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From biopolymers to Pickering emulsions: a green chemistry strategy to replace microplastics in next-generation cosmetics

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With the rising interest in eco-safe cosmetic products due to ongoing governmental restrictions and growing public concern regarding the effects of microplastics derived from synthetic products, research for biodegradable alternatives from renewable materials has been accelerated. Carbohydrate-based polymers can be considered suitable materials due to their excellent biodegradability, renewability, abundance, and versatility. In this study, microparticles based on starch, chitosan, and cellulose derivatives were produced using different methods to obtain micrometric particles with specific structural and rheological properties. In parallel, a formulation strategy was developed to establish a sustainable Pickering emulsion platform capable of incorporating and exploiting the functional properties of the produced biodegradable microparticles. Micrometric particles from native and chemically modified tapioca starch were found compatible with the optimized Pickering emulsion formulation. At the same time, the pseudoplastic flow behavior was maintained, and specific effects regarding droplet size distribution were achieved. The results provided evidence that the synthesized microparticles could serve effectively and safely as co-stabilizers and structuring-modifying agents for sustainable cosmetic emulsion formulation, confirming the appropriateness of the proposed biodegradable starch microparticles. In contrast, chitosan-based microparticles did not yield satisfactory texture or stabilization under the tested conditions, pointing toward additional optimization and investigation. This research confirms that chemically modified starch microparticles can be introduced effectively and safely as eco-safe, sustainable ingredients for next-generation, microplastic-free cosmetic formulations.

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1. Introduction

Plastic microbeads in cosmetics and personal care products have recently drawn global attention as major contributors to microplastic (MP) pollution.¹ Studies show that MPs are a risk to

terrestrial and aquatic ecosystems and exhibit toxicity to plants^{2,3} and human cells.⁴ MPs are tiny plastic particles (1 μm to 5 mm), classified as primary or secondary independent of their origin or shape.⁵ Primary MPs are intentionally manufactured for applications such as cosmetics, exfoliants, cleaning products, and biomedical uses, whereas secondary MPs result from environmental degradation. Cosmetic microbeads are typically round and smooth to prevent skin irritation,⁶ with about 93% made of polyethylene. Other polymers include polyethylene terephthalate, polypropylene, polymethyl methacrylate, polyester, polyurethane, and nylon.⁷

Plastic microspheres were first incorporated into cleansing and exfoliating products for their mild abrasive action, enabling effective yet gentle exfoliation with high skin compatibility. Over time, their role expanded to include film-forming, thickening, viscosity regulation, or emulsion stabilization, enhancing formula stability and prolonging shelf life. In creams, lotions, or makeup, MPs improve texture, spreadability and deliver a smooth, uniform sensory experience during skin application.

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MPs have long been valued for their chemical inertness, absence of odor, and skin compatibility.⁶ From an industrial perspective, the low cost of MP raw materials improved economic profitability for cosmetic manufacturers. However, these advantages come at a high environmental price: MPs persist in ecosystems and accumulate in aquatic environments;⁸ due to the limited efficiency of conventional treatment processes, a significant fraction escapes filtration and reaches natural ecosystems^{9,10} This growing evidence underscores the urgent need for sustainable alternatives to MPs in personal care products.

Beyond their long-lasting physical persistence, MPs can leach harmful additives, such as phthalates and bisphenol A, and act as carriers for contaminants, including heavy metals (Al, Cd, Co, Cr, Cu, Hg, Mn, Pb), hydrophobic organic compounds, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, pesticides and persistent organic pollutants.^{11,12} MPs enter the human body *via* ingestion, inhalation, or dermal absorption and may accumulate in blood, breast milk, and placental tissue.¹³

Chronic exposure is increasingly linked to inflammation, immune dysregulation, oxidative stress, and progression of diseases such as cancer and endocrine disorders.^{14,15} The effects of exposure to MPs on human health are multifactorial and largely depend on the route of exposure. Evidence consistently shows MPs trigger pathological alterations associated with long-term health outcomes.^{16–18} These concerns have driven governments, industries, and non-governmental organizations to act, yet current regulations remain partial and inconsistently enforced, mostly targeting rinse-off products, while leave-on cosmetics still contain large amounts of synthetic polymers.

A 2022 Plastic Soup Foundation report revealed that roughly 87% of major European cosmetic brands continue to use MPs, underscoring the urgent need for effective bans and sustainable alternatives.¹⁸ A major direction within the green transition involves the substitution of traditional petroleum-based polymers with natural or chemically modified biopolymers capable of reproducing the functional roles of MPs, such as texturizing, film-forming, viscosity control, and stabilization.¹⁹

The transition to natural, biodegradable materials offers long-term benefits, reducing environmental persistence of MP accumulation, eliminating toxic additives and aligning personal care products with circular economy principles. It also lowers ecological impact, enhances consumer trust and market competitiveness, and supports compliance with emerging regulatory pressures such as EU Regulation 2023/205.

Natural biopolymers are promising sustainable alternatives to synthetic polymers conventionally used in cosmetic formulation and packaging. Obtained from renewable sources, such as plant biomass and marine organisms, these polymers are biodegradable, biocompatible, and of low toxicity, making them an environmentally friendly substitute.²⁰ In this work, we have developed and characterized environmentally friendly microparticles obtained by three naturally occurring polysaccharides: starch, chitosan, and sodium carboxymethyl cellulose (CMC). Microparticles were produced using two different methods: precipitation or spray drying. The use of an environmentally

friendly alcohol as an antisolvent²¹ – such as ethanol – in the precipitation method further enhanced process sustainability by avoiding toxic solvents and high temperatures, achieving high yields. Similarly, spray drying enabled the production of microparticles without solvent usage, offering a scalable route for industrial use.

Starch, the second most abundant natural biopolymer after cellulose, consists of amylose and amylopectin in proportions and granular morphology that vary depending on the botanical origin. Amylose linear structure enables gel and film formation, while amylopectin branched conformation affects its crystallinity and physicochemical properties, key features for cosmetic applications: film formation, viscosity control, and moisture retention. Native starch is not directly used due to the poor solubility. Instead, physically, chemically, or enzymatically modified forms, (pregelatinized, oxidized, cationic, and esterified) are generally used in cream, lotion, and emulsion applications, as they improve dispersibility, stability, and tactile properties while adding moisturizing and absorbent benefits.²²

Chitosan is the deacetylated derivative of chitin and the second most abundant biopolymer after cellulose, a cationic polysaccharide widely recognized for its filmogenic, moisturizing, antimicrobial, and biocompatible characteristics.^{23,24} Widely applied in skin, hair, and oral care, it acts as a humectant and conditioning agent through electrostatic interactions with negatively charged biological surfaces, enhancing hydration, reducing transepidermal water loss, and forming a protective film.²⁴ Its antioxidant, antimicrobial, and wound-healing properties further extend applications in dermatological and cosmeceutical formulations.

Sodium carboxymethyl cellulose (CMC) is an important cellulose derivative widely employed in numerous fields. It is a water-soluble cellulose ether derived from the partially substituted ionic carboxymethyl ($-\text{CH}_2\text{COOH}$) of the cellulose hydroxyl group.²⁵ It acts as a thickener, stabilizer, and film former to provide better texture, retard the release of actives, and hydrate the skin for longer periods in cosmetic preparations.

In addition to their film-forming, thickening, and sensory-modifying properties, particulate biopolymers have recently attracted growing interest as functional components in emulsion systems. Solid particles can act as stabilizing agents in Pickering emulsions, a class of emulsions in which droplets are stabilized by particles adsorbed at the oil–water interface rather than by conventional molecular surfactants.²⁶ Once adsorbed at the interface, these particles form a protective barrier that prevents droplet coalescence, thereby enhancing emulsion stability. The stabilization mechanism is generally attributed to the strong and often irreversible adsorption of particles at the oil–water interface, which reduces the free energy of the system and creates a steric or electrostatic barrier around the droplets. The effectiveness of this process depends on several particle characteristics, including size, shape, surface chemistry, and amphiphilicity, which determine their ability to interact with both phases and remain anchored at the interface.²⁷

Due to their improved stability and reduced reliance on synthetic surfactants, Pickering emulsions have attracted



increasing attention in fields such as food science, pharmaceuticals, catalysis, and cosmetic formulations. In particular, the use of biodegradable and bio-derived particles as Pickering stabilizers represents a promising strategy to develop more sustainable formulations while maintaining desirable functional performance.²⁸ This study focuses on the synthesis and characterization of microparticles based on tapioca starch, chitosan, and carboxymethyl cellulose (CMC) as eco-friendly alternatives to conventional MPs, addressing growing environmental concerns. In addition, cosmetic formulations incorporating these microparticles were developed and systematically evaluated for performance and stability within representative emulsion systems.

2. Results

In this study, we investigated several methodologies for the synthesis of environmentally sustainable microparticles derived from starch, chitosan and carboxymethyl cellulose-based materials (Fig. 1).

First, tapioca starch microparticles were successfully synthesized using a solvent-precipitation approach with ethanol or 1-octanol as the solvent. The incorporation of oleic acid in the synthesis process was intended to enhance the hydrophobic character of starch by promoting the formation of starch-lipid complexes. Oleic acid, a long-chain monounsaturated fatty acid (C₁₈H₃₄O₂), was selected due to its low cost, non-toxicity, and chemical inertness, making it suitable for sustainable cosmetic applications.²⁹

During the reaction, heating the starch dispersion in the presence of oleic acid at 50 °C facilitated the partial gelatinization of starch granules and promoted molecular interactions between amylose helices and the hydrophobic tail of oleic acid.³⁰ The structural modification enhances the overall hydrophobicity of the polymeric matrix, thereby improving the compatibility of the resulting microparticles with lipidic environments and increasing their potential for adhesion and interaction with the skin surface. The precipitation of the modified starch phase in a hydroalcoholic solution allowed the controlled formation of microparticles through phase separation, yielding well-defined and easily recoverable structures after lyophilization.³¹

To investigate another alternative solvent approach for microparticle formation, the aqueous starch-oleic acid solution was precipitated into pure 1-octanol, a non-polar solvent immiscible with water. The immiscibility of 1-octanol with the aqueous phase allowed controlled formation of discrete microparticles through phase separation. Additionally, the use of octanol facilitated the recovery and reuse of the antisolvent, minimizing waste and enabling its recycling for subsequent syntheses. This approach provided an effective and sustainable strategy for producing starch-based microparticles with defined morphology and hydrophobic characteristics.

Overall, the introduction of oleic acid as a mild surface-modifying agent proved effective in tailoring the physico-chemical properties of tapioca starch microparticles. This modification strategy offers a simple, cost-effective, and environmentally benign route to enhance the surface

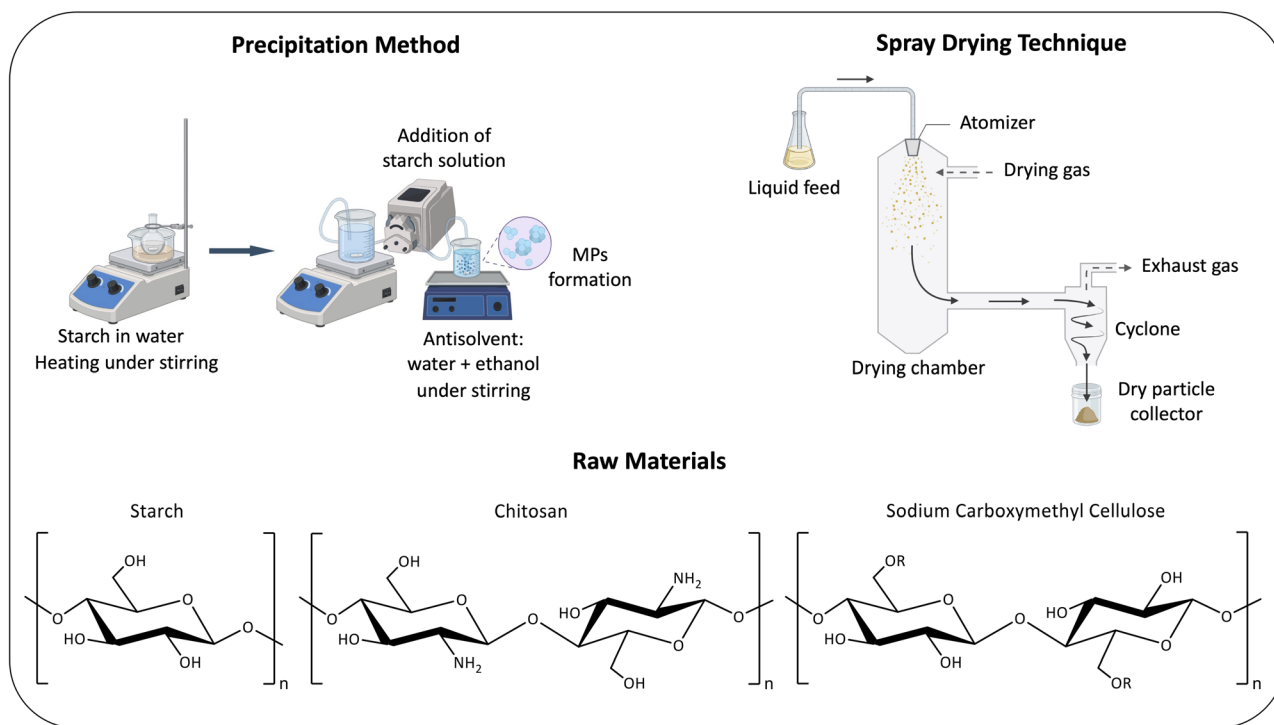


Fig. 1 Comparative illustration of the microparticle manufacturing methods used in this study. Precipitation process based on solvent-non-solvent mixing. Spray-drying process involving atomization of the polymer solution and instantaneous solvent evaporation to obtain dry microparticles.



hydrophobicity of starch-based materials, potentially improving their interaction with the skin, adhesion to lipidic layers, and functional performance in cosmetic and dermatological formulations.³²

The structural and morphological characterization of the tapioca starch microparticles provided further confirmation of the successful modification achieved through oleic acid incorporation. The chemical interactions between starch and oleic acid (Fig. 2A) within the microparticle matrix were evaluated using FTIR spectroscopy. The absorption band observed at 2900 cm^{-1} , corresponding to the symmetric and asymmetric C–H stretching vibrations of aliphatic $-\text{CH}_2$ groups, together with the characteristic C=O stretching band at 1749 cm^{-1} attributed to the carboxylic group of oleic acid, confirmed the occurrence of molecular interactions between the two components (Fig. 2B). These observations are consistent with the characteristic bands of oleic acid, typically reported at $2854\text{--}2923\text{ cm}^{-1}$ for $-\text{CH}_2$ groups and around $1708\text{--}1749\text{ cm}^{-1}$ for the C=O stretching vibration.³³

The microparticle morphology was analysed using scanning electron microscopy (SEM). Both unmodified and oleic acid-

modified starch microparticles exhibited a generally spherical morphology with diameters ranging from approximately 8 to $14\text{ }\mu\text{m}$ (Fig. 2C). The surface of the modified particles appeared slightly smoother and more compact compared to the native starch granules, suggesting a partial rearrangement of the polymeric chains upon complex formation. Despite the morphological resemblance, the incorporation of oleic acid was found to alter the rheological behavior of the starch-based material, indicating modifications in interparticle interactions and overall texture. These changes are particularly relevant in cosmetic formulations, as they may influence product stability, spreadability, and sensory performance.

Microparticles synthesized in the octanol medium exhibited comparable dimensions but showed an increased surface density and reduced hydrophilicity, likely due to the higher degree of lipid association promoted by the non-polar solvent environment. Such features highlighted the potential of solvent polarity and lipid content as key parameters to fine-tune the physicochemical and functional properties of starch-derived microparticles for cosmetic and dermatological applications.

To enhance the hydrophobicity and interfacial properties of tapioca starch, a two-step functionalization strategy was employed. Initially, tryptophan was reacted with poly(isobutylene-*alt*-maleic anhydride) (PMA) to form a modified polymer (PMW) (Fig. 2D). PMA was chosen as a biocompatible, safe, and reactive copolymer that could efficiently promote the attachment of the amino acid while introducing additional hydrophobic character through its aliphatic backbone. This approach facilitated the subsequent covalent interaction between the functionalized polymer and starch, enabling the formation of microparticles with tailored surface properties.³⁴ Unlike traditional synthetic beads, this polymeric linker is integrated at a molecular level onto the polysaccharide matrix; upon biological degradation of the starch component, the linker fragments do not form persistent solid microplastics, but rather result in dispersed, water-soluble oligomers, significantly reducing the environmental footprint of the formulation.

FT-IR analysis (Fig. 2E) of the resulting PMW-functionalized starch microparticles revealed a characteristic band in the $1700\text{--}1740\text{ cm}^{-1}$ region, suggesting the introduction of carbonyl-containing groups. Modifications in the carbohydrate fingerprint region ($1000\text{--}1150\text{ cm}^{-1}$) indicated alterations in the glycosidic network. These spectral changes are consistent with oxidative or structural modifications typically associated with PMW processing (Fig. S1), confirming that the treatment effectively altered the polysaccharide chemical environment.

SEM imaging showed that PMW-modified microparticles exhibited approximately spherical morphologies of $13\text{ }\mu\text{m}$, similar to native starch particles (Fig. 2F). Notably, the PMW-modified particles appeared more uniform and less aggregated compared to the PMA-modified polymer alone, confirming that the pre-functionalization with the amino acid promoted a more controlled particle formation and improved dispersion. This sequential functionalization strategy, using PMA as a polymeric linker to attach amino acid residues to starch, provided a simple and effective route to produce microparticles with enhanced hydrophobicity, improved

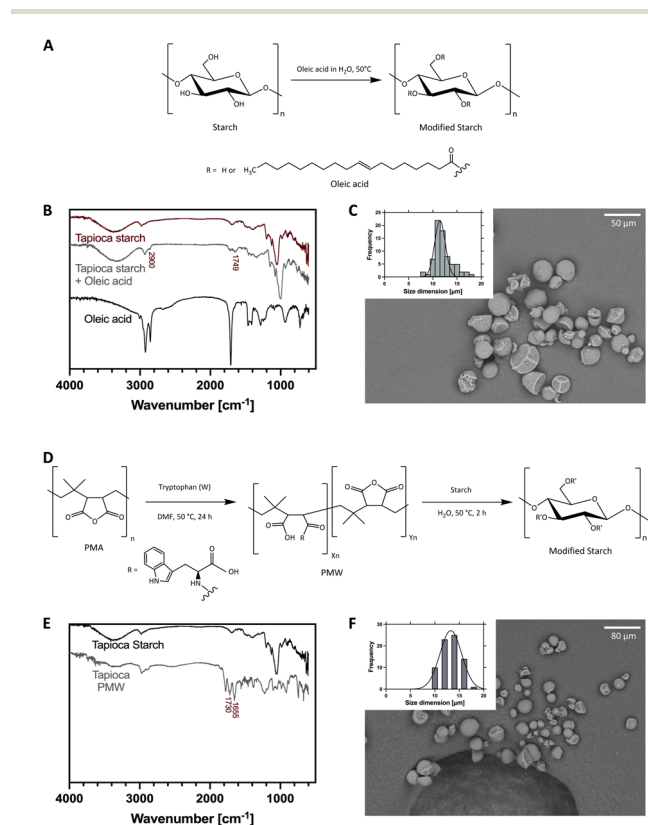


Fig. 2 Characterization of biopolymer modification and morphology. Chemical synthesis schemes. Proposed reaction mechanisms for the modification of (A) tapioca starch with oleic acid and (D) PMA-PMW-starch grafting. The chemical structures illustrate the transition from the native polymer to the hydrophobically modified derivatives. (B and E): FT-IR spectra. Fourier-transform infrared spectroscopy analysis comparing the native biopolymers with their modified counterparts. (C and F): SEM micrographs and particle size distribution. Scanning Electron Microscopy (SEM) images displaying the surface morphology and topography of the modified biopolymers.



particle stability, and potential application in cosmetic formulations. By combining the chemical versatility of PMA and the functional properties of amino acids, the resulting microparticles exhibited tunable surface properties that could facilitate better adhesion to skin and improved compatibility with lipid-containing products.

To explore the versatility of our natural biopolymer-based approach, chitosan and sodium carboxymethyl cellulose (Na-CMC) were selected as alternative matrices for the synthesis of microparticles. A spray-drying process, an environmentally friendly and scalable technique widely used for the encapsulation and stabilization of bio-based materials, was applied. Unlike precipitation methods, spray drying allows the continuous production of uniform, dry microparticles in a single step, eliminating the need for organic solvents and additional purification, thus aligning with the principles of green chemistry and sustainable manufacturing. Chitosan microparticles were successfully obtained by dissolving the polymer in dilute acetic acid and incorporating oleic acid as a hydrophobic modifier prior to atomization. Oleic acid was introduced to enhance the

hydrophobic character of the chitosan matrix (Fig. 3A) through ionic and hydrogen bonding interactions between its carboxylic group and the amino functionalities of chitosan. This modification aimed to improve skin adhesion, moisture retention, and overall compatibility with lipidic cosmetic formulations.

The FT-IR spectrum (Fig. 3B) of spray-dried chitosan microparticles revealed a characteristic absorption band at 1730 cm^{-1} , corresponding to the $\text{C}=\text{O}$ stretching vibration of the carboxylic group from oleic acid. The modified sample displayed a much stronger aliphatic $\text{C}-\text{H}$ stretching around $2920\text{--}2850\text{ cm}^{-1}$. Additionally, a reduction in the intensity of the $\text{N}-\text{H}$ bending region ($\sim 1590\text{ cm}^{-1}$) was noted, a feature compatible with amide bond formation following reaction between chitosan amino groups and the carboxyl function of oleic acid. These spectral signatures strongly suggested that oleic acid was not merely adsorbed but chemically grafted onto the chitosan backbone. SEM analysis showed that the chitosan microparticles possessed a spherical to slightly wrinkled morphology, typical of spray-dried particles, with a mean diameter ranging between 5 and $10\text{ }\mu\text{m}$ (Fig. 3C). The uniformity and low degree of aggregation indicated that the atomization and drying parameters were optimized. The surface morphology suggested the formation of dense particles with limited porosity, consistent with the hydrophobic modification induced by oleic acid. Similarly, Na-CMC, a water-soluble cellulose derivative rich in carboxyl and hydroxyl groups, was functionalized with oleic acid (Fig. 3D) and processed under optimized spray-drying conditions. The introduction of oleic acid into Na-CMC was intended to modulate its hydrophilic-hydrophobic balance and improve its film-forming ability in cosmetic applications.³⁵

FT-IR analysis (Fig. 3E) of Na-CMC microparticles displayed characteristic absorption bands at 2915 cm^{-1} (CH_2 stretching) and 1730 cm^{-1} ($\text{C}=\text{O}$ stretching of oleic acid). The coexistence and partial overlap of these bands confirmed that oleic acid was effectively associated with the polymer matrix, likely through ionic and hydrogen-bonding interactions. Morphological evaluation by SEM revealed that the Na-CMC microparticles exhibited a smooth, spherical surface, with diameters of $5\text{ }\mu\text{m}$ (Fig. 3F). The smooth surface and uniform size distribution are advantageous features for topical delivery systems, enhancing dispersibility and aesthetic performance in cosmetic formulations.

Overall, spray drying proved to be a simple, solvent-free, and energy-efficient approach for producing bio-based microparticles. The ability to control process parameters (feed rate, temperature, and air pressure) enabled fine-tuning of particle morphology and size distribution, while the incorporation of oleic acid provided a tunable strategy to modulate surface hydrophobicity, thereby improving compatibility with lipid-based and skin-contact applications.³⁶

2.1. Effect of chemical modification on sensory and functional skin-related properties

A preliminary consumer evaluation was performed to compare the sensory attributes of the native and chemically modified powders. Participants rated color, consistency, spreadability,

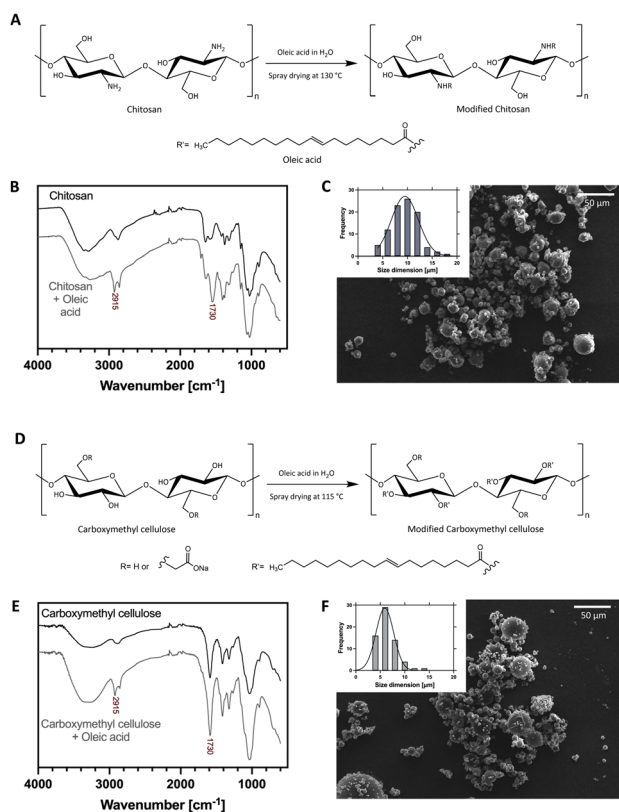


Fig. 3 Characterization of biopolymer modification and morphology. Chemical synthesis schemes. Proposed reaction mechanisms for the modification of (A) chitosan modification with oleic acid, and (D) carboxymethyl cellulose (CMC) modification. The chemical structures illustrate the transition from the native polymer to the hydrophobically modified derivatives. (B and E): FT-IR Spectra. Fourier-transform infrared spectroscopy analysis comparing the native biopolymers with their modified counterparts. (C and F): SEM micrographs and particle size distribution. Scanning Electron Microscopy (SEM) images displaying the surface morphology and topography of the modified biopolymers.

absorption, and softness according to the predefined protocol. Among the functional attributes assessed during and after application (spreadability, absorption, and softness), statistical analysis revealed distinct modification-dependent effects across the three biopolymers tested (Fig. 4).

For chitosan, the chemical modification with oleic acid resulted in a marked and consistent improvement across all evaluated attributes. Modified chitosan received significantly higher scores for spreadability, absorption, and softness compared with the native material ($p < 0.0001$ for all comparisons). This uniform enhancement suggests that functionalization substantially alters particle skin interactions, improving both tactile behavior during application and the perceived finish on the skin.

In contrast, the effect of modification on tapioca starch was more selective. No significant differences were observed for spreadability and softness (ns), indicating that the chemical modification did not perceptibly change the mechanical behavior of the powder during application or the tactile sensation after deposition. However, absorption increased significantly in the modified starch ($p < 0.0001$), suggesting an enhanced capacity of the treated particles to interact with skin moisture. This result indicates that the modification primarily influences hydration-related interactions without altering perceived handling properties.

CMC exhibited a response pattern comparable to modified chitosan, indicating enhanced performance. Statistical analysis confirmed markedly better spreadability, faster absorption, and increased softness compared to the control ($p < 0.0001$). The modified CMC scored consistently higher than the native powder, reflecting improved ease of distribution on the skin, faster perception of absorption, and a softer tactile finish (Fig. 4).

Collectively, these findings indicate that chemical modification can substantially alter the sensory performance of biopolymer-based powders, with the magnitude and nature of the improvement depending on the chemical structure of the base polymer.

2.2. Development of a sustainable Pickering base emulsion

Before evaluating how the developed microparticles might perform in cosmetic formulations, a preliminary formulation

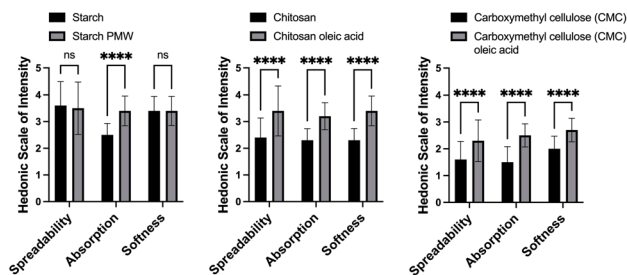


Fig. 4 Sensory evaluation of spreadability, absorption, and softness for formulations based on starch, chitosan, and carboxymethyl cellulose (CMC), with or without chemical modification ($n = 27$). Data are expressed as mean \pm SD. Statistical significance is indicated as ns or **** ($p < 0.0001$).

study was conducted to establish a stable and environmentally sustainable oil-in-water Pickering emulsion as a model base system. The goal was to minimize the use of conventional surfactants, which are often poorly biodegradable, by identifying natural particulate stabilizers capable of providing adequate emulsion stability while maintaining a reduced oil content and a low-impact INCI profile. A commercially available natural stabilizer powder (Vivapur) composed of microcrystalline cellulose, cellulose gum, and xanthan gum was selected as the primary stabilizer. This material was chosen for its natural origin, ease of dispersion in aqueous media, stabilizing ability, and white appearance.

The base emulsion was formulated using Vivapur as the stabilizer and a minimal oil phase consisting of sunflower oil and plum oil. The aqueous phase contained distilled water, glycerin, and potassium sorbate. This simple composition was intentionally chosen to emphasize the role of the stabilizer while maintaining a sustainable INCI profile. The resulting emulsion exhibited a homogeneous white appearance, high physical stability, and favorable rheological properties, making it suitable as a model system for further studies.

The resulting Vivapur-based emulsion exhibited a homogeneous white appearance, suitable rheological behavior, and an acceptable initial stability profile. However, minor limitations in texture and sensorial attributes suggested the need for further optimization.

To refine the physical and sensorial properties of the base system, an optimization study was performed using a Design of Experiments (DoE) approach. The DoE was structured to investigate the effect of two formulation variables: Vivapur concentration (3–8%) and oil content (10–40%) on the overall emulsion stability. The ten experimental formulations generated by the DoE were prepared using the standardized emulsification protocol under controlled storage conditions (4 °C, 25 °C, and 45 °C) and subsequently evaluated for macroscopic stability. As shown in Fig. S2, visual inspection revealed that three formulations (++, 0A, and A0) exhibited clear signs of instability, already indicating unfavorable combinations of the tested variables. Specifically, formulation ++ showed significant phase separation, with aggregates, as well as high heterogeneity. Significant flocculation was shown in formulation 0A, with large domains of dispersed oil drops, indicating insufficient structuring in the stabilization process for the liquid phase. Formulation A0 showed a visible yellowing on its top portion because of oil separation and coalescence.

From these observations, it can be determined that formulations ++, 0A, and A0 acted as true outliers within the experimental design, with clear visual instability even from the early evaluation. These particular variable combinations led to poor emulsification and poor kinetic stability, as was afterwards confirmed by the Turbiscan stability analysis. The remaining formulations visually appeared to be stable and after the quantitative investigation of their stability profiles using the Turbiscan, they were subsequently subjected to accelerated stability testing *via* centrifugation. Only two formulations (a0; -+) exhibited long-term stability under both Turbiscan and centrifugation analyses. Among these, a single formulation (a0)



was selected as the optimized model system, based on multiple criteria: stability under both Turbiscan and centrifugation analyses, minimal oil and stabilizer content, white coloration, favorable sensorial attributes and desirable rheological behavior, including shear-thinning and viscoelasticity.

The optimized formulation was further characterized for stability, rheological properties, and droplet size distribution, and subsequently employed as the reference matrix for the incorporation and evaluation of the sustainable microparticles developed in this study.

2.3. Incorporation of sustainable starch-based microparticles into the Pickering emulsion system

Following the development of the optimized sustainable Pickering base emulsion, preliminary incorporation trials were conducted to evaluate the feasibility of using the synthesized biodegradable microparticles as stabilizing or co-stabilizing agents. Given the objective of replacing microplastics in cosmetic formulations, particular attention was placed on determining whether microparticles derived from modified starch, chitosan or cellulose could contribute to emulsion stabilization while maintaining acceptable sensorial and physicochemical properties. To limit the use of modified powders during early formulation trials, the first series of experiments employed native tapioca starch. Native starch was dispersed and gelatinized prior to incorporation into the aqueous phase. However, an emulsion prepared using native starch as the sole stabilizing agent exhibited clear instability and rapid phase separation, confirming that native starch alone is insufficient to stabilize the oil-water interface in this system.

To overcome this limitation, a combination of native starch and Vivapur was tested (F1). This formulation displayed markedly improved stability and a homogeneous creamy texture, demonstrating that starch-based microparticles can function effectively only when used in synergy with a primary stabilizing agent. This finding guided the subsequent formulation strategy.

Building on the insights obtained with native starch, three additional formulations (F2–F4) were prepared incorporating

modified starch microparticles alongside Vivapur. Two types of modifications were investigated: oleic acid-modified starch and PMW-modified starch. The incorporation levels were selected based on preliminary dispersibility and compatibility tests.

All starch-containing formulations (Fig. 5A) exhibited pH values between 5.5 and 5.8, suitable for topical applications. According to visual inspection and Turbiscan stability profiling, formulations containing modified starches remained physically stable at time 0 and after 7 days of storage. Accelerated stability testing under centrifugation corroborated the absence of phase separation, confirming that modified starches do not negatively affect the emulsion's structural integrity under stress conditions (Fig. S4). The rheology of formulations is an important quality parameter. In this study, the apparent viscosity of the starch-based emulsions decreased with the increase of shear rate from 0.1–100 s⁻¹ as shown in Fig. 5B, indicating that the emulsions demonstrate a shear-thinning and non-Newtonian fluid behavior. The shear-thinning behavior is a desirable feature for topical formulations as it facilitates the application of the product on the skin and leaves a smooth sensorial feeling.

Formulations F1, F3, and F4 exhibited crossover values around 90%, indicative of a robust viscoelastic network, while F2, with oleic acid-modified starch, displayed a lower crossover value (63%), suggesting a reduced elastic contribution and earlier structural breakdown under strain.

The strength of the network structure can be determined from the storage modulus (G'), which indicates the elastic properties of the emulsion, and the loss modulus (G''), which indicates the viscous properties of the emulsion. The results of the dynamic oscillatory measurements of the Pickering emulsions with the frequency ranging from 0.01–10 Hz are shown in Fig. 5C.

Vivapur alone produced the most rigid network (highest G'), followed by Vivapur combined with PMW-modified starch, and finally the native or oleic acid-modified tapioca starch formulations. This trend reflects the reinforcing effect of the PMW-modified particles and the softer contribution of oleic acid-modified starches.

Droplet size distribution analysis further confirmed the strong influence of particle type on emulsion microstructure. The base emulsion (F0) exhibited a reduced mean droplet size and a more homogeneous distribution. In contrast, the incorporation of native starch or oleic acid-modified starch led to an increase in average droplet diameter. Among the tested systems, emulsions containing tapioca starch PMW (F3–F4) displayed the narrowest droplet size distribution, indicating enhanced droplet stabilization and improved uniformity (Fig. S3).

These findings demonstrate that modified starch-based microparticles integrate seamlessly into optimized Pickering emulsions, maintaining stability and rheological performance. Their ability to refine droplet size and enhance viscoelasticity confirms their role as effective co-stabilizers and positions them as a robust, sustainable alternative to microplastics in cosmetic formulations.

2.4. Preliminary assessment of chitosan-based microparticles

Two formulations (F5 and F6) were prepared using oleic acid-modified chitosan, alone or in combination with Vivapur.

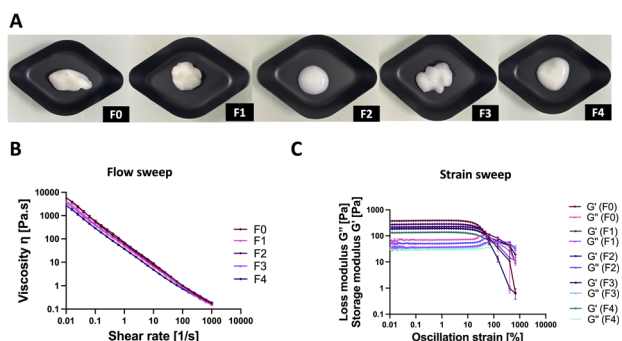


Fig. 5 Rheological characterization of the formulations. (A). Photographic images of the obtained formulations, illustrating their macroscopic appearance. (B). Flow sweep curves showing the shear-dependent viscosity and flow behavior. (C). Strain sweep profiles evidencing the viscoelastic region and structural integrity of the samples.



Contrary to starch-based systems, these emulsions exhibited sticky, pudding-like textures and lacked the structural cohesion required for cosmetic applicability. Moreover, stability assessments revealed discoloration at elevated temperatures (45 °C), indicating reduced robustness compared with starch-containing analogues.

These limitations suggest that, under the current formulation conditions, chitosan-based microparticles do not provide adequate stabilization and may interact unfavorably with the aqueous polymeric network formed by Vivapur. It is therefore likely that different processing parameters, modification strategies, or co-stabilizer ratios will be required to fully exploit chitosan microparticles in Pickering-type systems.

3. Conclusions

This study successfully engineered sustainable microparticles from three key biodegradable biopolymers, including starch, chitosan, and cellulose derivatives, through optimized preparation strategies that delivered distinct morphologies and tailored rheological profiles. By refining multiple techniques, we achieved particles with precisely controlled structural and functional properties, underscoring the remarkable versatility of these natural polymers. Their inherent biodegradability, renewability, and broad availability position them as compelling, high-performance alternatives to conventional MPs in cosmetic formulations.

A formulation strategy was established to develop a sustainable Pickering emulsion capable of incorporating these microparticles. Microparticles derived from native and modified tapioca starch demonstrated good compatibility with the optimized Pickering system. Modified starches played a fundamental role in achieving stable emulsions, preserving pseudoplastic rheological behavior, and refining droplet size distribution without triggering destabilization phenomena. These findings confirmed the potential of starch-based microparticles to function as co-stabilizers or structuring agents within sustainable cosmetic emulsions. Their performance supports further investigation into their role as functional and environmentally acceptable replacements for synthetic MPs. In contrast, chitosan-based microparticles, despite their biodegradability and intrinsic material appeal, failed to produce formulations with acceptable texture or stability under the tested conditions. This outcome highlights the need for more extensive optimization, focusing on the degree of chemical modification, dispersion protocol, and synergistic interactions with other natural stabilizers.

The findings of this work clearly establish modified starch microparticles as a viable and effective class of sustainable alternative to conventional MPs for next-generation cosmetic formulations. By integrating seamlessly into the optimized Pickering emulsion platform, these particles not only preserve stability and rheological integrity but also enhance formulation functionality. This platform provides a robust foundation for systematic exploration of biodegradable particles, accelerating innovation toward eco-safe, next-generation cosmetics.

Ultimately, these results lay the groundwork for fully sustainable systems, reinforcing the transition to MP-free

products and setting a new benchmark for responsible formulation strategies.

4. Experimental

4.1. Reagents

Tapioca starch was purchased from Nouryon Chemicals SPA (Milan, Italy). Poly (isobutylene-*alt*-maleic anhydride) MW 6 kDa, tryptophan, chitosan low molecular weight, carboxymethylcellulose sodium salt, potassium sorbate and oleic acid were purchased from Sigma-Aldrich (St. Louis, MI, USA). *N,N*-Dimethylformamide (DMF), acetic acid, ethanol, and 1-octanol were purchased from CARLO ERBA Reagents s.r.l. (Milan, Italy). Sunflower oil (commercial food grade Fruit d'Or) was acquired from a local retail market (Orléans, France) and used as received without further purification. The Glycerin and Plum oil were obtained from Aroma-zone (Paris, France). VIVAPUR® CS TEX Easy was generously supplied by JRS Rettenmaier (Rosenberg, Germany).

4.2. Synthesis of sustainable microparticles

4.2.1. Synthesis of tapioca starch microparticles. Tapioca starch (5 g, 100 g L⁻¹) was dispersed in 50 mL of distilled water and heated to 50 °C. After 30 min, oleic acid (0.285 mL, 0.5% w/v) was added, and the mixture was stirred at 50 °C for 4 h to promote starch-lipid complex formation. Microparticles were obtained by precipitating the aqueous phase dropwise into 50 mL of a water/ethanol solution (20% v/v) under continuous stirring for 30 min. The resulting suspension was filtered through a Büchner funnel equipped with a 200 nm cellulose filter. The collected microparticles were washed by centrifugation at 1000×g for 20 min to remove excess oleic acid, followed by lyophilization.

4.2.2. Synthesis of tapioca starch microparticles in 1-octanol. The procedure was similar to the previous method, except that the aqueous starch solution was precipitated into 30 mL of octanol (100% v/v) and stirred for 30 min. Microparticles were recovered by centrifugation at 1000×g for 20 min and lyophilized. Octanol, being immiscible with water, was recovered and reused.

4.2.3. Synthesis of tapioca starch microparticles functionalized with tryptophan-grafted- poly (isobutylene-*alt*-maleic anhydride) (PMW). PMW polymer was synthesized by dissolving PMA (1 g) and tryptophan (464 mg) in DMF (15 mL) at 60 °C overnight. The polymer was purified with 0.3 M HCl, centrifuged at 3200×g for 10 min, and lyophilized after freezing. Tapioca starch (5 g) and PMW (250 mg) were dispersed in 50 mL of distilled water at 50 °C for 2 h. Microparticles were formed by dropwise precipitation into 50 mL of ethanol (20% v/v), stirred for 30 min, filtered through a 200 nm cellulose filter, frozen and lyophilized.

4.2.4. Synthesis of chitosan microparticles. Chitosan (10 g L⁻¹) was dissolved in 50 mL of 1% (v/v) acetic acid at room temperature under stirring for 24 h. Oleic acid (0.285 mL, 0.5% w/v) was added, and the solution was spray-dried under the following conditions: feed rate 3 mL min⁻¹ (10%), inlet



temperature 130 °C, outlet temperature 90 °C, air pressure 6.0 bar, aspiration rate 90%, nozzle clear 2.

4.2.5. Synthesis of carboxymethyl cellulose sodium salt (Na-CMC) microparticles. Na-CMC (10 g L⁻¹) was dissolved in 60 mL of ultrapure water under stirring at room temperature for 24 h. Oleic acid (0.342 mL, 0.5% w/v) was added, and the mixture was stirred at 400 rpm for 2 h. The solution was spray-dried under the following conditions: feed rate 4 mL min⁻¹ (15%), inlet temperature 115 °C, outlet temperature 64 °C, air pressure 6.0 bar, aspiration rate 90%, nozzle clear 3.

4.3. Microparticles characterization

4.3.1. Fourier transform infrared (FT-IR) spectroscopy. Chemical structure and functional groups of native and modified powder were analyzed using FT-IR (FT-IR spectrometer platform INVENIO, Bruker Optics GmbH & Co. KG) in transmission mode over 500–4000 cm⁻¹, averaging 16 scans at 2 cm⁻¹ resolution. Samples subjected to analysis were positioned on a diamond crystal sampling plate and fixed in place with a pointed clamp. A background spectrum was collected before each sample scan using an empty plate. The ATR crystal and pointed tip were cleaned between measurements to eliminate any interference from previous samples.

4.3.2. Scanning electron microscopy (SEM). For scanning electron microscopy (SEM) analysis, the microparticle samples were mounted on conductive double-sided carbon adhesive tape attached to aluminum stubs. The samples were sputter-coated with a thin layer of gold and examined using a scanning electron microscope (Phenom Pro G6, Thermo Fisher Scientific) operated at an accelerating voltage of 10.0 kV. Photomicrographs were acquired at various magnifications to assess homogeneity, and particle diameters were measured using the ImageJ particle analyzer plugin.

4.4. Consumer evaluation of the sensory appeal of powders

A preliminary consumer sensory evaluation was conducted on 3 powders (starch, chitosan, and methylcellulose, both in their native and chemically modified forms). The test was carried out on a panel of 27 volunteers of both sexes. Each participant received a questionnaire in which five parameters had to be evaluated: color, consistency, spreadability, absorption, and softness. Specifically, color and consistency were assessed visually before powder application on the forearm, spreadability and absorption were evaluated during application, while softness was judged immediately after application. Each parameter was scored on a structured scale. For color and consistency, participants were asked to give a categorical judgment. For spreadability, absorption, and softness, a 4-point scale was used, where 1 represented the lowest intensity (absence of the characteristic) and 4 the highest intensity. The powders were presented to participants in designed plastic trays, each coded with a two-letter random code unknown to the panelists, to minimize external influences. Before starting, participants were instructed to clean their hands and forearms with paper. They were then shown how to apply the powders on the forearm using circular movements until the sample was fully spread.

Immediately afterward, participants filled in the questionnaire according to the predefined evaluation phases. In accordance with ISO 8589, the sensory evaluation was performed in a standardized environment under controlled conditions (temperature: 20.7 °C; relative humidity: 36%).

The results and the data collected were elaborated with two-way ANOVA analysis at a significance level of $p < 0.05$ to determine the statistical differences between the powder samples, based on the characteristics described by the panelists. All participants were informed about the nature of the study and provided informed consent prior to participation in the sensory evaluation.

4.5. Emulsion preparation

The base emulsion was prepared using a cold emulsification process. The aqueous phase was composed of distilled water, potassium sorbate, glycerin and Vivapur CS TEX Easy. Vivapur was pre-activated by dispersing it in the aqueous phase under mechanical stirring with a paddle stirrer at 2000 rpm for 5 minutes, followed by a 15-minute resting period to allow for complete hydration and stabilization of the dispersion. The aqueous phase was then combined with the oil phase, consisting of a defined blend of sunflower oil and plum oil. Emulsification was performed using a high-shear homogenizer (Polytron PT 10-35 GT, Kinematica AG, Switzerland) operating at 10,000 rpm for approximately 2 min. The resulting emulsion was collected in appropriate containers and stored at room temperature until further analysis.

4.5.1. Optimization of base emulsion using an experimental design approach. Following the initial preparation of the base emulsion, an optimization study was conducted to determine the optimal composition of ingredients for achieving a stable formulation. A design of experiments (DoE) approach was employed using JMP software. Response Surface Methodology (RSM) was selected as the most suitable strategy, as it enables the modeling of continuous responses as functions of multiple input variables, allowing for the assessment of both individual and interaction effects. The independent variables (X) were: oil content, ranging from 10% to 40%, using a combination of sunflower and plum oils in a fixed 1 : 2 ratio. Vivapur content, ranging from 3% to 8% as the stabilizing agent. The response variable (Y) was defined as the emulsion stability, which was quantitatively evaluated using a Turbiscan optical analyzer. The experimental design consisted of one level and two factors, generating 10 configurations. Every configuration was conducted by triplicate.

4.5.2. Development of the optimized emulsion. Based on the Design of Experiment (DoE), the formulation (a0) corresponding to the highest stability was selected as the optimized base emulsion. The detailed composition, including the exact quantities and percentages of each component, is reported in Table S1, and the emulsion was prepared according to the protocol described in Section Emulsion Preparation.

4.5.3. Emulsion preparation with starch-based microparticles. Tapioca starch powder (native or modified) was first dispersed in distilled water and subjected to controlled heating



in an oil bath at 90 °C for 1 h under mechanical stirring at 300 rpm to promote gelatinization. The resulting suspension was then allowed to cool to room temperature before incorporation into the aqueous phase of the emulsion.

After dispersion of the starch solutions, the suspensions were added to the remaining aqueous phase, consisting of distilled water, potassium sorbate and glycerin. The complete aqueous phase was then combined with the oil phase, prepared as a mixture of sunflower and plum oils. Emulsification was performed using a high-shear homogenizer operating at 10,000 rpm for 2 min. The resulting formulations were transferred into appropriate containers and allowed to equilibrate at room temperature before subsequent characterization. A summary of the tested microparticle types and incorporation quantity is reported in Table S2.

4.6. Characterization of the emulsions

4.6.1. Organoleptic properties. All formulations were characterized in terms of pH, color and texture. The pH of each sample was measured one day after the formulation was prepared at room temperature, using a calibrated digital pH meter (VWR avantor pH 1100 L Operating Manual).

4.6.2. Stability analysis. The physical stability of the emulsions was assessed using a Turbiscan LAB analyzer (Formulation, Toulouse, France). The instrument is equipped with a pulsed near-infrared light source ($\lambda = 880$ nm) and two synchronous detectors: transmission (T) and backscattering (BS). During the analysis, a scanning head moves along the height of the sample vial, recording BS and T signals across the emulsion column. After the emulsion formation, a fixed volume of sample was transferred into glass vials and analyzed under controlled conditions. The stability profile was monitored at different storage temperatures (4 °C, 25 °C, and 45 °C) and at defined time intervals (0 h, 1 h, 24 h, 48 h, and 7 days). The obtained backscattering (BS) curves, expressed as the percentage of reflected light as a function of sample height, provided information on destabilization phenomena such as droplet coalescence, creaming, or sedimentation.

4.6.3. Accelerated stability analysis. To predict physical instability phenomena, samples were subjected to strong mechanical stress conditions by using the centrifuge Eppendorf 5804 R. To perform the test, 10 g of each sample was placed in centrifugal tubes and centrifuged at 4000 rpm for 30 min at 25 °C. This process causes stress in the sample, simulating an increase in gravity and causing more particle movement, which predicts future instabilities.

4.6.4. Rheological analysis. The rheological properties of the emulsions were characterized using a rheometer (Discovery HR10, TA instruments) with a parallel plate geometry (40.0 mm parallel plate, Peltier plate Sandblasted, Solvent Trap). The temperature was set at 25 °C. The shear rate explored ranged from 0.01 to 1000 s⁻¹. Viscosity values were recorded, and flow curves were analyzed to determine the shear-thinning behavior and structural stability of the emulsions. Amplitude sweep tests were performed, increasing the strain from 0.01% to 1000%, at a fixed oscillation frequency of 1 Hz, to identify the sample's

linear viscoelastic region (LVER). All measurements were made in triplicate and data reported as mean \pm SD.

4.6.5. Particle size analysis. The droplet size distribution of the emulsions was determined by laser diffraction using a laser diffraction particle size analyzer (Shimadzu, SALD-2300). Before analysis, each sample was diluted 1:10 by dispersing 1 g of emulsion in 9 mL of distilled water. The dispersion was stirred to obtain a homogeneous sample. Measurements were made using a liquid cell at room temperature with the refractive index set to 3.00–0.20*i*. Each sample was measured in triplicate; results are given as mean \pm SD. The droplet size distribution was expressed as mean, median (D50), mode, standard deviation and percentile diameters (D10, D50, D90), reported in micrometers (μ m).

4.6.6. Light microscopy. Emulsions were observed under a light microscope (Leica DMI8, inverted microscope, Germany) at ambient temperature. A drop of each sample was placed between a glass slide and a cover slip and observed immediately. Images were acquired at 10 \times , 20 \times , and 40 \times magnifications. For each sample, five micrographs were taken, and representative images were selected to illustrate the microstructure of the emulsions.

Author contributions

All authors have given approval to the final version of the manuscript. M. C., D. P., and M. G. conceived the project. F. S. and M. G. designed the experiments. F. S. performed the experiments and analyzed the data. F. S., M. G. wrote the manuscript. B. D. S. and L. S. contributed to the manuscript writing. L. M. helped in the sensory evaluation. F. S. and M. G. prepared the figures. R. D. and D. H. supervised formulation experiments, with R. D. providing the resources. D. P., M. C., and M. G. conceptualized and supervised the project, guided experimental design and data analysis. M. G., P. G., M. C. and D. P. revised the final manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

All data are available in the manuscript or the supplementary information (SI). Supplementary information: experimental details, supplementary figures and tables, characterization data and supporting analyse. See DOI: <https://doi.org/10.1039/d6ra01252c>.

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