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Enhancement of Film-Forming Properties in Color Cosmetics Through Plasticizer Integration: Focus on Trimethylsiloxysilicate and Plasticizer System

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Abstract

This study investigates the optimization of film-forming systems in color cosmetics through the integration of plasticizers to enhance wear properties while maintaining skin comfort. Long-wear performance, a critical quality parameter in color cosmetics, traditionally relies on film-forming agents in water-in-oil and oil-dispersed systems. While these systems effectively provide water resistance and transfer resistance, conventional film-forming agents often create thick barriers that can cause skin discomfort. The research focuses on developing an improved formulation using trimethylsiloxysilicate as the primary oil-soluble film forming agent combined with diisobutyl adipate as a plasticizer. To investigate the correlation between film formation and plasticizer effects, the formulation was applied to foundation products. The film-forming capability, strength, durability, and quality were evaluated using Texture analyzer and colorimeter analysis. Results demonstrated that diisobutyl adipate at 20-25% concentration relative to trimethylsiloxysilicate creates an optimal flexible film. The resulting formulation exhibited superior water resistance and improved texture while maintaining the desired long-wear properties. These findings suggest a significant advancement in formulation design for water-in-oil and oil-dispersed color cosmetics, potentially leading to improved strategies that balance product durability with skin compatibility.

Keywords: *Color cosmetics, Film-forming agents, Trimethylsiloxysilicate, Diisobutyl adipate, Long-wear cosmetics, Plasticizer*

1. Introduction

Color cosmetics play a pivotal role in enhancing appearance and expressing individuality. The key attributes of color cosmetics include pigment quality, coverage, color payoff, adhesion, spreadability, sensory feel, safety, and, most importantly, long-lasting performance. In

recent years, consumer demand has shifted toward high-performance color cosmetics that not only provide vibrant color but also offer additional functionalities such as skin protection, moisturization, and antioxidant effects [1,7]. Among these attributes, long-lasting performance—often referred to as “long-lasting effect”—has emerged as a critical quality determinant and a major factor in consumer satisfaction. In today’s fast-paced society, consumers increasingly seek makeup products that can maintain a flawless appearance throughout the day, despite exposure to sebum, sweat, friction, and environmental stressors. The long-lasting effect is not limited to color retention; it also encompasses uniformity of coverage, resistance to smudging, and durability against water, oil, and abrasion [5,6]. Recent studies have proposed eco-friendly approaches to enhancing dye durability, such as the application of riboflavin phosphate-mediated photo-crosslinked casein biopolymer films, which significantly improve the longevity of water-soluble dyes on the skin. Furthermore, the choice of application tools (e.g., puffs, brushes) has been shown to influence both adhesion and long-lasting properties, with latex puffs demonstrating superior performance in terms of adherence and durability [2,3]. The development of innovative materials and advanced formulation strategies aimed at improving long-lasting performance remains a key research focus in the color cosmetics industry. Such advancements are essential for enhancing product competitiveness and meeting the evolving needs of consumers [4].

Film-forming agents are polymeric compounds that form a uniform protective layer on the skin surface, preventing pigment transfer and enhancing formulation durability [7]. They are broadly classified into synthetic polymers (acrylics, silicones) and natural-derived components (proteins, waxes), each offering distinct functional advantages [8]. For instance, silicone acrylate copolymers have gained attention as innovative materials offering both skin compatibility and environmental resistance [9]. Recent advancements emphasize multifunctional composite systems. 99% natural origin index under ISO 16128 standards while maintaining 93% durability in SPF 30 formulations, bridging functionality and sustainability. A bis-carboxydecyl dimethicone-based agent, enhances flexibility and transfer resistance simultaneously and forming a hydrating film while strengthening the skin barrier—a paradigm shift toward integrating skincare benefits into color cosmetics.

Plasticizers are a class of additives widely used in industry to impart flexibility, softness, and improved processability to polymers, most notably polyvinyl chloride (PVC). By definition, a plasticizer is a substance incorporated into a material—typically a plastic or elastomer—to increase its flexibility, workability, or distensibility [10]. The addition of plasticizers lowers the glass transition temperature of polymers, making them less brittle and more malleable, which is essential for manufacturing a wide range of flexible products [11]. Historically, the development of plasticizer technology began with the plasticization of nitrocellulose, leading to the creation of celluloid and later the widespread use of phthalates such as dibutyl phthalate and di-2-ethylhexyl phthalate (DOP) in PVC applications. Today, plasticizers are indispensable in the production of flexible PVC, which is used in products ranging from cables, flooring, and medical devices to coated fabrics and films [10,11]. The advantages of using plasticizers in industrial applications are numerous. Plasticizers significantly enhance the flexibility and softness of polymers, enabling the creation of products that can withstand repeated bending and mechanical stress without cracking. They also improve the processability of plastics by reducing melt viscosity, which simplifies molding and shaping operations and increases manufacturing efficiency [10]. Many plasticizers exhibit low volatility, helping preserve the material’s properties over time and extending product lifespan. Furthermore, plasticizers are compatible with a broad range of polymer systems, allowing for versatility in formulation and application across diverse industries. In addition to their mechanical and processing benefits, plasticizers contribute to the cost-effectiveness of polymer-based products by reducing

material costs and enabling the production of durable, long-lasting materials. Their ability to improve impact resistance, durability, and weatherability makes them ideal for applications requiring robust and flexible materials. As such, plasticizers remain a vital component in the modern plastics industry, supporting the development of innovative, high-performance materials for a wide array of end uses.

Conventional film-forming agents used in color cosmetics have become the industry standard due to their high durability and color retention. However, brittleness and insufficient flexibility have been identified as major limitations, often resulting in decreased user comfort. In particular, while these films exhibit excellent skin adhesion during prolonged use, the stiffness of the film has been reported to cause skin tightness and flaking, which directly contributes to reduced consumer satisfaction. Accordingly, this study aims to investigate the use of plasticizers to modulate the physical properties of film-forming agents as a novel solution to these challenges. In this work, we seek to build upon previous studies by systematically evaluating the effects of plasticizers on the mechanical properties of film-forming agents, optimizing durability and flexibility according to plasticizer concentration, and assessing these parameters within cosmetic formulations. Through this approach, we aim to overcome the performance limitations of film-forming agents in color cosmetics and lay the groundwork for the development of next-generation long-lasting formulations that combine both functionality and enhanced user comfort.

2. Materials and Methods

Materials

In this study, trimethylsiloxysilicate (Momentive, USA, hereinafter referred to as TMSS) was used as the film-forming agent, and isododecane (Lanxess, Germany) was employed as the volatile solvent. Various plasticizers were evaluated, including diisobutyl adipate (KAK, Japan), C12-15 alkyl benzoate (Innospec, USA), ethylhexyl methoxycinnamate (BASF, Germany), and isopentyl diol (Kuraray, Japan). The oil phase of the cosmetic formulation consisted of isononyl isononanoate (KAK, Japan), synthetic beeswax (Kahlwax, Germany), PEG-30 dipolyhydroxystearate (CRODA, England), and sorbitan isostearate (CRODA, England). For color expression in the foundation, titanium dioxide, iron oxide (CI 77492), iron oxide (CI 77491), and iron oxide (CI 77499) (sensient, USA) were utilized. The water phase incorporated butylene glycol (OQ chemical, Germany) as the polyol component, magnesium sulfate (MERCK, Germany) as the salt, and phenoxyethanol (Galaxy, India) as the preservative agent.

Method

TMSS was fixed as the film-forming agent, and several plasticizers were initially screened and tested. Subsequently, a suitable plasticizer was selected, and the film properties were evaluated according to its concentration. Finally, the selected plasticizer was applied to cosmetic formulations to assess both film-forming characteristics and foundation properties.

Film Hardening and Cracking Phenomena of Film-Forming Agents

TMSS and isododecane were mixed in a 1:1 ratio and stirred at room temperature until complete dissolution and transparency were achieved. The solution was then applied to a transparent acrylic plate at a uniform thickness using a bar coater. The morphological

changes of the film over time and the phenomena occurring when stress was applied to the film were observed using a digital camera (SONY HX300, Japan).

Plasticizer Screening

Four different plasticizers were investigated: diisobutyl adipate (hereinafter referred to as DBA) with branched alkyl groups, C12-15 alkyl benzoate as an aromatic ester type, ethylhexyl methoxycinnamate containing conjugated double bonds, and isopentyl diol as an alcohol complex. Each plasticizer was thoroughly mixed with TMSS 50% isododecane solution at a ratio of 8:2. The film formation process and changes occurring when stress was applied to the formed film were observed. Subsequently, an appropriate plasticizer was selected, and film formation evaluation according to concentration variation was conducted using digital camera observation.

Evaluation of Film Formation Ability According to Plasticizer Content

To observe the film formation phenomenon of the selected plasticizer with TMSS, equal amounts of varying plasticizer concentrations were applied to rubber film, and both the film formation time and the post-formation characteristics were compared. To investigate the cracking phenomena according to film strength after formation, a texture analyzer (Brookfield CT3, USA) was employed to apply uniform force and duration to stretch the rubber film, and the resulting phenomena were observed using a digital camera.

Table 1. Formulation of Foundation Containing Film-Forming Agent and Formulation Containing Both Film-Forming Agent and Plasticizer (flexible foundation).

Phase	Ingredients	Contents (wt%)	
		blank	flexible foundation
Oil phase	Trimethylsiloxysilicate		8.00
	Isododecane		10.00
	Isononyl Isononanoate	5.00	2.00
	Diisobutyl Adipate	-	3.00
	Synthetic Beeswax		1.20
	PEG-30 Dipolyhydroxystearate		2.00
	Sorbitan Isostearate		2.00
Color pigments	Titanium Dioxide		9.00
	Iron Oxide (CI 77491)		0.08
	Iron Oxide (CI 77492)		0.90
	Iron Oxide (CI 77499)		0.02
Water phase	Butyleneglycol		3.00
	Phenoxyethanol		0.50
	Magnesium Sulfate		1.00
	Water		QS to 100

Application to Foundation Formulation

The selected plasticizer at the optimal concentration was incorporated into a cosmetic formulation. A Water-in-Oil type foundation was chosen as the cosmetic formulation vehicle. The foundation formula is presented in Table 1. The oil and water phases were prepared separately, and the color pigments were ground using a powder-specific mixer to prepare the base. The oil phase was thoroughly dissolved at 65°C, after which the prepared color pigments were added and well dispersed. After confirming proper dispersion of the oil phase and colorants, the water phase was slowly introduced and emulsified using a homogenizer at 4000 rpm for 10 minutes, followed by cooling to complete the foundation preparation. The foundation formulations were designated as "blank" (without plasticizer) and "flexible foundation" (with incorporated plasticizer).

Evaluation of Film Properties in Foundation Formulation

The viscosity changes of the two prepared foundation formulations were measured over time, and color retention was evaluated by measuring color changes under various temperature conditions using a colorimeter (Minolta CM3700, USA). Additionally, the transfer area after film formation was measured and compared between formulations. To assess the moisturizing efficacy of the formulation containing only the film-forming agent versus the formulation containing both film-forming agent and plasticizer, skin hydration level and transepidermal water loss (TEWL) were measured and compared.

3. Results and Discussion

Film Formation and Cracking Phenomena of TMSS

TMSS films are widely applied in various cosmetic formulations; however, excessive use to enhance color longevity and makeup fixation can induce skin dryness and makeup breakdown. In particular, rather than forming a flexible film along the facial contours, the formation of a rigid film becomes pronounced during daily activities after makeup application, leading to film hardening that adversely affects both the makeup and the skin (Figure 1.).

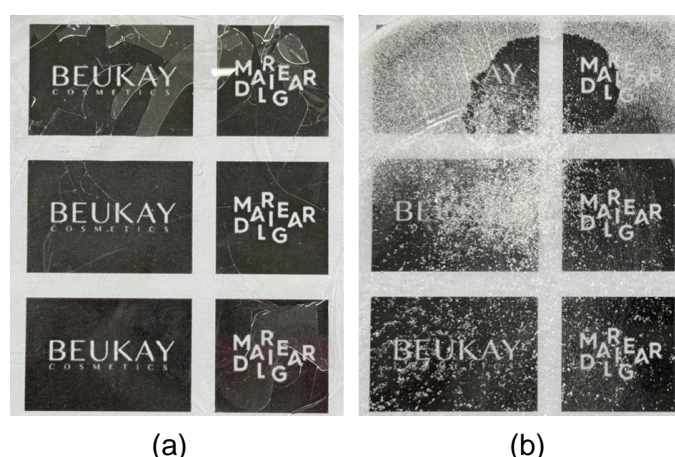


Figure 1. Digital camera images of (a) TMSS film hardening and (b) film cracking and powder formation after stress application to the hardened TMSS film

This phenomenon was determined to cause post-application dryness and was identified as the source of uncomfortable makeup sensation.

Observation of Compatibility Between TMSS Film and Plasticizers

As TMSS constitutes a component of the oil phase, its compatibility with carrier oils and other prescribed oils is of significant importance. To examine the compatibility of oil-based plasticizers with TMSS and isododecane as a carrier oil, TMSS solution was mixed with plasticizers to evaluate dissolution characteristics and film formation patterns.

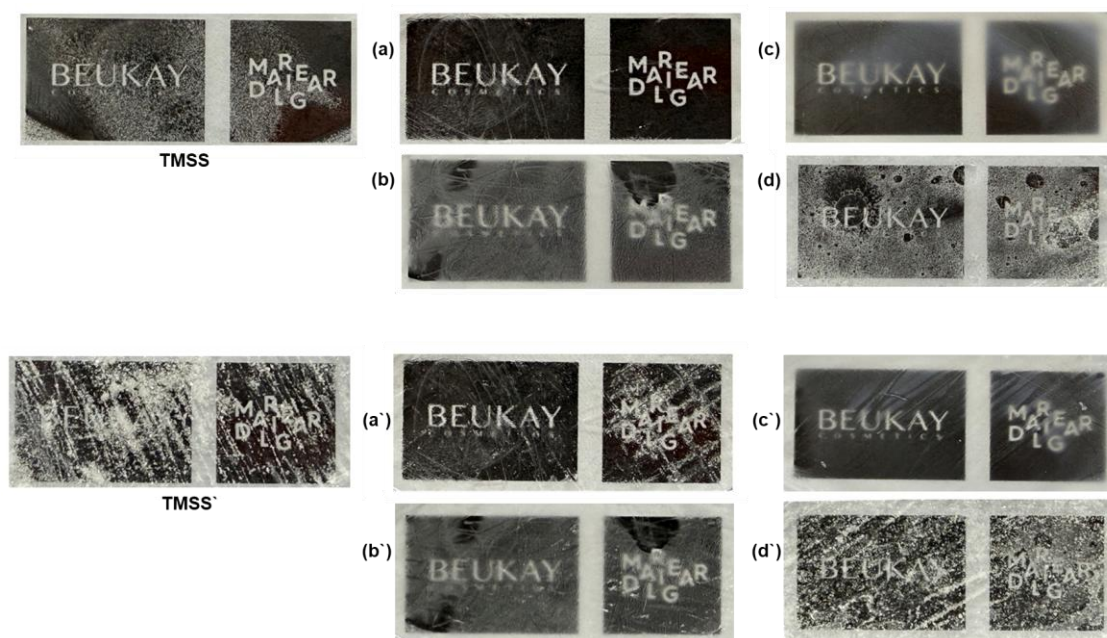


Figure 2. Observation of Film Formation After Reaction of TMSS Solution with Various Plasticizers: (a) TMSS and DBA, (b) TMSS and C12-15 Alkyl Benzoate, (c) TMSS and Ethylhexyl Methoxycinnamate, (d) TMSS and Isopentyldiol; Observation of Cracking Phenomena When Stress Was Applied After Film Formation: (TMSS'), (a'), (b'), (c'), (d')

Compatibility testing between TMSS solution and various plasticizers revealed that DBA maintained transparent solubility and film transparency after film formation. To verify the plasticizing function, appropriate stress was applied to mixtures of TMSS and different plasticizers to evaluate film flexibility and coating integrity. Results demonstrated increased flexibility in TMSS films containing DBA, C12-15 Alkyl Benzoate, and Ethylhexyl Methoxycinnamate as plasticizers. In summary, DBA was ultimately selected as the plasticizer for TMSS due to its excellent compatibility with TMSS film and its ability to modulate film strength to enhance flexibility.

Observation of TMSS Film Formation Ability According to DBA Concentration

To determine the optimal combination of TMSS as a film-forming agent and DBA as a plasticizer, concentration conditions for both film formation and post-formation flexibility were investigated.

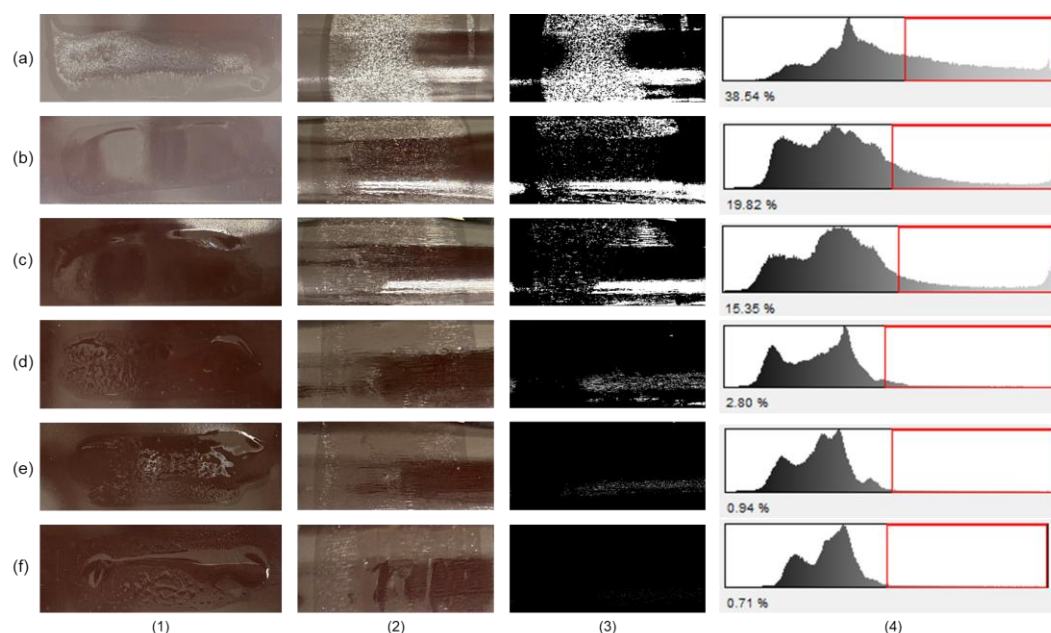


Figure 3. Experiment to Evaluate Film Images Formed at Various TMSS and DBA Concentrations and to Determine the Optimal Ratio for Film Flexibility: (a) TMSS film without plasticizer; (b) TMSS film with 1% DBA; (c) TMSS film with 2% DBA, (d) TMSS film with 3% DBA, (e) TMSS film with 4% DBA, (f) TMSS film with 5% DBA; (1) film on the rubber plate (50°C, 3hr), (2) Hardened film cracking phenomenon caused by pulling both ends with the same force (120G, CT3), (3) Histogram Representing Fragmented Film Areas (White Areas Indicate Fractured Film Surface), (4) Area Ratio of White Areas.

Film-forming capacity analysis across varying dibutyl adipate (DBA) concentrations revealed distinct phase behavior patterns. At 3% DBA, flexible continuous film formation was observed, whereas fragmented films resembling plasticizer-free formulations occurred at 1–2% concentrations (Figure 4). Excessive DBA content (>4%) induced complete film dissolution due to plasticizer oversaturation. As illustrated in Figure 4, increasing DBA content correlated with reduced viscosity in trimethylsiloxysilicate (TMSS)-based systems. This phenomenon is attributed to DBA's dual role as a plasticizer: while TMSS initially derived viscosity from isododecane carrier oil solubility, DBA-mediated TMSS solubilization into the bulk solution disrupted colloidal network integrity, ultimately lowering system viscosity. The concentration-dependent plasticization effect demonstrates critical formulation thresholds for optimizing film mechanical properties and rheological stability.

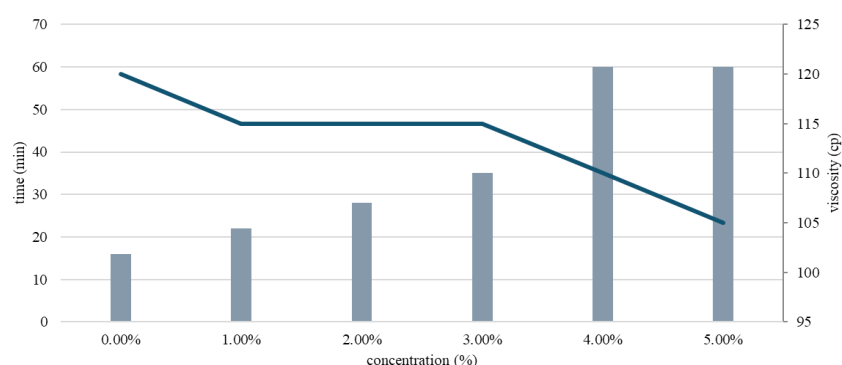


Figure 4. Film Kinetics and Rheological Analysis as Functions of DBA Concentration

Evaluation of Makeup Efficacy of Foundation

The stability of the formulation incorporating TMSS and DBA was evaluated by comparing its time-dependent changes with those of the TMSS-only formulation. As demonstrated in Figure 5, the viscosity stability remained consistent even with the addition of the plasticizer. Additionally, particle size changes exhibited trends similar to those observed in the emulsified foundation formulation without the plasticizer, indicating a stable state.

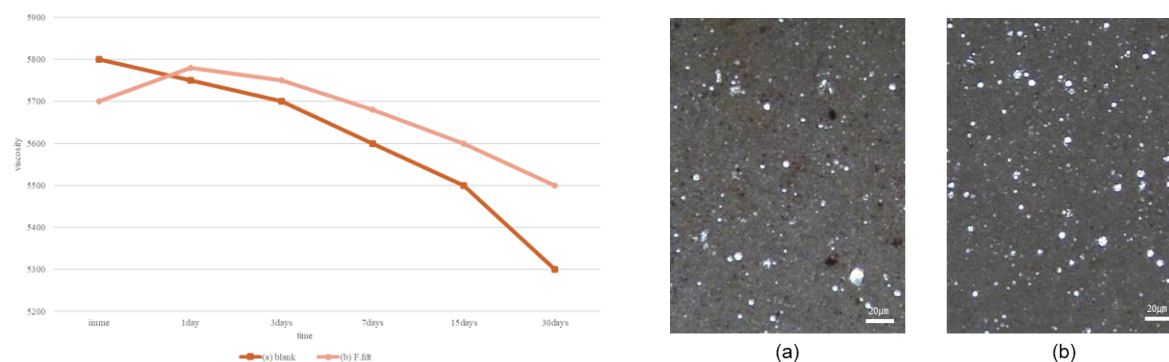


Figure 5. Time-dependent viscosity changes and microscopic images (100 \times magnification) of particle dispersion in foundation formulations: (a) TMSS-only formulation versus (b) TMSS-DBA hybrid film-forming agent formulation.

The makeup efficacy of a foundation formulation based on a TMSS film-forming agent was compared with that of a foundation incorporating both TMSS and dibutyl adipate (DBA) as a plasticizer. To evaluate color persistence, color difference (ΔL^* , Δa^* , Δb^*) was measured using a colorimeter under controlled conditions (30 $^{\circ}\text{C}$, 40 $^{\circ}\text{C}$, and 45 $^{\circ}\text{C}$ with 85% humidity). Initial measurements were taken at 25 $^{\circ}\text{C}$, followed by post-incubation measurements after 5 hours under each environmental condition. The results, summarized in Figure 6, demonstrated that the formulation combining TMSS and DBA exhibited smaller color deviations compared to the TMSS-only formulation. This improvement is attributed to DBA's role in preventing fragmentation of the hardened TMSS film, thereby enhancing resistance to external stressors (e.g., dust, moisture) and delivering superior color retention.

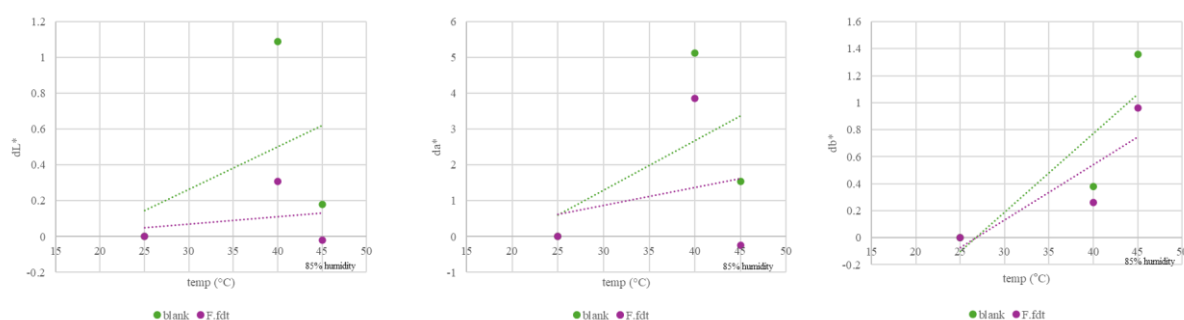


Figure 6. Measurement results of color differences (ΔL^* , Δa^* , Δb^*) under each temperature condition

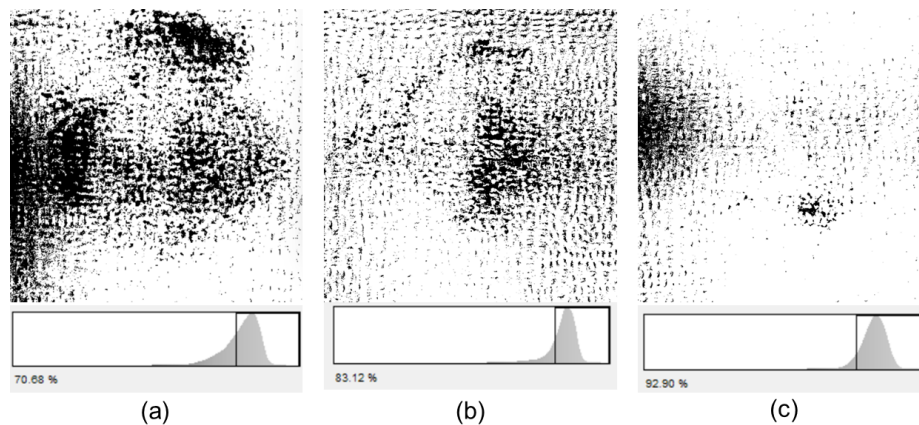


Figure 7. The amount of foundation transfer was quantified by measuring the surface area of transferred material. (Brookfield CT3, trigger : 90g, 2 sec); (a) general foundation without film forming agents, (b) blank foundation with TMSS, (c) F.foundation with TMSS and DBA

The observed increase in transfer was attributed to the migration of TMSS fragments inter-mixed with powder components from the foundation. This finding confirms that the TMSS-DBA plasticizer system enhances color persistence while reducing material transfer. To evaluate potential improvements in dryness caused by TMSS fragment accumulation and film rigidity, post-application skin hydration and transepidermal water loss (TEWL) measurements were conducted, as summarized in Figure 8.

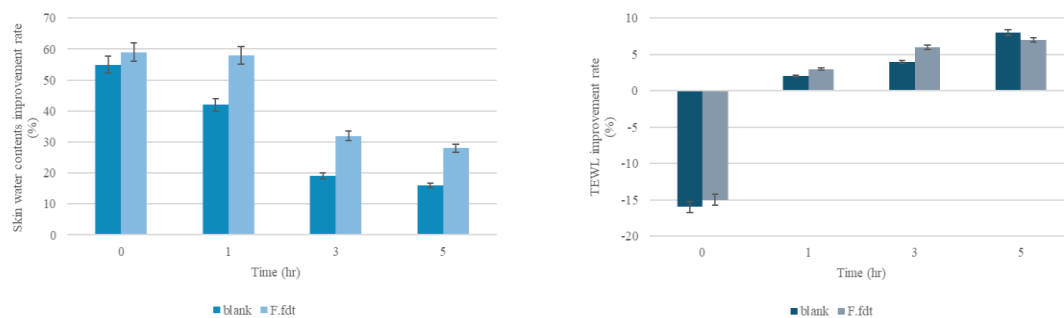


Figure 8. Skin moist contents improvement rate of TMSS with DBA; skin water contents rate and TEWL rate.

4. Conclusion

This study conducted a plasticizer screening to enhance the flexibility of TMSS as a film-forming agent. DBA was identified as the optimal plasticizer due to its compatibility and film-forming efficacy.

Compatibility and film flexibility: TMSS exhibited excellent compatibility with DBA, with a 20–25% concentration of DBA relative to TMSS producing a flexible film.

Performance in foundation formulations: The TMSS-DBA hybrid film demonstrated superior color retention and reduced transfer, enabling a long-wear foundation.

Skin hydration benefits: Foundations incorporating the TMSS-DBA hybrid film significantly improved skin hydration levels compared to TMSS-only formulations.

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