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RESEARCH ARTICLE

Pomegranate Peel Extract and Hyaluronic Acid-Integrated Water-in-oil-in-water Double Emulsion and its Sensory Analysis for Topical Application

Roswanira Abdul Wahab[a, b,*], Melanie Tan Hui Lin[a], Mohd Hamdi Zainal Abidin[a], Ni Made Suaniti[c]

[a]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia; [b]Investigative Forensic Sciences Research Group, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia; [c]Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Udayana, Jl. Campus Bukit Jimbaran, Badung, Bali (80361), Indonesia

Abstract Pomegranate peel extract (PPE) offers a rich source of natural polyphenols for cosmetic applications, yet its incorporation into stable topical formulations remains challenging due to poor bioactive stability and skin permeability. This study aimed to develop a stable water-in-oil-in-water (W/O/W) double emulsion co-loaded with PPE and hyaluronic acid (HA) using a high-energy two-step emulsification method, and to evaluate its physicochemical properties and consumer acceptability. The optimal formulation, identified through systematic screening of oil and xanthan gum concentrations, consisted of 15% grapeseed oil and 1.0% xanthan gum. Physicochemical characterization revealed that the emulsion possessed a mean droplet size of approximately 155 nm with a narrow size distribution (polydispersity index < 0.3), indicating a homogeneous system conducive to topical delivery. The formulation exhibited pseudoplastic (shear-thinning) rheological behavior, favorable for skin application, and maintained a skin-compatible pH (approximately 5.0) over 7 weeks of storage at 25°C. Stability studies demonstrated that the double emulsion resisted coalescence and Ostwald ripening throughout the storage period, with conductivity measurements confirming the structural integrity of the multiple emulsion system. Sensory evaluation by untrained panelists (n = 40) using a 9-point hedonic scale showed that the formulation achieved overall acceptance comparable to that of a commercial reference product, with particular preference noted for its fragrance and spreadability. These findings establish a foundational formulation strategy for incorporating PPE and HA into a physically stable W/O/W double emulsion with acceptable sensory properties. The systematic optimization approach and demonstration of resistance to key destabilization mechanisms distinguish this work from prior studies, though further biological and efficacy testing are required to substantiate any dermatological applications.

Keywords: Pomegranate peels, ethanolic-water extract, double emulsion, Water-in-oil-in-water, hyaluronic acid, topical.

***For correspondence:**
roswanira@utm.my

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Introduction

The global cosmetics industry continues to expand, driven by consumer demand for products that combine efficacy with safety and sustainability. A key trend shaping this market is the shift away from synthetic ingredients toward natural alternatives, particularly plant-derived bioactive compounds with demonstrable skin benefits (Mansoor *et al*., 2023). This transition is partly motivated by growing concerns regarding the long-term safety of synthetic additives commonly used in cosmetic formulations. For

instance, synthetic antioxidants such as butylated hydroxytoluene and butylated hydroxyanisole, while effective at preventing oxidative degradation, have been associated with potential health risks, including blood clotting abnormalities and genotoxic effects following prolonged topical exposure (Sharma *et al*., 2019; Alnuqaydan, 2024). Consequently, there is increasing interest in developing stable topical formulations incorporating natural bioactive ingredients that deliver comparable or superior functional benefits without the associated safety concerns.

Among promising natural sources, pomegranate (*Punica granatum* L.) peel has attracted considerable attention for cosmeceutical applications. While the edible arils are widely consumed, the peel, typically discarded as agricultural waste, is exceptionally rich in polyphenolic compounds, including hydrolyzable tannins (punicalagins, punicalin), anthocyanins, and phenolic acids (Lampakis *et al*., 2021). These phytochemicals exhibit potent antioxidant and anti-inflammatory activities, making pomegranate peel extract (PPE) a valuable candidate for topical formulations aimed at mitigating oxidative stress-mediated skin aging (Fateh *et al*., 2013). The use of peel extract specifically offers the dual advantage of valorizing agricultural by-products while harnessing a concentrated source of bioactive polyphenols.

However, incorporating PPE into topical products presents significant challenges. Its polyphenolic compounds are susceptible to degradation from light, oxygen, and temperature fluctuations (Pinho *et al*., 2021), while their hydrophilic nature limits skin permeability and bioavailability. These limitations necessitate advanced delivery systems that both protect labile bioactives and enhance their skin penetration. Water-in-oil-in-water (W/O/W) double emulsions offer a promising platform to address these challenges. This multiphase system, comprising an internal aqueous phase dispersed within oil droplets, themselves dispersed in an external aqueous continuous phase, provides distinct advantages for topical delivery: (i) compartmentalization and protection of hydrophilic actives, (ii) potential for sustained release, and (iii) capacity to co-deliver multiple bioactives with different solubility profiles (Mashhadian *et al*., 2022). Previous studies have demonstrated the feasibility of W/O/W emulsions for encapsulating plant extracts and hydrophilic actives, with stability dependent upon careful optimization of surfactant systems, osmotic balancing between aqueous phases, and rheological modification of the continuous phase (Schuch *et al*., 2014; Gharehbeglou *et al*., 2019).

Hyaluronic acid (HA), an endogenous glycosaminoglycan of the skin extracellular matrix, is widely incorporated into topical formulations for its moisturizing and viscoelastic properties (Juncan *et al*., 2021). Combining antioxidant-rich plant extracts with HA offers a potentially synergistic strategy to address both oxidative damage and moisture depletion in skin aging. However, successfully co-encapsulating hydrophilic HA and PPE within a W/O/W double emulsion demands careful formulation design to balance osmotic pressures, preserve interfacial film integrity, and achieve acceptable sensory attributes. Although previous research has explored pomegranate-based emulsions and HA-containing topical formulations individually, several gaps remain. First, the co-encapsulation of PPE and HA within a single W/O/W double emulsion system has not been systematically investigated. Second, while the importance of osmotic balance in double emulsion stability is well recognized, the specific interplay between xanthan gum concentration (as a continuous-phase rheology modifier) and oil-phase composition in stabilizing PPE-HA-loaded systems remains to be elucidated. Third, existing studies have primarily focused on physicochemical characterization, with limited attention to consumer sensory perception, a critical determinant of commercial viability. Fourth, many previous reports use pomegranate fruit extract rather than peel extract, despite the latter's higher polyphenolic content and greater potential for valorizing agricultural waste.

Therefore, this study aimed to develop and characterize a stable W/O/W double emulsion co-loaded with PPE and HA, optimized for topical application. Specifically, we investigated the effects of grapeseed oil and xanthan gum concentrations on emulsion stability, conducted comprehensive physicochemical characterization, including assessments of resistance to coalescence and Ostwald ripening, and evaluated consumer sensory acceptance relative to a commercial reference product. By systematically addressing formulation parameters critical to double emulsion stability while incorporating sensory evaluation, this work seeks to establish a foundation for further development of PPE-HA-loaded double emulsions as potential candidates for natural cosmetic applications, subject to subsequent biological and efficacy validation.

Materials and Methods

Pomegranate peel extract (PPE) and xanthan gum (from *Xanthomonas campestris*) were sourced from Personal Formula Resources (Malaysia), and hyaluronic acid (HA) was obtained from Take It Global (Penang, Malaysia). The surfactants Tween 80 (polyoxyethylene sorbitan monooleate; HLB 15.0) and

Span 80 (sorbitan oleate; HLB 4.0) were procured from Scharlau (Barcelona, Spain) and Sisco Research Laboratories (Maharashtra, India), respectively. Grapeseed oil was supplied by Aceites Borges Pont (Spain). Additional components included fragrance from Luzi Fragrance Compounds (Johor, Malaysia), phenoxyethanol from Thor Specialty (US), magnesium sulfate (electrolyte) from QREC (Asia) SDE Bhd (Malaysia), and glycerol from Fisher Scientific (UK). A commercial cream for sensory analysis was acquired from Guardian (Malaysia). Ultrapure water was produced in-house using the facilities of the Biotechnology and Biochemistry Laboratory, Faculty of Science, Universiti Teknologi Malaysia.

Preparation of the PPE-HA W/O/W Double Emulsion

A systematic screening approach was employed to identify the optimal composition for the PPE-HA W/O/W double emulsion. Based on preliminary literature review and preliminary experiments, grapeseed oil (15-18% w/w) and xanthan gum (1.0-1.5% w/w) were selected as variable factors due to their critical roles in emulsion stability and rheological properties. The concentration ranges were chosen based on preliminary trials: oil concentrations below 15% resulted in insufficient droplet coverage and rapid coalescence, while concentrations above 18% produced excessively viscous primary emulsions that hindered the second emulsification step. Xanthan gum concentrations below 1.0% failed to provide adequate continuous-phase viscosity for kinetic stability, whereas concentrations above 1.5% led to unacceptably high viscosity and poor spreadability during preliminary sensory assessment.

The concentrations of Span 80 (5% w/w) and Tween 80 (5% w/w) were maintained constant based on established principles for W/O/W emulsion formulation. This 1:1 ratio of lipophilic to hydrophilic surfactants was selected to achieve a balanced hydrophilic-lipophilic balance (HLB) approximately 9.5, which is within the optimal range for forming stable interfacial films in multiple emulsions (McClements *et al.*, 2012). The 5% concentration was chosen as it represents the minimum level required to fully coat the oil-water interfaces created during the two-step emulsification process, as calculated from the expected interfacial area based on target droplet sizes of <200 nm. Higher surfactant concentrations were avoided to minimize potential skin irritation and undesirable sensory attributes (tackiness).

Three formulations (Trials A1, A2, and A3) were prepared with the compositions shown in Table 1. Stability screening was conducted using centrifugation (10,000 rpm, 10 min) and six freeze-thaw cycles (4°C for 24 h, followed by 25°C for 24 h) as accelerated stress tests. The formulation demonstrating the highest stability (absence of phase separation) combined with optimal physicochemical properties (smallest droplet size, lowest PDI, and most negative zeta potential) was selected for comprehensive characterization.

The water-in-oil-in-water (W/O/W) double emulsions were prepared using an established two-step emulsification process involving ultra-homogenization and ultrasonication, with minor modifications. The primary emulsion (PE) was first formulated by ultrasonicating the oil phase for one minute at 100% amplitude in an ice bath. To ensure a uniform distribution of the internal aqueous phase, the mixture was subsequently stirred magnetically.

Prior to emulsification, the individual phases were heated separately to 75 ± 5°C for 10 minutes in a water bath. The internal aqueous phase was then added dropwise into the oil phase under constant homogenization at 12,000 rpm for 5 minutes. Concurrently, a mixture of Tween 80 and glycerol was ultrasonicated for one minute at 100% amplitude in an ice bath. Water, fragrance, and phenoxyethanol were then added to this mixture, followed by homogenization at 10,000 rpm for one minute. Subsequently, the primary emulsion was blended with this external aqueous phase assemblage and homogenized at 10,000 rpm for 9 minutes. During this homogenization, xanthan gum was deliberately added in a controlled manner. The final formulation was prepared in triplicate to ensure the precision of subsequent analyses. Furthermore, the stability of the formulation was found to be dependent on the concentrations of oil and xanthan gum.

Screening of the PPE-HA W/O/W Double Emulsion Formulation

To identify the optimal composition for a kinetically stable W/O/W double emulsion (DE) containing pomegranate peel extract (PPE) and hyaluronic acid (HA), this study screened various formulations for their grapeseed oil and xanthan gum content. The optimal formulation was confirmed by its resistance to phase separation during subsequent preliminary centrifugation and freeze-thaw stability tests, as described in the following Section 2.10.

Physical Characterization of W/O/W Double Emulsion

Mean Droplet Size, Polydispersity Index, Zeta Potential, and Organoleptic Assessment, for Thermodynamic Stability

The mean droplet size (MDS), polydispersity index (PDI), and zeta potential of the PPE-HA W/O/W DE were measured by dynamic light scattering (DLS) using Zetasizer Nano ZSP (Malvern Instrument, Malvern,

UK). All samples were liquefied in ultrapure water with a 1:20 ratio and were then transported to a capillary cuvette cell. The MDS and PDI of the PPE-HA W/O/W DE were monitored directly at weeks 3, 5, and 7 after formulation, with monitoring occurring every two weeks. To further check the stability of the formulation, an organoleptic test was also conducted. The organoleptic properties of the freshly prepared formulation were recorded and stored for 7 weeks at three diverse temperatures at 4°C, 25°C, and 40°C, and then assessed for their colour and appearance (Romes *et al*., 2021). The measurements were triplicated and reported as mean ± standard deviation.

pH, Conductivity and Viscosity Analysis

The pH value of the newly formulated W/O/W DE in every sample was tested with a Delta 320 pH meter (Mettler Toledo, USA) at 25ºC. The sample was tested for pH at one-week intervals for storage for up to 7 weeks i.e. 7 days, 14 days, 21 days, 28 days, 35 days, 42 days, and 49 days after formulation to inspect the distinction. All measurements were triplicated and reported as mean ± standard deviation.

Conductivity assessments were achieved for the W/O/W DE double emulsion by applying a conductometer (Mettler Toledo, USA). The sample was stored at 25ºC, and weekly conductivity measurements were taken at one-week intervals for 7 weeks, i.e., 7 days, 14 days, 21 days, 28 days, 35 days, 42 days, and 49 days after formulation.

Next, the viscosity of the DE was measured by using a viscometer (Engineering Laboratories, Inc., Middleboro, MA, USA) at 25ºC. The rheological behavior was evaluated at a shear rate of 10-50 s^{-1}, and the shear stress was measured. The viscosity of the W/O/W DE was evaluated by plotting a graph of viscosity versus shear rate, while the rheology of the W/O/W DE was determined by plotting a graph of shear stress against shear rate. All measurements were triplicated and reported as mean ± standard deviation.

Morphological Characterization

The morphology and mean droplet size (MDS) of the PPE-HA W/O/W DE were measured by applying JPK Instrument NanoWizard® 3 Atomic Force Microscope (Berlin, Germany) coupled with JPK data processing software system. The sample was diluted with distilled water at a ratio of 1:100, and a small aliquot of the PPE-HA W/O/W DE was deposited on a mica substrate. In all cases, the analysis was done under dry conditions.

Centrifugation and Freeze-Thaw Cycle Tests

The formulated (Trial A_1, A_2, and A_3) PPE-HA W/O/W DEs were subjected to ultracentrifugation at 10,000 rpm for 10 minutes to observe the phase separation. Next, the kinetic stability of this formulation was assessed using repeated freeze-thaw cycles. The formulated PPE-HA W/O/W DEs (Trial A1, A2, and A3) were transferred to sample bottles for the freeze-thaw cycles test and then stored at 4ºC for 24 hours, followed by thawing at 25ºC for 24 hours. The practice was repeated for six cycles to detect the separation of phases. Here, an absence of phase separation represents a kinetically stable DE and a potentially long shelf life.

Centrifugation and Freeze-Thaw Cycle Tests

To check the rate of phase separation in the PPE-HA W/O/W DE, a coalescence test was accomplished. In this study, the coalescence rate of DE was investigated by assessing the particle size over 7 weeks of storage at 25°C using Eq. (1).

$$\frac{1}{r^2} = \frac{1}{{r_0}^2} - \left(\frac{8\pi}{3}\right)\omega t \qquad (1)$$

Here, r refers to the mean radius after time, r_0 signifies the value at a certain time (s) and t characterizes the separation frequency per unit of the film surface.

For the Ostwald ripening test, Lifshitz-Slesov-Wagner's principle was applied to identify the rate of Ostwald ripening of the PPE-HA W/O/W DEs, stored for 7 weeks at 25 ºC. This is because smaller droplets with higher solubility tend to form larger droplets with time, consequently increasing the particle size. In this study, a plot of r^3 versus time was plotted to determine the rate of Ostwald ripening at 25ºC following Eq. (2).

$$\omega = \frac{dr^3}{dt} = \frac{8}{9}\left[\frac{C(\infty)V_m D}{\rho\, RT}\right] \qquad (2)$$

For Eq. (2), the parameters are defined as follows: ω is the frequency of rupture per unit surface area of the dialysis bag, r is the average droplet radius over time, t is the storage time (s), and C(∞) is the

solubility in the bulk phase. Furthermore, V_m represents the molar volume of the internal phase, and D is the diffusion coefficient of the dispersed phase through the continuous. Meanwhile, phase, ρ is the density of the dispersed phase, R is the gas constant, and T is the absolute temperature (Zhao *et al*., 2023).

Sensory Evaluation

A sensory evaluation was conducted with a panel of 40 untrained volunteers (aged 20-30 years) recruited from Universiti Teknologi Malaysia. The study was designed to assess consumer preference for the formulated emulsion relative to a commercial reference product. According to the guidelines of the Universiti Teknologi Malaysia Research Ethics Committee, this type of sensory evaluation for cosmetic product preference testing, involving healthy volunteers and products formulated with ingredients generally recognized as safe for topical use, was exempt from full ethical review. Nonetheless, all procedures were conducted in accordance with institutional guidelines for consumer testing.

Prior to participation, all volunteers were provided with detailed information about the study objectives, the composition of the test product, and the testing procedures. Written informed consent was obtained from all participants. Volunteers were informed that participation was voluntary and that they could withdraw at any time without consequence. The panel compared two products: a newly prepared cream (PPE-HA W/O/W DE) and a commercial face cream. Each sample was presented in an identical container labeled with a random three-digit code to ensure unbiased assessment.

Based on the sensory descriptive methodology of Gilbert *et al*. (2012), the panelists evaluated the creams against ten criteria: fragrance, texture, stickiness, spreadability, greasiness, absorbency and post-rub-in feeling. They rated each attribute using a 9-point hedonic scale (1 = "Dislike extremely" to 9 = "Like extremely"). Finally, panelists were asked to indicate their overall acceptance of the product.

Results and Discussion

Preliminary Screening of Stability of PPE-HA W/O/W Double Emulsion

In this study, the formulated PPE-HA W/O/W double emulsions (DEs) underwent short-term stability screening, including centrifugation and freeze-thaw cycle tests. Short-term stability screening, comprising centrifugation and freeze-thaw cycle tests, provides an accelerated assessment of the newly developed double emulsion formulation. These tests are crucial for predicting shelf-life under market conditions by expediting destabilizing processes.

Centrifugation accelerates creaming/sedimentation and phase separation in emulsions by imposing an external force field, allowing discrimination between physically stable and unstable formulations in a short time and enabling early detection of poorly stabilized systems. Likewise, repeated freeze-thaw cycles simulate thermal excursions and the associated droplet interactions (ice crystal formation, osmotic stress, and enhanced collision frequency), which can destabilize emulsions via coalescence, Ostwald ripening, or interfacial layer disruption (Plassard 2024).

In this study, three PPE-HA W/O/W double emulsion formulations (Trials A1, A2, and A3) were prepared with varying concentrations of grapeseed oil (15–18%) and xanthan gum (1.0–1.5%) and subjected to preliminary stability screening using centrifugation and freeze-thaw cycling. While all three formulations passed these accelerated stress tests without macroscopic phase separation (Table 1), quantitative physicochemical parameters revealed distinct differences that informed the selection of an optimal formulation for further characterization.

Trial A1 (15% grapeseed oil, 1.0% xanthan gum) was selected as the optimal formulation based on several complementary criteria. First, its mean droplet size (155.07 ± 5.85 nm) was within the optimal range (150–350 nm) reported for enhanced topical delivery, balancing interfacial surface area for release with manufacturing reproducibility (Rai *et al*., 2018). Second, its polydispersity index (0.280 ± 0.048) was substantially lower than those of Trials A2 (0.430 ± 0.016) and A3 (0.484 ± 0.004), indicating a more uniform droplet population with a reduced propensity for Ostwald ripening (Salvia-Trujillo *et al*., 2017). Third, its zeta potential (-24.77 ± 1.01 mV) was more negative than that of Trial A2 (-13.23 ± 0.80 mV), suggesting enhanced electrostatic contributions to colloidal stability.

Trial A2, despite having a slightly smaller mean droplet size (153.67 ± 2.29 nm), exhibited a substantially higher PDI and a less negative zeta potential, indicating a less homogeneous system with reduced electrostatic repulsion. Trial A3, containing higher xanthan gum (1.5%), showed the largest droplet size (166.33 ± 3.16 nm) and highest PDI, suggesting that excessive polymer concentration may promote

droplet aggregation or hinder efficient emulsification during the second homogenization step. The combination of favorable particle size, narrow size distribution, adequate surface charge, and successful stress test results thus justified selecting Trial A1 for subsequent characterization.

Table 1. Preliminary screening of the W/O/W DE containing PPE and HA

Components		Trial A_1	Trial A_2	Trial A_3
Grapeseed oil (%)		15	18	15
Xanthan gum (%)		1.0	1.0	1.5
Particle size (nm)		155.07 ± 5.85	153.67 ± 2.29	166.33 ± 3.16
Polydispersity index		0.280 ± 0.048	0.430 ± 0.016	0.484 ± 0.004
Zeta potential (mV)		-24.77 ± 1.01	-13.23 ± 0.80	-
Centrifugation		X	X	X
Freeze-thaw cycle	**1**	X	X	X
	2	X	X	X
	3	X	X	X
	4	X	X	X
	5	X	X	X
	6	X	X	X

(X) - No phase separation; (√) - Phase separation

Characterization of PPE-HA W/O/W Double Emulsion Organoleptic Evaluation

Organoleptic evaluation assesses product attributes using human senses such as sight, touch, and smell, and a critical consumer-facing analysis in emulsion development. The garnered information complements instrumental data by determining the subjective quality and user acceptance of a formulation (Merga *et al*., 2022). In this study, the PPE-HA W/O/W DE was physically observed for color, odor, and visual phase separation at room temperature. As shown in Figure 1a, the freshly prepared formulation was a homogeneous creamy white without liquefaction. The resultant coloration in the PPE-HA W/O/W DE seen here was the incorporation of the pale yellow to brown PPE into the internal aqueous phase. It is a common occurrence as natural extracts often impart characteristic hues to formulations (Akhtar *et al*., 2011). Next, stability assessments over seven weeks at 4°C, 25°C, and 40°C demonstrated the formulation's robustness, with no phase separation observed at any temperature (Figure 1b). While the creamy white color of the PPE-HA W/O/W DE was maintained at 4°C and 25°C, it transitioned to a light brown at 40°C by week six. This color change is likely attributable to internal and external factors, such as time, elevated temperature, and redox reactions that can alter the phytocompounds within the PPE-HA emulsion (Silvestre *et al*., 2000).

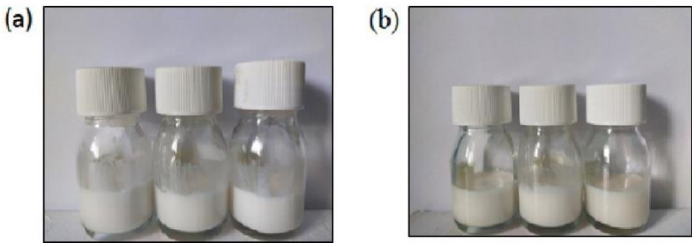


Figure 1 (a) Week 1 left to right: 4°C, 25°C, and 40°C and (b) Week 7 left to right: 4°C, 25°C, and 40°C.

MDS, PDI, and Zeta Potential

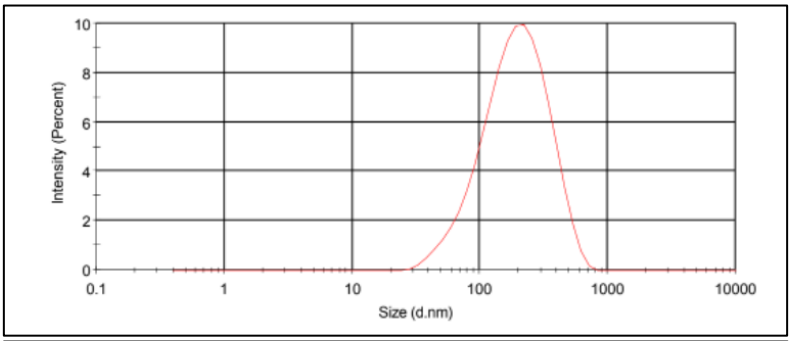
Established benchmarks for nanoemulsion stability include a particle size (Z-average) below 500 nm to enhance active delivery, a PDI < 0.3 indicating a monodisperse population, and a zeta potential > |±30| mV for electrostatic stability. However, for W/O/W double emulsions, the zeta potential requirement is often relaxed due to the dominant role of steric stabilization from surfactants and polymers (Salvia *et al*., 2017). A low PDI (<0.3) confirms an efficient emulsification process and reduces the risk of Ostwald ripening.

The optimized PPE-HA W/O/W DE exhibited a mean particle size of 155.07 ± 5.85 nm and a PDI of 0.280 ± 0.048 (Figure 2a). These values are significant not as standalone numbers, but for what they predict about formulation performance. The sub-200 nm droplet size suggests a large interfacial surface area for mass transfer, which could facilitate the release of encapsulated PPE and HA upon application. The low PDI (<0.3) indicates a monodisperse population, which is advantageous because uniform droplet sizes experience similar Laplace pressures, reducing the thermodynamic driving force for Ostwald ripening (Kaci *et al*., 2018). This uniformity likely contributed to the formulation's resistance to droplet growth during early-stage storage, as discussed in Section 4.2. The successful achievement of this size distribution confirms that the two-step emulsification process, combining ultra-homogenization and ultrasonication—was effective for this specific multi-component system.

The optimized formulation exhibited a zeta potential of -24.77 ± 1.01 mV (Figure 2b). While this value is below the ±30 mV threshold commonly cited as indicative of strong electrostatic stabilization, it must be interpreted within the context of this specific emulsion system. The ±30 mV benchmark is most relevant for systems where electrostatic repulsion is the primary stabilization mechanism. In W/O/W double emulsions, however, stability is multimodal: (i) steric stabilization provided by non-ionic surfactants (Span 80 and Tween 80), which form physically robust interfacial films, (ii) viscosity modification by xanthan gum in the continuous phase, which retards droplet movement and collision, and (iii) osmotic balancing with $MgSO_4$, which minimizes water diffusion between aqueous compartments.

The observed zeta potential of approximately -25 mV therefore indicates that while electrostatic repulsion contributes to colloidal stability, it is not the sole—or even primary—mechanism. The negative charge likely originates from hydroxide ions associated with glycerol and xanthan gum in the external phase (Gharehbeglou *et al*., 2019), while Tween 80 contributes an additional steric barrier through its hydrated polyoxyethylene chains. This combination of moderate electrostatic repulsion and robust steric stabilization appears sufficient to maintain droplet dispersion and resist aggregation over the seven-week study period, as evidenced by the absence of phase separation and the controlled nature of droplet growth (Section 4.2). Nevertheless, the borderline zeta potential suggests that the formulation may be more susceptible to destabilization under conditions that compromise the steric barrier (e.g., high electrolyte concentrations, extreme temperatures) than systems with stronger electrostatic contributions. This represents a consideration for future formulation optimization, should longer-term stability testing reveal limitations.

a)



b)

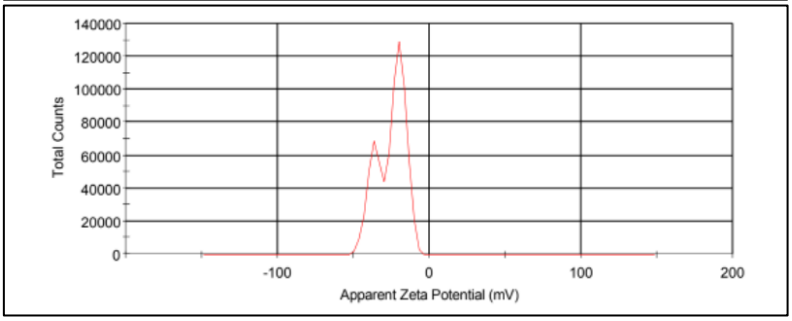


Figure 2. a) Particle size distribution and b) zeta potential scattering of the optimized PPE-HA W/O/W DE

pH, Conductivity and Viscosity

The initial pH of the PPE-HA W/O/W DE (5.42 ± 0.02) falls within the physiological range of healthy skin (4.0–6.0), indicating compatibility with the skin's acid mantle and a low likelihood of irritation upon application

(Hawkins *et al*., 2021). This pH value is not merely "acceptable" but may confer functional benefits, as slightly acidic formulations support skin barrier function and enzymatic activity involved in ceramide synthesis. Maintaining this pH over 7 weeks (mean 5.02 ± 0.24; Figure 6a) suggests that neither hydrolytic degradation of emulsion components nor microbial metabolism significantly altered the chemical environment during storage.

Meanwhile, the initial conductivity of 1.79 µS/cm is remarkably low for a system containing an aqueous phase. This low value provides indirect evidence that the oil membrane remained intact and that the encapsulated ions (from PPE, HA, and $MgSO_4$) were largely retained within the internal aqueous compartments (Schuch *et al*., 2014). If widespread coalescence or phase inversion had occurred, a sharp increase in conductivity would be expected as electrolytes were released into the continuous phase. The sustained low conductivity throughout the study period (1.70–1.91 µS/cm, Figure 6b) thus serves as a functional indicator of multiple emulsion integrity.

Rheological analysis revealed pseudoplastic (shear-thinning) behavior (Figure 3), a characteristic feature of xanthan gum-thickened systems. While this behavior itself is not novel, its confirmation in this specific formulation is significant for two reasons. First, it demonstrates that the complex multi-component system (containing oil droplets, internal aqueous compartments, and multiple surfactants) does not disrupt the expected rheological profile of the xanthan gum network. Second, the pseudoplastic behavior has direct practical implications: the formulation remains viscous and stable during storage but thins upon the shear stress of application, facilitating even spreading and potentially enhancing skin penetration (Berdey and Voyt, 2016). The viscosity at high shear (2.67 cP at 50 s^{-1}) suggests that the formulation spreads readily, consistent with the favorable spreadability scores (6.7) reported in the sensory evaluation.

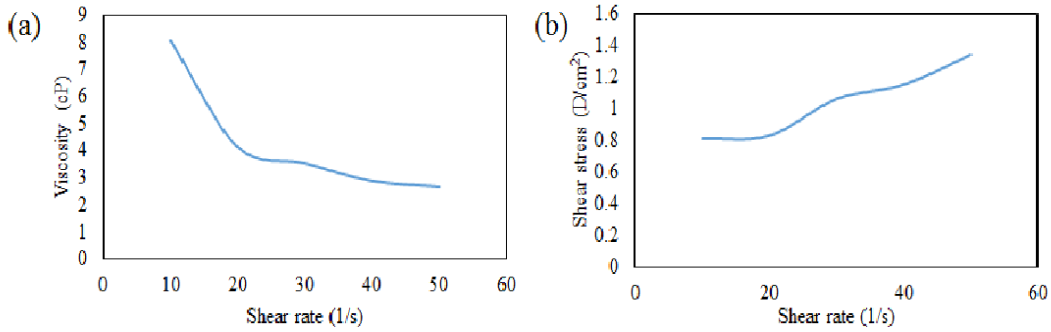


Figure 3. Rheological data showing the influence of (a) shear rate on the viscosity and b) the shear stress on the PPE-HA W/O/W DE

While pseudoplasticity is well-documented for xanthan gum-stabilized systems, its confirmation here is significant as it validates that the complex, multi-component PPE-HA W/O/W DE possesses the rheological profile necessary for a positive user experience and practical application. The data confirm that the optimized concentrations of grapeseed oil and xanthan gum successfully established this key quality attribute within the novel formulation.

Atomic Force Microscopy (AFM)

The morphology of the optimal PPE-HA W/O/W DE was further investigated using atomic force microscopy (AFM). As shown in Figure 4, the images provide qualitative visualization of the emulsion droplets, generally confirming their spherical nature. The droplet sizes observed in the AFM images (ranging from 61.99 nm to 157.3 nm, with an average of 127.40 ± 39.15 nm from five representative droplets) are in reasonable agreement with the mean droplet size obtained from dynamic light scattering (DLS), thereby corroborating the particle size analysis.

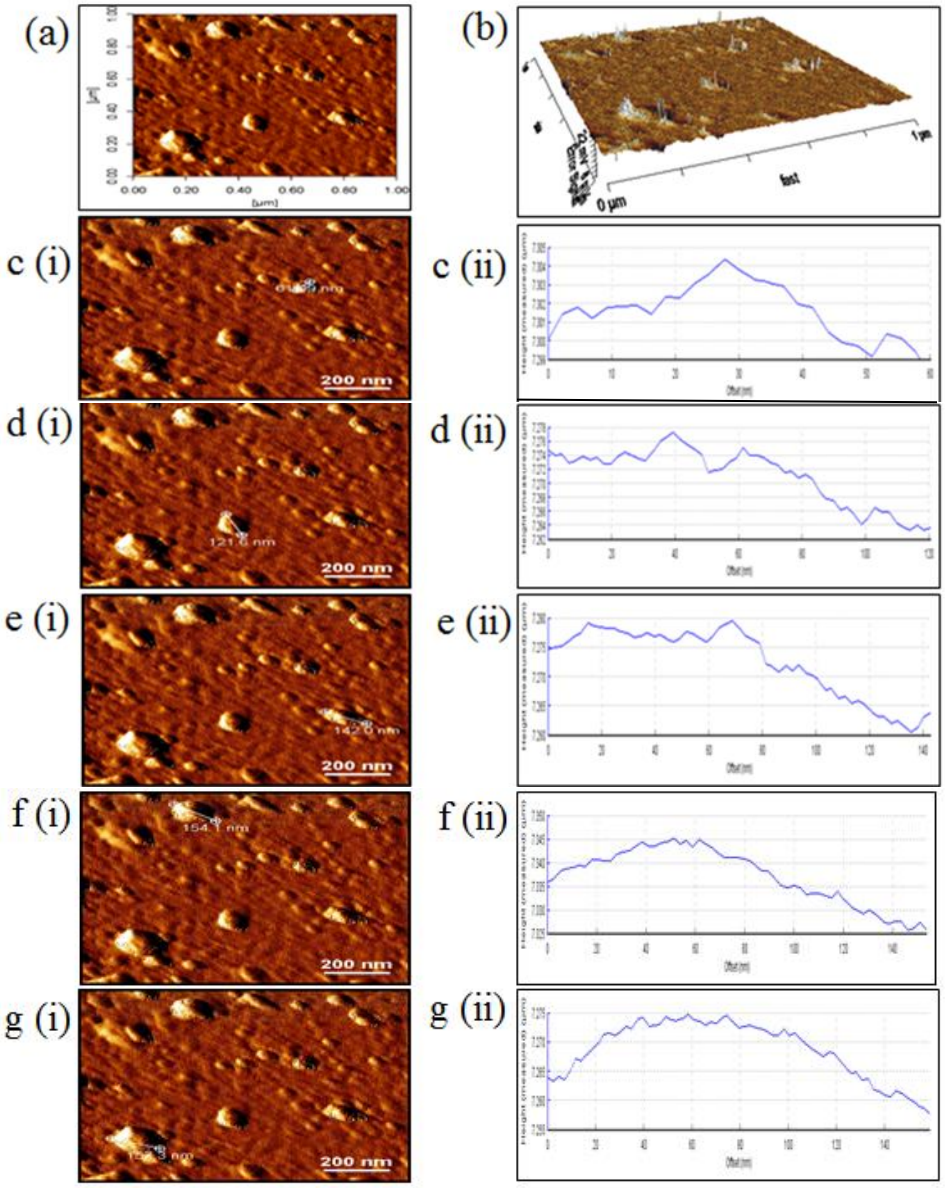


Figure 4. AFM images of the optimal DE (a) error signal of 1 x 1 µm^2 area; (b) 3D topography of 1 x 1 µm^2 area; c (i), d (i), e (i), f (i), g (i) are 2D topography of the selected droplets and c (ii), d (ii), e (ii), f (ii), g (ii) are height profiles of the selected droplets in the PPE-HA W/O/W DE

It is important to interpret these micrographs with caution, as the AFM sample preparation, which requires drying the emulsion on a mica substrate, can introduce artifacts. The presence of some micelles and elongated droplets (Figure 4a) is likely attributable to the partial evaporation of the external aqueous phase during the drying process, which can lead to droplet deformation, aggregation, or coalescence (Prasad *et al*., 2022). Consequently, while the AFM images offer valuable visual confirmation of droplet sphericity and an approximate size distribution, the quantitative particle size data presented in the derived DLS measurements of the emulsion in its native, hydrated state, are considered more reliable for assessing the formulation's true hydrodynamic diameter and polydispersity. Taken together, the DLS and AFM data suggest that the small mean droplet size and optimized composition work in concert to inhibit gross destabilization of the PPE-HA W/O/W DE.

Stability Tests

The stability of the PPE-HA W/O/W DE was assessed using centrifugation under various storage conditions, as the test represents the shelf-life of W/O/W DEs with high accuracy (Navarro-Pérez *et al*.,

202). All formulations (Trials A1, A2, and A3) withstood ultracentrifugation at 10,000 rpm for 10 minutes without evidence of phase separation, indicating robust resistance to gravitational stress. Similarly, all formulations remained stable throughout six consecutive freeze-thaw cycles, with no observable phase separation or creaming (Figure 5). These accelerated tests subject the emulsion to extreme mechanical and thermal stress, and the absence of failure suggests that the interfacial films—stabilized by the combination of lipophilic Span 80 and hydrophilic Tween 80, possess sufficient mechanical strength and elasticity to resist coalescence under these conditions. While these results are encouraging, accelerated tests are predictive but not definitive; they suggest good kinetic stability but cannot substitute for real-time stability data under normal storage conditions.

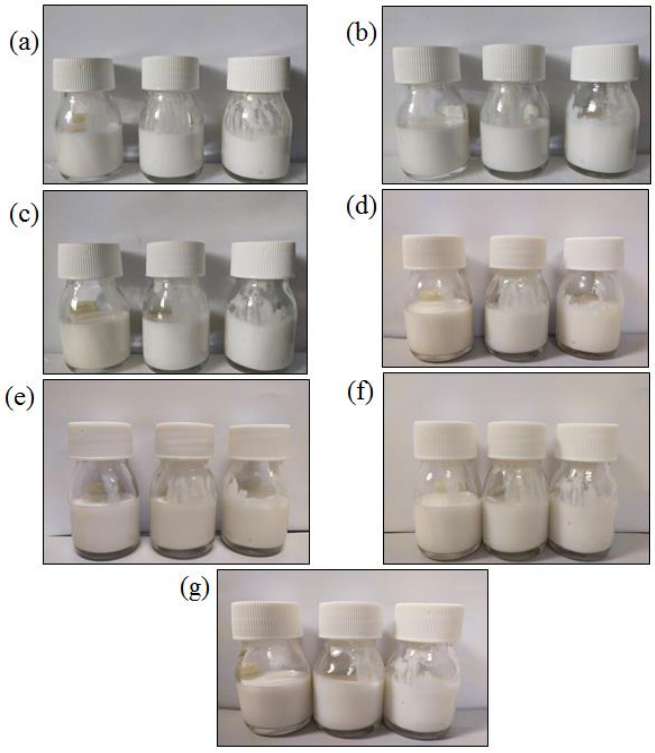


Figure 5. Freeze-thaw cycles (a) Freshly prepared PPE-HA W/O/W DE; (b) Cycle 1; (c) Cycle 2; (d) Cycle 3; (e) Cycle 4; (f) Cycle 5; (g) Cycle 6

Accelerated and Long-term Stability Test

The stability of the optimized PPE-HA W/O/W DE was further evaluated over seven weeks of storage at 4°C, 25°C, and 40°C. Macroscopically, the formulation showed no phase separation or liquefaction at any temperature throughout the study period (Table 2), confirming its resistance to gross physical destabilization. A color change from creamy white to light brown was observed at 40°C by week six, likely attributable to thermally induced oxidative changes in the polyphenolic constituents of PPE (Silvestre *et al*., 2000). This observation underscores the importance of temperature control during storage and suggests that refrigeration may be preferable for maintaining the formulation's aesthetic appearance over time.

Microscopic stability was assessed by monitoring pH, conductivity, droplet size, and polydispersity index (PDI) of samples stored at 25°C (Figures 6 and 7). The pH remained within the skin-compatible range (4.75–5.42; mean 5.02 ± 0.24) throughout the study, indicating no significant hydrolysis or generation of acidic degradation products. Conductivity remained consistently low (1.70–1.91 µS/cm), suggesting that the oil membrane remained intact and that electrolyte migration between the internal and external aqueous phases was minimal (Schuch *et al*., 2014; Khan *et al*., 2016).

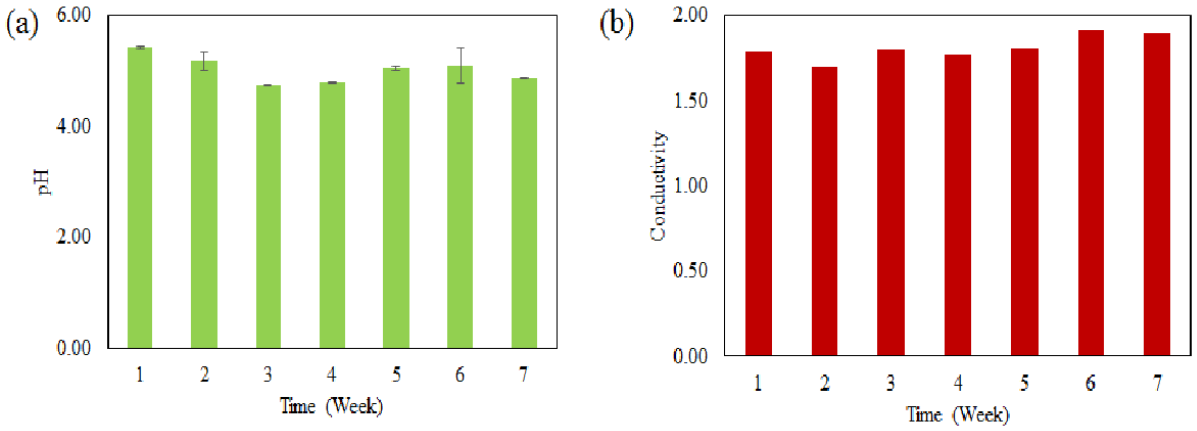


Figure 6. The a) pH value and b) the conductivity of the most stable PPE-HA W/O/W DE with incubation at 25°C)

Table 2. Stability of the PPE-HA W/O/W DE at different storage temperatures

Parameters	Colour			Liquefaction			Phase separation		
Time	4°C	25°C	40°C	4°C	25°C	40°C	4°C	25°C	40°C
Fresh	CW	CW	CW	X	X	X	X	X	X
Week 1	CW	CW	CW	X	X	X	X	X	X
Week 2	CW	CW	CW	X	X	X	X	X	X
Week 3	CW	CW	CW	X	X	X	X	X	X
Week 4	CW	CW	CW	X	X	X	X	X	X
Week 5	CW	CW	CW	X	X	X	X	X	X
Week 6	CW	CW	LB	X	X	X	X	X	X
Week 7	CW	CW	LB	X	X	X	X	X	X

CW – Creamy white; LB – Light brown; X – No liquefaction/ no phase separation

The mean droplet size (MDS) increased progressively over the 7-week period, from 155.07 ± 5.85 nm at week 1 to 404.84 ± 13.88 nm at week 7 (Figure 7a). The PDI increased correspondingly from 0.280 ± 0.048 to 0.560, indicating a transition from a monodisperse to a more polydisperse system. While this droplet growth is notable, it is important to contextualize its implications. An increase to approximately 400 nm remains within the size range generally considered acceptable for topical nanoemulsions (<500 nm) (Rai *et al*., 2018), suggesting that the formulation would likely retain its ability to facilitate skin penetration of encapsulated actives. However, this size progression may have functional and sensory consequences that warrant discussion. This elevated viscosity impedes the movement of oil droplets, thereby inhibiting creaming and phase separation,and ensuring long-term stability (Barradas and Holanda de Silva, 2020). Moreover, the successful use of this natural polysaccharide supported a key objective of the study: to replace synthetic ingredients with a natural alternative to formulate the PPE-HA W/O/W DE.

The increase in droplet size over time could potentially affect both product performance and user experience. Functionally, larger droplets exhibit a reduced interfacial surface area for mass transfer, potentially slowing the release rate of encapsulated actives (PPE and HA) upon skin application. While this could theoretically prolong the duration of action, it might also reduce the initial bioavailability of active ingredients. Sensorially, the observed increase in PDI and droplet size may correlate with the tactile perceptions reported in Section 4.4. Larger droplets and broader size distributions can alter the rheological properties of an emulsion, potentially contributing to the sensations of stickiness and greasiness noted by panelists. The moderate increase in viscosity that often accompanies droplet coalescence may explain why the PPE-HA W/O/W DE was perceived as stickier than the commercial comparator. This connection between microstructural evolution and sensory perception represents an important consideration for future formulation optimization. Furthermore, glycerol was added to the system to act as a cosurfactant, which could work synergistically to strengthen the interfacial film by integrating into its structurally weaker areas, thereby improving cohesion and preventing coalescence (Pavoni *et al*., 2020), in the PPE-HA W/O/W DE.

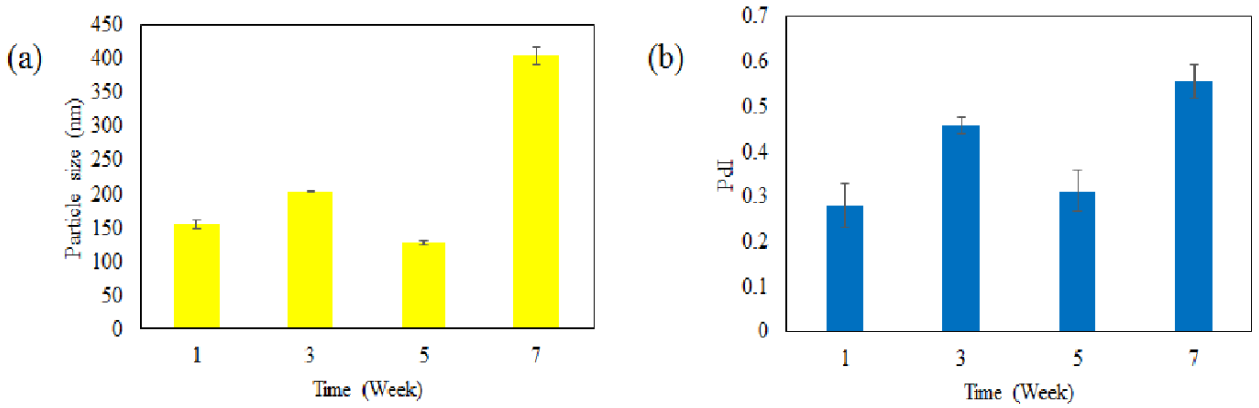


Figure 7. The (a) MDS (nm) and PDI of the optimized PPE-HA W/O/W DE with incubation at 25°C for up to 7 weeks

Rate of Coalescence and Ostwald Ripening

To elucidate the mechanisms underlying the observed droplet growth, the experimental data were fitted to kinetic models for coalescence and Ostwald ripening (Figure 8). While the coalescence rate is a valuable indicator, it is often complemented by other metrics, such as drainage (creaming/sedimentation), Ostwald ripening rate, interfacial rheology, and leakage tests, to provide a holistic stability assessment in W/O/W systems (Rhee *et al*., 2002). The non-linear relationship observed in the plot of $1/r^2$ versus time ($R^2 = 0.511$ for a linear fit) suggests that coalescence was not the dominant mechanism driving droplet growth in this system. Similarly, the poor linear fit of the r^3 versus time plot ($R^2 = 0.511$) indicates that Ostwald ripening, driven by the diffusion of dispersed-phase material from smaller to larger droplets, was not the primary instability mechanism.

These model-fitting analyses suggest that the PPE-HA W/O/W DE possesses inherent resistance to both classical destabilization pathways. This stability is likely attributable to several formulation design elements: (i) the combination of Span 80 and Tween 80 forming a robust, sterically stabilizing interfacial film, (ii) the inclusion of $MgSO_4$ (0.7%) in the internal aqueous phase to balance osmotic pressure and minimize water diffusion between aqueous compartments (Chen *et al*., 2019; Zhu *et al*., 2018; Romes *et al*., 2021), and (iii) the presence of xanthan gum in the external phase, which increases viscosity and retards droplet movement and collision.

The next part of this study investigates the occurrence of Ostwald ripening in the PPE-HA W/O/W DE, which was the primary mechanism causing the instability of emulsions. It is also a key mechanism of instability that describes the correlation between PDI and resistance to ripening, specifically emulsion stability. During this process, small droplets diffuse through the continuous phase to form larger droplets due to the difference in chemical potential (Liu *et al*., 2019). Moreover, the osmotic pressure gradient in a DE can drive diffusion of internal aqueous droplets to the external aqueous droplets, leading to Ostwald ripening (Leister and Karbstein, 2020). In this investigation, the stability of the PPE-HA W/O/W DE was investigated by plotting the graph of r3 versus time. The growth of MDS is said to be affected by Ostwald ripening if the r^3-time graph is linear. The stability mechanism of the PPE-HA W/O/W DE was further elucidated by the non-linear particle growth profile over seven weeks (Figure 8a-b). It was found that the notably low coefficient of determination ($R^2 = 0.511$) (Figure 8b) for a linear fit indicates that Ostwald ripening was not the dominant instability mechanism during extended storage of the PPE-HA W/O/W DE. This stability can be attributed to the inclusion of 0.7% $MgSO_4$ in the internal aqueous phase, which balanced the osmotic pressure and minimized water diffusion between the two aqueous phases, thereby suppressing Ostwald ripening (Zhu *et al*., 2018). The outcome seen here reflects the advantageous use of MgSO4 (0.7%) in the internal aqueous phase in osmotic-modulation of the PPE-HA W/O/W DE, as reported in a similar study, where the solute (MgSO4) addition modifies osmotic pressure gradients and reduces water diffusion between aqueous phases (Chen *et al*., 2019). Hence, it was shown that the increase in MDS of PPE-HA W/O/W DE from 128.13 ± 3.13 nm to 404.84 ± 13.88 nm during seven weeks of storage was not affected by coalescence and Ostwald ripening, conveying the suitability of the formulation produced in this study.

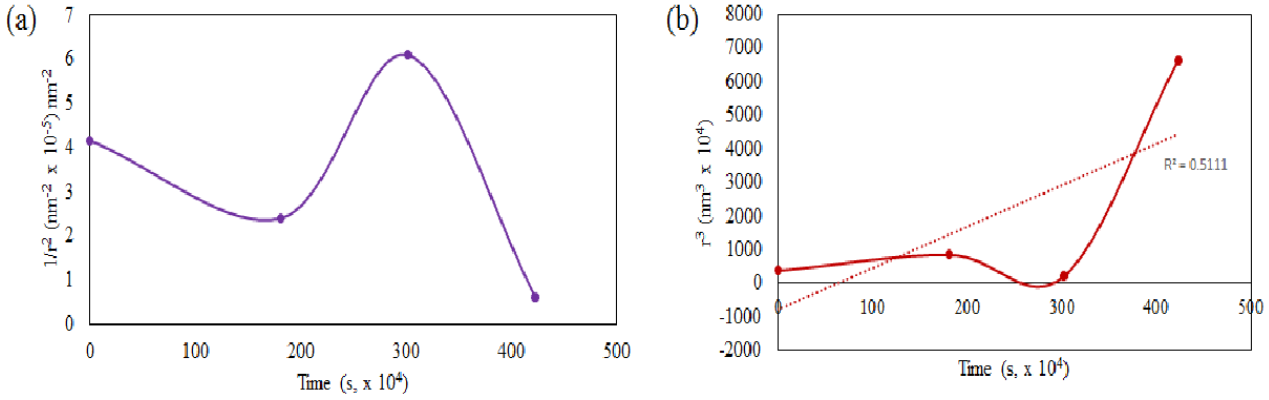


Figure 8. The (a) Plot of $1/r^2$ (nm^{-2}, x 10^{-5}) against time (s, x 10^4) at 25°C and (b) r^3 (nm^3, x 10^4) against time (s, x 10^4) for the PPE-HA W/O/W DE with incubation at 25°C for up to 7 weeks

However, it is important to acknowledge that these mechanistic interpretations are inferred indirectly from mathematical modeling of droplet-size data rather than directly observed. Techniques such as time-resolved microscopy or cryo-TEM would provide more definitive evidence of the specific microstructural changes occurring during storage and could confirm whether alternative mechanisms (e.g., partial coalescence, flocculation followed by fusion) contribute to the observed droplet growth. The absence of such direct visualization represents a limitation of the current study.

Furthermore, the seven-week duration of this stability study, while sufficient to observe initial trends in droplet evolution, is relatively short compared to the typical shelf-life requirements for commercial cosmetic products (typically 12–36 months). The data presented here should therefore be interpreted as evidence of promising short-to-medium-term kinetic stability, with long-term stability requiring confirmation through extended storage studies (≥12 months) conducted under ICH or analogous guidelines. The progressive droplet growth observed between weeks 5 and 7 (from 128.13 nm to 404.84 nm) underscores the importance of extended monitoring, as this trajectory, if continued, could eventually lead to droplet sizes exceeding the nanoemulsion range (>500 nm) with potential consequences for both efficacy and sensory acceptability.

Sensory Evaluation

Hedonic sensory evaluation of emulsions is a specific type of consumer testing that measures the degree of liking or acceptability of a product based on the personal preferences of a target user group. It is important to note that hedonic testing is purely subjective and focuses on the consumer's emotional and preference responses (Chigira *et al.*, 2017). The results, presented in the radar plot (Figure 9) and Table 3, provide insights into the formulation's perceptual strengths and areas requiring refinement. The PPE-HA W/O/W DE achieved overall acceptance scores (6.4) comparable to the commercial reference product (6.5), indicating that the prototype formulation is broadly acceptable to consumers despite being an unoptimized, first-generation prototype. This parity is notable, as achieving sensory equivalence to an established market product is a significant milestone in formulation development. Color (6.8) and fragrance (6.5) were the highest-rated attributes for the PPE-HA W/O/W DE, with the fragrance score exceeding that of the commercial product (6.1). The "berries" fragrance added during formulation likely contributed to this preference, suggesting that olfactory appeal can positively influence initial consumer perception. The color rating confirms that the pale hue imparted by PPE did not detract from visual acceptability.

The formulation demonstrated good spreadability (6.7), outperforming the commercial product (6.4) in this attribute. This finding aligns with the pseudoplastic rheological behavior discussed in Section 4.3. The shear-thinning properties imparted by xanthan gum allow the cream to thin upon application, facilitating even distribution across the skin. Glycerol also can act as an emollient and a co-surfactant to improve the formulation's texture (Mehling *et al.*, 2010). This is a functional advantage directly linked to the formulation's design.

However, the PPE-HA W/O/W DE received lower scores than the commercial product for several tactile attributes: stickiness (6.0 vs. 6.4), greasiness (5.5 vs. 6.2), and post-rub-in feeling (6.2 vs. 6.6). These lower ratings point to specific formulation shortcomings that impact the user experience upon and after

application. The elevated stickiness is likely attributable to two factors: (i) the presence of hyaluronic acid in the internal aqueous phase, which forms a highly viscous gel upon hydration, and (ii) the use of Tween 80, a surfactant known to increase viscosity and tackiness in topical formulations (Miastkowska *et al*., 2020). The greasiness perception, though rated only moderately (5.5 = "neither like nor dislike"), suggests that the oily phase components may impart a residual film that some users find less pleasant. These tactile perceptions likely contributed to the lower post-rub-in feeling score, indicating that the sensory experience after absorption requires improvement. While the formulation's absorbency (6.1) was only slightly lower than that of the commercial product (6.2), the combined tactile shortcomings suggest that the current formulation, while stable and functional, may not yet deliver the sensory elegance consumers expect. The glycerol content contributed positively to absorbency and texture, but it apparently was insufficient to fully offset the tackiness and greasiness imparted by other components.

Importantly, the overall acceptance score of 6.4 suggests that consumers are, on balance, willing to consider using this product despite its tactile limitations. This moderate level of acceptance provides a foundation for iterative optimization. Future iterations should focus on reducing greasiness and stickiness through several strategies: (i) optimizing the surfactant blend to reduce tackiness while maintaining stability, (ii) exploring co-emulsifiers or texture modifiers that can mitigate the greasiness of the oil phase, and (iii) adjusting the concentration of HA or its localization within the emulsion to minimize its viscosity-enhancing effects on bulk texture. Such refinements could elevate the sensory profile without compromising the physicochemical stability demonstrated in this study.

In summary, the sensory evaluation confirms that the PPE-HA W/O/W DE is broadly acceptable to consumers and performs comparably to a commercial benchmark in key attributes. However, the data also identify clear opportunities for improvement in tactile properties, providing specific targets for future formulation development to achieve both stability and sensory elegance.

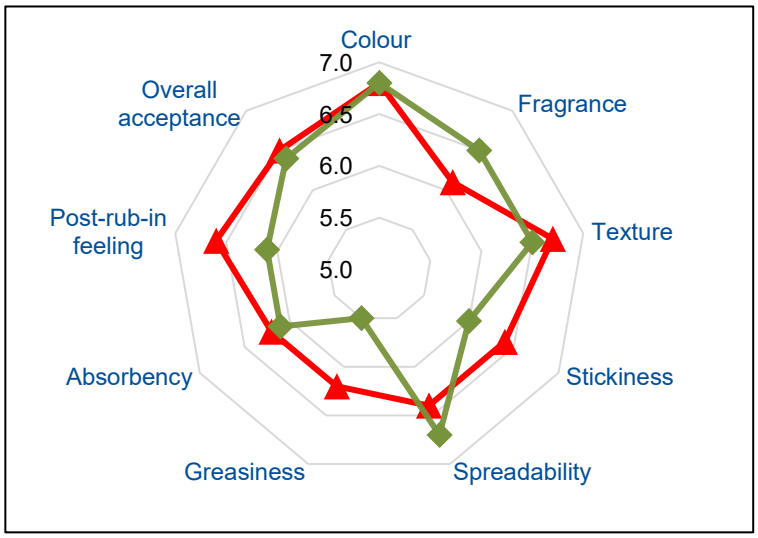


Figure 9. Radar plot of hedonic sensory evaluation of PPE-HA W/O/W DE and commercial product for nine parameters (Red–commercial product and Grey - PPE-HA W/O/W DE)

Table 3. Results of the mean hedonic sensory evaluation of the PPE-HA W/O/W DE and the commercial product tested on 40 volunteers

Samples/ Parameters	Commercial product	PPE-HA W/O/W DE
Color	6.8	6.8
Fragrance	6.1	6.5
Texture	6.7	6.5
Stickiness	6.4	6.0
Spreadability	6.4	6.7
Greasiness	6.2	5.5
Absorbency	6.2	6.1
Post-rub-in feeling	6.6	6.2
Overall acceptance	6.5	6.4

Conclusions

This study successfully developed a water-in-oil-in-water (W/O/W) double emulsion encapsulating pomegranate peel extract (PPE) and hyaluronic acid (HA) using a two-step emulsification process. The optimal formulation, comprising 15% grapeseed oil and 1.0% xanthan gum, produced stable double emulsions with a mean droplet size of 155.07 ± 5.85 nm, a polydispersity index of 0.280 ± 0.048, and a zeta potential of -24.77 ± 1.01 mV, as confirmed by AFM imaging. The formulation exhibited pseudoplastic rheological behavior, favorable for topical application, and maintained a skin-compatible pH (5.02 ± 0.24) throughout 7 weeks of storage at 25°C. Stability assessments demonstrated that the emulsion was resistant to coalescence and Ostwald ripening over the study period, with conductivity measurements (1.70–1.91 µS/cm) confirming the structural integrity of the multiple emulsion system. Sensory evaluation indicated comparable consumer acceptance to a commercial product, with particular preference for the formulation's fragrance and spreadability.

While these findings demonstrate the successful formulation and physicochemical stability of the PPE-HA W/O/W DE, the following limitations should be acknowledged. The stability study was conducted over a relatively short period (7 weeks), which may not fully account for long-term storage effects on formulation performance. Furthermore, this study focused exclusively on physicochemical characterization and sensory evaluation; no biological or efficacy testing (e.g., antioxidant activity assays, skin penetration studies, or in vivo efficacy trials) was performed. Consequently, claims regarding the formulation's dermatological benefits, therapeutic efficacy, or its capacity to serve as a direct replacement for synthetic cosmetic ingredients cannot be substantiated by the current data.

It is pertinent to indicate here that the primary contribution of this work is the establishment of a foundational formulation strategy for incorporating PPE and HA into a stable double emulsion system suitable for topical applications. These promising preliminary results provide a rationale for more comprehensive investigations. Future studies should prioritize extended stability assessments beyond seven weeks, incorporate biological evaluations including cell-based assays and skin permeation studies, and conduct controlled clinical trials to validate any potential dermatological benefits. Such work would be necessary before any substantive claims regarding the formulation's efficacy or its comparative performance against synthetic alternatives can be made.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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