concentration and  $\phi$  on the determined viscosity.

Fig. 9B illustrates the behaviour of Pickering emulsions regarding  $G'$  and  $G''$ .  $G'$  (storage modulus) indicates solid-like or elastic behaviour, whereas  $G''$  (loss modulus) reflects liquid-like or viscous behaviour. For emulsions V1 and V2, at low frequencies,  $G'$  exceeds  $G''$ , indicating a predominantly solid-like behaviour. This observation suggests a strong gel-like network for these samples, consistent with the morphological

observations. Such solid-like behaviour is advantageous for products like mayonnaise and salad dressings, as it helps to maintain their shape and stability during storage, effectively preventing phase separation [48,49]. However, as the frequency increases,  $G''$  surpasses  $G'$ , indicating a transition towards more liquid-like behaviour under higher deformation rates. This shear-thinning behaviour allows these emulsions to flow smoothly and be easily manipulated when mechanical forces are applied (e.g. scooping or spreading), particularly when dispensing a product from the container [50]. Additionally, the interfacial stabilisation provided by Pickering particles enhances the stability

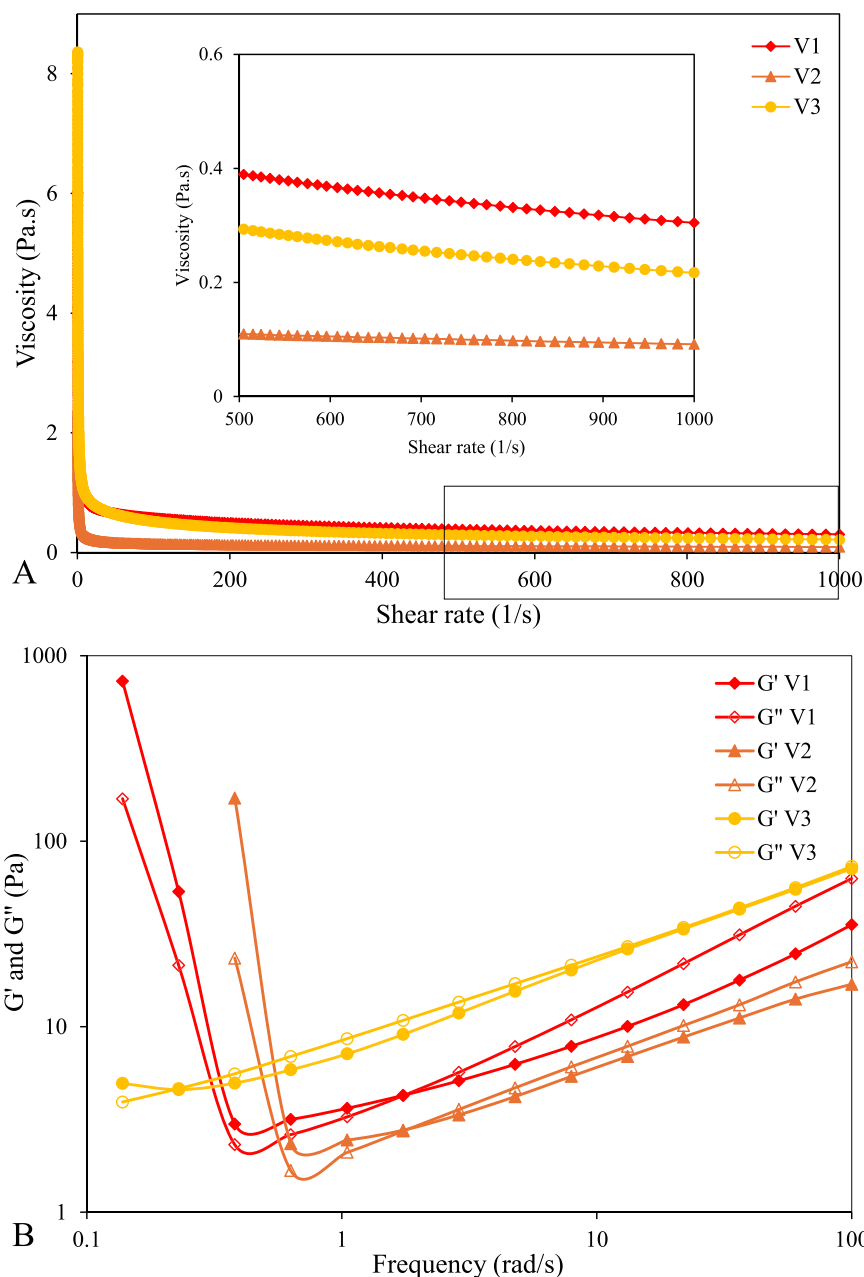


Fig. 9. Rheological properties of optimised emulsions (V1, V2 and V3): viscosity versus shear rate (A) and oscillatory frequency sweep curves,  $G'$  storage modulus and  $G''$  loss modulus (B).

of the emulsions, even when containing a bulk liquid-like behaviour under shear. In contrast, for emulsion V3, the difference between  $G'$  and  $G''$  is minimal across the frequency range, with both moduli converging at higher frequencies. When  $G'$  equals  $G''$ , it signifies that the sample exhibits ideal viscoelastic behaviour; that is, the emulsion behaves like a solid and a liquid simultaneously [51].

The emulsions' structural integrity, spreadability, and stability can ensure desirable texture, creaminess, and ease of manipulation, meeting consumer expectations for a consistent, high-quality product.

#### 4. Conclusions

This study explored the potential of curcumin-based solid dispersions (SDs) created with natural polymers such as pectin, maltodextrin, Arabic gum, potato starch, and k-carrageenan as Pickering stabilisers. Pectin-curcumin SDs (contact angle =  $48.0 \pm 3.6^\circ$ ) were the most effective,

providing a stable emulsion as confirmed by confocal microscopy. A design of experiments (CCRD  $2^2$ ) approach was used to examine how the formulation parameters, oil volume fraction ( $\phi$ ) and SD particle concentration affected emulsion stability. Creaming index (CI) and droplet size (D[4,3]) were the responses used to assess the emulsions' stability. The mathematical model indicated that intermediary  $\phi$  values (0.45) consistently reduced CI values (0–16.67 %) and D[4,3] (2.53–4.12  $\mu\text{m}$ ), regardless of SD particle concentration. CI decreased to 0 % when either  $\phi$  was low and SD concentration was high, or vice versa. This highlights the interdependency of these two factors in emulsion stability. Stable emulsions were achieved for formulations 2, 3, 8, and the central points (9–11).

Three optimised formulations were chosen to validate the mathematical models (V1 ( $\phi$  0.3, %SD 4.50), V2 ( $\phi$  0.45, %SD 3.00), and V3 ( $\phi$  0.60, %SD 1.55)). In all cases, the models pointed out higher CI and D [4,3] values than the experimental results, indicating that more stable

emulsions are obtained in practice (CI of 0 % and D[4,3] ranging from 3.45 to 12.73  $\mu\text{m}$ ). Optical microscopy corroborated their stability over 30 days and maintenance of colour parameters ( $\Delta E < 5$ ). From V1 to V3, the colour varied from orange to yellow ( $L^* = 64.06\text{--}72.00$ ,  $a^* = -11.09\text{--}12.50$ ,  $b^* = 55.10\text{--}60.70$ ), suggesting their potential for natural colouring applications. In terms of rheology, V1 and V2 emulsions demonstrated gel-like properties at low frequencies ( $G' > G''$ ) and liquid-like properties at high frequencies ( $G' < G''$ ), ensuring structural integrity and stability for products such as mayonnaise and salad dressings. In contrast, emulsion V3 exhibited ideal viscoelastic behaviour, showing a balance between solid and liquid characteristics across a broad frequency range.

This study highlights the potential of pectin-curcumin SDs in formulating stable, high-quality emulsions with desirable colour, texture, and stability. The findings provide valuable insights for designing emulsion-based products with tailored properties, offering an innovative approach to natural food product development.

### CRedit authorship contribution statement

**Santamaria-Echart Arantzazu:** Writing – review & editing, Supervision, Conceptualization. **de Rezende Stephany C.:** Writing – original draft, Methodology, Investigation, Conceptualization. **Dias Madalena M.:** Writing – review & editing, Supervision. **Ribeiro Andreia:** Methodology, Investigation. **Barreiro Filomena:** Writing – review & editing, Supervision, Resources, Funding acquisition, 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.

### Acknowledgements

FCT/MCTES (PIDDAC) support to CIMO (UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020)), UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020)); SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020); LSRE-LCM (UIDB/50020/2020 (DOI:10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI:10.54499/UIDP/50020/2020)); ALiCE LA/P/0045/2020 (DOI:10.54499/LA/P/0045/2020). FCT, for Stephany Cunha de Rezende's individual research grant (DOI: 10.54499/SFRH/BD/147326/2019), the institutional scientific employment program contract with Arantzazu Santamaria-Echart, and A. Ribeiro CEEC (DOI: 10.54499/2022.00798.CEECIND/CP1733/CT0009).

### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2025.137003.

### Data availability

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

### References

- R. Rayees, A. Gani, N. Noor, A. Ayoub, Z.U. Ashraf, General approaches to biopolymer-based Pickering emulsions, *Int. J. Biol. Macromol.* 267 (2024) 131430, <https://doi.org/10.1016/j.ijbiomac.2024.131430>.
- L. Chen, F. Ao, X. Ge, W. Shen, Food-grade pickering emulsions: preparation, stabilization and applications, *Molecules* 25 (2020) 3202, <https://doi.org/10.3390/molecules25143202>.
- J. Cheon, F. Haji, J. Baek, Q. Wang, K.C. Tam, Pickering emulsions for functional food systems, *J. Agric. Food Res* 11 (2023) 100510, <https://doi.org/10.1016/j.jafr.2023.100510>.
- A. Santamaria-Echart, I.P. Fernandes, S.C. Silva, S.C. Rezende, G. Colucci, M. M. Dias, M.F. Barreiro, New trends in natural emulsifiers and emulsion technology for the food industry, *Food Addit. IntechOpen* (2021) 1–32, <https://doi.org/10.5772/intechopen.99892>.
- W. Li, B. Jiao, S. Li, S. Faisal, A. Shi, W. Fu, Y. Chen, Recent advances on pickering emulsions stabilized by diverse edible particles: stability mechanism and applications, *Front Nutr.* 9 (2022) 1–17, <https://doi.org/10.3389/fnut.2022.864943>.
- L. Ming, H. Wu, A. Liu, A. Naem, Z. Dong, Q. Fan, G. Zhang, H. Liu, Z. Li, Evolution and critical roles of particle properties in Pickering emulsion: a review, *J. Mol. Liq.* 388 (2023) 122775, <https://doi.org/10.1016/j.molliq.2023.122775>.
- A. Sarkar, E. Dickinson, Sustainable food-grade Pickering emulsions stabilized by plant-based particles, *Curr. Opin. Colloid Interface Sci.* 49 (2020) 69–81, <https://doi.org/10.1016/j.cocis.2020.04.004>.
- X. Feng, H. Dai, L. Ma, Y. Fu, Y. Yu, H. Zhou, T. Guo, H. Zhu, H. Wang, Y. Zhang, Properties of Pickering emulsion stabilized by food-grade gelatin nanoparticles: influence of the nanoparticles concentration, *Colloids Surf. B Biointerfaces* 196 (2020), <https://doi.org/10.1016/j.colsurfb.2020.111294>.
- J. Wu, M. Shi, W. Li, L. Zhao, Z. Wang, X. Yan, W. Norde, Y. Li, Pickering emulsions stabilized by whey protein nanoparticles prepared by thermal cross-linking, *Colloids Surf. B Biointerfaces* 127 (2015) 96–104, <https://doi.org/10.1016/j.colsurfb.2015.01.029>.
- X. Hei, S. Li, Z. Liu, C. Wu, X. Ma, B. Jiao, H. Hu, J. Zhu, B. Adhikari, Q. Wang, A. Shi, Characteristics of Pickering emulsions stabilized by microgel particles of five different plant proteins and their application, *Food Chem.* 449 (2024) 139187, <https://doi.org/10.1016/j.foodchem.2024.139187>.
- S. Zhang, M. Holmes, R. Ettelaie, A. Sarkar, Pea protein microgel particles as Pickering stabilisers of oil-in-water emulsions: responsiveness to pH and ionic strength, *Food Hydrocoll.* 102 (2020) 105583, <https://doi.org/10.1016/j.foodhyd.2019.105583>.
- J.V.M. Benetti, J.T. do, P. Silva, V.R. Nicoletti, SPI microgels applied to Pickering stabilization of O/W emulsions by ultrasound and high-pressure homogenization: rheology and spray drying, *Food Res. Int.* 122 (2019) 383–391, <https://doi.org/10.1016/j.foodres.2019.04.020>.
- H. Dong, Q. Ding, Y. Jiang, X. Li, W. Han, Pickering emulsions stabilized by spherical cellulose nanocrystals, *Carbohydr. Polym.* 265 (2021) 118101, <https://doi.org/10.1016/j.carbpol.2021.118101>.
- N.A. Hadi, A. Marefati, M. Matos, B. Wiege, M. Rayner, Characterization and stability of short-chain fatty acids modified starch Pickering emulsions, *Carbohydr. Polym.* 240 (2020) 116264, <https://doi.org/10.1016/j.carbpol.2020.116264>.
- X. Wang, M. Heuzey, Chitosan-based conventional and Pickering emulsions with long-term stability, *Langmuir* 32 (2016) 929–936, <https://doi.org/10.1021/acs.langmuir.5b03556>.
- N. Nimaming, A. Sadeghpour, B.S. Murray, A. Sarkar, Hybrid particles for stabilization of food-grade Pickering emulsions: fabrication principles and interfacial properties, *Trends Food Sci. Technol.* 138 (2023) 671–684, <https://doi.org/10.1016/j.tifs.2023.06.034>.
- Z. Wei, Q. Huang, Edible Pickering emulsions stabilized by ovotransferrin – gum arabic particles, *Food Hydrocoll.* 89 (2019) 590–601, <https://doi.org/10.1016/j.foodhyd.2018.11.037>.
- Z. An, Z. Liu, H. Mo, L. Hu, H. Li, D. Xu, Preparation of Pickering emulsion gel stabilized by tea residue protein/xanthan gum particles and its application in 3D printing, *J. Food Eng.* 343 (2023) 111378, <https://doi.org/10.1016/j.jfoodeng.2022.111378>.
- W. Zhang, X. Gu, X. Liu, Z. Wang, Fabrication of Pickering emulsion based on particles combining pectin and zein: effects of pectin methylation, *Carbohydr. Polym.* 256 (2021) 117515, <https://doi.org/10.1016/j.carbpol.2020.117515>.
- Y. Jiang, D. Wang, F. Li, D. Li, Q. Huang, Cinnamon essential oil Pickering emulsion stabilized by zein-pectin composite nanoparticles: characterization, antimicrobial effect and advantages in storage application, *Int. J. Biol. Macromol.* 148 (2020) 1280–1289, <https://doi.org/10.1016/j.ijbiomac.2019.10.103>.
- Z. Ren, X. Huang, Y. Zhao, L. Shi, S. Yang, R. Jin, R. Lin, S. Liu, Z. Liu, Y. Zhang, W. Weng, Novel Pickering emulsions using polysaccharide-myosin complexes: effect of polysaccharide types, *Food Hydrocoll.* 157 (2024), <https://doi.org/10.1016/j.foodhyd.2024.110469>.
- Y. Du, L. Niu, X. Song, J. Niu, C. Zhang, K. Zhi, Dual-modified starch as particulate emulsifier for Pickering emulsion: structure, safety properties, and application for encapsulating curcumin, *Int. J. Biol. Macromol.* 266 (2024), <https://doi.org/10.1016/j.ijbiomac.2024.131206>.
- H. Li, X. Wu, W. Wu, Natural protein-polysaccharide-phenol complex particles from rice bran as novel food-grade Pickering emulsion stabilizers, *Int. J. Biol. Macromol.* 277 (2024), <https://doi.org/10.1016/j.ijbiomac.2024.134314>.
- S. Cen, Z. Li, Z. Guo, J. Shi, X. Huang, X. Zou, M. Holmes, Fabrication of Pickering emulsions stabilized by citrus pectin modified with  $\beta$ -cyclodextrin and its application in 3D printing, *Carbohydr. Polym.* 312 (2023), <https://doi.org/10.1016/j.carbpol.2023.120833>.
- L. Xu, Y. Xu, S. Hou, X. Zheng, Q. Cao, M. Chang, C. Feng, Y. Cheng, X. Geng, J. Meng, All-natural polysaccharide and protein complex nanoparticles from *Clitocybe squamulosa* as unique Pickering stabilizers for oil-in-water emulsions, *Int. J. Biol. Macromol.* 272 (2024), <https://doi.org/10.1016/j.ijbiomac.2024.132674>.
- C. Wang, J. Wu, C. Wang, C. Mu, T. Ngai, W. Lin, Advances in Pickering emulsions stabilized by protein particles: toward particle fabrication, interaction and arrangement, *Food Res. Int.* 157 (2022), <https://doi.org/10.1016/j.foodres.2022.111380>.

- [27] L.C. Ghirro, S. Rezende, A.S. Ribeiro, N. Rodrigues, M. Carochi, J.A. Pereira, L. Barros, B. Demczuk, M.F. Barreiro, A. Santamaria-Echart, Pickering emulsions stabilized with curcumin-based solid dispersion particles as mayonnaise-like food sauce alternatives, *Molecules* 27 (2022) 1250, <https://doi.org/10.3390/molecules27041250>.
- [28] S.C. de Rezende, A. Santamaria-Echart, H.H.S. Almeida, I. Marcet, M. Carpintero, M. Rendueles, M. Lopretti, M.M. Dias, M.F. Barreiro, Solid dispersions as effective curcumin vehicles to obtain κ-carrageenan functional films for olive oil preservation, *Int. J. Biol. Macromol.* 286 (2025) 138446, <https://doi.org/10.1016/j.ijbiomac.2024.138446>.
- [29] Y. Huang, W.-G. Dai, Fundamental aspects of solid dispersion technology for poorly soluble drugs, *Acta Pharm. Sin. B* 4 (2014) 18–25, <https://doi.org/10.1016/j.apsb.2013.11.001>.
- [30] S.C. de Rezende, O. Ferreira, A. Santamaria-Echart, M.M. Dias, M.F. Barreiro, Evaluating the potential of natural polymers for water-dispersible curcumin-based solid dispersion colourant systems for food applications, *J. Food Eng.* 371 (2024) 111986, <https://doi.org/10.1016/j.jfoodeng.2024.111986>.
- [31] Convert | EasyRGB, (n.d.). (<http://www.easyrgb.com/en/convert.php>) (accessed October 14, 2023).
- [32] V. Chandel, D. Biswas, S. Roy, D. Vaidya, A. Verma, A. Gupta, Current advancements in pectin: extraction, properties and multifunctional applications, *Foods* 11 (2022), <https://doi.org/10.3390/foods11172683>.
- [33] M. Krempel, K. Griffin, H. Khouryieh, Hydrocolloids as emulsifiers and stabilizers in beverage preservation. in: *Preservatives and Preservation Approaches in Beverages: Volume 15: The Science of Beverages*, Elsevier, 2019, pp. 427–465, <https://doi.org/10.1016/B978-0-12-816685-7.00013-6>.
- [34] J. Liu, J. Tan, X. Hua, Z. Jiang, M. Wang, R. Yang, Y. Cao, Interfacial properties of ultrahigh methoxylated pectin, *Int. J. Biol. Macromol.* 152 (2020) 403–410, <https://doi.org/10.1016/j.ijbiomac.2020.02.264>.
- [35] S. Huang, H. Wang, S. Wang, X. Sha, N. Chen, Y. Hu, Z. Tu, Pectin stabilized fish gelatin emulsions: physical stability, rheological, and interaction properties, *Front Nutr.* 9 (2022), <https://doi.org/10.3389/fnut.2022.961875>.
- [36] Q. Guo, J. Su, X. Shu, F. Yuan, L. Mao, J. Liu, Y. Gao, Production and characterization of pea protein isolate-pectin complexes for delivery of curcumin: effect of esterified degree of pectin, *Food Hydrocoll.* 105 (2020), <https://doi.org/10.1016/j.foodhyd.2020.105777>.
- [37] E.F. Ribeiro, P. Morell, V.R. Nicoletti, A. Quiles, I. Hernando, Protein- and polysaccharide-based particles used for Pickering emulsion stabilisation, *Food Hydrocoll.* 119 (2021) 106839, <https://doi.org/10.1016/j.foodhyd.2021.106839>.
- [38] C. Sun, S. Gunasekaran, Effects of protein concentration and oil-phase volume fraction on the stability and rheology of menhaden oil-in-water emulsions stabilized by whey protein isolate with xanthan gum, *Food Hydrocoll.* 23 (2009) 165–174, <https://doi.org/10.1016/j.foodhyd.2007.12.006>.
- [39] M. L'Estimé, M. Schindler, N. Shahidzadeh, D. Bonn, Droplet Size Distribution in Emulsions, *Langmuir* 40 (2024) 275–281, <https://doi.org/10.1021/acs.langmuir.3c02463>.
- [40] A. Araiza-Calahorra, A. Sarkar, Pickering emulsion stabilized by protein nanogel particles for delivery of curcumin: effects of pH and ionic strength on curcumin retention, *Food Struct.* 21 (2019) 100113, <https://doi.org/10.1016/j.foosr.2019.100113>.
- [41] M.I. Rodrigues, A.F. Iemma, Boca Raton, FL. *Experimental Design and Process Optimization*, CRC press, 2014, <https://doi.org/10.1201/b17848>.
- [42] J. Marto, L. Gouveia, A. Duarte, L.M. Gonçalves, S.M.C. Silva, F. Antunes, A.A.C. C. Pais, E. Oliveira, A.J. Almeida, H.M. Ribeiro, Starch-based Pickering emulsions for topical drug delivery: a QbD approach, *Colloids Surf. B Biointerfaces* 135 (2015) 183–192, <https://doi.org/10.1016/j.colsurfb.2015.07.024>.
- [43] L.E. Low, S.P. Siva, Y.K. Ho, E.S. Chan, B.T. Tey, Recent advances of characterization techniques for the formation, physical properties and stability of Pickering emulsion, *Adv. Colloid Interface Sci.* 277 (2020) 102117, <https://doi.org/10.1016/j.cis.2020.102117>.
- [44] Y. Chevalier, M.A. Bolzinger, Emulsions stabilized with solid nanoparticles: Pickering emulsions, *Colloids Surf. A Physicochem Eng. Asp.* 439 (2013) 23–34, <https://doi.org/10.1016/j.colsurfa.2013.02.054>.
- [45] N.P. Aditya, I.E. Hamilton, I.T. Norton, Amorphous nano-curcumin stabilized oil in water emulsion: physico chemical characterization, *Food Chem.* 224 (2017) 191–200, <https://doi.org/10.1016/j.foodchem.2016.12.082>.
- [46] A. Ribeiro, Y.A. Manrique, I.C.F.R. Ferreira, M.F. Barreiro, J.C.B. Lopes, M.M. Dias, Nanohydroxyapatite (n-HAp) as a pickering stabilizer in oil-in-water (O/W) emulsions: a stability study, *J. Dispers. Sci. Technol.* (2022) 1–13, <https://doi.org/10.1080/01932691.2020.1845199>.
- [47] S. Kinra, R. Pal, Rheology of Pickering emulsions stabilized and thickened by cellulose nanocrystals over broad ranges of oil and nanocrystal concentrations, *Colloids Inter.* 7 (2023) 36, <https://doi.org/10.3390/colloids7020036>.
- [48] A. Akcicek, S. Karasu, F. Bozkurt, S. Kayacan, Egg yolk-free vegan mayonnaise preparation from Pickering emulsion stabilized by gum nanoparticles with or without loading olive pomace extracts, *ACS Omega* 7 (2022) 26316–26327, <https://doi.org/10.1021/acsomega.2c02149>.
- [49] Z.H. Tekin-Cakmak, I. Atik, S. Karasu, The potential use of cold-pressed pumpkin seed oil by-products in a low-fat salad dressing: the effect on rheological, microstructural, recoverable properties, and emulsion and oxidative stability, *Foods* 10 (2021), <https://doi.org/10.3390/foods10112759>.
- [50] A.A. Gkinali, A. Matsakidou, T. Moschakis, A. Paraskevopoulou, Egg-free mayonnaise-type emulsions stabilized with proteins derived from the larvae of *Tenebrio molitor*, *Food Hydrocoll.* 156 (2024), <https://doi.org/10.1016/j.foodhyd.2024.110249>.
- [51] H. Nciri, N. Huang, V. Rosilio, M. Trabelsi-Ayadi, M. Benna-Zayani, J.-L. Grossiord, Rheological studies in the bulk and at the interface of Pickering oil/water emulsions, *RheologicaActa* 49 (2010) 961–969, <https://doi.org/10.1007/s00397-010-0471-8>.