IFSCC 2025 full paper (IFSCC2025-396)

"Development of Environmentally Friendly Amino Acid-Based Surface Treatment Agents"

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1. Introduction

In recent years, the diversification of formulation design in cosmetics has led to increasing demands for "texture design" and "functional enhancement" of powder materials. A particularly valuable approach involves the surface treatment of powders to improve the dispersion, application, adhesion, color development, and longevity of the final product. Traditionally, metal soaps and silicone-based agents have been used for such surface treatment of powders. However, to increase environmental compatibility, enhance skin affinity, and adapt to diverse textures, new technologies must be developed to enable more flexibility in design.
N-acyl amino acids contain amide bonds between fatty acids and amino acids, thus offering wide variability in terms of properties depending on the fatty acid chain length and type of amino acid. These compounds have garnered attention as ingredients for cosmetics owing to their excellent biodegradability [1], as well as their lower irritation and higher skin safety compared with typical anionic surfactants, like soaps [2].
Additionally, N-acyl amino acids can form complexes with divalent or higher-valent metal salts, similar to metal soaps with fatty acids. Nonomura and coworkers [3] studied fatty acid-Ca complexes with varying degrees of saturation in the fatty acid moiety and reported that their structure significantly affected their lubricity. Although most research on Ca-surfactant complexes pertains to fatty acids, Sakai and coworkers investigated complexes comprising Ca ions with acylglycine and acylglutamic acid. They found that the physical properties of acyl amino acid Ca salts varied depending on the acyl amino acid type and fatty acid chain length [4].
This research focuses on complexes of divalent or higher-valent metal ions with N-acyl amino acids. On this basis, a new technology is developed to treat powders by precipitating metal ion-surfactant complexes on the powder surface. This method simply involves mixing the powder with an aqueous solution of acyl amino acid salt and then adding an aqueous solution of the metal ions. Thus, it requires no special equipment and is a more straightforward process than those used in conventional advanced surface treatments. Moreover, the precipitation mechanism enables wide application of this method for diverse powder types. Any aqueous single- or multi-component surfactant solution that forms complexes with polyvalent metal ions can be used to treat powders with various physical properties. Overall, the developed method enables simple production of treated powders with designed functions, thereby expanding the range of raw materials available for cosmetic development.

2. Materials and Methods

2.1 Materials

The amino acid- and fatty acid-based surfactants used in this study included disodium stearoyl glutamate ($C18GluNa_2$) (Ajinomoto Co., Inc.), potassium cocoyl glycinate (CocoGlyK) (Ajinomoto Co., Inc.), potassium cocoyl glutamate ($CocoGluK_2$) (Ajinomoto Co., Inc.), sodium cocoyl alaninate (CocoAlaNa) (Ajinomoto Co., Inc.), and potassium cocoyl fatty acid (CocoFAK). The carbon chain length distributions of CocoGlyK, $CocoGluK_2$, CocoAlaNa, and CocoFAK were similar, primarily consisting of C12 chains.

2.2 Preparation of Powder Treatment Solution

Unless otherwise specified, the following aqueous acyl amino acid and $CaCl_2$ solutions were used for the powder surface treatments. The acyl amino acid (fatty acid) solution was adjusted to 20 wt.% and pH 10. The $CaCl_2$ solution was prepared to obtain a 2:1 molar ratio of calcium ions to monovalent anions (CocoGlyK, CocoAlaNa, and CocoFAK) or a 1:1 molar ratio of calcium ions to divalent anions ($CocoGluK_2$ and $C18GluNa_2$); this ensured complete complexation of Ca ions with acyl amino acids for the subsequent powder treatment. When preparing mixed solutions comprising multiple acyl amino acids, the $CaCl_2$ concentration was adjusted accordingly to achieve the appropriate molar ratio for each component.

2.3 Surface Treatment of Powders

An acyl amino acid (fatty acid) solution was added to the powder and mixed for 1 minute using a lab mixer. Then, the $CaCl_2$ solution was added and mixed for 1 additional minute. Each final mixture was dried overnight at room temperature under air to obtain the treated powders. The obtained surface-treated powder was used for evaluation without washing, thus further highlighting the practicality of the developed method.

2.4 Sensory Evaluation of Various Powders

Six expert panelists performed sensory evaluations of the surface-treated powders in terms of their spreadability, adhesion to the skin, moistness, smoothness, and softness. Each powder was tested on either the back of the hand or the inner forearm and graded on a scale of 1-5, with 5 being the best.

2.5 Water Contact Angle Measurements

A plastic plate was covered with double-sided tape, and powder was sprinkled over the entire surface. Excess powder was tapped off to create a uniform coating. A droplet of Milli-Q water was applied to the test sample using an automatic contact angle goniometer (CA-VP type, Kyowa Interface Science), and the contact angle was measured 1 second after application. Measurements were repeated three times, and the average value was used for evaluation.

2.6 Shearing Cohesion Measurements

The shearing cohesion of each surface-treated powder was measured using a dynamic mechanical analyzer (Discovery HR 20, TA Instruments) equipped with a powder rheology accessory. The geometry was Shear cell powder-14334.

2.7 Dynamic Friction Coefficient Measurements

First, 100 mg of surface-treated powder was placed on artificial leather (Idemitsu Technofine, approximately 2 mm thick), and measured using a tribometer (TL201Ts, Trinity Lab) with a tactile contactor (finger model, fingerprint type, Trinity Lab). The measurement conditions for the friction tester were as follows: load = 50 g; test stage movement rate = 25 mm/sec; measurement distance = 25 mm; reciprocations = 20; dynamic friction coefficient measured on the 20th reciprocation. Measurements were repeated three times, and the average value was used for evaluation.

2.8 X-Ray Diffraction Measurements

X-ray diffraction was used for structural analysis of the Ca-acyl amino acid complexes. Each Ca-acyl amino acid complex sample was prepared by mixing the acyl amino acid (20 wt.%) and $CaCl_2$ (35 wt.%) solutions in a 6:1 ratio and drying at room temperature for 3 days. The measurements were performed using an X-ray diffractometer (D8 ADVANCE, Bruker) with a Cu-Kα source (λ = 0.154 nm) and a voltage and current of 30 kV and 40 mA, respectively.

2.9 Oil Dispersibility Test

Oil was gradually added to the powder while the powder was kneaded. The wet point per gram of powder was determined as the amount of oil added up to the point at which the mixture became a lump. The flow point per gram of powder was determined as the amount of oil added up to the point at which the mixture became fluid. The oil dispersity was calculated according to Eq. (1):

$$\text{Oil dispersity (g/g)} = \text{Flow point (g/g)} - \text{Wet point (g/g)} \quad (1)$$

A lower value indicates better oil dispersibility.

2.10 Microscopic Observations

The pigment dispersibility of the prepared liquid foundation samples was observed with an optical microscope (ECLIPSE LV100POL, Nikon) 1 month after preparation.

2.11 In vitro SPF Measurement

A beige pigment obtained by mixing titanium dioxide and iron oxides (yellow, red, and black iron oxides) was surface-treated using an aqueous solution of C18Glu ($C18GluNa_2$: 15 wt.%; arginine: 5 wt.%; glycerin: 40 wt.%; water: 40 wt.%) and a $CaCl_2$ solution (35 wt.%). The resulting surface-treated powder was used to prepare a water-in-oil (W/O) liquid foundation containing 9.6% of the treated powder and 5% ethylhexyl methoxycinnamate. For comparison, non-treated and dimethicone-treated beige pigments were also prepared, and the corresponding W/O liquid foundations were obtained using the same formulation. The in vitro sun protection factor (SPF) of each liquid foundation was measured using an SPF analyzer (UV-2000S, Labsphere). Samples were prepared by evenly spreading 32 mg of each liquid foundation onto a poly methyl methacrylate (PMMA) plate.

2.12 TOF-SIMS Measurements

To determine the distribution of components on the surface of the treated powders, time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements were performed (M6 IONTOF) using a high spatial resolution measurement mode (delayed extraction). The primary ion species was Bi_3^{++}, and the primary ion acceleration voltage was 30 kV.

3. Results and Discussion

3.1 Preparation of Acyl Amino Acid-Ca Salt-Treated Powders

An overview of the powder surface treatment is presented in Figure 1. Acyl amino acids and fatty acids reacted with polyvalent metal salts to form complexes, which precipitated as an acyl amino acid gel on the powder surface. This strategy can be applied to surface-treat powders used in cosmetics, such as extender pigments, color pigments, and organic powders. Most of these non-treated powders are hydrophilic, and therefore, surface treatments aim to impart hydrophobicity and increase oil dispersibility. As a commonly used cosmetic raw material, mica was selected as the powder for this study. Mica is an inorganic powder with numerous surface hydroxyl groups, which impart hydrophilic properties. Divalent calcium ions are also widely used as a cosmetic raw material, and in this study, they served as the polyvalent metal ion. Ultimately, the surface-treated powders were prepared by stirring mica in aqueous acyl amino acid solution to adsorb the acyl amino acid onto the powder surface; then, the aqueous $CaCl_2$ solution was added with stirring.

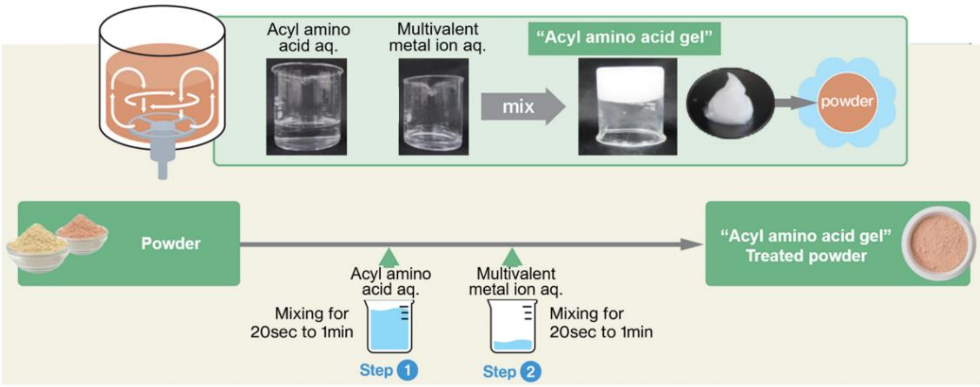

Figure 1. Schematic diagram of acyl amino acid gel (Ca-acyl amino acid complex) treatment.

To demonstrate that the developed powder treatment method can alter the powder characteristics, C18Glu was used as the exemplary material, because it is already used as an acyl amino acid-based surface treatment agent and is expected to impart hydrophobicity when adsorbed owing to its long acyl chain. The sensory profile, water contact angle, and oil dispersibility of mica treated with a calcium acylglutamate complex (Ca-C18Glu) (i.e., (Ca-C18Glu)-mica) were compared with those of non-treated mica (Figure 2).

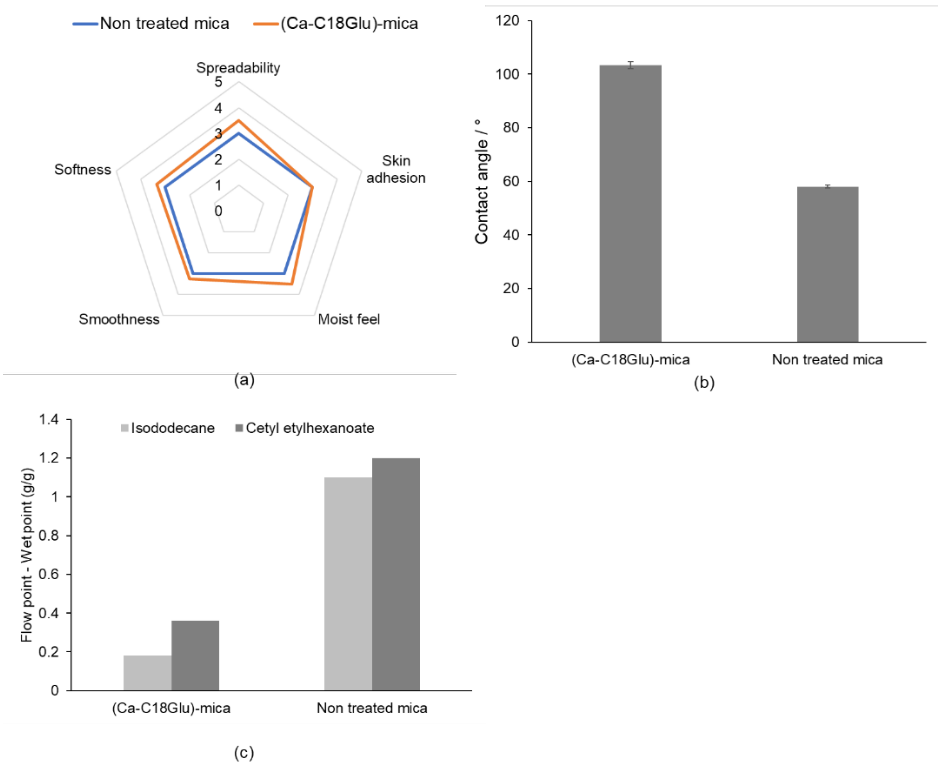

Figure 2. (a) Sensory evaluations, (b) water contact angles, and (c) oil dispersibility of non-treated mica and (Ca-C18Glu)-mica.

Figure 2a indicates that (Ca-C18Glu)-mica exhibited superior spreadability, adhesion, moistness, and smoothness compared with non-treated mica. Additionally, Figure 2b,c reveals that the hydrophobicity and oil dispersibility both improved after the powder treatment. This improvement was attributed to the surface adsorption of hydrophobic Ca-C18Glu. These findings suggest that simple successive mixing of the powder with acyl amino acid and $CaCl_2$ solutions constitutes an effective surface treatment, leading to powders with distinct properties.

3.2 Differences in Physical Properties of Surface-Treated Powders by Acyl Amino Acid Type

The influence of the acyl amino acid type on the physical properties of surface-treated powders was investigated. In addition to C18Glu, CocoGlu with a cocoyl chain was used in this study, considering its versatility in cosmetic raw materials. Glycine (Gly) and alanine (Ala), which have distinct amino acid structures, and their derivatives with cocoyl chains (CocoGly and CocoAla) were used for comparison. Figure 3 shows the sensory evaluations of mica samples surface-treated with these Ca-acyl amino acid complexes. Mica treated with CocoGlyCa (Ca-CocoGly) (i.e., (Ca-CocoGly)-mica) exhibited superior spreadability and smoothness, whereas mica treated with CocoAlaCa (Ca-CocoAla) (i.e., (Ca-CocoAla)-mica) was characterized by superior moistness. The texture of mica treated with CocoGluCa (Ca-CocoGlu) (i.e., (Ca-CocoGlu)-mica) and (Ca-C18Glu)-mica were intermediate, although (Ca-CocoGlu)-mica had higher moistness and skin adhesion than (Ca-C18Glu)-mica. These results highlight the possibility of tuning the texture of powders by varying the amino acid type and acyl chain length used in the surface treatment.

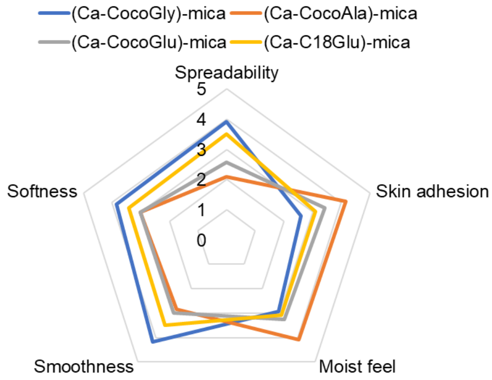

Figure 3. Sensory evaluations of surface-treated mica samples.

Next, the physicochemical properties related to the sensory attributes of the Ca-acyl amino acid-treated mica were measured, i.e., the shearing cohesion, water contact angle, and dynamic friction coefficient (Figure 4). Shearing cohesion is a physical property that reflects the adhesiveness between powder particles. Notably, a high shearing cohesion may contribute to higher moistness [5], making it a useful physicochemical indicator for usability and texture considerations. The (Ca-CocoAla)-mica exhibited the highest adhesiveness. Additionally, this treated powder had the smallest contact angle, indicating that it was the most hydrophilic among those examined (Figure 4b). Dynamic friction measurements were conducted to investigate the spreadability and smoothness of the treated powders, and the results showed that (Ca-CocoGly)-mica had the lowest value, consistent with its superior spreadability and smoothness in the sensory evaluation (Figure 4c). Together, these results

explain the resistance, adhesion, and moistness experienced when spreading the powder on the skin, as recognized in the sensory evaluations, thus supporting their validity.
The high adhesiveness and moistness of (Ca-CocoAla)-mica are likely related to the hydrophilic groups on the surface. Specifically, the hydrophilic NaCl, which is a byproduct of the complexation between CocoAlaNa and $CaCl_2$, on the surface may partially dissolve in the moisture on the skin, thereby increasing the adhesiveness and moistness of the treated powder. Furthermore, (Ca-C18Glu)-mica, which had the longest acyl chain, was the most hydrophobic, followed by (Ca-CocoGlu)-mica and (Ca-CocoGly)-mica, which exhibited similar hydrophobicity because of their similar acyl chain lengths (Figure 4b). Thus the hydrophobicity of the surface-treated powders is also influenced by the acyl chain length.

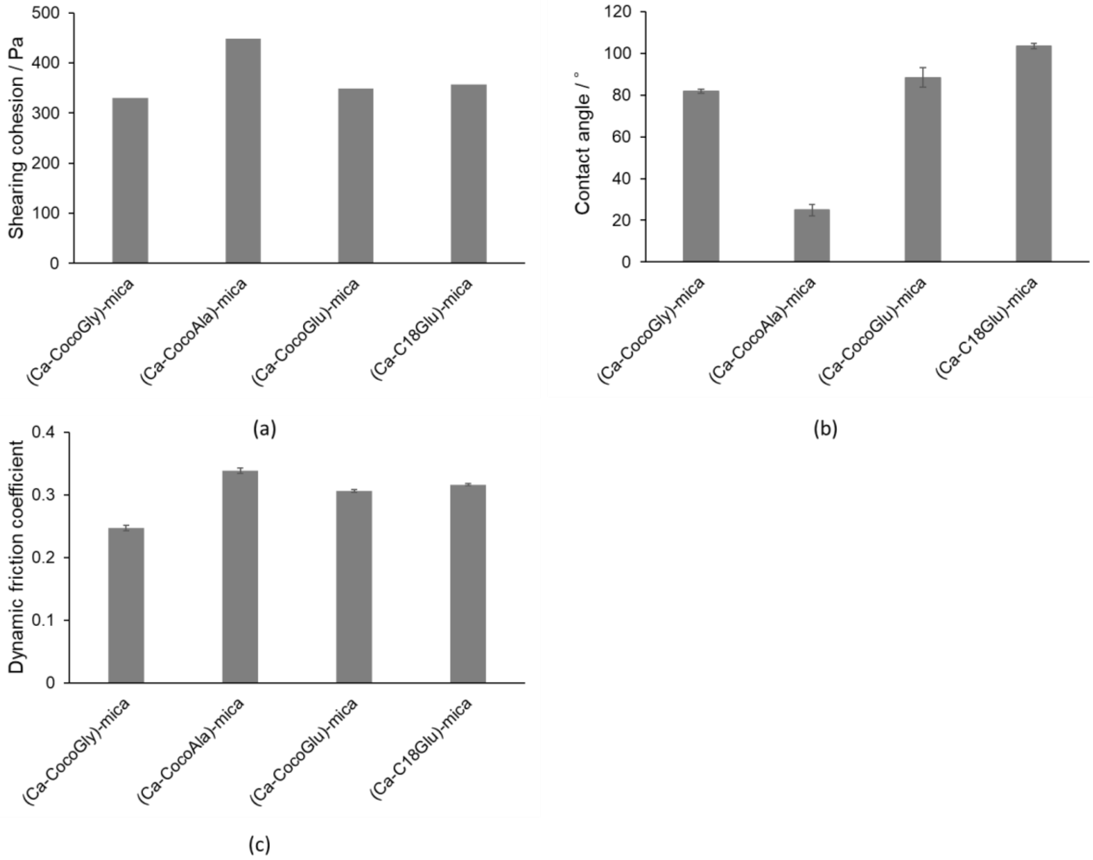

Figure 4. (a) Shearing cohesion, (b) water contact angle, and (c) dynamic friction coefficient of each surface-treated mica sample.

The smoothness and low dynamic friction coefficient of (Ca-CocoGly)-mica were attributed to the multilayer lamellar structure of Ca-CocoGly, as indicated by the strong diffraction peak characteristic of a lamellar structure (Figure 5). It has been reported that powders forming a lamellar structure exhibit lubricity due to the delamination of the lamellar layers [6], although the detailed mechanism has not yet been elucidated.

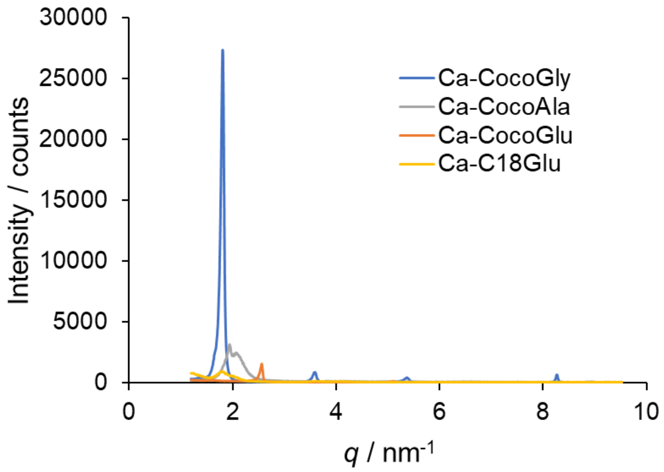

Figure 5. X-ray diffraction patterns of Ca-acyl amino acid complexes.

Figure 6 shows the oil dispersibility of each surface-treated mica sample. Oil dispersibility is an important property, especially in terms of incorporating powders into emulsion systems. In general, surface treatment with Ca-acyl amino acid complexes increased the oil dispersibility of mica. This is because the mica surface becomes more hydrophobic after being treated with Ca-acyl amino acid complexes. A comparison of the Ca-acyl amino acid-treated micas revealed that (Ca-C18Glu)-mica exhibits superior oil dispersibility relative to samples containing acyl amino acids with cocoyl chains. This suggests that the oil dispersibility of surface-treated mica is influenced by the amino acid moiety's acyl chain length.

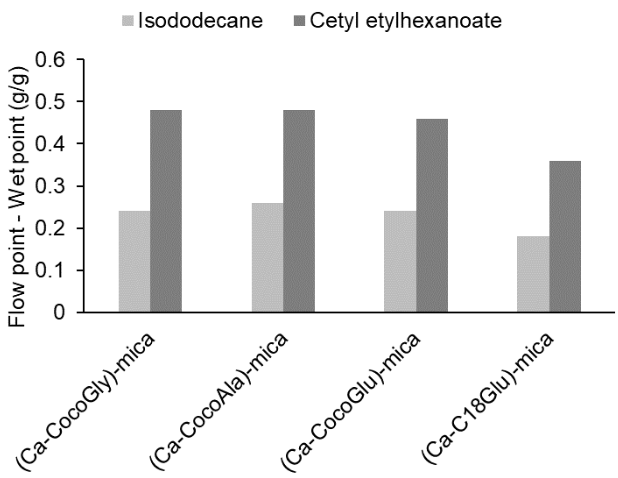

Figure 6. Oil dispersibility of each surface-treated mica sample.

3.3 Efficacy of Ca-C18Glu Surface-Treated Powders in Liquid Foundation

The efficacy of powders treated with Ca-acyl amino acid complexes was evaluated in liquid foundation to assess their practical applicability in cosmetics. The experiments focused on C18Glu, which exhibited the best oil dispersibility. Figure 7a shows the oil dispersibility of non-treated or surface-treated titanium dioxide and iron oxide mixed powders used in liquid foundation. Ca-C18Glu surface-treated powders demonstrated better oil dispersibility than dimethicone-treated powders and non-treated powders in both isododecane (hydrocarbon oil) and cetyl ethylhexanoate (ester oil), which are commonly used cosmetic raw materials.

Additionally, microscopic images of the liquid foundation samples (Figure 7b) revealed that liquid foundation containing Ca-C18Glu surface-treated powder achieved stable dispersion without powder aggregation, in contrast to liquid foundation containing dimethicone-treated powder or non-treated powder. Furthermore, the liquid foundation containing Ca-C18Glu surface-treated powder had the highest SPF, likely because of the inhibition of powder aggregation, which led to a more uniform liquid foundation film [7].

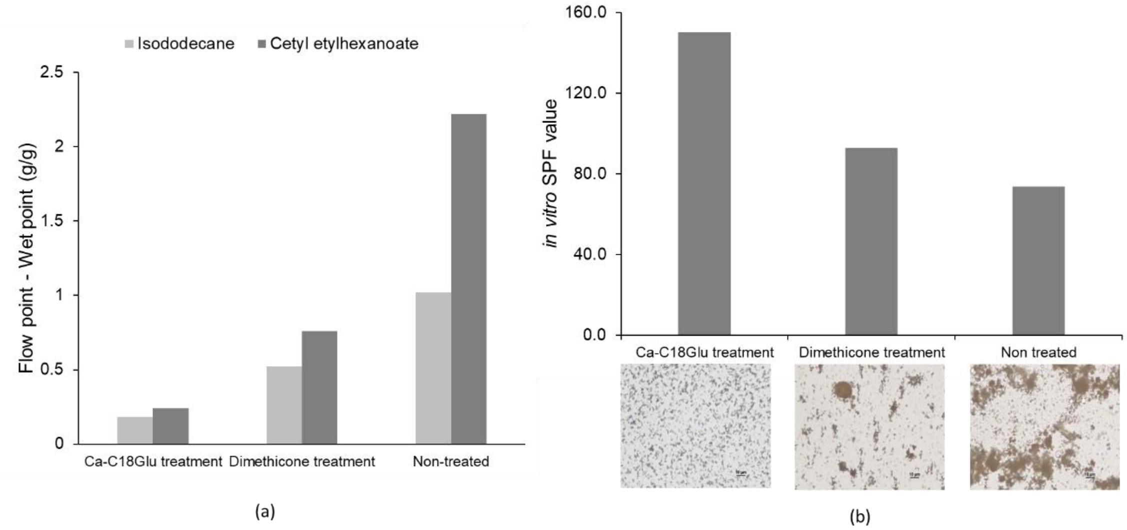

Figure 7. (a) Oil dispersibility of each powder and (b) *in vitro* SPF values and microscopic images of liquid foundations containing the powders.

3.4 Physical Properties of Powders Treated with Multiple Acyl Amino Acids and Fatty Acids

The physical properties of powders subjected to a composite acyl amino acid treatment with CocoGlyK, $C18GluNa_2$, and CocoFAK were investigated. The objective was to examine whether synergistic effects would be observed following a surface treatment with multiple acyl amino acids. Notably, fatty acids (CocoFAK) were included as texture modifiers because they form complexes with calcium ions, leading to high lubricity [8].

The distributions of CocoGly, C18Glu, and CocoFA on the surface of the treated powder were observed using TOF-SIMS (Figure 8). The images confirmed that each component was uniformly distributed on the surface of the treated powders.

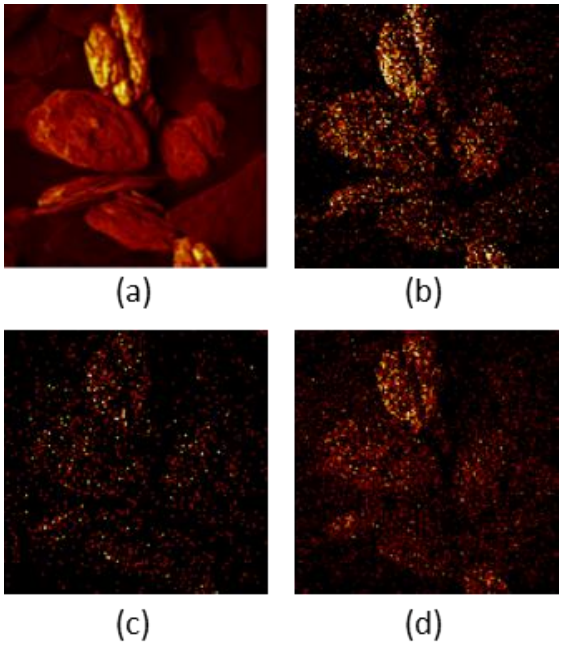

Figure 8. TOF-SIMS images: (a) total negative secondary ions; (b) CocoGly (*m/z* 74.03, $C_2H_4NO_2^-$); (c) C18Glu (*m/z* 98.03, $C_4H_4NO_2^-$); and (d) CocoFA (*m/z* 199.18, $C_{12}H_{23}O_2^-$).

Next, the texture of mica subjected to the composite treatment was comparatively examined (Figure 9).

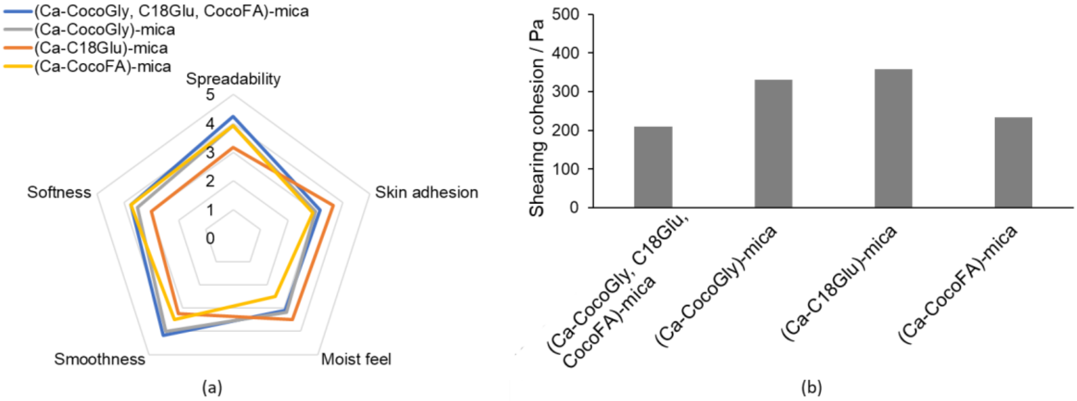

Figure 9. (a) Sensory evaluations and (b) shearing cohesion of each surface-treated mica sample.

When the composite treatment was applied, the evaluated spreadability and smoothness were higher than expected based on the results of the individual components, and were equal to or greater than those of the highest-rated single component, (Ca-CocoGly)-mica (Figure 9a). Additionally, the shearing cohesion was lower than those of powders treated with the single components (Figure 9b). This result suggests that using multiple surfactants with different acyl chain lengths and hydrophilic structures can induce synergistic effects on the treated powders. Indeed, adding acyl amino acids with a long C18 chain along with those having a Coco chain increases chain length heterogeneity in the Ca-acyl amino acid complex mixture. Although the detailed mechanism remains unclear, it is reasonable to conclude that this would weaken the interactions between carbon chains, thereby reducing the adhesion between powders.

4. Conclusion

This study evaluated surface-treated powders processed with acyl amino acid solutions and $CaCl_2$ solutions. The surface treatment involved mixing the powders sequentially with aqueous acyl amino acid and $CaCl_2$ solutions, thus offering a simpler method than those used in conventional surface treatments. Compared with non-treated powders, the obtained surface-treated powders exhibited enhanced functional properties, such as texture, hydrophobicity, and oil dispersibility. Further investigations into the effects of different acyl amino acids on the properties of treated powders revealed the potential for modulating the ultimate properties of surface-treated powders, i.e., their texture, dynamic friction coefficient, shearing cohesion, and hydrophobicity.

Powders treated with Ca-C18Glu demonstrated high oil dispersibility and no aggregation in liquid foundation, as confirmed by microscopic images. Additionally, in vitro SPF measurements showed that these powders exhibited higher SPF than formulations with non-treated or dimethicone-treated powders.

A composite treatment using multiple acyl amino acids and fatty acids was also explored. TOF-SIMS measurements confirmed uniform distributions of all components following the surface treatment. Moreover, the powders treated with multiple surfactants exhibited synergistic effects, particularly in terms of spreadability, smoothness, and shearing cohesion, compared with those treated with a single surfactant.

Overall, a simple method was developed for the surface treatment of powders using acyl amino acids, which have high environmental and biocompatibility, and calcium ions, which are commonly used in cosmetics. This strategy offers an alternative approach to conventional surface treatment techniques that require advanced technologies. Evaluations of the treated powders demonstrates the possibility of tailoring their properties through the selection and combination of surfactants. The application of this method is expected to broaden the scope of functionality and uniqueness in future cosmetic design.

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