







Article

Chemical and Rheological Characterization of a Facial Mask Containing an Olive Pomace Fraction

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Abstract: Cosmetic interest in agro-industrial byproducts is growing. In fact, many studies have shown that these residues present bioactive compounds with several skincare applications. One example is olive byproducts, such as olive pomace, which has a composition rich in phenolic compounds. As the production of olive oil is increasing, the amount of byproducts being generated is escalating, with significant constraints in their safe disposal due to their phytotoxic nature. The present study aimed to, from a zero-waste perspective, characterize and add value to a sub-byproduct, a semi-solid paste (SSP) derived from a patent process of olive pomace extraction. The chemical analysis of this residue revealed high moisture and significant protein, fat, and ash contents. Furthermore, vitamin E total phenolics and flavonoid content were assessed, as well as antioxidant activity, using DPPH• (2,2-diphenyl-1-picrylhydrazyl radical) and FRAP (ferric reducing antioxidant power) methods. Based on this primary assessment, a facial mask with antioxidant properties was developed. Rheological analysis showed that the developed mask presented shear thinning behavior, thixotropy, and texture characteristics desirable for skincare use. The results of this study showed the successful incorporation of SSP into facial masks and provides a preliminary assessment of this byproduct's impact on the appearance and performance of these formulations.

Keywords: olive pomace; cosmetics; sustainability; facial mask; antioxidant; rheology



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1. Introduction

In recent years, sustainability has been a major driver of industry innovation, leading to new procedures and products while bearing in mind waste reduction and eco-friendly processes [1]. Considering the widespread use of skincare products in everyday life, cosmetic industry practices have a significant environmental impact [1]. Designing more sustainable products also complies with newer consumer concerns about environmental footprints. Sustainable development represents a pressing issue as the population increases and resources are depleted. The concept of a circular economy is based on the reduction/elimination of wastes through the upscaling of residues, thus adding value and expanding their life cycle [2]. In that sense, agri-food byproducts have been a recent focus of investigations. In fact, each year, byproducts represent billions of tons of residues that are discarded from various industries, posing a significant disposal problem [1]. Agri-food byproducts are promising sources of compounds with biological properties, representing renewable, low-cost, and sustainable raw materials [3].

One example of a circular economy in the agro-industrial sector is the olive byproduct valorization. The olive oil industry generates high amounts of waste, such as leaves, olive

pomace (OP), olive stones, and olive mill wastewater (OMWW), particularly during the agricultural phase and oil production stage [4]. OP, the main residue of olive oil production, is a semi-solid residue that contains olive husk and pulp, crushed olive stones, and water, with a moisture content of more than 60% depending on the cultivation region and the employed extraction method [4–6]. OP also contains a substantial amount of compounds, such as dietary fiber, unsaturated fatty acids, minerals, and phenolic compounds [7]. In fact, this byproduct is particularly rich in phenolic compounds—such as hydroxytyrosol, oleuropein, tyrosol, and others—that, due to their polar character, remain in the residues [8]. Phenolic compounds have demonstrated biological activities with cosmetic potential, such as antioxidant, anti-aging, photoprotector, and anti-inflammatory activities [9]. In turn, olive pomace is a major ecological concern due to its high phenolic and organic load and low pH, contributing to potentially hazardous effects on soil and water [4]. Aside from bringing environmental benefits, byproduct recycling strategies can provide social and economic advantages, thus increasing the sustainability of the olive oil industry [4]. As olive oil has been used as a cosmetic and skin protector since ancient times, olive pomace application in skincare is promising. A literature review suggests there are few cosmetics developed based on other olive byproducts, such as olive leaves [5,10] or OMWW [11], with potential antioxidant, anti-aging, and photoprotector claims; however, to the best of our knowledge, there are no olive pomace-based topic formulations.

The olive pomace fraction used in this study is a secondary byproduct that resulted from the extraction of bioactive components through an eco-friendly physical process (PCT/IB2018/060111). After centrifugation, a semi-solid paste (SSP) was obtained. This extraction method did not involve the use of organic solvents and presented economic advantages when compared with emergent non-conventional extraction processes. This strategy also provided the particular advantage of retaining various functional compounds—namely, fatty acids, polysaccharides, minerals, and phenolics. Achieving synergy between these components can favor multiactivity cosmetic formulations, thus adding functional properties and improving skin benefits. Considering the results of the chemical characterization, a facial mask with moisturizing and antioxidant properties, containing SSP as an ingredient, was developed. Facial masks are increasingly popular as they are accessible, can be easily applied, show instant effects on the skin, and are available in different forms adjusted to consumer needs. Facial masks with clay minerals are frequently used in skincare regimens due to their cleansing properties and skin-toning effects. Other ingredients, such as vitamins, proteins, or substances with exfoliating or moisturizing properties, can also be added to facial masks [12]. In fact, anti-pollution skincare is one of the latest cosmetic trends and is based on ingredients and formulations that can, on one hand, purify and remove chemical pollutants from the skin, and on the other hand, possess biological activities that counteract the negative effects of airborne pollutants, particularly oxidative damage through the formation of reactive oxygen species (ROS) [13]. Air pollution, along with other exogenous factors, such as ultraviolet (UV) radiation and smoking, are recognized factors that lead to premature aging [13]. As a result of an imbalance between endogenous antioxidant production and ROS formation, oxidative damage to the skin cell components escalates [13]. Plant extracts are often rich in bioactive compounds, whose antioxidant and chelating activities can be exploited in anti-pollution formulations by reducing skin oxidative stress [13]. Phenolic compounds act as free radical scavengers preventing cell damage, thus delaying the skin aging process [14]. In that sense, this work presents a preliminary study on the valorization of olive pomace for a specific cosmetic application within a circular economy context.

2. Materials and Methods

2.1. Standards and Reagents

Folin-Ciocalteu's reagent, sodium carbonate, ferrous sulfate, 2,4,6-tri-(2-pyridyl)-S-triazine (TPTZ), ferric chloride, sodium nitrite, aluminum chloride, sodium hydroxide, 2,2-diphenyl-1-picrylhydrazyl radical (DPPH[•]), 6-hydroxy-2,5,7,8-tetramethylchroman-2-

carboxylic acid (Trolox), gallic acid, catechin, and butylated hydroxytoluene, were acquired from Sigma-Aldrich (St. Louis, MO, USA). Absolute ethanol was obtained from Fisher Chemical (Loughborough, England). Kjeldahl catalyst tablets, sulfuric acid, boric acid, potassium hydroxide, anhydrous sodium sulfate, and n-hexane (HPLC grade) were obtained from Merck (Darmstadt, Germany). Tocol (2-methyl-2-(4,8,12-trimethyl-tridecyl) chroman-6-ol) was obtained from Matreya Inc. (State College, PA, USA). Vitamin E standards were received from Calbiochem (La Jolla, CA, USA). For mask formulation, bentonite, glycerin, and panthenol were acquired from Acofarma (Madrid, Spain), and ethanol was purchased from Aga (Prior Velho, Portugal). Water was purified in a Milli-Q system (Millipore, Bedford, MA, USA). All other reagents were of an analytical grade.

2.2. Methods

2.2.1. Sample and Sample Preparation

Fresh olive pomace, collected immediately after olive oil production, was kindly provided by different olive oil producers (two samples from the North of Portugal, Trás-os-Montes, and two from the South, Alentejo). The samples were equally mixed in order to be representative of the Portuguese panorama regarding the main areas of olive oil production. A sample of the final olive pomace (200 g) was subjected to a patented process of extraction (PCT/IB2018/060111). Briefly, the sample was pressed using a hydraulic press (30 min), and the obtained semi-liquid fraction was collected. This fraction was further centrifuged (5000 rpm; 20 min), the supernatant was discarded for other applications, and the obtained pellet (SSP) was freeze-dried ($-80\text{ }^{\circ}\text{C}$, 0.015 mbar; Cryodos, Telstar, Barcelona, Spain) for further characterization and mask development (Figure 1).

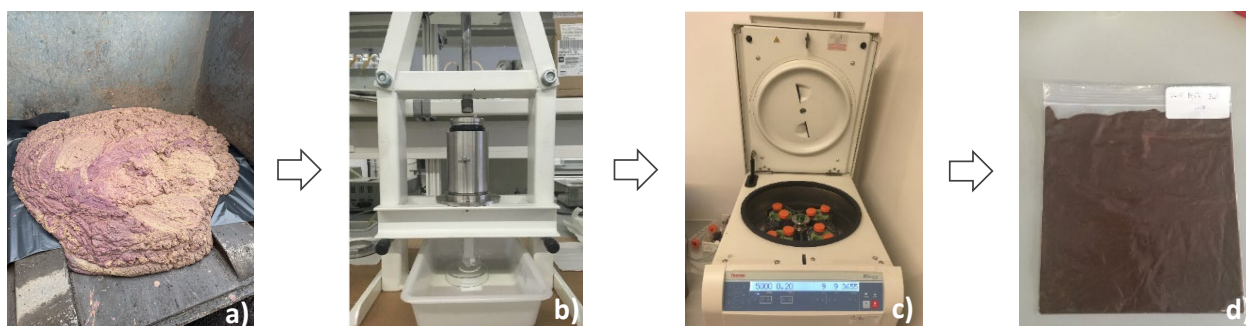


Figure 1. Summary of the steps employed to obtain the semi-solid paste (SSP) from fresh olive pomace. (a) fresh olive pomace (b) hydraulic press; (c) centrifugation; (d) SSP.

2.2.2. Proximate Analysis

Sample moisture was determined using an infrared balance (Scaltec model SMO01, Scaltec Instruments, Heiligenstadt, Germany). Total fat and total protein were determined using Soxhlet and Kjeldahl methods, respectively, according to AOAC standard methods [15]. The total protein content was calculated using 6.25 as the nitrogen conversion factor [16]. Ash content was determined through incineration at $500\text{ }^{\circ}\text{C}$ (Thermolyne 48000 Furnace, Barnstead/Thermolyne, Dubuque, IA, USA), following AOAC standard methods [15]. Each analysis was performed in triplicate.

2.2.3. Extracts Preparation

A sample aliquot (150 mg of the SSP or 2 g of the mask) was extracted with 50 mL of ethanol/water (80%/20%). The mixture was continuously stirred at 600 rpm in a heating plate (MS-H-S10 10-Channel Classic Magnetic Hotplate Stirrer, DLAB Instruments Ltd., Beijing, China) at $40 \pm 1\text{ }^{\circ}\text{C}$, for 60 min. Then, it was filtered (Whatman No. 4) and stored at $-20\text{ }^{\circ}\text{C}$ until analysis. The extraction was performed in triplicate for the evaluation of antioxidant activity and phenolic and flavonoid content.

2.2.4. Antioxidant Activity

Ferric Reducing Antioxidant Power (FRAP)

The FRAP assay was carried out according to Costa et al. [17]. Briefly, using a microplate, 35 μL of a diluted extract was mixed with 265 μL of the FRAP reagent (0.3 M of acetate buffer, 10 mM of TPTZ solution, and 20 mM of ferric chloride). The mixture was incubated at 37 °C for 30 min and protected from light. Absorbance was measured at 595 nm (Synergy HT Microplate Reader, BioTek Instruments, Inc., Winooski, VT, USA). The analysis was performed in triplicate, and the results were expressed as g of ferrous sulfate equivalents (FSE) per 100 g.

2,2-diphenyl-1-picrylhydrazyl radical (DPPH \bullet) Scavenging Ability

The radical scavenging potential was assessed according to Costa et al. [18]. In brief, 270 μL of an ethanolic DPPH \bullet solution (6.0×10^{-5} mol/L) was mixed with 30 μL of the extract. The absorbance decrease was measured every 2 min, at 515 nm, in order to observe the kinetic reaction (Synergy HT Microplate Reader, BioTek Instruments, Inc., Winooski, VT, USA). The reaction endpoint was reached at 20 min. The analysis was performed in triplicate, and the results were expressed as g of Trolox equivalents (TE) per 100 g.

2.2.5. Phenolic and Flavonoid Content

Total phenolic content was determined using spectrophotometry (Synergy HT Microplate Reader, BioTek Instruments, Inc., Winooski, VT, USA), according to Costa et al. [18] with minor modifications. Briefly, 30 μL of the extract was mixed with 150 μL of the Folin–Ciocalteu reagent (1:10). Then, 120 μL of sodium carbonate (7.5% *m/v*) was added, and the mixture was incubated at 45 °C for 15 min and protected from light. After 30 min at room temperature, absorbance was measured at 765 nm. The analysis was performed in triplicate, and the results were expressed as g of gallic acid equivalents (GAE) per 100 g.

Total flavonoids were estimated using a colorimetric assay based on Costa et al. [17]. In brief, 1 mL of the extract was mixed with 4 mL of deionized water and 300 μL of 5% sodium nitrite. After 5 min at room temperature, 300 μL of aluminum chloride 10% was added to the previous solution. After an additional 1 min at room temperature, 2 mL of sodium hydroxide and 2.5 mL of deionized water were added. The solution was mixed, and the absorbance was read at 510 nm (Microplate reader Synergy HT, BioTek Instruments, Inc., Winooski, VT, USA). The analysis was performed in triplicate, and the results were expressed as g of catechin equivalents (CE) per 100 g.

2.2.6. Vitamin E Profile

For vitamin E analysis, the SSP oil was first extracted using a cold extraction procedure, according to Alves et al. [19]. Briefly, an antioxidant (0.1% BHT, 75 μL), an internal standard (100 $\mu\text{g}/\text{mL}$ of tocol; 50 μL), and absolute ethanol (1 mL) were added to a 200 mg sample, being homogenized for 30 min in an orbital vortex mixer (VV3, VWR Int., Lutterworth, UK) with multiple sample supports. Then, 2 mL of n-hexane was added, and the solution was mixed again for 30 min. After that, 1 mL of NaCl 1% (*m/v*) was added. The mixture was vortexed and centrifuged (2 min, 5000 rpm; Labofuge Ae, Heraeus Sepatech, Germany), and the organic phase was collected. The residue was re-extracted twice with 2 mL of n-hexane, and the organic phases were combined. Then, a sufficient amount of anhydrous sodium sulfate was added to the final extract. The mixture was vortexed and centrifuged to collect the upper layer. The solvent was evaporated under nitrogen until reaching a volume of 500 μL . The chromatographic analysis was carried out using an HPLC system (Jasco, Tokyo, Japan) equipped with a multiwavelength diode array detector (MD-2015) that was coupled with an FP-2020 fluorescence detector (Jasco, Tokyo, Japan) and programmed for excitation at 290 and emission at 330 nm. The chromatographic separation of the compounds was achieved using a normal phase SupelcosilTM LC-SI column (75 mm \times 3.0 mm, 3.0 μm ; Supelco, Bellefonte, PA, USA). The vitamin E vitamers were identified based on

their UV spectra and by comparing their retention times with those of existing standards. Quantification was obtained using the internal standard method of fluorescence signals.

2.2.7. Facial Mask Formulation

A control base formulation (without SSP) and a base with 5% of SSP as an ingredient were developed. Powders (SSP and bentonite) were mixed in a mortar, and panthenol was added as a moisturizer. The mask vehicle was prepared by mixing water, ethanol, and glycerin at room temperature. Then, the vehicle was slowly added to the solid mixture through manual stirring until reaching complete homogenization.

Clay minerals, such as bentonite, are used in cosmetics—not only as rheology modifiers but also in facial masks—due to their high absorbency capabilities, in order to clean impurities, such as excess sebum or toxins [20,21]. Ethanol, due to its lower vapor pressure compared to water, is frequently used as a drying agent that controls the application time of facial masks, as these should dry quickly after being applied [12]. The correct balance between ethanol and glycerin (glycerin has hygroscopic properties, which delay mask drying) contributes to the acceptability and efficiency of the mask formula. The detailed composition of each mask is presented in Table 1.

Table 1. Composition of facial masks (% *w/w*): the control and the 5% SSP-containing mask.

Composition (INCI)	Control	SSP Mask
Bentonite	38.0	33.0
Glycerin	23.1	23.1
Alcohol	23.1	23.1
Panthenol	10.0	10.0
SSP	-	5
Purified water (<i>Aqua</i>)	5.8	5.8

2.2.8. pH Measurement

Measurements of the pH were carried out in dispersions (1%, *w/w*) of masks 15 days after preparation, in neutral water, using a potentiometer (Metrohm 827 pH lab, Herisau, Switzerland).

2.2.9. Texture and Rheological Analysis

The evaluation of texture and viscosity was performed 15 days after the preparation of the masks (base and 5% SSP mask) and storage at room temperature while protected from light.

The evaluation of the texture parameters (firmness and adhesiveness) was performed using a texturometer, Stable Micro Systems TA-XT2i (Haslemere, UK). The following test conditions were used: compression mode, cylindrical probe (13 mm, P/0.5), penetration distance of 5 mm, test speed of 3 mm/s, trigger force of 0.049 N, and load cell of 5 kg. The viscosity and the rheological behavior of the facial masks were evaluated using a rotational viscometer, Thermo Haake VT550 (Karlsruhe, Germany). Measurements were obtained at progressively higher shear rates (up to 500 s⁻¹) to obtain the ascending curve, and the procedure was repeated in reverse with progressively slower rates to obtain the descending curve. All measurements were made at room temperature (20.00 ± 0.04 °C), in triplicate, for each analyzed sample.

2.2.10. Statistical Analysis

Data are reported as mean ± standard deviation. Statistical analyses were performed using the statistical package IBM SPSS v 26 for Windows (SPSS Inc., Chicago, IL, USA). Student's *t*-test was used to discriminate between any two groups under consideration.

3. Results and Discussion

3.1. Proximate Analysis

Table 2 shows the results for the SSP chemical composition. The proximate analysis demonstrated a high moisture content (68.1%) and significant protein and fat contents (9.9 % and 9.6% in dry weight (dw), respectively). A previous study by Nunes et al. [22], regarding the chemical characterization of olive pomace, revealed lower values for these parameters—namely, 5.8% of fat and 7.4% of protein, expressed in dw. The ash content in SSP was also notably higher, with 5.2% dw versus olive pomace with 1.9% dw being mentioned in the cited work. In fact, olive pomace contains crushed olive kernels, which contributed to the weight of the sample, whereas olive the SSP used in this study was a smooth paste without kernels. This could be a contributing factor to the differences observed. Further, geographical and cultivation differences can account for the variations observed in chemical composition [4]. The samples in this work resulted from a mixture of two different geographical locations, whereas the sample used in the study of Nunes et al. [22] was derived from only one olive oil producer. The observed chemical features of SSP can be of interest in cosmetic applications. As demonstrated by Nunes et al. [22], the olive pomace oil fraction is essentially rich in monosaturated fatty acids, such as oleic acid. These substances provide structural stability to cell membranes and contribute to skin barrier integrity. Further, their emollient properties increase the hydration and softness of the skin. The unsaponifiable fraction also contains squalene, a natural component of human sebum, which has emollient qualities, as well as an effect as a skin barrier against solar radiation and antioxidant proprieties. Minerals have hygroscopic characteristics and are part of the natural moisturizing factor, which is essential to the stratum corneum hydration plasticity and homeostasis [4].

Table 2. Proximate analysis of the semi-solid paste (SSP) obtained from fresh olive pomace.

Moisture	Total Fat	Total Protein	Ash
68.1 ± 0.2	9.6 ± 1.3	9.9 ± 0.9	5.2 ± 0.1

Results expressed in dry weight (dw), g per 100 g of sample, as mean ± standard deviation.

3.2. Vitamin E Profile

In a previous study by Nunes et al. [22], it was evidenced that the vitamin E profile of olive pomace was comprised of the following vitamers: α -tocopherol, β -tocopherol, α -tocotrienol, and γ -tocopherol. α -Tocopherol was the major form (7.64 mg/100 g, dw), while the other vitamers were present in lower amounts. In the SSP, the same vitamers were also observed and, similarly, α -tocopherol was found to be the major vitamin E form (6.83 mg/100 g dw). α -Tocopherol is the most biologically active form of vitamin E, having a major role in the prevention of lipid peroxidation and the scavenging of lipid peroxy radicals; hence, its use in cosmetics formulations is extensive [22].

3.3. Phytochemicals and Antioxidant Activity

Plants often produce secondary metabolites with antioxidant characteristics as a response to environmental stressors, such as ultraviolet (UV) radiation or high temperatures, in order to preserve physical and metabolic integrity [3]. Olive phenolics have been widely studied for their health-promoting properties, especially oleuropein, hydroxytyrosol (HT), and tyrosol [9]. HT, in particular, is the main phenolic present in olive pomace and has been reported as a powerful antioxidant with anti-aging proprieties, including collagen metabolism influence, radical scavenging activity, and melanogenesis inhibition [6,23,24]. Flavonoids are bioactive polyphenols found in fruit and vegetables with extended nutraceutical, pharmaceutical, and cosmetic applications, due to their antioxidative, anti-inflammatory, anti-mutagenic, and anti-carcinogenic properties [25]. The flavonoids described in olive pomace include quercetin, apigenin, rutin, luteolin glucoside, luteolin, dismetin, taxifolin, and apigenin glucoside [26]. The results for total phenolic

content (TPC), total flavonoids (TF), and antioxidant activity are presented in Table 3. The content of phenolic compounds in olive pomace paste was 3.57 g/100 g dw. TPC was also evaluated in the masks, with values of 0.01 g/100 g for the control and 0.17 g/100 g for the 5% SSP-containing mask, showing a significant improvement in this parameter due to SSP incorporation. As phenolic compounds show low stability regarding environmental conditions, such as exposure to light, oxygen, and temperature, chemical assessment through stability testing should be performed in order to guarantee antioxidant efficacy during shelf-life [27].

Table 3. Phytochemical analysis, vitamin E content, and antioxidant activity of the semi-solid paste (SSP) obtained from the fresh olive pomace.

TPC (g GAE/100 g)	TF (g CE/100 g)	Vitamin E (mg/100 g)	DPPH• Inhibition (g TE/100 g)	FRAP (g FSE/100 g)	
3.57 ± 0.15	3.18 ± 0.17	Total	7.04 ± 0.10	4.95 ± 0.28	6.79 ± 0.32
		α-tocopherol	6.83 ± 0.11		
		β-tocopherol	0.08 ± 0.01		
		γ-tocopherol	0.12 ± 0.01		
		α-tocotrienol	0.01 ± 0.01		

Results expressed in dry weight, as mean ± standard deviation. GAE, gallic acid equivalents; CE, catechin equivalents; TE, Trolox equivalents; FSE, ferrous sulfate equivalents.

3.4. Facial Masks' Organoleptic Characterization

The masks developed in this study presented a homogenous appearance and similar green to grey coloring across both types. The formulations exhibited an opaque appearance with semi-solid consistency and no particular smell. Figure 2 shows the two masks' visual aspects: (A) a base mask (without SSP) as a control, and (B) the mask with 5% of the SSP incorporated.

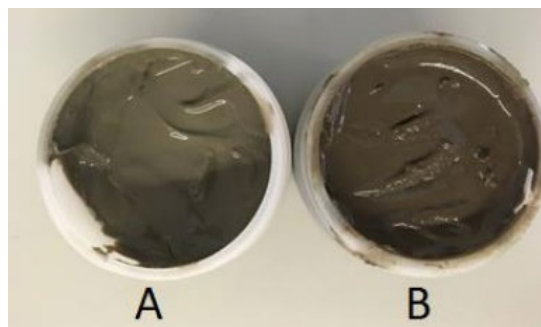


Figure 2. Control mask (A) and OPP mask (B).

3.4.1. pH Measurement

The pH of the control and SPP-based masks were both considerably high: 9.65 ± 0.01 and 9.39 ± 0.01 , respectively. The pH values of cosmetic products are important to maintain optimal skin balance. The acidic skin surface pH (4.0–4.5) is a key factor in its barrier function influencing various factors, such as the composition of stratum corneum lipids and hydration, as well as the resident microflora [28]. Increased skin surface pH may be associated with the pathogenesis or the severity of many skin disorders, including acute eczema, irritant contact dermatitis, atopic dermatitis, ichthyosis, acne vulgaris, and *Candida albicans* infections [28]. For topical application, suitability formulations should comply with natural skin pH, presenting an acidic to neutral pH [28]. As bentonite has alkaline properties, the addition of citric or lactic acid could enhance skin compatibility by lowering the formulation pH. It is worth mentioning that the SSP presented in the mask slightly lowered the pH, probably due to the acidic characteristics of phenolic and organic acids present in olive pomace.

3.4.2. Textural and Rheological Analysis

Effortless spreading and product adherence to the skin are important characteristics to consider when formulating cosmetic masks [29]. Once applied, the mask layer should remain in place and not drip. Rheology and texture analyses are valid tools to assess the impact of raw materials on the final formulation as well as quality control since these parameters can provide essential information about the structure, which can influence shelf-life as well as sensory and processing attributes [30].

Figure 3 shows the rheograms of the SSP-based mask and the control after 15 days of storage at room temperature. At the highest shear rate (500 s^{-1}), the control presented a lower apparent viscosity compared to the SSP mask ($901.7 \text{ Pa}\cdot\text{s}$ vs. $1164 \text{ Pa}\cdot\text{s}$). However, the increase in the shear rate produced a reduction in the viscosity of both masks, therefore displaying a shear thinning behavior. Formulations with this behavior improve application and spreading, thus providing a pleasant sensory feeling and skin coverage [31]. It is also possible to observe the presence of a hysteresis loop in both masks, thus indicating that these formulations are thixotropic materials. Thixotropy corresponds to a decrease in viscosity with time, which is also desirable in topical formulations because it helps to maintain the suspending components' stability and indicates a more cohesive structure [31]. Thixotropy was more pronounced in the base mask, which can indicate that SSP inclusion had an impact on the mask structure. In fact, SSP was incorporated by replacing 5% of bentonite in the base formula; since bentonite composition provides better holding water capacity, this fact should also be accounted for in the changes observed. It should also be noted that, since the SSP-containing mask and the respective control are suspensions, powders tend to deposit over time and separate from the vehicle [32]. Further, powders, such as bentonite, tend to hydrate progressively during storage, which can alter the viscosity and hinder spreadability. Therefore, further studies should include stability testing in order to predict shelf-life and ensure that the formulation's physical characteristics remain constant.

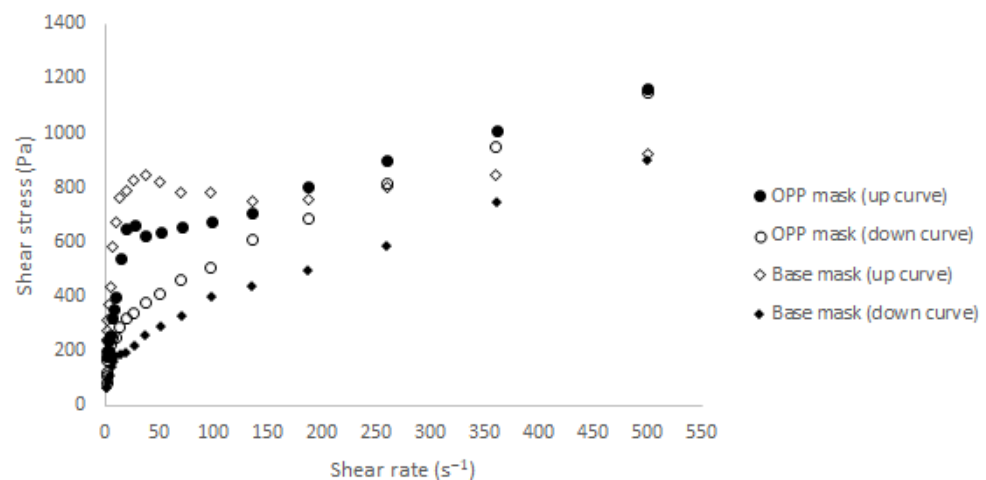


Figure 3. Rheograms, obtained for the control and 5% SSP-containing mask, at $20.00 \pm 0.04 \text{ }^\circ\text{C}$.

Figures 4 and 5 present the graphs corresponding to the evaluation, respectively, of the maximum force (firmness) and negative area (adhesiveness) of facial masks after 15 days of storage at room temperature. Similar values of adhesiveness were observed in both masks. Less adhesive facial masks may slide during application time, reducing their effectiveness and having a negative impact on the consumer experience; thus, these results favor SSP incorporation. Regarding firmness, the SSP-based mask presented higher values ($0.329 \pm 0.008 \text{ N}$) than the base mask ($0.221 \pm 0.011 \text{ N}$).

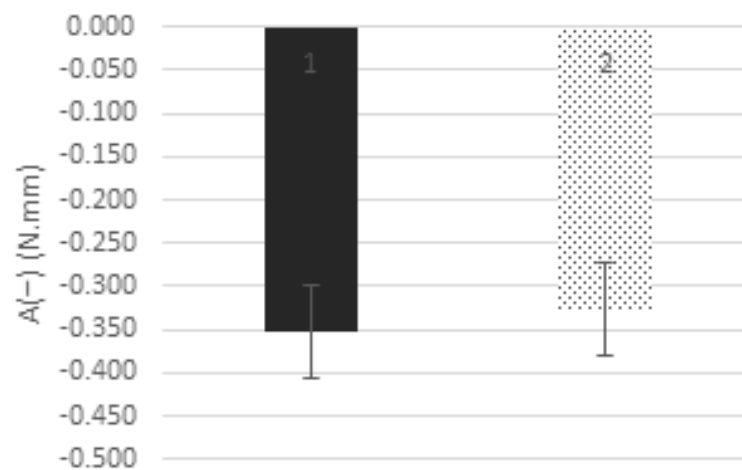


Figure 4. Texture analysis of the facial masks. (1) mask containing 5% of SSP; (2) control. Adhesiveness ($A(-)$) is represented in the bars as mean \pm standard deviation. No significant differences were found between samples ($p > 0.05$).

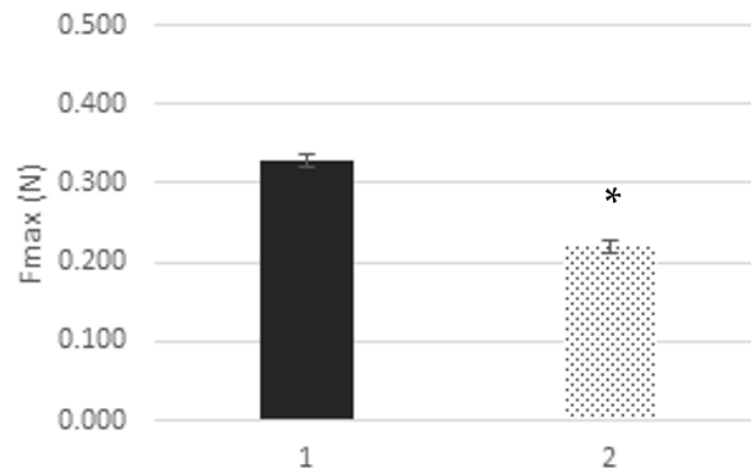


Figure 5. Texture analysis of the facial masks. (1) mask containing 5% of SSP; (2) control. Firmness (F_{max}) is represented in the bars as mean \pm standard deviation. *, Significant differences ($p < 0.05$) were found between samples.

4. Conclusions

This work highlights the potential of olive pomace to obtain an innovative ingredient (a semi-solid paste) to be used in facial mask formulations, as a sustainable source of both lipid and polar bioactive compounds. Indeed, the lipid fraction of this new ingredient is a source of antioxidants (such as vitamin E) and hydrosoluble compounds (such as phenolics) that protect the skin against oxidative stress. The 5% SSP-containing mask showed a 17-fold increase in total phenolic content compared to the base mask. This study also demonstrated that the SSP facial mask had a pleasant visual aspect, with no odor and good spreadability. This mask shows a pseudoplastic behavior with thixotropy, which are important characteristics for application and consumer acceptance. However, the SSP inclusion had an impact on the mask formulation, reducing thixotropy, which can be predictive of loss of stability. As this was a preliminary study, some important studies are missing. Further development should be focused on stability testing regarding microbiological, chemical, and physical properties to assess the efficacy, safety, and cosmetic quality of these types of facial masks.

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References

1. Mellou, F.; Varvaresou, A.; Papageorgiou, S. Renewable Sources: Applications in Personal Care Formulations. *Int. J. Cosmet. Sci.* **2019**, *41*, 517–525. [[CrossRef](#)] [[PubMed](#)]
2. Romani, A.; Pinelli, P.; Ieri, F.; Bernini, R. Sustainability, Innovation, and Green Chemistry in the Production and Valorization of Phenolic Extracts from *Olea europaea* L. *Sustainability* **2016**, *8*, 1002. [[CrossRef](#)]
3. Hoang, H.T.; Moon, J.-Y.; Lee, Y.-C. Natural Antioxidants from Plant Extracts in Skincare Cosmetics: Recent Applications, Challenges and Perspectives. *Cosmetics* **2021**, *8*, 106. [[CrossRef](#)]
4. Rodrigues, F.; Pimentel, F.B.; Oliveira, M.B.P.P. Olive by-products: Challenge Application in Cosmetic Industry. *Ind. Crops Prod.* **2015**, *70*, 116–124. [[CrossRef](#)]
5. Nunes, A.; Goncalves, L.; Marto, J.; Martins, A.M.; Silva, A.N.; Pinto, P.; Martins, M.; Fraga, C.; Ribeiro, H.M. Investigations of Olive Oil Industry By-Products Extracts with Potential Skin Benefits in Topical Formulations. *Pharmaceutics* **2021**, *13*, 465. [[CrossRef](#)]
6. Nunes, M.A.; Pimentel, F.B.; Costa, A.S.G.; Alves, R.C.; Oliveira, M.B.P.P. Olive By-Products for Functional and Food Applications: Challenging Opportunities to Face Environmental Constraints. *Innov. Food Sci. Emerg. Technol.* **2016**, *35*, 139–148. [[CrossRef](#)]
7. Ribeiro, T.B.; Oliveira, A.; Coelho, M.; Veiga, M.; Costa, E.M.; Silva, S.; Nunes, J.; Vicente, A.A.; Pintado, M. Are Olive Pomace Powders a Safe Source of Bioactives and Nutrients? *J. Sci. Food Agric.* **2021**, *101*, 1963–1978. [[CrossRef](#)]
8. Granados-Principal, S.; Quiles, J.L.; Ramirez-Tortosa, C.L.; Sanchez-Rovira, P.; Ramirez-Tortosa, M.C. Hydroxytyrosol: From Laboratory Investigations to Future Clinical Trials. *Nutr. Rev.* **2010**, *68*, 191–206. [[CrossRef](#)]
9. Nunes, A.; Marto, J.; Gonçalves, L.; Martins, A.M.; Fraga, C.; Ribeiro, H.M. Potential Therapeutic of Olive Oil Industry By-Products in Skin Health: A Review. *Int. J. Food Sci. Technol.* **2021**, *57*, 173–187. [[CrossRef](#)]
10. Kesente, M.; Kavetsou, E.; Roussaki, M.; Blidi, S.; Loupassaki, S.; Chanioti, S.; Siamandoura, P.; Stamatogianni, C.; Philippou, E.; Papaspyrides, C.; et al. Encapsulation of Olive Leaves Extracts in Biodegradable PLA Nanoparticles for Use in Cosmetic Formulation. *Bioengineering* **2017**, *4*, 75. [[CrossRef](#)]
11. Galanakis, C.M.; Tsatalas, P.; Galanakis, I.M. Implementation of Phenols Recovered from Olive Mill Wastewater as UV Booster in Cosmetics. *Ind. Crops Prod.* **2018**, *111*, 30–37. [[CrossRef](#)]
12. Nilforoushzhadeh, M.A.; Amirkhani, M.A.; Zarrintaj, P.; Salehi Moghaddam, A.; Mehrabi, T.; Alavi, S.; Mollapour Sisakht, M. Skin Care and Rejuvenation by Cosmeceutical Facial Mask. *J. Cosmet. Dermatol.* **2018**, *17*, 693–702. [[CrossRef](#)] [[PubMed](#)]
13. Juliano, C.; Magrini, G. Cosmetic Functional Ingredients from Botanical Sources for Anti-Pollution Skincare Products. *Cosmetics* **2018**, *5*, 19. [[CrossRef](#)]
14. Liu, J.K. Natural Products in Cosmetics. *Nat. Prod. Bioprospect.* **2022**, *12*, 40. [[CrossRef](#)] [[PubMed](#)]
15. AOAC. *Official Methods of Analysis of AOAC International*, 19th ed.; AOAC International: Gaithersburg, MD, USA, 2010.
16. Tontisirin, K. Chapter 2: Methods of food analysis. In *Food Energy: Methods of Analysis and Conversion Factors: Report of a Technical Workshop*; Food and Agriculture Organization of the United Nations: Rome, Italy, 2002; pp. 7–17.
17. Costa, C.S.G.; Nunes, M.A.; Almeida, A.A.; Santos-Silva, A.; Oliveira, M. Nutritional, Chemical and Antioxidant/Pro-Oxidant Profiles of Silverskin, a Coffee Roasting By-Product. *Food Chem.* **2018**, *267*, 28–35. [[CrossRef](#)]

18. Costa, A.S.G.; Alves, R.C.; Vinha, A.F.; Barreira, S.V.P.; Nunes, M.A.; Cunha, L.M.; Oliveira, M.B.P.P. Optimization of Antioxidants Extraction from Coffee Silverskin, a Roasting By-Product, Having in View a Sustainable Process. *Ind. Crops Prod.* **2014**, *53*, 350–357. [[CrossRef](#)]
19. Alves, R.C.; Casal, S.; Oliveira, M.B.P.P. Determination of Vitamin E in Coffee Beans by HPLC Using a Micro-extraction Method. *Food Sci. Technol. Int.* **2009**, *15*, 57–63. [[CrossRef](#)]
20. Carretero, M.I. Clay Minerals and Their Beneficial Effects Upon Human Health. A Review. *Appl. Clay Sci.* **2002**, *21*, 155–163. [[CrossRef](#)]
21. Benson, H.A.E.; Roberts, M.S.; Leite-Silva, V.R.; Walters, K. *Cosmetic Formulation: Principles and Practice*; CRC Press: Boca Raton, FL, USA, 2019; p. 230.
22. Antónia Nunes, M.; Costa, A.S.G.; Bessada, S.; Santos, J.; Puga, H.; Alves, R.C.; Freitas, V.; Oliveira, M. Olive Pomace as a Valuable Source of Bioactive Compounds: A Study Regarding its Lipid- and Water-Soluble Components. *Sci. Total Environ.* **2018**, *644*, 229–236. [[CrossRef](#)]
23. Jeon, S.; Choi, M. Anti-Inflammatory and Anti-Aging Effects of Hydroxytyrosol on Human Dermal Fibroblasts (HDFs). *Biomed. Dermatol.* **2018**, *2*, 21. [[CrossRef](#)]
24. Uchida, R.; Ishikawa, S.; Tomoda, H. Inhibition of Tyrosinase Activity and Melanine Pigmentation by 2-Hydroxytyrosol. *Acta Pharm. Sin. B* **2014**, *4*, 141–145. [[CrossRef](#)] [[PubMed](#)]
25. Panche, A.N.; Diwan, A.D.; Chandra, S.R. Flavonoids: An Overview. *J. Nutr. Sci.* **2016**, *5*, e47. [[CrossRef](#)]
26. Nunes, M.A.; Palmeira, J.D.; Melo, D.; Machado, S.; Lobo, J.C.; Costa, A.S.G.; Alves, R.C.; Ferreira, H.; Oliveira, M. Chemical Composition and Antimicrobial Activity of a New Olive Pomace Functional Ingredient. *Pharmaceuticals* **2021**, *14*, 913. [[CrossRef](#)] [[PubMed](#)]
27. Paini, M.; Aliakbarian, B.; Casazza, A.A.; Lagazzo, A.; Botter, R.; Perego, P. Microencapsulation of Phenolic Compounds From Olive Pomace Using Spray Drying: A study of operative parameters. *LWT Food Sci. Technol.* **2015**, *62*, 177–186. [[CrossRef](#)]
28. Barel, A.O.; Paye, M.; Maibach, H.I. *Handbook of Cosmetic Science and Technology*, 3rd ed.; Informa Healthcare Inc.: New York, NY, USA, 2009; pp. 221–232.
29. Klimaszewska, E.; Zieba, M.; Gregorczyk, K.; Markuszewski, L. Application of Blue Honeysuckle Powder Obtained by an Innovative Method of Low-Temperature Drying in Skincare Face Masks. *Molecules* **2021**, *26*, 7184. [[CrossRef](#)]
30. Semenzato, A.; Costantini, A.; Meloni, M.; Maramaldi, G.; Meneghin, M.; Baratto, G. Formulating O/W Emulsions with Plant-Based Actives: A Stability Challenge for an Effective Product. *Cosmetics* **2018**, *5*, 59. [[CrossRef](#)]
31. Di Mambro, V.M.; Fonseca, M.J. Assays of Physical Stability and Antioxidant Activity of a Topical Formulation Added with Different Plant Extracts. *J. Pharm. Biomed. Anal.* **2005**, *37*, 287–295. [[CrossRef](#)]
32. da Silva Favero, J.; dos Santos, V.; Weiss-Angeli, V.; Gomes, L.B.; Veras, D.G.; Dani, N.; Mexias, A.S.; Bergmann, C.P. Evaluation and Characterization of Melo Bentonite Clay for Cosmetic Applications. *Appl. Clay Sci.* **2019**, *175*, 40–46. [[CrossRef](#)]

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