Influence of monomer on structure, processing and application characteristics of UV curable urethane acrylate composite coatings

Z Grigale-Sorocina¹, M Kalnins² and K A Gross²

¹Environment, Bioenergetics and Biotechnology Competence Centre, Aizkraukles street 21, 339, Riga, LV-1006, Latvia
²Riga Technical University, Faculty of Material Science and Applied Chemistry, Institute of Polymer Materials, P. Valdena Street 3, Riga, LV-1048, Latvia

E-mail: zane.grigale@gmail.com

Abstract. Increased interest in the esthetical natural nail coatings have encouraged more in-depth studies particularly of UV curable coatings: their formation, processing, structure, characteristics and removing. Typical requirement for nail coatings is good adhesion, but preferably for the short time of functioning (usual 2-4 weeks). This study investigated the impact of four different monomers (tert obutyl cyclohexyl acrylate (TBCHA), ethylene glycol dimethacrylate (EGDMA), tetrahydrofurfuryl acrylate (THFA), hydroxypropyl methacrylate (HPMA)) to viscosity of uncured mixture and degree of conversion, mechanical properties, surface gloss, micro hardness and adhesion loss for cured films. Specific coating application requires comparatively high coating flexibility and stability of deformation characteristics. This can be achieved with composition containing 30% of monomer TBCHA, what shows ultimate elongation $\varepsilon_B = 0.23 – 0.24$, modulus of elasticity $E = 670-710$ MPa and comparatively constant properties in 72 hours ($\Delta E = 1.3\%$, $\Delta \varepsilon_B = 6.0\%$). A composition with 40% of TBCHA shows the fastest coating destruction achieving adhesion loss within 3 min.

1. Introduction

During last decades, a great deal of attention has been given to UV curing applications as an alternative to traditional solvent-borne coatings [1, 2, 3] due to their environmental soundness, lower energy consumption, rapid curing at room temperature and curing on heat sensitive substrates [4, 5, 6, 7]. In the last decade new market space for coating applications with short-term requirements has appeared. The market space includes coatings on natural nail for aesthetic and medical reasons [8, 9]. Typical coating requirement is good adhesion, but for these novel applications adhesion is desired only for the time of functionality (usual 2-4 weeks).

The formulation of appropriate coatings is critical to achieve required characteristics: firstly, for uncured gel - pigment stability of the suspension and reduced viscosity (3000-4500mPas) – secondly, for cured coating - adhesion loss from substrate (after 5-10 min soak off in the solvent permitted in cosmetics), increased elasticity (20-50%), high surface gloss (70-90), surface hardness (>110MPa) and efficient polymerization (90-95%), what can be achieved with accurate ingredient selection. Short-term coating applications haven't been widely reported yet, only some patent applications have been submitted [10, 11, 12]. Desired ingredients in radically cured formulations are polyurethane acrylates as precursors to produce cross-linked networks giving high-performance final materials.
UV curable resins they prove excellent adhesion, flexibility, chemical and scratch resistance, high hardness and gloss, but often suffer from the high viscosities [1, 4, 7]. To overcome the deficiency low viscosity monofunctional monomers or low viscosity oligomers as reactive diluents can be used. Degree of conversion of the cross-linked system is one of the most important parameters which can strongly affect adhesion loss and required short-term characteristics. Degree of conversion can be controlled with light intensity, time of curing and photoinitiator amount [4, 6, 13]. For coatings on natural nails all these 3 aspects are constant as temperature on natural nails cannot exceed 70°C. Curing time is usually 30 s in the lamp with UV spectrum 395-405nm and photoinitiator amount 1-2%. Other possibility to affect the degree of conversion is optimization of standard system. Some studies have been done by varying with different photoinitiators [4, 14], urethane acrylate oligomers [6] and monomers [14]. Biopolymers [15, 16, 17] and their effect on the short-term characteristics of UV curing coating have been studied by us previously [18, 19]. There still is a need to optimize the standard systems, varying with monomer type, functionality and its content what may accelerate the adhesion loss in the solvent due to the incomplete curing and less dense network. We put forward the hypothesis that less assembled systems and monomers with lower functionality provide weaker adhesion to the substrate and ensure the possibility to eliminate the adhesion interaction between the coating and the substrate.

The objective of this study is to optimize the composition of the UV curing varnish system composed of urethane acrylate oligomers, photoinitiator and monomers of various types and functionalities.

2. Experimental

Materials were selected to ensure two different goals: long term properties - with good adhesion and short term properties –quick removal in solvent media. For uncured gel viscosity was determined. For cured coatings degree of conversion, mechanical characteristics, surface gloss, microhardness and adhesion loss in solvent media were evaluated.

2.1. Materials and methods

Main composite ingredients (oligomers, monomers, photoinitiator) were selected to confirm the requirements of EU Cosmetic Regulation. Tri-functional urethane acrylate oligomer Ebecryl 1258 (Allnex) was chosen for its film forming properties. Hexa-functional urethane acrylate oligomer Ebecryl 1291 (Allnex) was added as adhesion promoter. Four different monomers were evaluated to study their effect on the degree of conversion and adhesion of the cured film: Tertiobutyl cyclohexyl acrylate (TBCHA), Ethylene glycol dimethacrylate (EGDMA), Tetrahydrofurfuryl acrylate (THFA), Hydroxypropyl methacrylate (HPMA). For the initiation of radical photopolymerization reactions Ethyl - 2,4,6 – Trimethylbenzoylephosphinate (Lucirin TPO_L) (BASF) photoiniciator was applied.

2.2. Composition preparation

All components - reactive diluent/monomer (conc.10, 20, 25, 30, 35, 40, 45, 50 weight %) (TBCHA, EGDMA, THFA, HPMA), adhesion promoter (2,5 weight %) (Ebecryl 1291), photoinitiator (2 weight %) (Lucirin TPO_L), and base oligomer (rest amount) (Ebecryl 1258) - were mixed (100-300rpm) at room temperature (23°C) in yellow light (589nm) for 10 min. Uncured gels were stored in a thermostatically controlled environment T=40°C for 24h to remove the trapped air. The mixed gels were used for viscosity/flowability tests or were applied on the substrate (Teflon or aluminium sheets) in thickness 200 µm and cured for 30s under UV lamp (KP800LED) with luminous intensity 130mw and spectrum maximum λ = 405nm (Yi Liang electron technology Co, China) yielding cross-linked films for mechanical properties, microhardness, surface gloss and adhesion loss tests.
2.3. Test methods
The effect monomer concentration on the viscosity of urethane acrylate mixture was determined by Brookfield viscometer DV-II + Pro (Brookfield Engineering Laboratories). The systems with a viscosity in the range from 1000 up to 6000 mPas were searched.

The degree of conversion was determined by evaluation of gel fraction of the cured coating. To evaluate post curing effects gel fraction of the coatings was determined immediately after cure (GF) and after 72 hours of storage (GF₀). Samples were inserted in a Soxlet apparatus and maintained in a condensing acetone vapor atmosphere for 48 hours. Residual gel was dried in vacuum to constant weight. GF was calculated as follows (1), were m₀ is the initial sample's weight and m is the mass of tested samples after drying.

\[ \%GF = \left( \frac{m}{m_0} \right) \times 100 \] (1)

The mechanical properties of UV-cured films were determined by standard tensile stress-strain tests to measure tensile strength (σ) and elongation (ε) immediately after cure and after 72h of storage. Standard tensile stress-strain experiments were performed at room temperature using BDO FB020TN (Zwick Roell, Germany) universal testing machine according to the requirements of LVS EN ISO 527-3:2000 [20].

Gloss measurements of the coatings immediately after cure (G) and after 72 hours of storage (G₀) were carried out using the Novo Gloss Lite Gloss Meter (Rhopoint Instruments Ltd.) on a black substrate at an angle of 60°.

Micro hardness of the coatings immediately after cure (H) and after 72 hours of storage (H₀) experiments were performed using Vickers microscope M41 at 200g statistic loading.

Adhesion loss of the coatings to the substrate was evaluated by a following procedure. Initially 200 µm thick 5 cm x 5 cm cured films on aluminum sheets were left for 72 hours to assure complete polymerization and afterwards removability of the coating was evaluated. Coatings were wrapped in paper, impregnated in 95% acetone solution with water, coated with aluminum foil (100 µm thick) and kept for 10 minutes. Consequently scratch resistance, an indicator of coating adhesion to the substrate, was measured with SAM (Scratch Adhesion and Mar Tester) device S.A.M PA-5050 (Gardco) where the Hoffman tester concept is used [21]. After each 30 second period, coating adhesion to the substrate was evaluated using 5 SAM scratches (with distance 5mm, force 250g), horizontally and vertically. When 100% adhesion loss between the substrate and the coating appeared, effective soak-off time was detected.

3. Results and discussions
Natural nail has a complicated porous structure and there is no close material to natural nail to test the adhesion. Fingernails are composite structures containing fibrils and plate-like structures of keratin bound together by a keratinous matrix material [23]. Based on previous experience [18, 19] we put forward the hypothesis that adhesion is dependent on the degree of conversion of the coating. Our assumption is that the lower the degree of conversion – the faster should be the adhesion loss from the substrate. At the same time degree of conversion should be enough high to provide the required mechanical characteristics: elasticity, toughness, surface gloss and adhesion in the time of use. Also degree of conversion cannot be lower than 90% due to the health issues, where residual monomers should not be found in the cured coating [24].

3.1. Viscosity
For the coating application and other processing activities, viscosity is the most important parameter. It should be in the range of 3000-4500 mPas to provide the good leveling, but not smaller, to avoid flowing. To select the optimum monomer concentrations this range has been expanded from 1000 to 6000 mPas. To find the optimal concentrations, first 8 different concentrations were tested and results are shown in Figure 1.
All four monomers ensure the required viscosity by considering that their concentrations in the formulation are 30%, 35% and 40%. Formulations with 30% and 40% concentrations of the monomers have been chosen to evaluate the influence of the monomer on the exploitation characteristics of the cured coatings. Nail coating application requirements (viscosity 3000-4500 mPas) have been met for the compositions containing 30% EGDMA, 40% HPMA and 30-40% TBCHA. Further investigations for aged uncured samples are necessary to predict the storage time for uncured compositions.

### 3.2. Degree of Conversion

In this test eight different samples were prepared and characterized. Samples differed with the monomers included and weight ratio between oligomers and monomers: 70:30 and 60:40. Gel contents of polymeric films were determined immediately after cure (GF) and after 72h of storage (GF₀). Results were found to be between 94 and 99% as it is shown in Table 1. Degree of conversion of monomer EGDMA was the highest, providing the GF between 96.4% and 98.5%. Such behavior was expected due to the higher functionality of the acrylate monomer.

**Table 1. Monomer effect on the gel fraction (GF), surface gloss (G) and micro hardness (HV) of the cross-linked films.**

| Monomer | Conc. | Gel fraction | Surface gloss | Micro hardness |
|---------|-------|--------------|---------------|---------------|
|         | %     | %            | %             | %             | Mpa           | Mpa | %            |
| 1 TBCHA | 30    | **97,4**     | 98,0          | 0,61          | 46            | 68  | 32           | 104 |
| 2 TBCHA | 40    | 94,0         | **94,1**      | 0,11          | 51            | 72  | 29           | 69  |
| 3 EGDMA | 30    | 98,5         | 99,3          | 0,81          | 47            | 59  | 20           | 204 |
| 4 EGDMA | 40    | 96,4         | 98,9          | 2,53          | 47            | 57  | 18           | 220 |
| 5 THFA  | 30    | 96,0         | 96,3          | 0,31          | 59            | 73  | 19           | 25  |
| 6 THFA  | 40    | 95,7         | 96,7          | 1,03          | 54            | 61  | 11           | 28  |
| 7 HPMA  | 30    | 97,0         | 97,6          | 0,61          | 50            | 63  | 21           | 99  |
| 8 HPMA  | 40    | 95,0         | 99,9          | 4,90          | 43            | 58  | 26           | 65  |

*ΔGF = (GF₀ – GF) **ΔG = (G₀ – G) ***ΔHV = (HV₀ – HV)

Gel contents of all the investigated systems increased in time by 0.1% - 4.9% (after 72 hours of storage) due to post-curing. The extracted uncured parts of 4 different kinds of monomers increase with increasing content of the monomer (40%). In other studies it has been found that microstructure, crosslink density as well as degree of conversion are strongly related to the mechanical and other properties of the materials [6, 23]. In this study we found correlation between degree of conversion not only with mechanical properties, but also with adhesion.

### 3.3. Mechanical properties

Young’s modulus of natural nail at relative humidity 55% is 2.32 GPa [24]. Deformation characteristics of the coating on the nail should have as close as possible to those of the natural nail to ensure good adhesion and avoid air pockets. No one of the tested compositions reached so high modulus of elasticity. Films containing bi-functional monomer EGDMA reached the highest E values, but cured films were brittle and with the smallest ultimate relative deformation εB values (Fig.2.). Stability of mechanical properties in time is very important for natural nail coatings. Modulus of elasticity increases for all studied compositions along with storage time, whereas the highest increase -
57% - have been found for the composition containing 30% THFA, and for both concentrations with HPMAs (37% and 54%). Systems containing TBCHA showed the most stable E values; post-cure time have almost no effect on the characteristic of the cured films.

As natural nail coating should have the ability to move together with natural nail plate, coating should have $\varepsilon_B$ at least 0.6% [22]. Initial tests showed that $\varepsilon_B$ should be in range 20-50%, to avoid too high brittleness or the softness of the film. Compositions with TBCHA and HPMA fit in the requested range. These compositions should be tested more carefully to detect their long term adhesion, removability, surface hardness and surface gloss.

### Figure 1.
Effect of monomer concentration on the viscosity of uncured system in requested viscosity range

### Figure 2.
Elastic modulus and elongation at break values for the films with 30% and 40% of monomers measured immediately after cure (0) and after 3 days of storage (3).

#### 3.4. Gloss

The effect of the monomer type and concentration on the gloss were investigated using the constant curing conditions (time, intensity, layer thickness) and constant photoinitiator amount. Used monomer affected the final gloss of the samples in the range from 43 to 73 GU (Table 1.). Monomer concentration increase in the system differently affects the gloss values. Concentration of EGDMA doesn’t affect the gloss, TBCHA increases it, but other 2 lower molecular weight monomers (HMPA and THFA) decrease it.

For all the coatings the surface gloss values increase in the time due to the post cure effect. Values increase by 15-35%. For top coat the gloss values are very important characteristic to ensure good esthetic look of the coating. Thus compositions with 30% or 40% of TBCHA are recommended especially for top coats.

#### 3.5. Adhesion loss

Coating stability is one of the most important properties for the chosen application. All previous studies have been done mostly on long term adhesion properties, but this application requires both: good adhesion in the time of functionality and fast adhesion loss at coating removal. Soak–off tests have been performed after 72h of storage and results are presented in the figure 3. Obtained results correlate with the GF data obtained after 72h of storage. The greatest adhesion loss was obtained for the composition containing 40% TBCHA for which adhesion from substrate was lost after 3 min and it correlates with the smallest GF values.
Compositions with EGDMA took the longest time for the removal. This monomer has the closest mechanical properties to the natural nail, but ensures too strong adhesion with natural nail, due to its higher reactivity (bi-functionality). TBCHA shows average mechanical characteristics and good adhesion loss ability; therefore compositions with 30% and 40% of TBCHA should be developed further to improve mechanical properties.

3.6. The composition influence on coatings characteristics

Short term coatings challenges with, at least, seven characteristics, which should meet the requirements: viscosity, efficient polymerization, gloss, surface hardness, toughness, elasticity, removability. All ingredients in the composition affect the final product properties.

In this study we evaluated the monomer effect on the coating characteristics, but no one of the monomers have been found to be perfect and could improve all the characteristics. The results obtained are presented in figure 4, where requested values for adhesion loss (0-4 min.) and gloss (70-80 GU) are compared. As shown, only one composition (with 40% TBCHA) fits with requested levels of both of the parameters. Although the compositions with 30% of TBCHA show the results quite close to the requested, their film toughness should be increased.

4. Conclusions

Assumption, that lower degree of conversion promotes the destruction of adhesion between the substrate and the coating, was confirmed. Presence of 40% of the monomer TBCHA in the composition showed the smallest GF value (94%), what provided the fastest adhesion loss.

Good coating flexibility and consistency of mechanical properties can be achieved by using 30% of the monomer of TBCHA in the composition, which showed the optimal $\varepsilon_B$ values (23.07-24.58%), high E values (670-712MPa) and comparatively constant properties in 72 hours ($\Delta E =1.25\%$, $\Delta \varepsilon_B =6.14\%$). A composition with 40% of TBCHA showed the fastest coating destruction times, achieving adhesion loss from the substrate after 3 min.

Acknowledgements

The authors thank the Investment and Development Agency of Latvia (Project No. LKC/2.1.2.1.1/10/01/006, Contract No. L-KC-11-0005) for their financial support.
References

[1] Liu P, Gu A, Liang G, Guan Q and Yuan L. 2012 Prog. Org. Coat74 150
[2] Sauro S, Vijay S and Deb S 2012 Eur. Polym. J48 1474
[3] Milinavičiūtė A, Jankauskaitė V and Narmontas P 2011 Mater. Sci-medzg 17216
[4] Jančovičová V, Mikula M, Havlinová B and Jakubiková Z 2013 Prog. Org. Coat 76 438
[5] Wang F, Hu J, Q and Tu W. P 2008 Prog. Org. Coat 62 250
[6] Kayaman-Apohan N, Demirci R, Cakir M and Gungor A 2005 Prog. Org. Coat 73 3262
[7] Pichavant L and Coqueret X. 2008 Prog. Org. Coat 62
[8] Łopaciuk A and Łoboda M. Global Beauty Industry Trends in the 21st Century Managemant, Knowledge and Learning International Conference 2013 Zarad.
[9] Drummey C. 2013-2014 Industry Statistics Highlights Nails Magazine 2013
[10] Vu T and Chad C. Compositions and Methods for Nail Coatings, United States Patent 20110182838, 28 July 2011
[11] Haile D.L Compositions for Removable Gel Applications for Nails and Methods of their Use, USA Patent WO 2011/011304 A2, 27 January 2011
[12] Koschar M. Easily Removable Nail Polish Composition, Germany Patent DE102011102661 A1, 29 November 2012
[13] Wu N, Zhang Y and Wang Y 2013 Int. J. Adhes
[14] Oguri M, Yoshida Y, Yoshihara K, Miyachi T, Nakamura Y, and Shimoda S 2012 Acta Biomater
[15] Misbah S et al. 2012 Carbohydr. Polym 87 404
[16] Gällstedt M, Törmqvist J and Hedenqvist M.S 2001 J. Polymer Sci. Part B: Polymer Phys 39 992
[17] El-Shafee et al. 2001 Eur. Polymer J 37 2104
[18] Grigale-Sorocina Z, Kalnins M et al. Mater. Sci. (Medziagotyra) in print.
[19] Grigale-Sorocina Z, Kalnins M et al. 2015 P. Est. Acad. Sci 64 93
[20] Determination of tensile properties. Part 3: Films and sheets, test conditions (in Latvian), BS EN ISO 527-3: 2000th Plastic.
[21] Koleske J. V 1995 Paint and Coating Testing Manual. American Society for Testing and Materials, Philadelphia
[22] Farran L. et al. 2009 J Biomech 42 1235
[23] Taki K and Nakamura T. J Cosmet., Dermatol. Sci. Appl
[24] Alishiri M, et al. 2014 Mater. Sci. Eng 42 773