

Article

Clay-Based Cosmetic Formulations: Mineralogical Properties and Short-Term Effects on Sebum Regulation and Skin Biomechanics

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Abstract

The growing demand for dermocosmetics with ingredients of natural origin reflects the pivotal role of cutaneous health and appearance in consumer self-esteem. Under this context, clays have attracted attention for their potential applications in dermatological care. Our research work aimed to increase knowledge on the short-term impact of cosmetic formulations containing a blend of red, green, and black clays, assessing their effects on sebum regulation and in cutaneous biomechanical behavior (firmness/elasticity). Unlike daily skincare products, clay masks are used infrequently and for short durations; thus, an *in vivo* assessment was conducted after a 2-h application to reflect typical consumer use. The mineralogical and physicochemical properties of the different clays were characterized. Mineralogical analysis revealed distinct compositions among the clays: black clay exhibited a simpler mineral profile, lower density, and smaller particle size; green clay contained expandable smectite and was the densest; and red clay displayed the largest average particle size and highest iron content. Thermal analysis identified two major transitions: dehydration and kaolinite dehydroxylation. *In vivo* studies conducted in participants showed a significant reduction in skin oiliness across all clay-based formulations compared to baseline, control, and placebo following a 2-h application, and the rebound sebum production was dependent on clay concentration. Cutometry measurements did not reveal statistically significant improvements in skin firmness or elasticity compared to the control and placebo. The findings suggested that while clay-based formulations effectively reduced skin oiliness in the short term, their impact on sebum regulation and on skin biomechanical properties was limited after such a short product application period. Additional studies are warranted to elucidate the distinct effects of each clay, assess their behavior in different formulation bases, and evaluate their efficacy after repeated use.

Keywords: clays; sebumetry; cutometry; thermal analysis; mineralogical analysis



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1. Introduction

In recent years, consumer preference has shifted towards natural and sustainable cosmetic ingredients [1]. Within this paradigm, clays—mineral materials empirically used in health and beauty care—have re-emerged as a compelling option. The therapeutic potential of “medicinal earth” was reported by ancient civilizations, such as those of China,

Egypt, and Greece [2,3]. However, robust scientific assays have rarely been employed to substantiate their effectiveness.

Clays are mainly composed of inorganic minerals (clay minerals) and correspond to the inorganic fraction of several soil types. They may also contain organic matter, impurities, residual, and amorphous minerals. Clays utilized in cosmetics often incorporate metals like aluminum, iron, magnesium, and titanium, contributing to their diverse functionalities [4,5]. Different dermatological benefits can result from this blend of materials, such as reducing sebum production, hydrating the skin, enhancing firmness, and providing a whitening effect [6]. As a result, clays hold strong potential for applications in products targeting both acne-prone and mature skin.

As active ingredients, clays are widely employed in skin cleansing, sebum control, substance adsorption, anti-aging, UV protection, and ion exchange with the skin. These properties are attributed to their specific mineralogical composition, particle size, shape, structure, and ion exchange capacity [2,7–10]. However, the unique composition, properties, and versatility of clays can also render them valuable in Cosmetology. In addition to serving as active ingredients, clays can play a significant role as adjuvants, influencing key parameters such as stability, rheology, and color. Additionally, their aesthetic appeal has led to their incorporation into various makeup formulations.

Clays are categorized based on their color, which reflects their mineral composition and, consequently, their physicochemical properties [4,5,8,10–12]. This coloration arises from their crystalline structure, water content, and associated matter [13]. Although the specialized literature directly correlating specific clay colors with improvements in hair and skin health remains limited, with most studies emphasizing photoprotective effects [14], clays continue to be widely utilized worldwide.

Our investigation aimed to comprehensively characterize commercially available clays and evaluate, through *in vivo* analysis, the effect of formulations containing varying clay concentrations on critical skin attributes, including firmness, elasticity, and sebum regulation. Unlike other facial skincare products that are applied daily, clay masks are typically used only once or a few times per week or month, with relatively short contact periods. Therefore, an *in vivo* assessment was performed following a 2-h application to reflect realistic consumer usage.

2. Materials and Methods

2.1. Provenance of Clay Samples

The selected clay samples were commercially available cosmetic clays denominated as “red clay” (Internacional Nomenclature of Cosmetic Ingredients [INCI]: Kaolin), “black clay” (INCI: Kaolin) and “green clay” (INCI: Kaolin), all supplied by Terramater® (Santo André, Brazil). Samples were all from the same batch and were not submitted to any previous treatment.

2.2. Characterization of Clay Samples

Clays used in the formulations were characterized by thermal analysis concerning differential scanning calorimetry (DSC), thermogravimetry (TG), and differential thermal analysis (DTA), particle size distribution, X-ray diffraction, and X-ray fluorescence.

2.2.1. DSC Analysis

The DSC analysis of the clay samples was performed with Differential Scanning Calorimeter DSC 7020 (Seiko Instruments, Tokyo, Japan) using hermetic aluminum pans. The assay was performed under a heating ramp of 30–450 °C and a heating rate of 10 °C/min. As an inert atmosphere, nitrogen was employed at a 50 mL/min flow.

2.2.2. TG/DTA

The TG/DTA of clay samples was performed with Exstar TG/DTA 7200 Analyzer (Seiko Instruments, Tokyo, Japan). Samples were transferred to hermetic alumina pans, and the assay was performed under a 30–600 °C heating ramp and heating rate of 10 °C/min. Nitrogen was selected as an inert atmosphere at a 100 mL/min flow.

2.2.3. Particle Size Distribution Analysis

The particle size distribution was determined by laser diffraction using a CILAS 1090 high-resolution laser analyser (CILAS, Orléans, France). A wet dispersing module was used for green clay samples: purified water was used as a dispersing agent without sonication; stirring activation and measurement time of 60 s were employed, maintaining obscuration between 15 and 20%. A dry dispersing module was employed for black and red clays: samples were dispersed in a compressed air jet at a pressure of 200 mbar, and measurement time of 30 s, with obscuration between 1 and 5%. For both wet and dry dispersion modules, the Fraunhofer model was used to calculate the diameters, and the graphs were obtained using CILAS SizeExpert software version 9.51 (CILAS, Orléans, France).

2.2.4. X-Ray Diffraction Determination

Mineralogical composition analysis was performed by X-ray diffraction analysis, where clay diffractograms were obtained. The analysis was performed with Bruker D8 Da Vinci X-ray diffractometer, with copper K-alpha radiation ($\lambda = 1.5418$ Angstrom), operating at 40 KV and 40 mA, and angle sweep of 2 to 70° 2-teta. Data were analyzed with Match! Software from the Crystallographic Open Database.

2.2.5. X-Ray Fluorescence Assessment

Clay samples were submitted for chemical assessment (elements' determination) by X-ray fluorescence diffraction technique. Samples were prepared and pressed into a briquette and inserted in the X-ray fluorescence analyzer Epsilon 4.

2.3. Formulation Development

Three formulations were developed and coded as F01 (placebo), F02 (low clay concentrations) and F03 (high clay concentrations). Their compositions are described in Table 1. The previously characterized commercially available red, green, and black clays were incorporated as active components in the formulations. Red clay was chosen for its antiaging activity, green clay for its astringent and acne reduction efficacy, and black clay due to its rejuvenating, antioxidant, and oil absorption effect [5].

Table 1. Formulations' qualitative and quantitative compositions.

Formulation Composition			Concentration (%w/w)		
			F01	F02	F03
Base formulation with pH between 5.5 and 6.5 (gel base with Ammonium Acryloyldimethyltaurate/VP Copolymer as thickener at 2%)			Until 100% *	Until 100% *	Until 100% *
Active compounds	Tersil® CDR (red clay)	INCI: Kaolin	0.0	3.0	7.0
	Tersil® G (green clay)	INCI: Kaolin	0.0	3.0	7.0
	Tersil® CB (black clay)	INCI: Kaolin	0.0	3.0	7.0

Legend: * Enough quantity to obtain 100% formulation weight. INCI = International Nomenclature of Cosmetic Ingredients.

2.4. *In Vivo* Efficacy Assessment of Red, Green, and Black Clay-Based Cosmetic Formulations

This protocol was approved by the Ethics Committee of the Faculty of Pharmaceutical Sciences, University of São Paulo, located in São Paulo, Brazil (approval code 5.532.318). All participants gave their written informed consent before participating in the study. The authors have no ethical conflicts to disclose.

2.4.1. Specific Inclusion Criteria

The specific inclusion criteria for the study participants were the following: both genders; healthy participants with intact skin on their face; skin phototypes between I and IV; neither irritation nor allergy history to the material used; agreement to participate in the research and aptitude to accomplish protocol demands.

2.4.2. Specific Exclusion Criteria

The specific exclusion criteria were: participants allergic to the test product category; pregnant or lactating (for female participants); immunodeficient; participants with active atopic dermatitis; participants that had received kidney, heart and/or liver transplant; solar erythema on the face due to intense solar exposure up to one month before study beginning; use of corticoids, antihistamines, immunosuppressants, retinoids, anti-inflammatory medications; forecast of intense UV rays exposure (either sun or UV lamps) during the study; history of non-adherence to study protocols; participants that refuse to participate in the study; people who are directly involved with the protocol and their families; and any other conditions not mentioned that may interfere with the research study according to the investigator.

2.4.3. Assessment of Skin Firmness and Elasticity by Cutometry

Skin firmness and elasticity was analyzed by cutometry assessment using Multi Probe Adapter—MPA (Courage & Khazaka, Köln, Germany) equipment coupled with the Cutometer[®] (Courage & Khazaka, Germany) probe. The technique is based on suction, where the equipment and probe generate a negative pressure on the skin, causing it to enter the probe's opening (suction) followed by its release to the original position (return). The probe's sensor detects skin dislocation inside the probe during suction and return [15–17].

Each reading was set to be performed with 3 suction and relaxation cycles (2 s each). For each cycle, a graph was obtained. From the graph, firmness and elasticity results were determined as follows:

- Skin firmness: R0 (or Uf) parameter—Maximum amplitude—highest point in the curve
- Skin biologic elasticity: R7 (Ur/Uf)—Skin's ability to return to its initial position after deformation.

We selected twenty participants of 30 to 60 years old and submitted them to a 30 min acclimatization period at 20 ± 2 °C temperature and $50 \pm 5\%$ relative humidity before measurements. Three sites were marked on the malar region on the cheeks for baseline measurements (t0). Then, each product was applied on the marked sites in a standardized manner with disposable syringes (2.0 mg/cm^2), according to a randomization table. After 2 h of contact, the products were uniformly removed with a cotton pad, and subsequent measurements were performed at t2h (immediately after removal) and t4h (4 h after application, corresponding to 2 h after removal). To minimize the effect of inter-individual variability, the results were expressed as the ratio of each sample site value to the corresponding basal value for all volunteers across the analyzed parameters. The ratios were calculated for each time point (t2h/t0h and t4h/t0h).

2.4.4. Assessment of Skin Oiliness by Sebumetry

Oiliness assessment was conducted by sebumetry, using Multi Probe Adapter—MPA (Courage & Khazaka, Germany) equipment coupled with the Sebumeter® (Courage & Khazaka) probe. The probe contains a matte synthetic tape, the exposed surface of which contacts the participant's skin for 30 s. Meanwhile, sebum from the skin is adsorbed onto the tape, causing it to become partially transparent (an effect proportional to the amount of sebum collected) [18]. After sebum collection, the probe is inserted in the equipment's aperture, where a photocell is located to measure transparency. The light transmission represents sebum content, measured as $\mu\text{g sebum/skin cm}^2$.

We selected twenty participants who were 18 to 45 years old with oily skin on the face T-zone and submitted them to a 30 min acclimatization period at $20 \pm 2^\circ\text{C}$ temperature and $50 \pm 5\%$ humidity before measurements. Then, three sites were marked on the forehead for baseline measurements (t0). Subsequently, each product was applied on the marked sites in a standardized manner with disposable syringes (2.0 mg/cm^2), according to a randomization table. After 2 h of contact, the products were uniformly removed with a cotton pad, and new measurements were performed on t2h (immediately after removal) and t4h (4 h after application, corresponding to 2 h after removal). The same type of data analysis was conducted, with ratios in comparison to the basal values being calculated for each time point (t2h/t0h and t4h/t0h). Statistical comparisons between ratios were conducted using ANOVA ($\alpha = 0.05$) followed by the Tukey post-test using Minitab® Statistical Software 21.1.0 (Minitab LLC, State College, PA, USA).

2.4.5. Statistical Treatment

Statistical comparisons between ratios were conducted using ANOVA ($\alpha = 0.05$) followed by the Tukey post-test using Minitab® Statistical Software 21.1.0 (Minitab LLC, USA).

3. Results

3.1. Clay Sample Characterization

3.1.1. DSC

Figure 1 presents the DSC curves for black, green, and red clays. Data is summarized in Table 2.

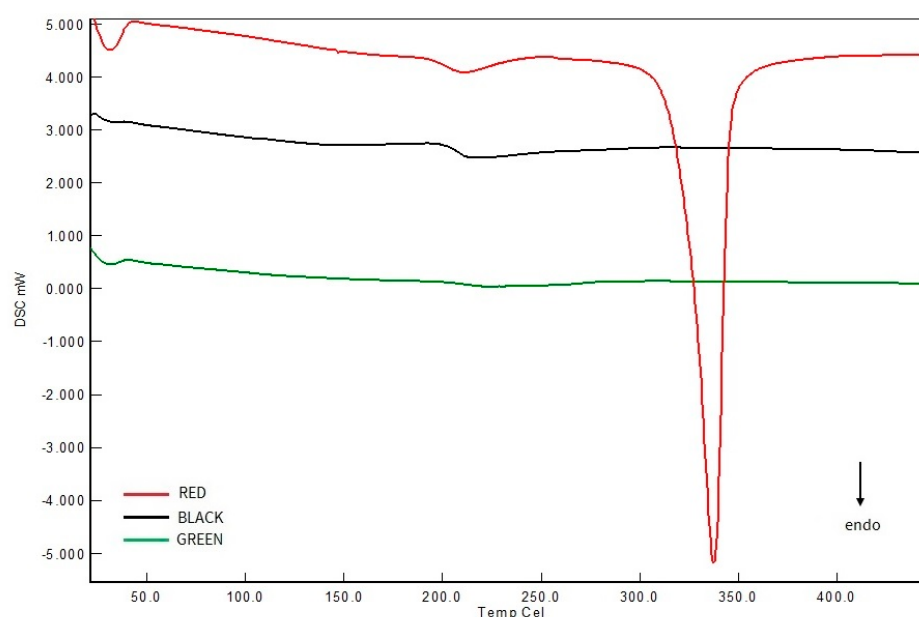


Figure 1. DSC curves of black, green, and red clays.

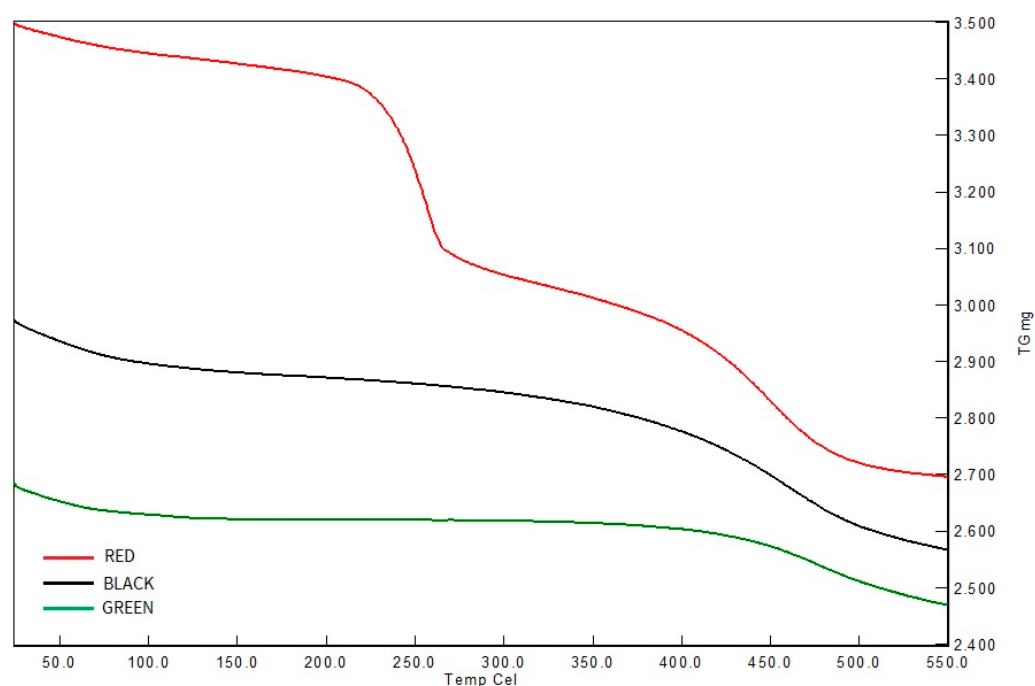
Table 2. Clays' DSC data (exothermic events).

Clay Sample	Event's Start (°C)	Event's End (°C)	Event's Peak (°C)	Area (mJ/mg)	Area (uV.s/mg)
Black	201.7	263.0	217.7	21.2	-
Red	322.5	345.6	337.7	161.7	152
Green	203.4	245.9	230.6	8.74	-

All clays presented exothermic peaks: black clay's peak was at 217.7 °C (from 201.7 to 263.0 °C), red clay at 337.7 °C (from 322.5 to 345.6 °C) and green clay at 230.6 °C (from 203.4 to 245.9 °C).

3.1.2. TG/DTA

Figure 2 presents the obtained TG curves for black, green, and red clays. Data is summarized in Table 3.

**Figure 2.** TG curves of black, green, and red clays.**Table 3.** TG data for each clay type.

Clay Sample	Mass Loss Between 25 and 125 °C	Mass Loss Between 425 and 550 °C	Residue at 540 °C
Black	2.87%	6.10%	86.64%
Red	1.08%	3.80%	85.57%
Green	0.98%	1.95%	96.61%

All clays presented two thermal events: one at lower temperatures (between 25 and 125 °C), and one at higher temperatures (between 425 and 550 °C). Black, red and green clays have shown mass loss, respectively, of 2.87%, 1.08% and 0.98% at lower temperatures, and of 6.10%, 3.80% and 1.95% at higher temperatures.

3.1.3. Particle Size Distribution

Clay samples' particle size distribution (granulometric assessment) is summarized in Table 4.

Table 4. Particle size distribution profile (CILAS readings) per clay type.

Clay Sample	10% DM	50% DM	90% DM	Average DM
Black	4.10	59.62	121.86	61.70
Red	22.65	91.33	189.12	101.64
Green	7.44	81.47	157.78	82.67

DM = diameter.

Analysis of particle size distribution showed mean diameters of 61.70 μm for black clay (smallest), 82.67 μm for green clay, and 101.64 μm for red clay (largest).

3.1.4. X-Ray Diffraction

Diffractionograms were obtained for clay samples under different conditions to allow mineralogical composition determination. Results and assay conditions are described in Table 5.

Table 5. X-ray diffraction results (clays' mineralogical compositions).

Clays	Sample Treatment Condition	Mineralogical Composition				
		Kaolinite	Illite	Smectite *	Quartz	Hematite
Black	TC	✓			✓	
	CF	✓			✓	
Red	TC	✓			✓	✓
	CF	✓			✓	
	EG	✓			✓	
Green	TC		✓	✓	✓	
	EG	✓	✓	✓		

Legend: TC = total clay sample was pressed on the glass slide; CF = clay fraction sample was decanted on glass slide; EG = clay fraction sample was saturated with ethylene glycol. * Expandable clay mineral, possibly montmorillonite. ✓ indicates the presence of the clay mineral for each clay and experimental condition.

The results allowed us to infer that black clay sample was composed mostly of kaolinite clay mineral and quartz. As the assay did not detect manganese minerals in black clay samples, we inferred that its color probably comes from its content of organic matter.

We also found that red clay sample's composition was kaolinite and quartz, as well as gibbsite ($\text{Al}(\text{OH})_3$), and hematite. Hematite is the component likely to cause this clay's reddish color. Gibbsite indicates that red clay is a material lixiviated by weathering. Green clay was composed of kaolinite and quartz, as well as illite, and smectite. The identification of the expandable clay mineral (smectite) in the sample was carried out after sample saturation with ethylene glycol, where a peak expansion from 14 to 17 Angstrom was observed.

3.1.5. X-Ray Fluorescence

The X-ray fluorescence assay allowed a semi-quantitative determination of elements in oxide state in clay samples, described in Table 6.

The X-ray fluorescence analysis revealed that all assessed clay samples were predominantly composed of Al_2O_3 and SiO_2 , with black and green clays containing a notably higher proportion of the latter. Red clay was distinguished by its elevated levels of Fe_2O_3 and TiO_2 . These findings are further explored in the Discussion Section.

Table 6. Clays' X-ray fluorescence results.

Element/ Clay	Multielement Calibration/Screening (%)		
	Black	Green	Red
Na ₂ O	0.0 ppm	1.148	0.0 ppm
MgO	0.0 ppm	0.643	0.0 ppm
Al ₂ O ₃	24.658	19.749	37.259
SiO ₂	56.417	58.182	33.948
P ₂ O ₅	0.028	0.018	0.025
SO ₃	0.212	0.151	0.120
Cl	0.003	0.002	0.0 ppm
K ₂ O	0.416	1.840	0.264
CaO	0.235	0.721	0.027
TiO ₂	1.157	0.303	2.151
V ₂ O ₅	0.022	0.006	0.047
Cr ₂ O ₃	0.011	0.014	0.030
MnO	0.017	0.013	0.015
Fe ₂ O ₃	1.539	2.330	13.295
NiO	0.002	0.001	0.005
CuO	0.002	0.001	0.004
ZnO	0.003	0.006	0.004
Ga ₂ O ₃	0.004	0.002	0.007
As ₂ O ₃	4.2 ppm	1.1 ppm	0.006
SeO ₂	0.9 ppm	0.0 ppm	/
Rb ₂ O	0.002	0.005	0.001
SrO	0.014	0.032	0.002
Y ₂ O ₃	0.004	0.001	0.004
ZrO ₂	0.053	0.016	0.136
Nb ₂ O ₅	0.010	0.011	0.022
MoO ₃	3.1 ppm	2.2 ppm	7.5 ppm
PdO	2.4 ppm	2.6 ppm	0.2 ppm
Ag ₂ O	0.077	0.077	0.112
CdO	0.0 ppm	0.4 ppm	1.2 ppm
SnO ₂	0.008	0.007	0.011
Sb ₂ O ₃	0.002	0.002	0.003
BaO	0.032	0.051	0.013
CeO ₂	0.022	0.007	0.012
Eu ₂ O ₃	0.008	0.010	0.038
HfO ₂	7.1 ppm	4.1 ppm	0.004
Ta ₂ O ₅	0.006	0.010	0.022
WO ₃	8.9 ppm	0.003	0.0 ppm
IrO ₂	0.0 ppm	0.0 ppm	0.0 ppm
PtO ₂	0.0 ppm	0.0 ppm	0.0 ppm
HgO	5.0 ppm	0.0 ppm	1.7 ppm
Tl ₂ O ₃	0.0 ppm	0.0 ppm	0.0 ppm
PbO	0.005	0.001	0.002
Bi ₂ O ₃	0.0 ppm	0.0 ppm	0.0 ppm
ThO ₂	0.002	2.5 ppm	0.005
F	15.026	14.628	12.397
Rh	0.0 ppm	0.0 ppm	0.9 ppm
Re	0.0 ppm	0.0 ppm	0.0 ppm
Au	0.1 ppm	0.0 ppm	0.0 ppm
U	4.0 ppm	1.3 ppm	7.2 ppm
Yb ₂ O ₃	8.8 ppm	0.003	0.006
Nd ₂ O ₃	0.0 ppm	0.0 ppm	/
TeO ₂	/	0.006	/
GeO ₂	/	0.4 ppm	/
Br	/	/	3.0 ppm

3.2. Skin Parameters: Cutometry (Firmness and Elasticity) and Sebumetry (Oiliness)

The ratio of skin firmness and elasticity values per experimental time (t2h/t0h and t4h/t0h) and treatment (Control, F01, F02 and F03) were determined and are described in Figures 3 and 4, whereas the ratios for skin oiliness values per experimental time (t2h/t0h and t4h/t0h) and treatment (Control, F01, F02 and F03) are in Figure 5.

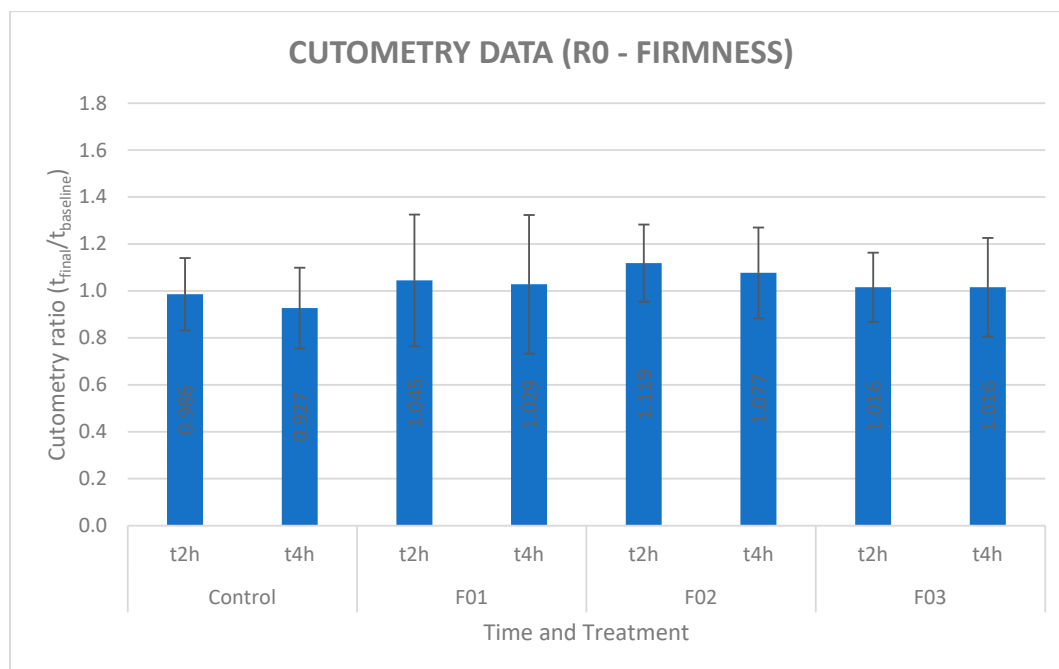


Figure 3. Average ratio cutometry per time (t2h and t4h) and treatment (Control, F01, F02, F03)—R0 (skin firmness) (mean $\pm$ SD, $n = 20$). No statistically significant difference ($p > 0.05$) was observed either between times or treatments concerning R0 ratio values (skin firmness).

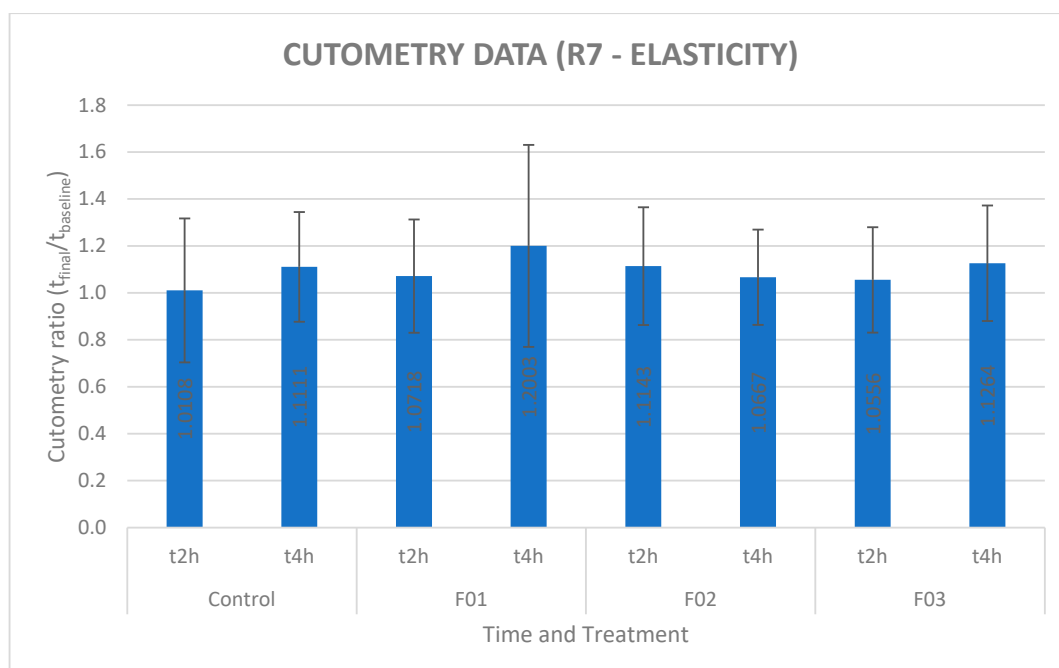


Figure 4. Average ratio cutometry values per time (t2h and t4h) and treatment (Control, F01, F02, F03)—R7 (skin elasticity) (mean $\pm$ SD, $n = 20$). The same behavior was observed regarding R7 ratio values (skin elasticity).

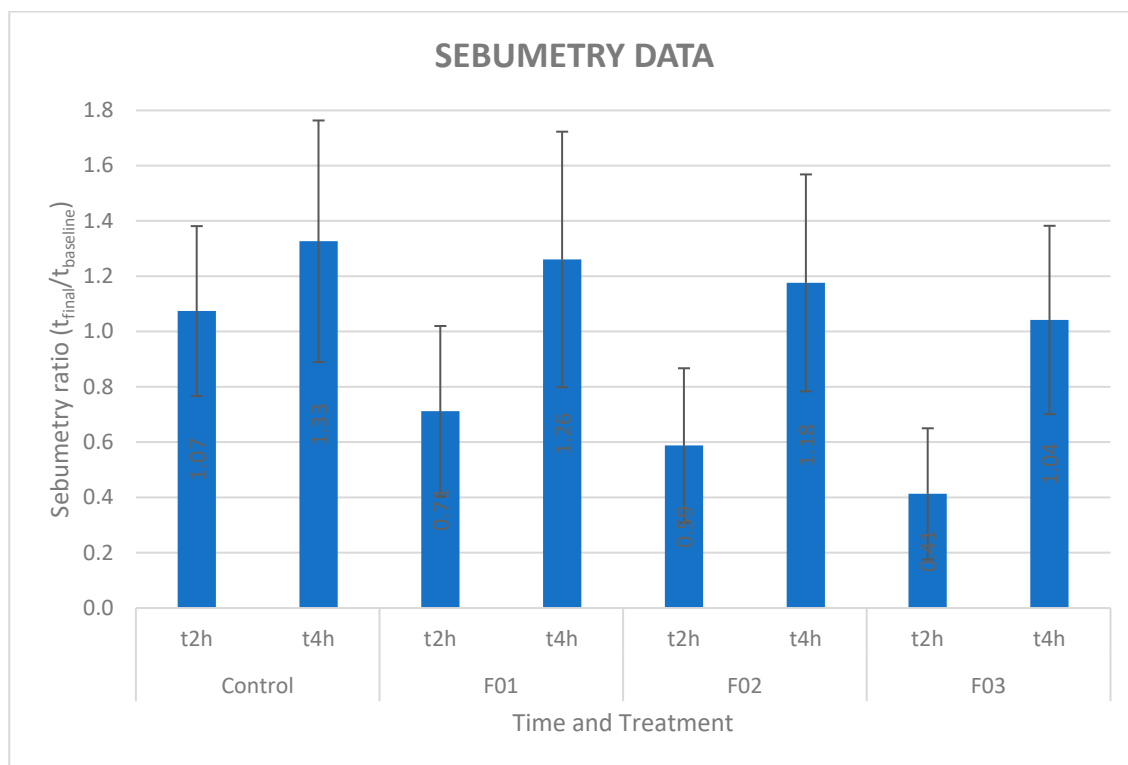


Figure 5. Average ratio sebumetry values per time and treatment (mean $\pm$ SD, $n = 20$). At 2 h (t2h), Sebumetry ratios showed a statistically significant reduction in all treatment groups compared to the control. No significant differences were observed between F01 and F02 or between F02 and F03, whereas F01 and F03 differed significantly, indicating greater sebum reduction with higher clay concentrations. At 4 h, no significant differences were detected among any groups ($p > 0.05$).

4. Discussion

The DSC analysis revealed that all three clays exhibited exothermic peaks, likely attributed to the decomposition of kaolinite. However, the amplitude and intensity of these peaks varied among the clays, aligning with Bretzke's findings [19]. Previous studies mention that kaolinite dihydroxylation's extent can vary depending on clays' chemical, physical, and mineralogical characteristics, resulting in exothermic peaks with different temperatures. When kaolinite suffers dihydroxylation (removal of hydroxyl group), it is converted to metakaolinite. This occurs, because elevated temperatures induce kaolinite's calcination, leading to structural water loss. The resulting metakaolinite is an amorphous aluminum silicate characterized by a disordered structure [19]. In our findings, exothermic events occurred with peaks at 217.7 °C for black clay (201.7–263.0 °C); 337.7 °C for red clay (322.5–345.6 °C); and 230.6 °C for green clay (203.4–245.9 °C). In 2007, Zague conducted thermal behavior assessment of green clay and reported distinct findings [4]. Her study identified an endothermic peak at 96.93 °C, attributed to clay dehydration, corresponding to the evaporation of water from the particles' internal and external surfaces. She observed no thermal events for green clay near 200 °C. However, an additional endothermic event was detected for pink clay and aluminum–magnesium silicates at approximately 270 °C, which the author associated with the onset of dihydroxylation of the layers within the crystalline lattice [4].

Thermogravimetric (TG) analysis of clays typically reveals two distinct thermal events. At lower temperatures (50–200 °C), dehydration occurs, involving the evaporation of water from both internal and external surfaces. At higher temperatures (usually above 400 °C), mass loss is predominantly attributed to the dihydroxylation of kaolinite [4,19,20].

In the present study, the first thermal event, corresponding to dehydration, was observed between 25 and 125 °C. Black clay exhibited a 2.87% mass loss, while red and green clays showed lower losses of 1.08% and 0.98%, respectively. These findings suggest that black clay undergoes more substantial dehydration compared to the other clays.

The other (second) thermal event, associated with kaolinite dihydroxylation, occurred at 425–550 °C. Black clay experienced a mass loss of 6.10%, significantly higher than the losses observed for red clay (3.80%) and green clay (1.95%). These results indicate that black clay is more prone to mass loss under thermal conditions in both dehydration and dihydroxylation phases.

Granulometric and compositional analyses provide additional insights. Black clay exhibited the smallest average particle diameter (61.70 µm), compared to red clay (101.64 µm) and green clay (82.67 µm). The smaller particle size of black clay likely results in a larger exposed surface area, which could enhance its susceptibility to dehydration and thermal reactions. Moreover, black clay's simpler composition may further contribute to its thermal behavior.

While these observations suggest a correlation between particle size, composition, and thermal sensitivity, further research is needed to confirm these hypotheses and better understand the mechanisms driving these differences.

When analyzing TG assay's results, green clay had the lowest mass loss. Also, it was the only sample with an expandable clay mineral (smectite), as determined by X-ray diffraction analysis. Clays are complex mixtures of substances with varying particle sizes, composed of at least two clay minerals combined with differing proportions of non-clay components such as quartz, feldspars, carbonates, oxides, amorphous phases, and organic matter [19,21–24]. Clays with higher quartz content, often characteristic of lighter-colored clays, typically exhibit larger particle sizes, which contribute to a rougher texture when applied to the skin [19]. Based on our findings, black clay is likely to provide the smoothest application, while red clay is expected to be the roughest. This aligns with observations from Silva-Valenzuela et al. (2018), who emphasized that “softness and small particle size are important for skin therapeutic and cosmetic applications, such as face masks and clay body creams” [24].

Mineralogical analysis revealed the presence of kaolinite in all three clays and smectite (an expandable clay mineral) exclusively in green clay. These mineral components suggest significant potential for dermatological applications, including protective effects against external agents (e.g., pollution), absorption of exudates, and management of liquid secretions. These minerals adhere to the skin, forming a protective film that absorbs exudates, and creates a low-moisture environment unfavorable to microbial growth. Furthermore, they are capable of adsorbing bacteria, viruses, grease, and toxins, thereby exhibiting antiseptic properties [2,25–27]. Kaolinite and smectite, with their high sorption capacity, are effective in forming protective films, concealing imperfections, and reducing excessive oiliness and toxins. These properties make them particularly suitable for oily and acne-prone skin [6,26–28].

The compositional analysis of the clays revealed that all evaluated samples were predominantly composed of Al_2O_3 and SiO_2 . Clays with high silicon content exhibit hydrating properties, help mitigate skin inflammatory responses and contribute to skin regeneration and protection. Conversely, clays enriched with aluminum demonstrate hydrating effects, facilitate pigment dispersion, and enhance melanin adsorption [6,29]. Among the clays analyzed, red clay exhibited the highest Fe_2O_3 content, which can be attributed to the presence of hematite identified via X-ray diffraction analysis. Iron oxide-rich clays have been associated with enhanced photoprotective properties in cosmetic

formulations [8]. This finding aligns with the results reported by Bretzke (2015), who also identified red clay as having the highest iron content among various clay types tested [19].

Clay minerals are capable of absorbing substances such as heavy metals, depending on their characteristics. Therefore, heavy metals' content of clays is an important aspect to be considered for cosmetic applications regarding toxicology [6]. The FDA established limits for heavy metal content in cosmetic products, as exemplified: mercury cannot exceed 65 ppm in the finished product (1 ppm = 1 µg/g) and 1 ppm in colorants; lead cannot exceed 10 ppm as impurity in cosmetics including lip care products and 20 ppm in colorants; arsenic limit for color additives in cosmetics is 3 ppm (ABED, MOOSA, ALZUHAIRI, 2024; FDA, 2025). X-ray fluorescence showed the presence of 5.0 ppm of HgO in black clay and 1.7 ppm in red clay; 0.005 ppm of PbO in black clay, 0.001 ppm in green clay and 0.002 ppm in red clay; and 4.2 ppm of As₂O₃ in black clay, 1.1 ppm in green clay and 0.006 ppm in red clay. Therefore, green and red clays fulfill FDA requirements and black clay must be more accurately studied concerning fulfillment of arsenic limits.

When statistically analyzing skin firmness values (R0), we did not observe significant differences over time for any site. These findings contrast with some of the existing literature, as clays similar to those incorporated into these formulations have been reported to cause a lifting effect [30]. Previous studies, such as those by Balduino et al. (2016) and Silva et al. (2011), have highlighted the use of red and black clays in skin rejuvenation, attributing to them lifting properties and other characteristics that justify their inclusion in anti-aging cosmetic formulations [5,10]. However, despite claims regarding clays' potential to enhance skin firmness, few studies to date have shown significant improvements in cutometry measurements between clay-treated and control sites. Velasco et al. evaluated the effects of clay-based face masks on skin firmness and elasticity using cutometry [12]. Their findings showed no significant differences in cutometry values across time points or formulations, suggesting that variations in clay composition had little impact on skin viscoelasticity over the short duration of the study.

Sebumetry measurements taken after 2 h of product application demonstrated that all formulations significantly reduced superficial sebum levels compared to the untreated control site, including the placebo. We hypothesize that the activity of the placebo may be attributed to its polymer component, which possesses mild emulsifying properties, facilitating the emulsification of skin lipids during contact with water during product removal. However, the formulations with clays caused a more marked reduction in skin oiliness at both tested concentrations, with statistically significant differences relative to the placebo detected at the maximum concentration (7% of each clay). These results highlight the efficacy of the active components and confirm the importance of concentration under the tested conditions. The findings were consistent with existing literature, which attributes clays' effectiveness in adsorbing skin lipids, exudates, and impurities to their porosity and cation exchange capacity, conferring excellent astringent properties [2,6,14,20]. Nevertheless, more studies are needed to evaluate each clay individually and identify which exhibits the greatest efficacy in sebum reduction. Based on existing evidence, green clay is hypothesized to be the most effective in this regard.

For the t4h reading (2 h after product removal), the objective was to assess whether the clays could influence a possible rebound effect in sebum production. The results showed that the mean ratios at t4h were greater than 1 across all application sites, indicating that sebum levels not only recovered but exceeded the baseline values. This upward trend suggests that the skin resumed its natural sebaceous activity after the initial reduction, with no evidence of a compensatory regulation induced by the clays. Consequently, these findings do not support a sustained sebum-regulating effect of the formulations

when applied only once, highlighting the transient nature of their action and the need to investigate repeated or long-term applications for a more reliable evaluation of efficacy.

5. Conclusions

Commercially available clays used in the cosmetic industry, identified by their color (black, green, and red), were selected for characterization and evaluation following their incorporation into a cosmetic formulation. Each clay exhibited distinct mineralogical compositions, elemental profiles, and particle sizes, with variations in compositional complexity. Among them, black clay was found to be the simplest in composition and had the smallest particle size.

The combination of these three clays, incorporated into an oil-free cosmetic formulation, demonstrated efficacy in reducing skin oiliness immediately after application. However, under the conditions of this study, the clays did not regulate sebum production or improve skin firmness and elasticity. Further research is warranted to investigate the isolated effects of each clay and their performance in different formulation vehicles and after repeated applications.

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