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Examining Adhesion Promoters in UV-Cured Nail Coatings: A Comprehensive Investigation into Composition, Polymerization, and Performance Characteristics

Zane GRIGALE-SOROCINA [*]**, Ingmars BIRKS, Estefanija NOVICKA**

R&D, Kinetics Nail Systems, Kurzemes prospekts 3K, Riga, LV-1026, Latvia

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UV curing nail coatings have gained immense popularity for their rapid curing time and enhanced performance. Achieving strong adhesion to natural nails is crucial for these coatings. This study investigates various adhesion promoters used in UV-cured nail coatings. Key composition characteristics such as polymerization temperature (T), post-production viscosity, and viscosity stability over three months at 50°C were evaluated. Adhesion with pull-off testing and physico-mechanical properties of cured coatings were examined. Various adhesion promoters including aliphatic acrylates, silanes, dimethacrylate succinate adduct, dimethacrylate maleate adduct, and acid-based adhesion promoters were tested. Silane compounds exhibited superior adhesion and viscosity stability, making them suitable for long-lasting formulations. Polymerization temperature varied, requiring optimization for each formulation. The choice of adhesion promoter strongly influenced physico-mechanical properties, with dimethacrylate/maleate adduct showing superior durability. The findings offer a comprehensive understanding of the influence of adhesion promoters on coating composition and performance, aiding in the development of high-quality, long-lasting UV curing nail coatings for the cosmetics industry.

Keywords: coatings, acrylate monomers, adhesion, polymerization, nail coatings.

1. INTRODUCTION

UV-cured coatings on natural nails represent a significant advancement in the field of nail cosmetics and treatments. These coatings rely on ultraviolet (UV) light exposure to initiate a polymerization process, resulting in a durable and glossy finish. Ensuring strong adhesion between the UV-cured coating and the natural nail substrate is paramount for the longevity and effectiveness of such coatings [1].

Several potential strategies exist to enhance adhesion in this context. One approach involves the utilization of specialized primers or adhesive promoters tailored for natural nail surfaces. These formulations are designed to facilitate molecular-level interactions between the coating and the nail, thereby improving overall adhesion strength [2].

Furthermore, surface preparation techniques play a crucial role in optimizing adhesion. Mechanical treatments, such as gentle abrasion or buffing, can be employed to create micro-roughness on the nail surface. This micro-roughness provides an improved substrate for the coating to adhere to, enhancing the overall bond strength [3]. In addition, chemical modifications may be considered to enhance adhesion. Surface treatments involving non-harsh acids or mild chemical agents can be explored, provided they are compatible with the natural composition of the nail. These treatments can introduce functional groups or alter surface energies, leading to enhanced intermolecular interactions with the UV-cured coating [2, 4 – 7].

The advancements in adhesion properties of UV-cured coatings on natural nails predominantly rely on proprietary knowledge within the industry, which companies are generally hesitant to disclose, aiming to maintain a competitive edge in product performance within the market. Consequently, only a limited body of scientific research findings is accessible on this subject matter [2].

The selection of adhesion promoters for UV curing coating compositions intended for application on natural nails depends on several factors, including the specific chemical composition of the coating and the natural nail substrate.

Functional Monomers: Certain functional monomers, such as methacrylated silanes or phosphates, can act as adhesion promoters by forming covalent bonds with the nail surface. These functional groups enhance the interfacial adhesion between the coating and the natural nail [4, 8].

Cross-Linking Agents: Cross-linking agents like multifunctional acrylates or methacrylates can promote adhesion by facilitating a stronger chemical bond formation between the coating and the nail substrate [9].

Surface Modifiers: Silane coupling agents or organofunctional silanes can be used as adhesion promoters. These molecules possess both organic and inorganic components, allowing them to enhance adhesion by creating a chemical bridge between the coating and the nail surface [10, 11].

Polymeric Adhesion Promoters: Some polymers, such as functionalized polyurethanes or acrylic copolymers, can be designed to enhance adhesion by forming strong interactions with the nail surface [12].

Surfactants and Wetting Agents: Certain surfactants and wetting agents can improve adhesion by reducing surface tension and ensuring better wetting of the natural

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[*] Corresponding author. Tel.: +371-28323467.
E-mail: *zane.grigale@kineticsbeauty.com* (Z. Grigale-Soročina)

nail, facilitating a more intimate contact between the coating and the substrate [13].

Primer Systems: While not strictly adhesion promoters in themselves, primer systems consisting of a combination of functional monomers, cross-linking agents, and surface modifiers can be tailored to specifically enhance adhesion in UV curing coating compositions for natural nails [2].

Compatibility with UV Initiators: It's crucial to ensure that the chosen adhesion promoter is compatible with the UV initiator system used in the coating composition. Incompatibility may lead to reduced curing efficiency and compromised adhesion [8, 14].

Compatibility with Formulation Components: The adhesion promoter should be compatible with other components in the formulation to prevent any negative interactions that could hinder the overall performance of the coating [15].

Ultimately, the selection of an adhesion promoter should be based on thorough compatibility testing with both the UV curing composition and the natural nail substrate, as well as consideration of the specific requirements and constraints of the application.

It's also important to follow the industry's traditions and requests for the adhesion promoter and UV curing coating to achieve the best results. Additionally, regulatory considerations and potential health and safety implications of using certain adhesion promoters should be considered [16, 17].

The available strategies for enhancing adhesion are constrained in this context. Harsh acids and surface treatments are precluded since the substrate is a natural nail. The extant research findings pertaining to enhanced adhesion for UV coatings on natural nails indicate that the isolated application of primers confers a superior increase in adhesion compared to the application of coatings without the use of primers [2].

The objective of this study is to evaluate potential adhesion promoters for enhancing the adhesion of UV-cured compositions on natural nails in the absence of primers.

2. METHODOLOGY

2.1. Composition and formulation

In pursuit of enhancing adhesion properties, a comprehensive assessment was conducted involving the incorporation and evaluation of 9 distinct adhesion promoters into the system. This assortment predominantly encompassed silanes, adhesion promoters reliant on acid chemistry, and aliphatic urethane acrylates. The available characteristics of tested adhesion promoters are listed in Table 1.

The formulation consisted of a 61 % weight urethane acrylate oligomer (Urethane Dimethacrylate, Exothane 26, Esstech), 33 % monomer - hydroxypropyl methacrylate (HPMA, Esstech), complemented by a 1% photoinitiator (ethyl-2,4,6-Trimethylbenzoylphenylphosphate, Lucirin TPO_L, Basf) and 5 % of an adhesion promoter.

2.2. Test methods

Rheological behavior was assessed using a KNX5112 rheometer (Kinexus) at 25 °C. The average of three measurements with a 3 – 5 % standard deviation was considered. Viscosity measurements were taken after formulation preparation and at intervals of 2, 12, 36, and 72 days.

Table 1. Characteristics of tested adhesion promoters

Formula code / Adhesion promoter	Funcionality	Acid value, (mgKOH/g)	Viscosity, cps or mPas, 25°C
RAW-01 Aliphatic urethane *Esstech*	2		
RAW-02 Gamma-methacryloxypropyltrimethoxysilane *Esstech*	2.5	85 – 105	700 – 900
RAW-03 Gamma-methacryloxypropyltrimethoxysilane *Esstech*	1.5	220 – 350	1100
RAW-04 Dimethacrylate/Succinate Adduct *Esstech*	1		
RAW-05 Dimethacrylate/maleate adduct *Esstech*	1		
RAW-06 2-Propenoic acid, 2-methyl-, 2-hydroxyethyl ester, reaction products with phosphorus Oxide *Sartomer*	1	130 – 195	10 – 35
RAW-07 2-Propenoic acid, 2-methyl-, 2-hydroxyethyl ester, reaction products with phosphorus Oxide *Sartomer*	1	280 – 310	2500
RAW-08 Bis(methacryloyloxyethyl) acrylate compound *BASF*	1		
RAW-09 Aliphatic polyether urethane methacrylate *BASF*	3		60000

Components were mixed at 1800 rpm for 4 minutes using a Dispermill KK 250, followed by Film Applicator (BYK) deposition to achieve a 200 μm thickness. UV/LED curing (KP800LED, $\lambda = 400 - 410$ nm, YI Liang electron technology Co, China) for 60 seconds ensued.

Differential thermal analysis was employed to study photopolymerization using a K-type thermocouple and a data logger (KTT-310 Meter Dual). A constant sample mass of 0.16 g ± 0.01 g was used, placed within a 10 mm diameter silicon matrix under a UV lamp. Temperature differentials between thermocouples were recorded.

Cure depth was ascertained by measuring the thickness of the polymerized coating using a Hegman gauge grindometer for a transparent composition. The clear coatings, incorporating nine different adhesion promoters, were applied to a 200 μm thickness onto the grindometer, then subjected to UV/LED (KP800LED lamp curing for 60 seconds. Subsequently, any non-polymerized oxygen inhibition layer was eliminated using a cotton pad, and the thickness of the removed layer was measured.

Mechanical properties: The mechanical properties of UV polymerized films were determined by standard tensile stress-strain tests to measure ultimate tensile strength (σ), modulus of Elasticity (E) and elongation at break (ε). The formula used was $E= \sigma/ \varepsilon$. Standard tensile stress-strain experiments were performed at room temperature on tensile tester BDO FB020TN (Zwick Roell, Germany) according to the requirements of LVS EN ISO 527-3:2000 (sample shape: double blade films; the speed of the upper crosshead: 10 mm/min). Samples were placed in a universal testing facility holder and deformed at a rate of 25 mm/min. The results are the mean values of 5 independent measurements.

Adhesion strength was evaluated using the pull-off adhesion test (ISO 4624) on glass and aluminum panels. After application, curing, and 1-hour polymerization, the coating was lightly abraded, cleaned with 90 % acetone solution, and a metal dolly (*D* = 20 mm) with a hot glue-coated contact surface was pressed against the coating. The dolly was left for 30 minutes to dry, after which pull-off testing was conducted.

3. RESULTS AND DISCUSSION

The adhesion properties of short-term UV-curable coatings applied to natural nails have not been extensively documented [1, 2, 18 – 22]. Furthermore, there is a scarcity of studies addressing methods to enhance the adhesion of these coatings [2]. Some available reports have studied primers as adhesion-promoting substances [2]. Consequently, we conducted experiments involving nine distinct adhesion promoters, assessing their impact on the properties of the UV curing gel polish base composition. The research goal was to identify an optimal system with outstanding adhesion qualities (2 – 3 MPa) and other coating characteristics summarized in Table 2.

Table 2. Criteria defined for optimal UV curable nail coatings

Response	Goal limits
Viscosity, mPas	1000 – 5000
Polymerization temperature	< 70
Cure depth, μm	200 – 250
Elongation at break, %	10 – 30
Tensile strength, MPa	10 – 15
Pull-off adhesion on glass, MPa	2 – 3
Pull-off adhesion on aluminum, MPa	2 – 3

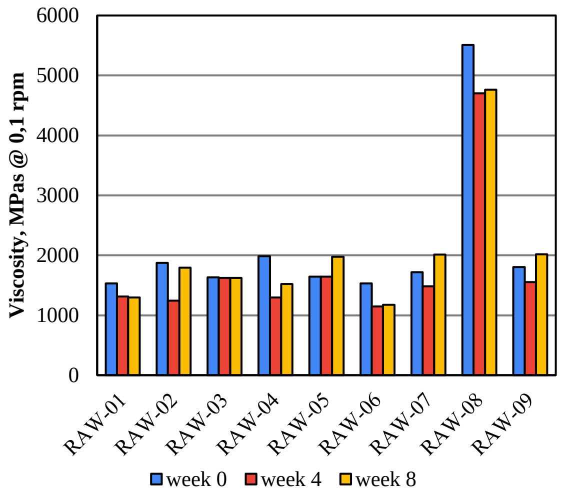

Fig. 1. Viscosity variation of composition over 8 weeks at 50 °C with eight distinct adhesion promoters measured @ 0.1 rpm

Throughout the novel product development protocol, viscosity constitutes the primary parameter under consideration. Viscosity was examined over eight weeks, to observe the viscosity changes in time at aging conditions (50 °C) (Fig. 1). The findings indicate that the majority of adhesion promoters lead to an elevation in composition viscosity, ranging from 5 % to 30 %. Notably, RAW-08 demonstrated a substantial increase in viscosity, exceeding 2.5 times the initial value. While the initial viscosity of the composition did not meet the specified requirements, it exhibited the highest degree of viscosity change during the aging tests. RAW-03 exhibited the most favorable viscosity characteristics among the compositions evaluated.

The thermal analysis principles were applied to characterize these systems. The findings are shown in Fig. 2. RAW-02, gamma-methacryloxypropyltrimethoxysilane, attains the highest polymerization temperature. In contrast, all other adhesion promoters lead to a reduction in the polymerization temperature of the base system.

Typically, the maximum polymerization temperature is achieved within the initial 20 seconds of the polymerization process, with the except for RAW-08. To meet the specified requirements, it is advised to refine the composition and decrease the concentration of the monomer. This adjustment is crucial to produce a coating that aligns with the specified standards, as a majority of the systems surpass the T_{MAX} threshold (70 °C). For systems exceeding the specified maximum temperature, the concentration of monomer or photoinitiator must be reduced to slow down the reaction rate, thus preventing any discomfort or pain during polymerization on human nails.

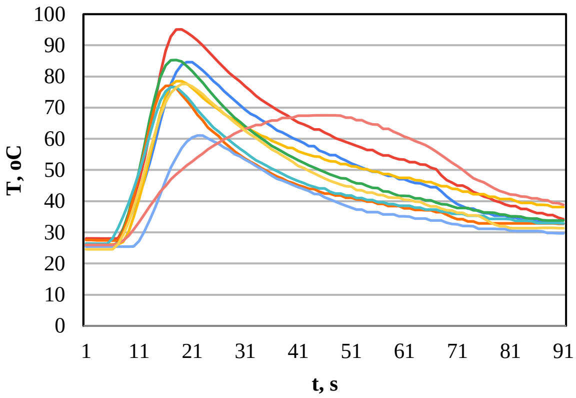

Fig. 2. Temperature fluctuations during polymerization in systems utilizing eight different adhesion promoters. RAW-01 base composition without adhesion promoters

The subsequent parameter under investigation was the cure depth, a metric delineating the extent of polymerization activity. This parameter serves to characterize the activity of the adhesion promoters within the system. A higher value in cure depth signifies heightened polymerization activity within the thicker layer. The findings indicate that, in the case of clear coatings, the activity of the majority of adhesion promoters is commensurate and surpasses the maximum (250 μm), with the exception of RAW-07 and RAW-08, where polymerized layer was less than required 200 μm.

The Young's modulus of a natural nail at a relative humidity of 55 % has been reported as 2.32 GPa [21]. It is imperative for the deformation characteristics of the nail coating to closely approximate those of the natural nail, as this ensures optimal adhesion and prevents any adhesion failure. All examined compositions fell short of attaining a modulus of elasticity equivalent to that of a natural nail. This is attributed to the fact that the film applied onto the nail did not surpass a thickness of 200 micrometers.

Films containing the RAW-05 adhesion promoter (Dimethacrylate/Maleate Adduct) exhibited the highest Young's modulus values. However, these cured films displayed heightened brittleness and the lowest ultimate relative deformation (εB) values, as depicted in Fig. 3 and Fig. 4. Notably, only this composition met the stipulated acceptance criteria, as all other compositions were too elastic.

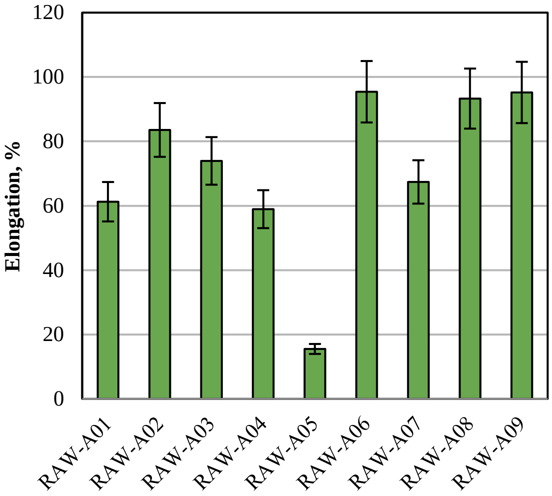

Fig. 3. Elongation at break values for coatings with different adhesion promoter

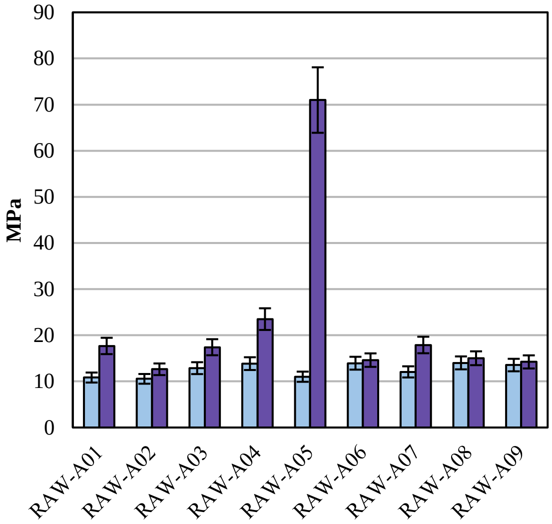

Fig. 4. Elastic modulus and tensile strength values for coatings with different adhesion promoters

RAW-05 adhesive promoters facilitated the system's curing and the formation of a denser cross-linking network. The lack of information from the raw material manufacturer regarding the adhesive promoter itself prevents making broader conclusions. Films containing RAW-04 also could be one of the options, as an added adhesion promoter increases the modulus of Elasticity. All other adhesion promoters increase elongation properties but decrease the modulus of elasticity, however, the requirements for natural nail coatings demand systems with higher elasticity modulus and lower elongation at break.

The adhesive strength is defined as the maximum tensile stress experienced when a direct load is applied perpendicular to the surface under examination [23]. The pull-off adhesion test methodology has proven effective in establishing relative rankings for a set of coated panels that exhibit significant disparities in adhesion. This test, classified as a partially destructive method situated near the surface, enables the measurement of tensile strength across diverse materials [24]. The application of a defined pull-head plate, affixed to the test area, imparts the tensile load. The adhesive strength is represented by the ratio of the failure load to the test area [23]. Ten coating samples, parallel in nature, were prepared and evaluated on glass and aluminum panels. All compositions displayed a similar level of differentiation within a range of +/- 0.35. The outcomes are graphically depicted in Fig. 5.

Previously, a cross-cut tester was employed to assess coating adhesion on the substrate. However, this method exhibited a notably high degree of variability in results and lacked correlation with in-vivo tests [23]. By utilizing the pull-off adhesion tester, results can be consistently reproduced and directly compared with in-vivo tests. The pull-off adhesion strength methodology has demonstrated superior utility in contrast to preceding testing techniques, owing to its expeditious and comparable results. These attributes hold considerable significance for research and development laboratories within small enterprises [24].

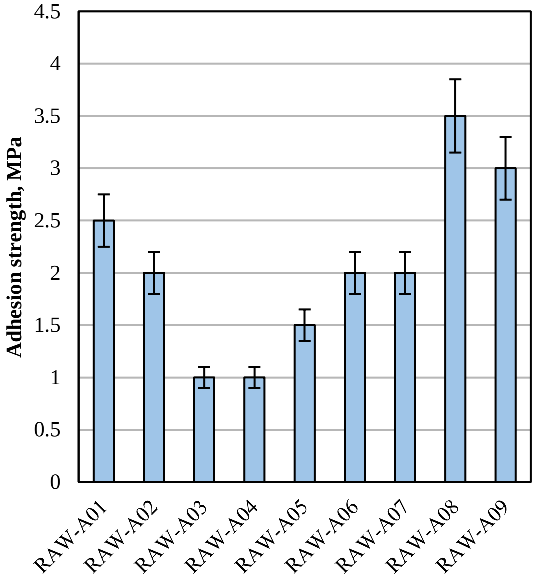

Fig. 5. Adhesion strength on aluminum sheets for coatings with different adhesion promoters

Using the Pull-off adhesion technique, it was observed that five formulations exhibited improved adhesion to aluminum compared to the baseline composition (Fig. 6). Adhesion of the base formulation was 2.5 MPa. Conversely, two formulations exhibited heightened adhesion on aluminum substrates. Specifically, only composition RAW-08 is deemed suitable for subsequent assessments on natural nails, as exhibiting an increase in adhesion on aluminum from 2.5 MPa to 3.5 MPa.

4. CONCLUSIONS

This research comprehensively evaluated various adhesion promoters for UV curing nail coatings, considering critical factors including composition polymerization temperature, viscosity, physico-mechanical characteristics, and adhesion. The findings offer valuable insights into optimizing adhesion for UV-cured nail coatings without the use of primers.

The choice of adhesion promoter significantly influenced the mechanical properties of the cured coatings. For instance, RAW-05 Dimethacrylate/Maleate Adduct displayed superior modulus of elasticity (71 MPa) and tensile strength (11 MPa), ensuring durability and wear resistance.

Two formulations exhibited enhanced adhesion on aluminum substrates. Compositions RAW-08 and RAW-09 showed promise for further assessments on natural nails due to their consistent adhesion on aluminum sheets (3.5 MPa and 3 MPa).

However, the viscosity of RAW-08 did not meet the acceptance criteria (> 5000 mPas). Each system that excelled in one parameter failed to meet requirements when compared to other system parameters. None of the compositions tested can be utilized as a natural nail coating. Further formulation adjustments are necessary.

Overall, this research provides valuable insights into the selection and optimization of adhesion promoters for UV curing nail coatings. It addresses critical aspects such as polymerization temperature, viscosity stability, and cured coating properties, contributing to the development of high-quality, long-lasting UV curing nail coatings for the cosmetics industry.

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