



RIGA TECHNICAL
UNIVERSITY

Zane Grigale-Soročina

UV ACTIVATED COPOLYMERIZATION COATINGS OF URETHANE ACRYLATES FOR USE IN THE COSMETIC INDUSTRY

Summary of the Doctoral Thesis



RIGA TECHNICAL UNIVERSITY

Faculty of Materials Science and Applied Chemistry

Institute of Polymer Materials

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DOCTORAL THESIS PROPOSED TO RIGA TECHNICAL UNIVERSITY FOR THE PROMOTION TO THE SCIENTIFIC DEGREE OF DOCTOR OF SCIENCE

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Science (Ph. D.) is my own. I confirm that this Thesis has not been submitted to any other university for the promotion to a scientific degree.

Zane Grigale-Soročina

Date:

The Doctoral Thesis has been written in the Latvian language; it contains an introduction; 3 chapters; conclusions; 107 figures; the total number of pages is 140. The Bibliography contains 197 titles

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LIST OF MOST IMPORTANT ABBREVIATIONS

- A – spectral absorption value
 A_N – durability of adhesion bond
 A_S – adhesion strength
BDA – base diacrylates
 c – mass concentration
CAB – cellulose acetate butyrate
 c_{in} – initiator mass concentration
 D_∞ – droplet diameter at equilibrium state
DTA – differential thermal analysis
 E – modulus of elasticity
E10 – base diacrylate *Exothane 10*
E26 – base diacrylate *Exothane 26*
E8 – base diacrylate *Exothane 8*
EGDMA – Ethylene glycol dimethacrylate
 ΔE – colour difference parameter in time
FTIR – Fourier-transform infrared spectroscopy
 G – gel fraction
 Gl – surface gloss
 Gl^* – surface gloss after abrasion test
HPMA – hydroxypropyl methacrylate
 HV – Vickers micro hardness
 $K_{C=C}$ – degree of conversion of acrylate vinyl groups
CM – comonomers
 M_C – the magnitude of the statistical molecular weight of the cross-linked structure between adjacent cross-links
NC – nitrocellulose
 Q – degree of swelling
 R^\bullet – free radical
 R_0 – $(A_{810}/A_{1716})_0$ or $(A_{1636}/A_{1716})_0$ relative absorption before exposure to UV radiation
 R_t – $(A_{810}/A_{1716})_t$ or $(A_{1636}/A_{1716})_t$ relative absorption after determined t_{UV}
SB – sucrose benzoate
TBCHA – 4-tert-Butylcyclohexyl acrylate
THFA – tetrahydrofurfuryl acrylate
 T_{MAX} – maximum reaction temperature
TMBFF – ethyl-2,4,6-Trimethylbenzoylphenylphosphinate
 t_p – polymerization time
 T_R – reaction temperature
 T_S – heating temperature
 t_{UV} – UV exposure time
 ϵ_B – relative deformation at break
 θ – contact angle on the solid surface
 λ_{MAX} – maximum polymerization wavelength
 λ_p – polymerization initiation wavelength
 ρ – density of cross-linked polymer
 σ_B – tensile strength at break
 σ_L – surface tension energy on the interface between a liquid and a solid
 σ_S – solid surface tension value
 η – viscosity

ν – cross-link density
 ϕ – cross-linking functionality
 ψ_{POL} – mass fraction of polymer
 ψ_{Solv} – mass fraction of solvent
 ϕ_{SOLV} – volume fraction of solvent
 ϕ_{POL} – volume fraction of polymer

GENERAL CHARACTERISTICS OF THE DOCTORAL THESIS

Topicality of the Research

The use of UV-curable liquid bifunctional monomers for cosmetic coatings is a rapidly evolving direction. These coatings are able to provide a significantly higher set of performance characteristics of the resulting coating compared to the coatings formed by drying polymer solutions.

The practical idea of the research is to create a composition that effectively polymerizes under the dosed UV radiation and forms a coating that meets all the requirements set for nail coatings.

Acrylates are most often used as the main components of the coating composition, which in the presence of UV radiation and the initiator form chemically cross-linked structures with the required properties of the coating in a relatively short period of time.

Evaluating the set of the most important properties of various acrylates, it must be concluded that urethane acrylates are particularly suitable for the intended purpose. They are able to form cross-linked structures with a wide range of mechanical properties. Their viscosity before curing and the rate of curing vary widely. This allows to select the basic components entering the system and create compositions that meet the requirements of the applied application technology and the performance of the created coating.

Initially, the raw materials for the UV-curable coating were taken from the dental, varnish, paint and coating industries. The use of raw materials from these industries in the cosmetics sector is associated with the development of products that are dangerous to consumers and causes an increased risk of occupational diseases. Thus, it is important to find and study the components entering the coating that meet the requirements of the EU Cosmetics Regulation.

In order to use the composition for cosmetic coatings and fill the requirements, it must meet a number of technological properties and form coatings with specific physico-mechanical, surface and adhesion properties. Therefore, the experience of current UV-curable coatings is not applicable.

The principles for selecting output components are not clear. It is necessary to develop methodologies for researching and testing the properties of the composition, the curing process and the cured product, which would ensure the possibility to create coatings with the desired set of properties.

Aim of the Doctoral Thesis

The aim of the work is to develop a methodology for the formation of UV-activated polymerization compositions of urethane acrylates and to obtain cosmetic coatings that meet the full range of requirements and limitations.

The Tasks of the Doctoral Thesis

The following tasks have been set for the research:

- 1) to develop a methodology for component selection, composite system development and coating acquisition;
- 2) to develop a methodology for the evaluation of the structures and set of properties of the obtained coatings;
- 3) to study the influence of the chemical nature and ratio of urethane diacrylates and monoacrylates on the indicators of cross-linked structures formed in the process of UV-activated copolymerization and corresponding indicators of coating properties suitable for the formation of cosmetic coatings;
- 4) to evaluate the effect of individual additives on the properties of cross-linked coatings, their adhesion to the surface and the durability of the coating removal.

Scientific Novelty of the Doctoral Thesis

A complex methodology has been developed for the formation of acrylate composite systems and obtaining the appropriate cosmetic coatings in the process of UV-activated copolymerization, as well as for the adequate evaluation of the set of structural parameters and properties of the obtained coatings.

Compositions of urethane diacrylates and individual monoacrylates have been developed, which upon curing under the conditions of UV-activated copolymerization process in accordance with the requirements of cosmetic varnishes form cross-linked structural coatings with high strength-deformation, surface hardness, surface light reflectance, adhesion bond and other parameters.

It has been found that the strength-deformation indices of hardened coatings are mainly determined by the degree of cross-linking of components achieved in the copolymerization process, which can be controlled by the comonomer content ratio.

Practical Value of the Doctoral Thesis

Raw materials have been researched and found for the development and application of new UV-curable composite coatings for human nail coatings. The components which are friendly to human health and thus reduce the risk of occupational diseases, risk factors of working environment for technicians and allergy / irritation risks for end users / composite material users.

A methodology for the development and testing of new coatings has been developed.

A methodology for creating formulas for three-layer coatings has been developed.

The coatings have been tested in laboratory and in-vivo on natural nails.

Adhesion tests of coatings to natural nails have been developed, and the composition of coatings has been compared in relation to their functionality and effects on human health (the results are shown in the Thesis).

The developed formulations have served as basic systems, from which *Kinetics Nail Systems Ltd.* manufactures world-class UV-curable nail coatings.

Thesis Statements to Be Defended

Forming the UV-activated copolymerization compositions of urethane diacrylates and monoacrylates, it is possible to comply with all the requirements and limitations of the specific cosmetic coating industry without exception: those that determine the initial performance of the composition, the conditions of the coating application and photocuring processes, and those that define the set of performance and post-performance characteristics of the cured coating.

The developed optimal composition of compositions is able to ensure the required system coating – substrate (nail) structure integrity in the process of operation (coating strength-deformation indices, surface hardness, coating adhesion strength to the substrate) and at the same time easy and convenient disintegration of the formed structure during removal with solvents.

The Structure and Volume of the Thesis

The Doctoral Thesis has been written in Latvian; it contains an introduction and 3 main chapters: a review of literary sources, the methodological part, a summary of experimental results and their evaluation, conclusions, and a list of references with 197 sources of information. It has been illustrated with 107 figures and 32 tables. The volume of the Doctoral Thesis is 140 pages.

Approbation of the Research Results

The main scientific achievements and results of the dissertation have been presented at 9 international scientific conferences.

The results of the Thesis have been published in 10 scientific journals (SCOPUS cited), 1 publication in full-text conference proceedings and 11 publications in books of abstracts of scientific conferences.

The main results of the research are reflected in the following articles:

1. Grigale-Sorocina Z., Birks I., Vindedze E. Evaluation of Photoinitiator and Fluorescent Pigments Impact on Color Stability in Pigmented UV-curable Coatings. *Solid State Phenomena*. 2021, 320, 77–82. (Scopus)
2. Grigale-Sorocina Z., Birks I., Vindedze E. Evaluation of Reactive Diluent Impact on Stability of Systems Viscosity in UV-Curable Compositions. *Solid State Phenomena*. 2021, 320, 150–154. (Scopus)
3. Z. Grigale-Sorocina, I. Birks. Hectorite and bentonite effect on water-based polymer coating rheology. *Comptes Rendus Chimie*. 2019, 22, 169–174. (Scopus)

4. Grigale-Sorocina Z, Pilipavica R, Birks I. Spectrophotometric Evaluation of Pigmented Urethane Acrylate Colour Stability. *IOP Conference Series: Materials Science and Engineering*. 2019, 660, 012058. (Scopus)
5. Grigale-Sorocina Z, Pilipavica R, Birks I. Spectrophotometric Evaluation of Urethane Acrylate Based Pigment Colour Stability. *SOJ Materials Science & Engineering*. 2018, 6(1): 1–4.
6. Grigale-Sorocina Z., Kalnins M., Birks I. Analysis of Pigment Process and Production techniques for Use in Nail Polish Systems, *Solid State Phenomena*. 2017, 267, 109–113. (Scopus)
7. Grigale-Sorocina Z., Kalnins M., Birks I. Processing Technology Development for Organic Clay Suspension System, *Solid State Phenomena*. 2017, 267, 7–11. (Scopus)
8. Grigale-Sorocina Z., Kalnins M., Simanovska J., Vindedze E., Birks I., Brazdauska E. Effect of Additives on UV-activated Urethane Acrylate Polymerization Composite Coatings. *Materials Science (Medžiagotyra)*. 2016, 22(1), 54–59. (Scopus)
9. Grigale-Sorocina Z., Kalnins M., Gross K.A. Influence of monomer on structure, processing and application characteristics of UV curable urethane acrylate composite coatings. *IOP Conference Series: Materials Science and Engineering (Mse)*. 2016, 111. (Scopus)
10. Simanovska J., Grigale-Sorocina Z. Design for Sustainability Approach During Product Development – A Case Study Using Innovative Nail Polishes Developed By A Small Enterprise. *Proceedings of the Estonian Academy of Sciences*. 2016, 65 (3), 297–303. (Scopus)
11. Grigale-Sorocina Z., Kalnins M., Simanovska J., Vindedze E., Birks I., Brazdauska E. Additives in UV-activated urethane acrylate polymerization composite coatings. *Proceedings of the Estonian Academy of Sciences*. 2015, 64(1), 88–93. (Scopus)

The main research results reflected in conference proceedings:

1. Z. Grigale-Sorocina, E. Vindedze, I. Birks. Evaluation of adhesion for polymer composite coatings. *Materials Science and Applied Chemistry. Programme and abstract book*, Latvia, Riga, 24 October, 2019.
2. Z. Grigale-Sorocina, E. Vindedze, I. Birks. Correlation of mechanical properties of polymer composite coatings with viscosity of unpolymerized system. *Materials Science and Applied Chemistry. Programme and abstract book*, Latvia, Riga, 24 October, 2019.
3. Z. Grigale-Sorocina, I. Birks, R. Pilipavica. Spectrophotometric evaluation of pigmented urethane acrylate coating colour stability. *4th International conference Innovative Materials, Structures and Technologies 2019*, Latvia, Riga, 25–27 October, 2019, RTU Faculty of Civil Engineering.
4. Z. Grigale-Sorocina, I. Birks. Hectorite and bentonite effect on water-based polymer coating rheology. *2nd International symposium Clays and ceramics. Book of abstracts*, University of Latvia, Latvia, Riga, 29–31 January, 2018. University of Latvia, p. 38.

5. Z. Grigale-Soročina, M. Kalniņš, I. Birks. Analysis of Pigment Process and Production techniques for Use in Nail Polish Systems. *26th International Baltic Conference Materials Engineering 2017*, Lithuania, Kaunas, 26–27 October, 2017.
6. Z. Grigale-Soročina, M. Kalniņš, I. Birks. Processing Technology Development for Organic Clay Suspension System. *26th International Baltic Conference Materials Engineering 2017*, Lithuania, Kaunas, 26–27 October, 2017.
7. Z. Grigale-Sorocina, M. Kalnins. Methods to evaluate the adhesion behavior for UV-activated urethane acrylate composite coatings for short term applications. *MSAC conference proceedings and programme*, Latvia, Riga, 21 October, 2016. Riga RTU Press, pp. 63–67.
8. Grigale-Sorocina Z., Kalnins M., Birks I., Brazdauska E. Impact of Monomer Nature on Short-Term Coating Characteristics of UV Curing Urethane Acrylate Composite System. *Baltic Polymer Symposium 2015*, Latvia, Sigulda, 16–18 September, 2015, p. 122.
9. Grigale-Sorocina Z., Kalnins M., Simanovska J., Vindedze E., Birks I., Brazdauska E. UV-Activated Polymerization Composite Coatings. *Baltic Polymer Symposium 2014*, Laulasmaa, Estonia, 24–26 September, 2014, p. 101.
10. Grigale-Sorocina Z., Kalnins M. UV-Activated Polymerization Composite Coatings. *23rd International Baltic Conference Materials Engineering 2014, Book of Abstracts*, Lithuania, Kaunas, 23–24 October, 2014, Kauno Technologijos universitetas, pp. 64–65.
11. Grigale-Sorocina Z., Kalnins M., Vindedze E. UV-Activated Polymerization Composite Coatings. *Riga Technical University 55th International Scientific Conference*, Abstracts, Latvia, Riga, 14–17 October, 2014. Riga, RTU Press, p. 57.

BRIEF CONTENT OF THE DOCTORAL THESIS

In the introduction the topicality of the Doctoral Thesis is substantiated, the aim and main tasks are formulated, the guidelines of the Thesis are presented.

The literature review summarizes information on the types of natural nail coatings and the basic components entering them. Restrictions on the choice of basic components entering the system are described. The effect of conditions and components on the natural nails are described.

The methodological part characterizes the materials used in the study and describes the research methods.

Diurethane diacrylates of the *Exothane* family (manufactured by *Esstech Ltd.*), which are differently structured alkyl diurethane diacrylates (Fig. 1), were used as the main components for the formation of UV-activated polymerization compositions (Table 1).

Several acrylates with low viscosity were used as comonomers (KM) (Table 2).

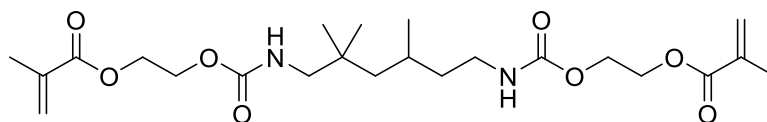


Fig.1. Schematic formula of di-2-methacryloxyethyl 2,2,4-trimethylhexathylenedicarbamate.

Table 1

Characteristics of Used Base Diacrylates

| Name/property | <i>Exothane 8</i> | <i>Exothane 26</i> | <i>Exothane 10</i> |
|-------------------------|-------------------|--------------------|--------------------|
| Abbreviation | E8 | E26 | E10 |
| Molecular weight, g/mol | 600–300 | 700–1400 | 400–1000 |
| Viscosity, Pa·s | 31.5 | 16.2 | 72.1 |

Table 2

Characteristics of the Comonomers Used

| Chemical name | Hydroxypropyl methacrylate (<i>Esstech Ltd</i>) | 4-tert-Butylcyclohexyl acrylate (<i>Sartomer Ltd</i>) | Ethylene glycol dimethacrylate (<i>Sartomer Ltd</i>) | Tetrahydrofurfuryl acrylate (<i>Sartomer Ltd</i>) |
|-------------------------|---|---|--|---|
| Abbreviation | HPMA | TBCHA | EGDMA | THFA |
| Structural formula | | | | |
| Molecular weight, g/mol | 144.17 | 210.31 | 198.22 | 156.18 |
| Funkcionalitāte | 1 | 1 | 2 | 1 |
| Viscosity, mPa·s | 12.5 | 19.22 | 13.58 | 17.82 |

Based on the patent study, the recommendations of the raw material manufacturer and the spectral range of the UV lamp used, ethyl-2,4,6-trimethylbenzoylphenylphosphinate (TMBFF, supplier *BASF*) was used as a photoinitiator, with a UV absorption spectrum close to that required: (390–420 nm).

Additional additives were used in the research: nitrocellulose (NC), cellulose acetate butyrate (CAB), sucrose benzoate (SB), pyrogenic silica dioxide, and pigments.

The main content of the chapter consists of the characterization of the obtained composite system, coating research methods and the parameters to be determined:

- 1) evaluation of viscosity and flowability;
- 2) evaluation of surface tension and surface wetting of non-polymerized compositions;
- 3) evaluation of stability and sedimentation of non-polymerized pigmented compositions over time;
- 4) differential thermal (DTA) and spectroscopic (FTIR) analysis of polymerisation process; determination of polymerization depth;
- 5) determination of the content of the cross-linked part of polymerized systems;
- 6) determination of tensile strength-deformation indices of coating;
- 7) studies of surface hardness, surface gloss and surface abrasion resistance of coatings;
- 8) assessment of coating adhesion strength and coating durability;
- 9) spectroscopic analysis of pigmented coatings and evaluation of color invariance;
- 10) comparison of coating compositions in terms of their functionality and effect on human health.

SUMMARY OF THE EXPERIMENTAL RESULTS AND THEIR ESTIMATION

1. Selection of Research Object

The main goal of the work was to create composite systems that would be safe and effective for obtaining high quality natural nail coating.

The strategy to achieve this goal is largely determined by the mandatory requirements for nail polish.

Requirements for the polish components

1. The components of the polish composition must comply with EU Cosmetics Regulation No. 1223/2009 requirements [1], and USA FDA (*Food and Drug Association*) requirements, which ensures that the composition is safe to use and is not harmful for human health [2], [3].

Requirements for the polish application

1. Polish must be applied with a brush at room temperature.
2. Polish must ensure the thickness of the obtained layer in the range of 30– 50 μm in one application. Long-term experience shows that this can be achieved if the viscosity of the polish during application is in the range of 1–5 Pa·s.
3. Polish should wet the nail surface well.
4. Polish should flow optimally over the nail surface.

Requirements for polish polymerization

1. The applied layer of polish must harden within 30–60 s.
2. When curing by UV-activated polymerization, the excitation wavelength λ_p must be 390–420 nm, the maximum of the spectrum 405 nm.

Requirements for polymerized coating

1. Coating must have a certain set of optical properties (surface gloss $Gl > 70$ GU, light transmittance 75–100 %).
2. Coating must comply with the following strength-deformation characteristics:
 - a) modulus of elasticity $E = 200\text{--}2000$ MPa,
 - b) elongation at break $\varepsilon_B = 20\text{--}160$ %,
 - c) surface hardness (by Vicker) $HV > 50$ MPa.
3. The coating must adhere well to the nail surface.
4. The adhesion strength (A_S) of the coating to the substrate according to ISO 4624 should be at least 2 MPa (using metal as a substrate).

Durability requirements for polymerized coating

1. The polymerized layer must maintain all the above indicators for 2–4 weeks.

2. The durability of the coating on natural nails should be at least 2 weeks.
3. The gloss of the coating surface during wear must remain $Gl^* > 60$ GU.

Requirements for the removal of polymerized coating

1. The coating must be easy to remove by nail-friendly techniques.

2. Formation of a Starting Composition

To find the optimal concentration of initiator, it was necessary to create a starting composition for urethane acrylates. The determining factor was the viscosity (η) of the composition.

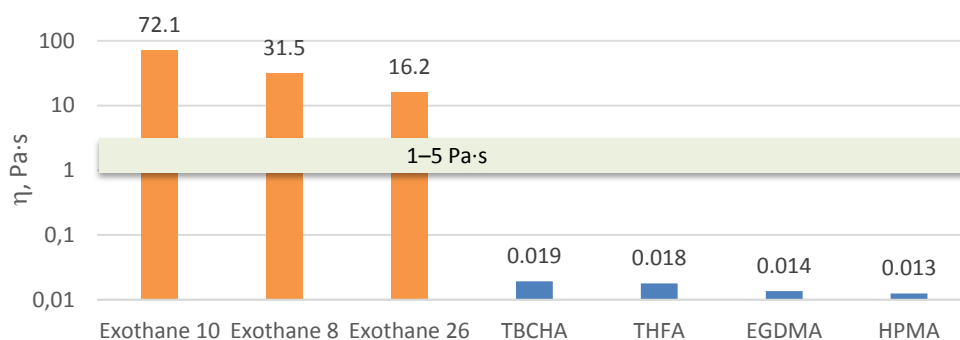


Fig. 2. Viscosity η of the selected acrylates and the range of viscosity requirements set for the final composition.

As can be seen in Fig. 2, the BDA viscosity of all selected base diacrylates is almost one order of magnitude higher than the viscosity range allowed for the composition (1–5 Pa·s). This means that the BDA must be combined with KM, which has a significantly lower viscosity, to create a starting composition.

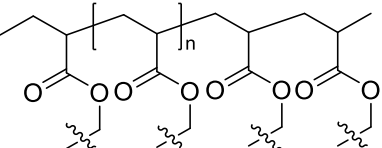
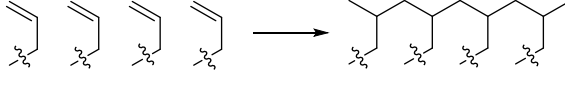
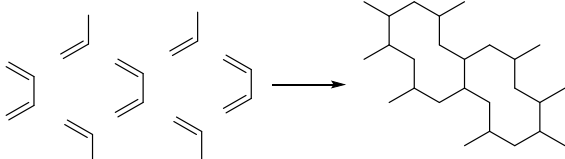
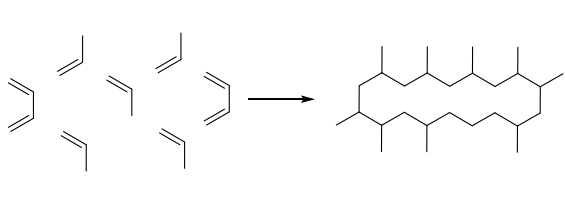
It is not possible to form a composition from KM alone, because their viscosity is more than two orders of magnitude lower than the allowable.

The need to combine BDA with KM is associated with the formation of a cross-linked polymerization product of a specific structure (see the scheme in Table 3).

Table 3

Acrylate Polymerization Scheme

| Description of the polymerization step | Scheme |
|--|--------|
| The radical R^\bullet formed as a result of UV-indicated homolytic decomposition of the initiator molecule joins the vinyl group of the acrylate molecule, forming a growing macroradical. | |
| Acrylate molecules join the growing macroradical. | |

| | |
|--|--|
| During the polymerization process a series of polymers are formed. |  |
| Polymerization of monofunctional acrylates results in linear polymers. |  |
| If the acrylate functionality is 2 or more, branched and cross-linked polymerization products are formed (idealized structure of diacrylate polymerization product). |  |
| When monoacrylates are added to diacrylates, copolymerization of monoacrylate and diacrylate takes place. Monoacrylate molecules are chaotically incorporated into the cross-linked structure formed by diacrylates, thinning cross-links in proportion to their content in the copolymer. |  |

3. Determination of the Optimal Content of the Initiator

To create the starting composition, we choose BDA from the selected compounds with the lowest viscosity E26 ($\eta = 16.2 \text{ Pa}\cdot\text{s}$) and comonomer (KM) with the lowest viscosity (HPMA, $\eta = 12,5 \text{ mPa}\cdot\text{s}$). This makes it possible to obtain a composition with the desired viscosity using a lower content of monofunctional comonomer.

From Fig. 3, we chose the HPMA content in the composition 45.0 %, which corresponds to the minimum permissible limit of the viscosity of the composition – 1 Pa·s.

The content of initiator TMBFF in the composition was varied in the range of 0.4–1.0 % (Fig. 4). The course of UV-activated photo-copolymerization at different initiator contents was studied using the process differential thermal analysis (DTA) (Fig. 4).

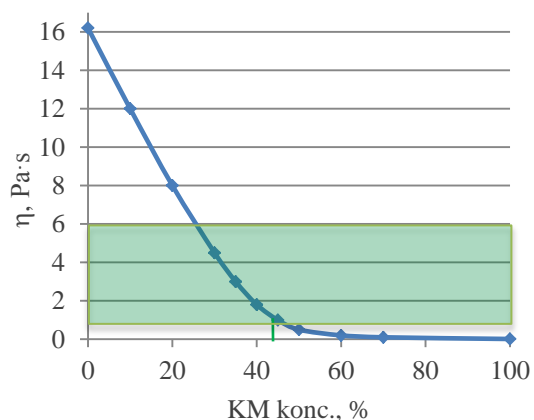


Fig. 3. Compositions of *Exothane 26* – HPMA viscosity η depending on HPMA content.

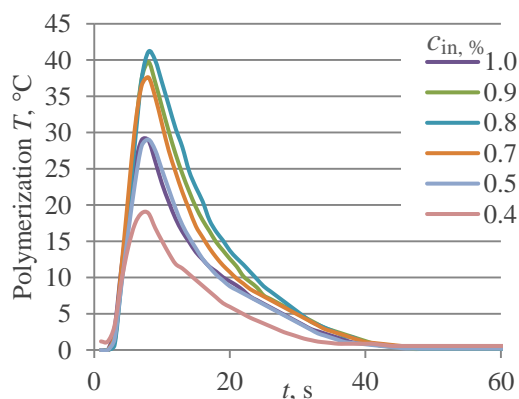


Fig. 4. Systems: *Exothane 26* – HPMA polymerization temperature T_R in the process of photopolymerization of change curve at different content of initiator TMBFF.

From the curves in Fig. 4, we determined the following values (Table 4):

- below curve $T_R(t)$, the value of full area Q corresponding to the amount of heat released during the polymerization;
- area under curves up to reaction time 30 s, Q_{30} ;
- maximum temperature T_R growth rate $T^\bullet = dT/dt$;
- T_R maximum value – T_{MAX} ;
- $(T_R + T_S)$ maximum value T^*_{MAX} , where T_S – UV the temperature of the heating caused by the lamp;
- time, according to the end of the reaction – t_∞ .

Table 4

Polymerization Reaction Characteristics of *Exothane 26* and HPMA at Different Initiator TMBFF Contents

| $c_{in}, \%$ | Q , not.uni. | Q_{30} , not.uni. | $T_{MAX}, ^\circ C$ | $T^*_{MAX}, ^\circ C$ | $T^\bullet, ^\circ C/s$ | t_∞, s |
|--------------|----------------|---------------------|---------------------|-----------------------|-------------------------|---------------|
| 0.4 | 244 | 243 | 18 | 43 | 6.1 | 43 |
| 0.5 | 383 | 359 | 29 | 56 | 7.3 | 45 |
| 0.7 | 487 | 450 | 37 | 64 | 9.9 | 48 |
| 0.8 | 556 | 520 | 41 | 68 | 10.5 | 49 |
| 0.9 | 516 | 481 | 40 | 66 | 10.3 | 47 |
| 1.0 | 390 | 363 | 29 | 54 | 8.3 | 46 |

As can be seen from Table 4, the highest Q value and the highest polymerization reaction yield are reached at $c_{in} = 0.8 \%$.

At the same initiator content, the highest reaction yield is reached in 30 s – Q_{30} .

The initiator TMBFF concentration 0.8 % in the *Exothane 26* – HPMA system was considered as optimal and was used in further studies.

For the *Exothane 26* – HPMA system with an initiator content of 0.8 %, FTIR spectra were recorded after different exposure times of the samples in UV radiation (Fig. 5).

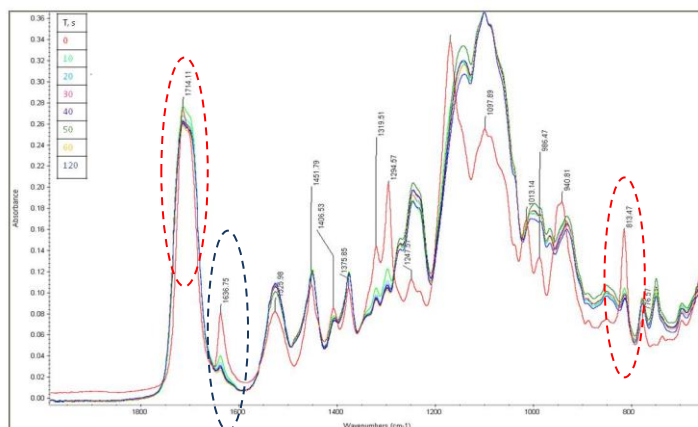


Fig. 5. FTIR absorption spectra in the range of 2000–600 cm^{-1} after different UV exposure times t_{UV} of the system: *Exothane 26* – HPMA.

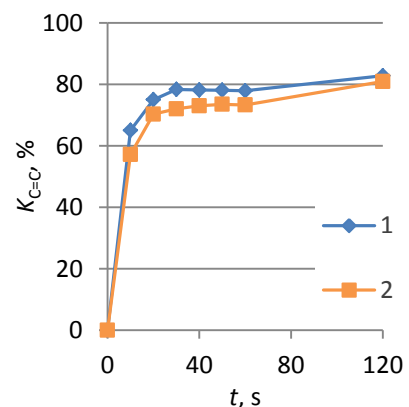


Fig. 6. The degree of conversion of unsaturated bonds $K_{C=C}$ depending on t_{UV} (calculated: 1 – after 813 cm^{-1} , 2 – after 1636 cm^{-1} band).

The fluctuations associated with the acrylate vinyl group are of interest:

- 1) 813 cm^{-1} – C=C acrylate vinyl group twisting fluctuations;
- 2) 1636 cm^{-1} – C=C acrylate vinyl group stretching oscillations.

As vinyl groups of acrylates are involved in the polymerization process, the absorption intensity in these spectral bands decreases [6], [7].

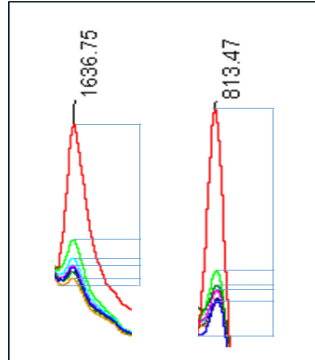


Fig. 7. FTIR-IR absorption spectra in the 813 cm^{-1} and 1636 cm^{-1} bands of system: *Exothane 26* – HPMA.

As can be seen from the spectra (Fig. 7), the absorption value A in the band of these fluctuations decreases with increasing time t_{UV} .

It can be used to estimate the degree of conversion of acrylate vinyl groups $K_{C=C}$ (1) [6], [7]:

$$K_{C=C} = (R_0 - R_t)R_0, \quad (1)$$

where $R_0 = (A_{810}/A_{1716})_0$ vai $(A_{1636}/A_{1716})_0$ is relative absorption before exposure to UV radiation; $R_t = (A_{810}/A_{1716})_t$ or $(A_{1636}/A_{1716})_t$ is relative absorption after determined t_{UV} ; A_{1716} – absorption at 1716 cm^{-1} range (acrylate C=O group stretching) fluctuations which do not change during the polymerization process.

As can be seen from Fig. 5, a sufficiently high $K_{C=C}$ value is reached after the first seconds of UV exposure. The extreme value of $K_{C=C}$ does not exceed 80 %. This means that the remaining 20 % of the acrylate vinyl groups do not participate in the copolymerization process.

4. Selection of Base Diacrylate and Comonomers and Determination of Their Content Ratios

4.1. Choice of Base Diacrylates

The most important task was to find the most suitable compounds and their content ratios using the range of selected comonomers, which would allow to create compositions whose photo copolymerization process can obtain coatings that meet many conflicting requirements.

The strength-deformation indices ($E = 47\text{ MPA}$ and $\varepsilon = 16\%$) of the coating formed by the system found in the previous chapter do not meet the requirements set for the coating in Chapter 1 ($E = 200\text{--}2000\text{ MPa}$; $\varepsilon_B = 20\text{--}160\%$).

Therefore, for further studies, systems with other base diacrylates were tested. We used compositions containing one of the selected base diacrylates (*Exothane 26* (K1), *Exothane 8*

(K2), *Exothane 10* (K3)), the comonomer hydroxypropyl methacrylate (HPMA, 45.2 %) and the photoinitiator 2,4,6-trimethylbenzoylphenyl phosphate. (TMBFF 0.8 %).

The viscosity of all compositions was evaluated before the UV-activated cross-linking (Fig. 8). The developed compositions were polymerized and the strength-deformation indices of the UV-activated copolymerization products of the compositions were evaluated (Figs. 9 and 10). The factored zone corresponds to the range of characteristics specified in the requirements.

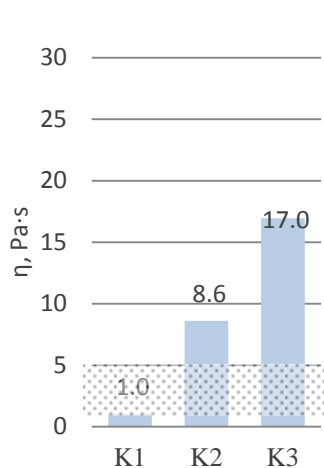


Fig. 8. Viscosity η values of non-polymerized compositions.

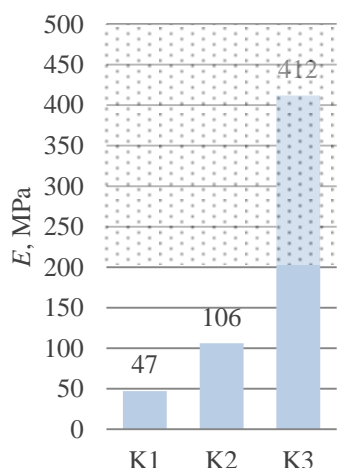


Fig. 9. Modulus of elasticity E of polymerized compositions.

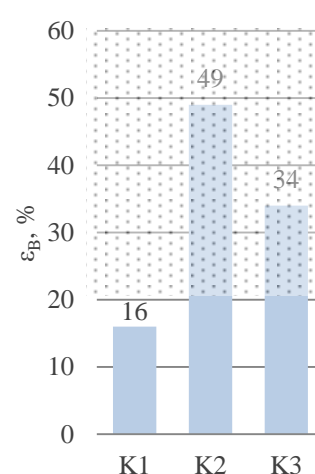


Fig. 10. Elongation at break ϵ_B of polymerized composition.

The value of E increases in the composition row: E26 (K1) < E8 (K2) < E10 (K3). The values of the BDA own modulus of elasticity increase in the same sequence.

The manufacturer did not disclose the chemical structure of the *Exothane* family diacrylates. It was known that Exothanes are mixtures of urethane dimethacrylate modification products of different molecular weights. Judging by the values of the modulus of elasticity E of the investigated cross-linked BDA (which is proportional to the degree of cross-linking ν for the cross-linked polymers), the values of the studied BDA ν increase in the row E26 > E8 > E10. As acrylic groups are located at the ends of diacrylate molecules, this is only possible if the length (molecular weight) of the BDA molecule decreases in this sequence.

In a similar line as in the case of BDA, the value of the modulus of elasticity of the copolymer also increases. This means that if it is necessary to obtain a copolymer with a higher E value, BDA with a lower molecular weight should be used.

The elongation at break values of polymerized compositions increase in the row: E26 < E10 < E8. These data suggested that the diacrylates of the *Exothane* family were not linear.

When evaluating the compositions according to the mechanical parameters, the system with *Exothane 10* (K3) was the only one whose values fell within the set of requirements, but the viscosity of this system significantly exceeded the required one.

Prior to further testing, the DTA polymerization process of these systems was performed. From the experimental curves $(T_R + T_S)(t)$ and $(T_R)(t)$ the amount of heat released by the polymerization Q and the maximum temperature reached during the polymerization, T_{MAX} were determined.

Judging by the Q and T_{MAX} values, under the existing UV activation conditions, all *Exothane* group diacrylates are within the T_{MAX} requirements, so all three of the selected BDAs were used for further studies.

In order to obtain the coatings meeting the requirements of viscosity and mechanical properties, compositions were formed in which the content of KM and initiator remains unchanged (respectively, 45.2 % and 0.8 %), but variations were made in the composition of BDA including all 3 studied BDAs in a ratio 1:1:1 and in a ratio of 2:1:1. The total BDA content remains unchanged 54 % (Table 5).

Table 5

Content of BDA Entering the Compositions

| Composition No. | <i>Exothane 26</i> | <i>Exothane 8</i> | <i>Exothane 10</i> |
|-----------------|--------------------|-------------------|--------------------|
| | Conc., mass % | | |
| K6 | 18 | 18 | 18 |
| K7 | 26 | 14 | 14 |
| K8 | 14 | 26 | 14 |
| K9 | 14 | 14 | 26 |

The viscosity of all systems before UV-activated cross-linking (Fig. 11) and the strength-deformation indicators of polymerized samples were evaluated (Figs. 12 and 13).

The eligible area is textured in the images.

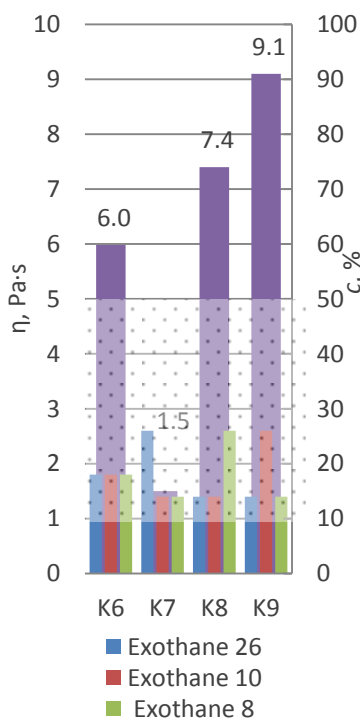


Fig. 11. Viscosity η value of non-polymerized compositions depending on the concentration of BDA.

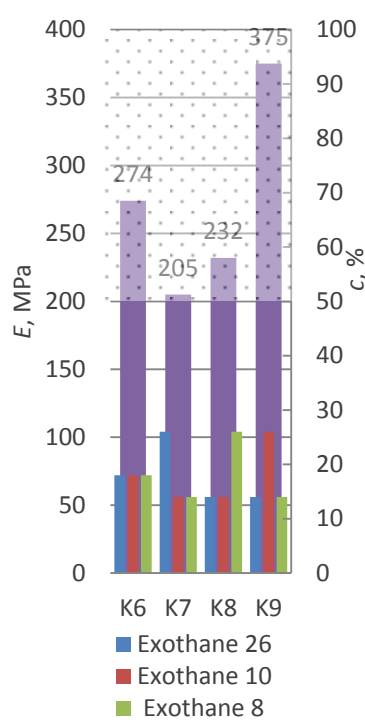


Fig. 12. Tensile elastic modulus E value of polymerized compositions depending on the concentration of BDA.

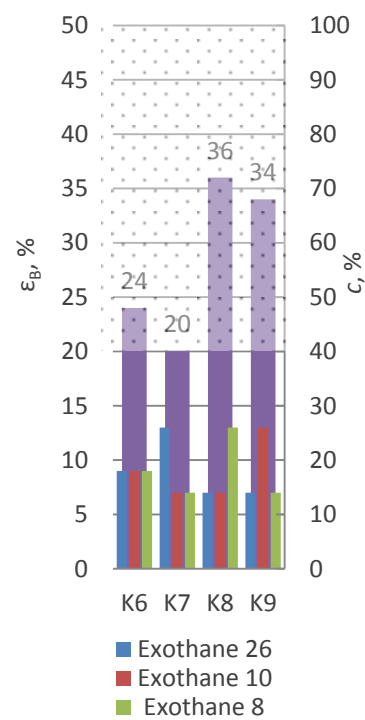


Fig. 13. Elongation at break ϵ_B values of polymerized compositions depending on the concentration of BDA.

The composition K7, which contains all three *Exothane* group diacrylates studied, meets the requirements of all specified parameters. Although the mechanical properties are very close to the lowest range of requirements, the properties of this composition are closest to the set requirements, so this composition was used for further studies.

Further analysis of the UV-activated polymerization process of this composition, showed that the value of the actual polymerization temperature ($T_R + T_S$) exceeds 70 °C – the maximum allowable temperature in the coating hardening process. Therefore, in further studies it was necessary to find out the effect of several other KMs and their content on the viscosity of the non-polymerized system, as well as the temperature achieved during polymerization.

4.2. Choice of comonomers

The KM acts in the system as a less viscous component that allows the viscosity of the overall system to be regulated, and as a component it participates in copolymerization reactions with BDA. By participating in copolymerization cross-linking reactions, KM can influence the polymerization process and the amount of heat released during the polymerization, and thus also the value of the maximum temperature to be reached during the polymerization T_{MAX} [4].

Three selected monofunctional monomers have been studied: hydroxypropyl methacrylate (HPMA), tetrahydrofurfuryl acrylate (THFA), tert-butylcyclohexyl acrylate (TBCHA), and one bifunctional monomer ethylene glycol dimethacrylate (EGDMA) with a viscosity value close to the values of monofunctional KM.

The composition of the tested systems is derived from K7: photoinitiator – 0.8 %; BDA ratio 2:1:1 (*Exothane 26: Exothane 8: Exothane 10*). KM tested at concentrations range from 10 % to 45 %.

The dependence of KM content on the viscosity η of non-polymerized systems is shown in Fig. 14. The viscosity of the system is determined by the viscosity of the KM itself and its content.

At the same KM content, the higher the viscosity of pure KM, the higher is the value of the viscosity of the system.

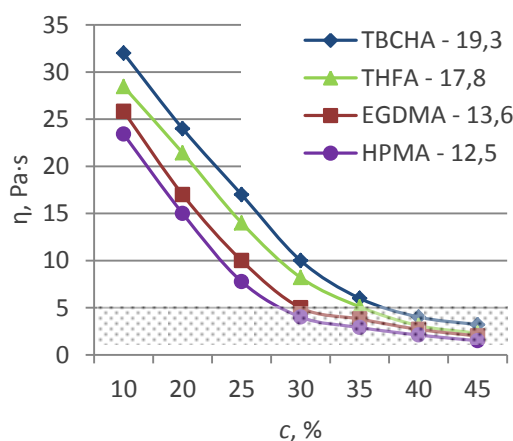


Fig. 14. Effect of viscosity value η of non-polymerized compositions on KM concentration (numbers at KM notations – KM viscosity, mPa·s).

As can be seen from the data in Fig. 14, practically all studied KMs are able to provide the value of system viscosity in the required range if their concentration is equal or exceeds 40 %.

The requirement that the viscosity of non-polymerized systems should not exceed 5 Pa·s and be not less than 1 Pa·s is related to the need to ensure optimal flowability of the composition during the coating application process. Experience has shown that if $\eta > 5$ Pa·s, the applied amount of the composition does not flow sufficiently over the surface to be coated, and the coating forms a thicker layer than 50 μm , which can promote an increase of polymerization temperature $T > 70$ °C. If $\eta < 1$ Pa·s, the coating flows over the nail surface outside the area to be covered.

The experimental determination of the viscosity of the composition is sufficiently labor-intensive and requires a relatively large volume of the test sample (at least 100 mL). It seemed useful to evaluate the ability of the composition to flow over the surface to be coated using our standardized drop method.

After placing the drop on the surface, the first correctly measured measurement of the diameter of the fuzzy drop can be made after 1 min (D_0).

The diameter of the effluent droplet increases over time and reaches equilibrium after ≈ 5 min – D_∞ . The value of D_0 and D_∞ increases with increasing KM content, respectively with a decreasing system viscosity. In Fig. 15, it can be seen that the values of D_0 and η form a single s-type curve, which can be satisfactorily described by a third-order polynomial¹ (line in the figure). This makes it possible to estimate the viscosity η value of the system by measuring diameter D of the effluent droplet. In order to obtain the value of the system viscosity η in the permissible range 1–5 Pa·s, the value of D_0 must be in the range of 17–25 mm.

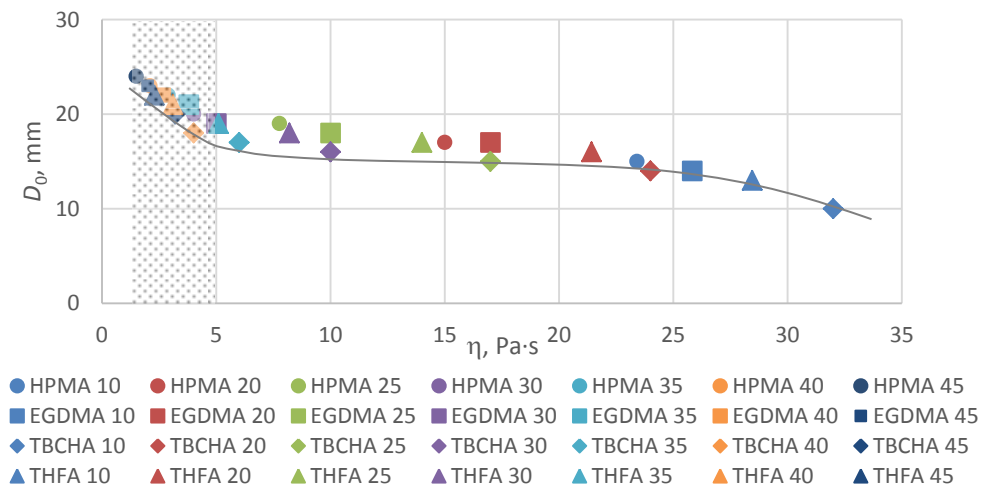


Fig. 15. D_0 and η interrelation in KM containing systems.

Based on the data of viscosity and flow studies, the range of investigated compositions was narrowed for further studies, excluding systems with KM concentrations of 10 %, 20 % and 25 %, which do not meet the requirements of rheological properties.

¹ $D = 24.969 + 1.3975\eta + 0.072\eta^2 - 0.0013\eta^3$, $R^2 = 0.9394$.

In order to determine the effect of KM on the copolymerization process, we considered it possible to limit ourselves to two sufficiently important characteristics: the conversion of acrylate unsaturated bonds $K_{C=C}$ during the change of degree and the change of the polymerization differential temperature by fixing the maximum polymerization temperature T_{MAX} .

The change of the degree of conversion of unsaturated bonds $K_{C=C}$ during time is one of the most important criteria for the course of UV-activated polymerization.

A similar nature of $K_{C=C}$ change is also observed for systems with different KM (Fig. 16). At the same concentration, the value of T_{MAX} , as well as the equilibrium value of $K_{C=C}$, increases in the row: THFA < HPMA < TBCHA < EGDMA (Fig. 17).

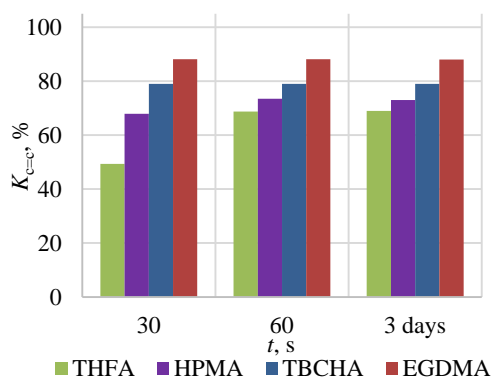


Fig. 16. Degree of conversion of unsaturated bonds $K_{C=C}$ (according to the intensity of oscillations of acrylate vinyl groups IR at 813 cm^{-1}) after 30 s and 60 s exposure to UV radiation and after 3 days exposure at room temperature.

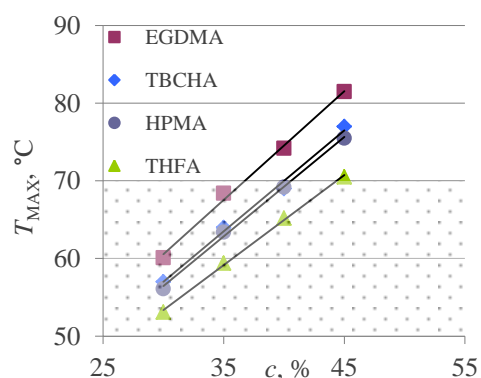


Fig. 17. Dependence of polymerization temperature T_{MAX} on KM concentration.

$K_{C=C}$ and T_{MAX} values should be considered as comparative indicators for the evaluation of the activity of a particular KM in the copolymerization process. By far the highest activity is for diacrylate – EGDMA.

It is difficult to judge why such a series of KM activities is formed in connection with the chemical structure of these compounds without further research. Another significant obstacle to this is that the chemical structure of the copolymerization base diacrylates is not directly known to us.

4.3. Influence of Different KM on More Important Parameters of the System Copolymerization Product

At lower KM content the viscosity of the non-polymerized system exceeds the required ($>5\text{ MPa}\cdot\text{s}$), at higher KM content – T_{MAX} value is higher than required ($>70\text{ °C}$).

As because of technical reasons it was not possible to determine all the cross-linked product parameters immediately after photopolymerization, measurements were taken after 24 hours (1 day). Samples were also tested after 72 hours (3 days) to determine if any post-cure effects occurred.

The formation of cross-linked structures during copolymerization is characterized by the content of the cross-linked part in the final product – gel fraction G .

In the case of all KM, a high G value is achieved – above 95 %. The achieved G values increase in the KM line: THFA < HPMA < TBCHA < EGDMA. The value of G increases noticeably after 3 days of polymerization in a similar sequence.

The gel fraction characterizes the content of the cross-linked (insoluble) part of the polymer in the system but does not give an idea of the density of the cross-linked arrangement.

The degree of cross-linking of the cross-linked part can be estimated from the experimentally determined value of the equilibrium swelling degree of the cross-linked part – Q (2).

$$Q = [(m_S - m_D) / m_D] \cdot 100, \% \quad (2)$$

where m_S is the mass of the sample of the cross-linked part in the swollen state and m_D is the mass of the dried sample. Q value depends entirely on the parameter characterizing the degree of cross-linking of the cross-linked polymer M_C – the average statistical molecular weight between the nearest cross-links [6].

The higher the Q value, the higher is the M_C value.

In our case, it was not possible to use Flory–Rehner equation [162], which connects the volume fraction of cross-linked polymer ϕ_{POL} in the expanded polymer to its M_C value. This is because the equation can be used for weakly cross-linked (high M_C values) superelastic polymers.

Regardless of the KM used, the experimentally determined swelling degree Q values of the cross-linked samples are very small (0.9–1.8 %) and was characterized by a relatively large dispersion.

The corresponding ϕ_{POL} values were in the range of 0.95–0.99, which shows a high degree of gel cross-linking and then low M_C values.

Regardless of the KM used, the Q values of the swelling degree of the experimentally determined cross-linked samples were very small: 0.9–1.8 %. The calculated ϕ_{POL} values from them were 0.97–0.99. These figures clearly indicate a high degree of gel cross-linking and, thus, a low M_C value.

The most important indicator of the deformation properties of a cross-linked polymer, the value of which is unambiguously determined by the degree of cross-linking, is the initial modulus of tensile elasticity $E = \lim d\sigma/d\varepsilon \big|_{\varepsilon \rightarrow 0}$ [10]. This characterizes the tensile strength of the polymer at the beginning of the deformation process.

As can be seen from Fig. 18, The E value of cross-linked coating samples with different KM differs sharply. The value of E increases significantly in the KM sequence THFA < HPMA < TBCHA < EGDMA. In the case of EGDMA, the E value is almost 10 times higher than THFA. This means that EGDMA can provide an order of magnitude of cross-linking at the same content in the system.

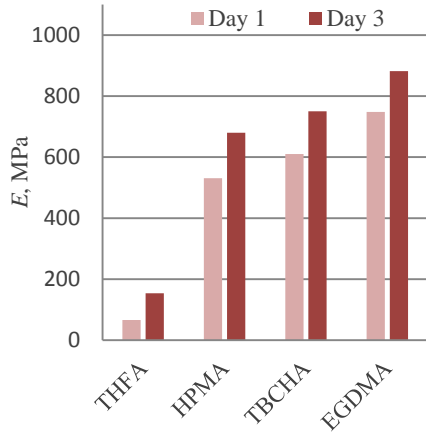


Fig. 18. Value of tensile modulus E of the coating for compositions containing different KM (KM content – 35 %).

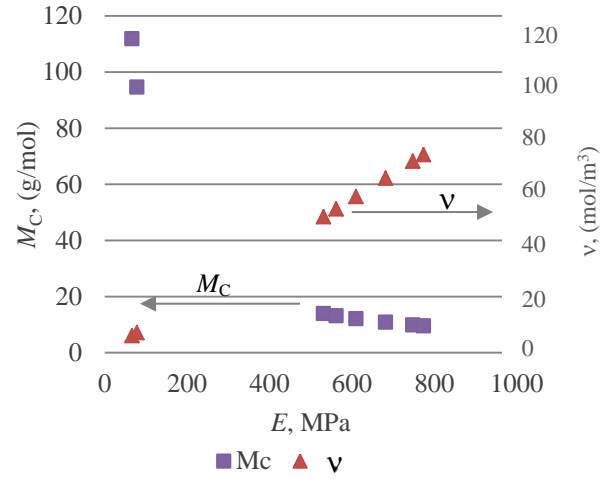


Fig. 19. Values of modulus of elasticity E , M_C and ν for different KM.

The values of the modulus of elasticity E (Pa) and M_C (g/mol) of the cross-linked polymer are related by a simple Formulation (3) [10]:

$$M_C = 3\rho RT / E, \quad (3)$$

where ρ is density of cross-linked polymer, g/m^3 ; R is universal gas constant, $(\text{m}^3\text{Pa})/\text{kmol}$; and T is temperature, K.

As can be seen, the M_C value of the cross-linked polymer is inversely proportional to the E modulus value of the polymer.

To assess the degree of cross-linking, the value of cross-link density is also used (4).

$$\nu = 2\rho / 3M_C. \quad (4)$$

This value is inversely proportional to the value of M_C [10], thus directly proportional to the value of E .

As the modulus E increases, the value of M_C decreases, but the value of ν increases.

As can be seen from Fig. 19, for most monomers, a significant degree of cross-linking is achieved – a low M_C value.

The monomers studied separately, according to the values of the modulus of elasticity E of the compositions containing them, the corresponding values of M_C and ν can be ranked in the same series as before for T_{MAX} (Fig. 17), $K_{\text{C=C}}$ (Fig. 16) and G : THFA < HPMA < TBCHA < EGDMA.

The most effective of the monomers studied after all the determined parameters is diacrylate EGDMA.

The values of the elongation at break ϵ_B of the studied cross-linked systems vary within wide limits: 1–85 % (Fig. 20). There is a traditional correlation between E and ϵ_B values (Fig. 21).

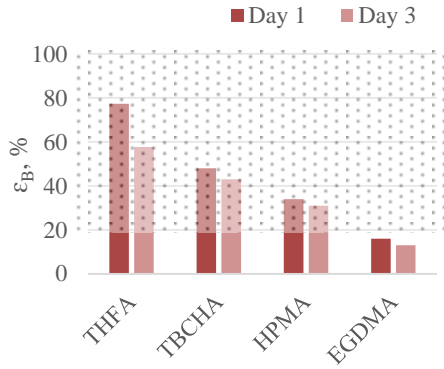


Fig. 20. Value of the elongation at break of the coating depending on the system KM (35 %) were determined on day 1 and day 3 after polymerization.

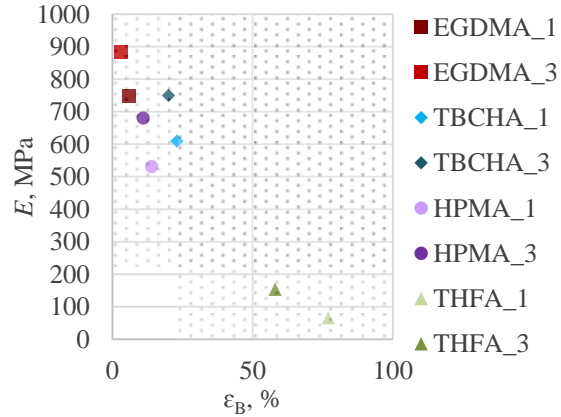


Fig. 21. The modulus of elasticity and elongation at break values in the set of requirements for systems with 35 % KM are determined on day 1 and day 3 after polymerization.

HV values of cured coating microhardness were determined for base compositions with different monomers. They line up in a similar sequence as for the modulus of elasticity: THFA < HPMA < TBCHA < EGDMA.

The values of *HV* and the corresponding *E* values correlate well with each other (Fig. 22).

Surface hardness *HV* characterizes the resistance of a material to deformation in a relatively thin layer (200 μm) at the surface.

Surface hardness of polymers correlates with the value of the yield stress σ_y of the polymer [11]. In our case, we encountered a particularly large (>40 %) dispersion of experimental data of σ_y and also in the case of tensile stress at break σ_B . For the studied compositions (at KM content 35 %) σ_B values were in the range of 5–45 MPa, but σ_y in the range of 2–41 MPa. Due to the large variance of values, the correlation *HV* – σ_y was not considered.

In the case of all studied compositions, the values of modulus of elasticity *E* and surface hardness *HV* measured after 1 day and 3 days after photopolymerization differ (Fig. 22). *E* and *HV* values increase.

There can be no reason for the increase of *E* and *HV* values other than the entry of unreacted vinyl groups in the copolymerization reactions and the increase of the cross-linking density already after UV-activated copolymerization. Similar post-copolymerization has been observed for UV-polymerized urethane acrylate coatings [12], [13].

When measuring the value of the modulus of elasticity *E* for the composition with HPMA 35 %, in a longer period of time after UV-activated copolymerization (Fig. 23), we found that the increase of *E* value after three days of exposure is small. This leads to the conclusion that 3 days is a sufficient time to assess the post-cross-linking effect.

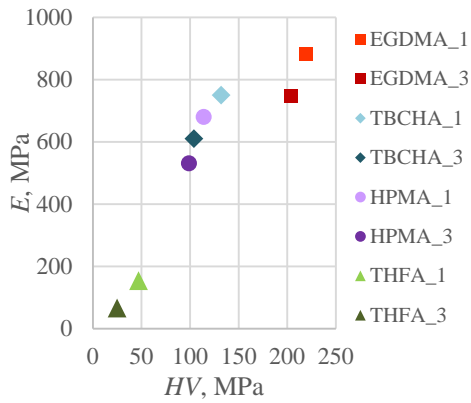


Fig. 22. Values of modulus of elasticity E (MPa) and surface hardness HV (MPa) for coatings after 1 day and 3 days after polymerization.

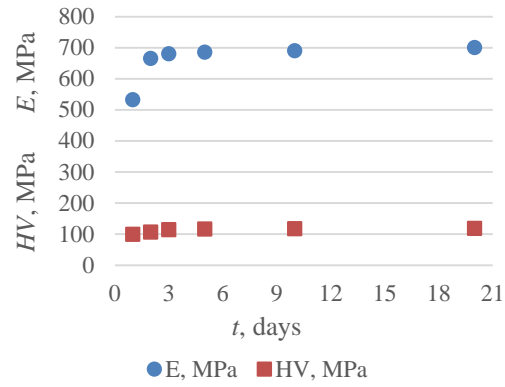


Fig. 23. Change in modulus of elasticity E and surface hardness HV during coatings with 35 % HPMA.

It can be concluded from Fig. 23 that both parameters for E and HV coatings are stable over the period corresponding to the actual service life of the coating.

It was interesting to compare the increase in the value of E and HV for systems with different KM.

Figure 24 shows the increase of the modulus value E_3/E_1 .

It can be seen (curve E in Fig. 24) that the higher the value of E reached after 1 day (higher the achieved cross-link density ν , Fig. 18), the lower is the value of E increase E_3/E_1 (less cross-link density ν). The increase in surface hardness HV values is similar (Fig. 24, curve HV).

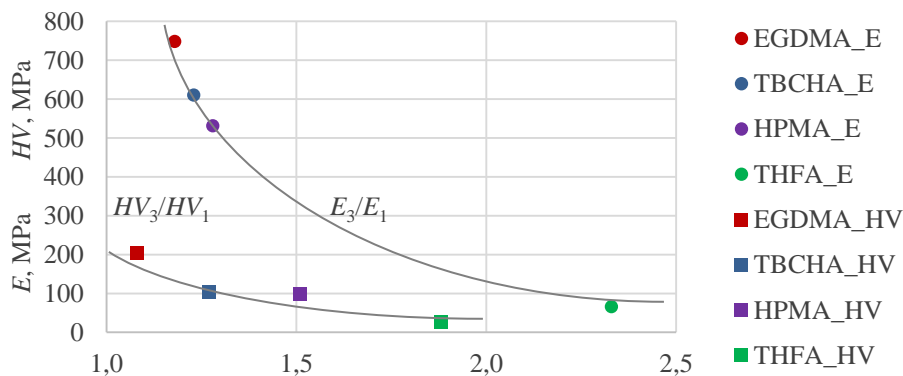


Fig. 24. Ratio of changes of elasticity E and surface hardness (HV) values in the results for day 3 and day 1 in coatings with 35 % HPMA.

Surface gloss was assessed using a Novo Gloss Lite gloss meter from *Rhopoint Instruments Ltd*.

As shown in Fig. 25, the surface gloss values range from 57 GU to 83 GU. This indicator is important for surface coatings. The minimum requirement for surface coatings is 70 GU [14].

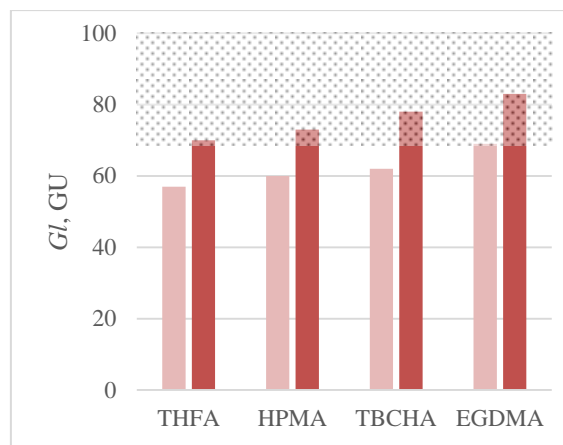


Fig. 25. GI (GU) values of the coating surface gloss 1 day and 3 days after polymerization. KM content 35 %.

It should be noted that the surface gloss of all studied coatings, i.e., the reflectance of light increases by 17–21 % over time (comparing day 1 and day 3 after photopolymerization).

The gloss of the polymer surface depends on several parameters characterizing the optical properties of the coatings [15]: refractive index, light absorption, transmittance, etc.

Surface gloss depends significantly on surface roughness (ratio of real surface size to imaginary) [16]. The larger it is, the larger is the part of the incident light scattered by the surface.

Analysis of the ASM surface showed that the amplitude of the surface relief practically does not change for 10 days.

It is possible that the increase in surface gloss over time is determined by a change in the optical properties of the coating with an increase in cross-linking density.

4.4. Effect of KM on the Wetting Ability of an Unpolymerized Composition

The ability to wet the nail (substrate) surface of the investigated compositions (adhesives) and its relationship with the strength of the adhesive compound was evaluated.

For this purpose, we selected four compositions containing 35 % of different comonomers: EGDMA, THFA, TBCHA and HPMA. The rest of the system contained a mixture of BDA (*Exothane 26*, *Exothane 10*, *Exothane 8*, respectively 2:1:1) and photoinitiator TMBFF – 0.8 %.

For these compositions, the values of surface tension σ_{AG} and suppress angle θ on the model surface of the natural nail (beef nail) were determined.

As can be seen from Fig. 24, the wetting angle decreases during the measurement. The rate of angle change is higher due to the lower viscosity of the composition. The equilibrium value is reached within 5–8 minutes (Fig. 26).

This is an important fact, because when applied to the coatings in practice, wetting will have reached a state close to equilibrium before curing in the UV polymerization.

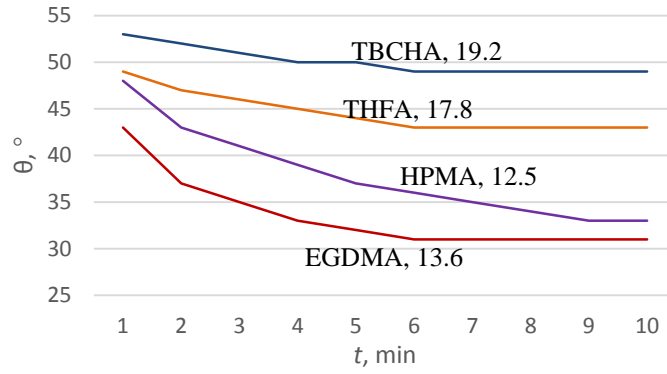


Fig. 26. Change in wetting angle in a time during systems under study; numbers at the comonomer designations – viscosity η , Pa·s.

The wetting properties of the studied compositions and the values of the parameters characterizing the adhesion conjunction are given in Table 6.

Table 6

Wetting Properties of Compositions and Values of Parameters Characterizing Adhesion Strength

| Compositons No. | KM | Viscosity η , Pa·s | Surface tension σ_{AG} , mJ/m ² | Value of the suppress equilibrium angle θ , ° | $\cos \theta$ | A_S , MPa (Fig. 27) |
|-----------------|-------|-------------------------|---|--|---------------|-----------------------|
| K24 | EGDMA | 3.8 | 36 | 31 | 0.88 | 3.3 |
| K10 | HPMA | 4.0 | 38 | 33 | 0.87 | 2.9 |
| K31 | THFA | 5.1 | 41 | 43 | 0.78 | 2.5 |
| K17 | TBCHA | 6.0 | 43 | 49 | 0.72 | 2.3 |

As can be seen from Table 6, the value of θ decreases with decreasing adhesive surface tension (σ_{AG}). The wetting ability of the adhesive increases.

This is in line with the Young's equation (σ_{SA} – surface tension on the interface adhesive-substrate)

$$\cos \theta = (\sigma_{SG} - \sigma_{SA}) / \sigma_{AG}. \quad (5)$$

In our case, the substrate (beef nail) surface tension $\sigma_{SG} = \text{const} \approx 40 \text{ mJ/m}^2$ [17].

As expected, as the wetting capacity of the adhesive increases (the θ value decreases), the strength of the achieved adhesion increases sharply (the value of A_S increases), see Table 6.

We can conclude that all four studied compositions wet the nail surface well enough ($\theta < 50^\circ$) [18] and are able to provide sufficiently high values of adhesive strength.

4.4. Effect of KM on Coating Adhesion Bond and Bond Durability

In nail coating technology, the strength of adhesion and the durability of the adhesion are highly controversial. The adhesion strength of the coating ($A_S > 2 \text{ MPa}$) must be high enough and maintained during operation (2–4 weeks). At the same time, the coating must be removed by contact with the solvent as quickly as possible.

The coatings of all four studied KM-containing (35 %) compositions were tested 3 days after UV polymerization by distracting the coating from surface (pull-off method was used)

and by scratching the coating from the surface (using Cross-Cut tester *BYK*), which has been immersed in the solvent, up to 65 % of the coating loses adhesion from the substrate.

The values of both parameters for all systems meet the set requirements (Fig. 27). Further studies have shown the possibility of reducing the adhesion durability A_N (adhesion loss time) to reduce the contact time of the natural nail with the solvent when removing the coating.

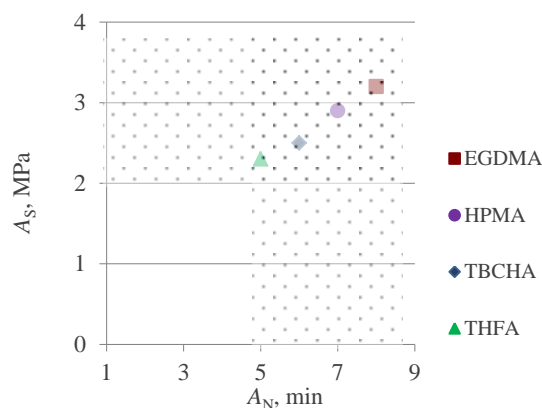


Fig. 27. Adhesion bond and adhesion bond stability for systems with different KM (35 %).

As can be seen, there is a logical correlation between the two parameters: higher values of adhesion strength correspond to longer adhesion durability.

Due to the high degree of cross-linking that can be achieved for all compositions, it is reasonable to assume that the swelling and permeability of the coating are not critical. The coating fragments lose adhesion from the surface as the solvent accesses the contact surface around the perimeter of the fragment.

4.5. Summary

The performed studies show that all studied KM: THFA, HPMA, TBCHA and EGDMA in compositions with BDA urethane diacrylates: *Exothane 8*, *Exothane 10*, *Exothane 26* can be used for nail coating base formulation.

They provide:

- possibility to obtain compositions with the desired viscosity (< 5 Pa·s);
- rapid course of UV-activated co-polymerization of compositions (<60 s), not exceeding the maximum allowable temperature (<70 °C) caused by the heat effect of polymerization;
- sufficient values of the strength-deformation indices of the polymerized coating;
- sufficient adhesion of the coating to the material to be coated (2.0 MPa);
- desired adhesion durability when removing the coating (10 min).

5. Additives and Their Effect on the Properties of the Compositions

5.1. Effect of Additives on the Properties of a Non-Polymerized Composition

Additives for various purposes are used in the development of UV-activated copolymerization systems for cosmetic coatings [19].

Certain additives that are soluble in the comonomer composition without participating in the copolymerization process can locally reduce the cross-link density of the coating by volume curing and the density of the adhesion bonds at the interface. This may facilitate the disintegration of these structures in solvent media and facilitate the separation of the worn coating [20]–[22].

Additives can also increase the stability of pigmented compositions (reduce the tendency of pigment sedimentation) over time [23].

Finally, the presence of additives may affect the rheological properties of the non-polymerized composition [24].

For the research we chose additives that are soluble in the non-polymerized composition and also in acetone (acetone is a traditionally used solvent for the removal of worn coatings).

The following additives were selected:

- 1) nitrocellulose (NC) [4], [5];
- 2) cellulose acetate butyrate (CAB) [25];
- 3) sucrose benzoate (SB) [15].

Several types of dispersed pyrogenic SiO₂ with different hydrophilicity were also tested. The composition used in the experiments was as follows: BDA: *Exothane 26* – 31 %, *Exothane 8* – 17 %, *Exothane 10* – 17 %; photoinitiator – 0.8 %; KM: EGDMA = 10 %, HPMA = 24.1–24.2 % (depending on the additive conc). Additive content: 0.5–3.0 %.

As the content of additives increases, the viscosity of the non-polymerized system increases (Fig. 28).

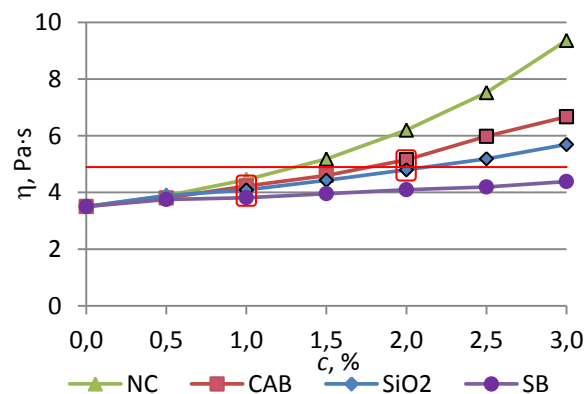


Fig. 28. Dependence of non-polymerized systems viscosity on additive concentration. Concentrations where the dots have a black frame indicate that the pigmented systems are stable over time. The optimal concentrations of additives are marked with a red frame.

The polymers of cellulose origin NC and CAB increase the viscosity the most. A concentration of 3 % NC increases the initial basic viscosity almost triple.

The effect of additives on the stability of individual pigmented non-polymerized systems was also visually assessed.

Three additives can ensure the pigment stability of the tested system over time. These are $\text{SiO}_2 - 1\%$, CAB - 2%, NC - 2%.

The dependence of the shear rate on the viscosity of additive-containing compositions was found (Fig. 29).

The non-polymerized composition is applied to nail surface by manicure technician with a brush. Moving the brush with a speed $\approx 10\text{ mm/s}$ (10^{-2} m/s), the shear speed $\dot{\gamma}$ between composition layer on the substrate $10\text{--}100\ \mu\text{m}$ ($10^{-5}\text{--}10^{-4}\text{ m}$) and the brush plane can significantly exceed 10^2 s^{-1} .

As can be seen, in the range of shear rate $\dot{\gamma}$ $3\text{--}20\text{ s}^{-1}$, the viscosity of both the base composition and the compositions containing the additive (CAB and $\text{SiO}_2\text{ N20}$) does not depend on the shear rate. From a rheological point of view, these compositions are Newtonian fluids.

Systems containing dispersed SiO_2 H15 and H20 are pseudoplastic: their viscosity decreases significantly (even in the narrow $\dot{\gamma}$ study range).

This condition can be considered positive from the point of view of application of the composition. The viscosity of the composition during its application (brush stroke) (at $>10^2\text{ s}^{-1}$) will be significantly lower than at rest point.

The dependence of the viscosity of the additive-containing compositions on the shear duration was determined (Fig. 30). As can be seen from the figure, the systems containing SiO_2 H15 and H20 show a marked decrease in viscosity during the first 60–90 s.

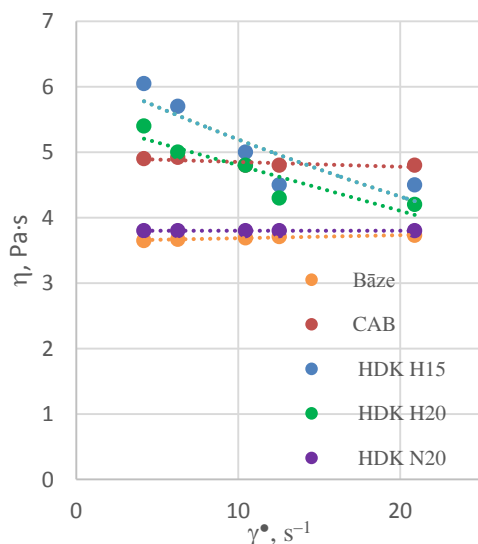


Fig. 29. Dependence of viscosity η of compositions containing additives on shear rate $\dot{\gamma}$.

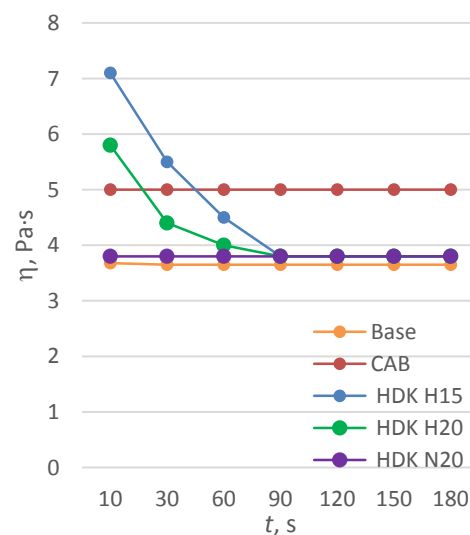


Fig. 30. Dependence of additive compositions viscosity η on shear duration t^* (used shear rate $\dot{\gamma} = 20.90\text{ s}^{-1}$).

This indicates the collapse of the dispersed structure of SiO_2 particles in the composition during the shear process. Our viscosity measurements show that this structure fully recovers in 20–30 s.

The presence of such a thixotropic effect is essential in the process of applying the composition. During shear, the viscosity value decreases and facilitates the application of the composition layer. Also, increase of the viscosity after application ensures that the applied layer does not leak too much.

5.2. Effect of Additives on Coating Properties

The presence of all four studied additives causes a decrease in the *HV* values of the microhardness of the cured coating (Fig. 31).

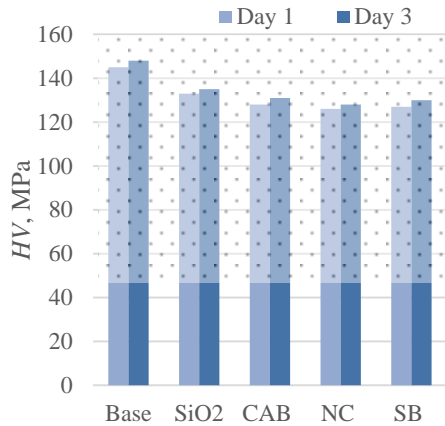


Fig. 31. Surface hardness for systems containing additives (1 and 3 days after polymerization).

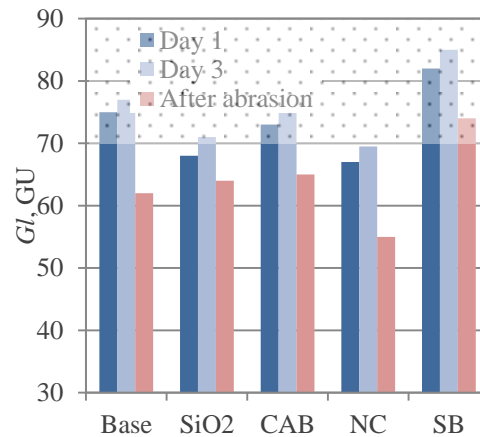


Fig. 32. Surface gloss for systems containing additives (1 and 3 days after polymerization).

GI values of the coating surface gloss for the studied compositions are shown in Fig. 32.

Sucrose benzoate acts as an additive that increases the gloss of the coating surface. The coating containing CAB has the least effect on gloss changes, but the addition of SiO₂ and NC reduces the gloss values of the coating.

Gloss resistance over time is important for coatings on natural nails, so the gloss of the coating surface was determined after the surface scratch test (Fig. 30). The surface gloss of all coatings decreases in the range of 10–20 %. The largest gloss reduction is for the system with NC, the smallest for coatings with silica and SB.

The strength-deformation properties of additive-containing coatings were studied in the tensile mode. The values of the modulus of elasticity *E*, the yield stress σ_Y and the corresponding elongation ε_Y , the fracture stress σ_B and the corresponding elongation at break ε_B are summarized in Table 7.

All studied composites under the given test conditions were characterized by stress-strain curves with a pronounced peak flow. A relatively large scattering was observed between the ‘strength-deformation’ relationships of the parallel samples (7–12 %).

The studied additives have little effect on the *E* value (Fig. 33).

Table 7

Strength-Deformation Properties of Additives-Containing Coatings

| Comp. No. | Additives | Additive contents, % | Elastic modulus E | Yield stress σ_Y | Elongation at yield stress σ_Y | Fracture stress σ_B | Elongation at break ϵ_B |
|-----------|------------------|----------------------|---------------------|-------------------------|---------------------------------------|----------------------------|----------------------------------|
| | | | MPa | MPa | % | MPa | % |
| K37 | Base | 0 | 784 | 25 | 14 | 24 | 23 |
| K57 | SiO ₂ | 1 | 792 | 25 | 13 | 24 | 27 |
| K47 | CAB | 2 | 791 | 26 | 13 | 27 | 34 |
| K41 | NC | 2 | 824 | 30 | 14 | 26 | 20 |
| K53 | SB | 2 | 810 | 27 | 14 | 25 | 18 |

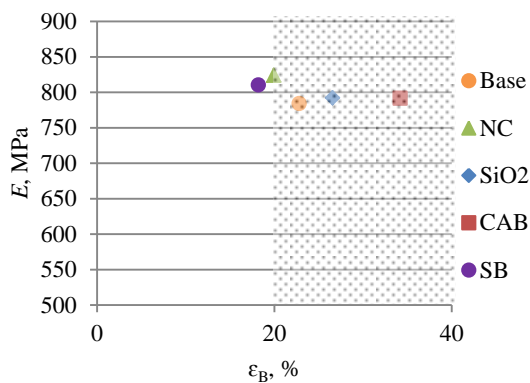


Fig. 33. Elastic modulus and elongation at break values for coatings with different additives.

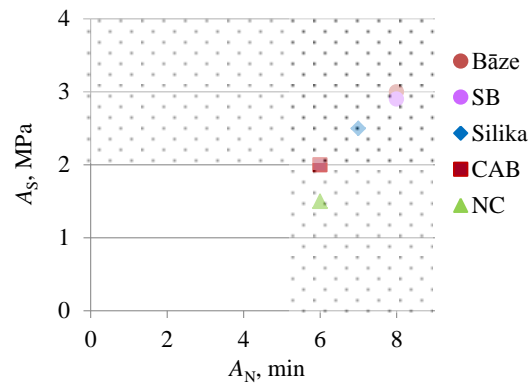


Fig. 34. Adhesion strength and adhesion durability values for coatings with different additives.

5.3. Effects of Additives on Adhesion Bond and Adhesion Bond Durability

For the coatings of all investigated additive-containing compositions 3 days after UV polymerization, the adhesion strength A_S and the adhesion durability A_N were determined (Fig. 34).

The addition of sucrose benzoate does not affect coatings A_S and A_N . All other additives reduce the stability of the adhesion strength and the adhesion durability. The addition of CAB, silica and SB can provide the required A_S (>2 MPa) for the studied composite system. NC reduces the adhesion strength to the substrate too much and does not meet the requirements for the coating.

Evaluating the effect of additives on the durability of the coating and adhesion strength, we conclude that they facilitate the loss of coating adhesion under the influence of the solvent. A particularly recommended additive for such removable coatings is CAB.

5.4. Effect of Additives on Coating Properties. Summary

In the practical part, the effect of additives on the properties of urethane acrylate coatings is studied. As a result of the experiments, the influence of four different additives: pyrogenic SiO₂, CAB, NC and SB on the polyurethane acrylate system and its properties was evaluated.

The effect of additives on the properties of the non-polymerized gel and on the properties of the polymerized coating has been determined.

The most important characteristics obtained during the research are summarized in Table 8.

CAB and SiO₂ are the most effective additives for improving the properties of pigmented urethane acrylate systems.

The stability of the pigmented suspension can be ensured by 2 % CAB, NC and 1 % SiO₂.

Table 8

Effect of Additives on Coating Properties

| Comp. No. | Additive | Additive conc. | Pigm. susp. stab. | η | E | ϵ_B | GF | HV | Gl | Gl^* | A_N | A_S |
|--------------|------------------|----------------|-------------------|--------|----------|--------------|------|------|------|--------|-------|-------|
| | | mass % | | Pas | MPa | % | % | MPa | GU | GU | min | MPa |
| Requirements | | | is | 1–5 | 200–2000 | 20–160 | >90 | >50 | >70 | >60 | <10 | >2 |
| K37 | Base | 0 | not | 3.5 | 784 | 23 | 98 | 148 | 77 | 62 | 8 | 3 |
| K57 | SiO ₂ | 1 | is | 4.1 | 792 | 27 | 97 | 135 | 71 | 64 | 7 | 2.5 |
| K47 | CAB | 2 | is | 5.0 | 791 | 34 | 96 | 131 | 75 | 65 | 6 | 2 |
| K41 | NC | 2 | is | 6.2 | 824 | 20 | 96 | 128 | 69 | 55 | 6 | 1.5 |
| K53 | SB | 2 | not | 4.1 | 810 | 18 | 97 | 130 | 85 | 74 | 8 | 2.9 |

The most effective way to improve the deformation properties of the coating is addition of CAB, increasing the elongation at break by 9 %, and NC, increasing the modulus of elasticity by 40 MPa (5 %).

CAB and NC promote the removal of the coating or the loss of adhesion in the solvent environment most effectively.

In the development of further coatings, SB is recommended to be used as an additive to the surface coating, as it effectively increases the gloss of the surface and is able to maintain it after the abrasion test of the coating.

SiO₂ and CAB are recommended for pigmented systems, as they are able to ensure the stability of the pigmented suspension and the increase in viscosity of the system is within the set requirements.

CAB is recommended for base coatings as it improves the deformation properties of the coating and promotes reduced adhesion resistance in the presence of solvent, thus facilitating coating removal.

6. Results of Coating Adhesion Tests

Adhesion strength A_S and adhesion durability A_N for coatings have been determined.

The experimentally determined adhesion durability A_N was characterized by an adhesion loss time when >65 % of the coating has detached from the substrate. Systems with a 35 % comonomer mixture were selected for the study, where 10 % is EGDMA, which is the primary KM, and the remaining 25 % are the previously tested KM (secondary KM): THFA, TBCHA and HPMA.

The previously tested BDA mixture 61.2 % in ratio 2:1:1 (*Exothane 26*; *Exothane 8*; *Exothane 10*) was used as the base diacrylates. The photoinitiator TMBFF used is 0.8 %. SiO₂ 1 % and CAB 2 % were used as additives. The obtained results are summarized in Fig. 33.

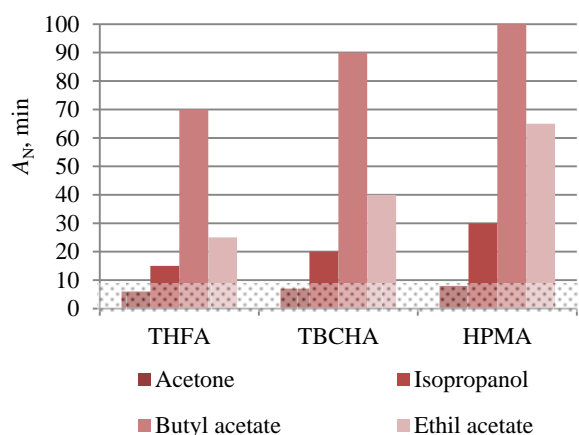


Fig. 35. Influence of comonomers on the adhesion durability of the coating in 4 different solvents.

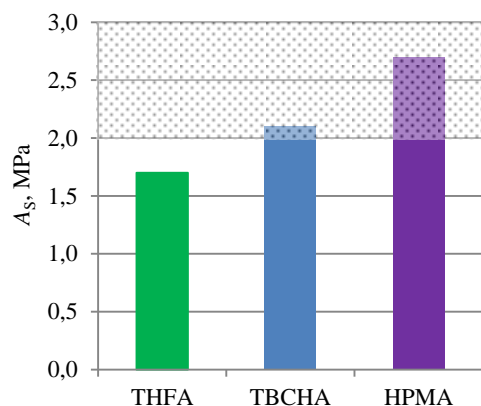


Fig. 36. Effect of monomers on coating adhesion binding.

The most effective solvent for all compositions was acetone, which was able to separate the coating from the substrate in less than 10 min (Fig. 35). It was used in further tests.

In terms of adhesion strength, compositions are in a similar order as with 30 % KM: THFA < TBCHA < HPMA.

In addition to adhesion durability tests in various solvents, the adhesion strength A_S to these systems was determined, both in laboratory and *in-vivo*, on natural nails.

Metal plates were used as a substrate. The adhesion strength results are ranked analogously to the adhesion durability tests (Fig. 35): THFA < TBCHA < HPMA. Eligible coatings ($A_S > 2$) are with KM TBCHA and HPMA.

The adhesion results obtained in the laboratory correlated with the results obtained in *in-vivo* tests on natural nails.

7. Color Stability of Pigmented Compositions

An important criterion for pigmented coatings is color stability and consistency over time. It is, therefore, important to predict changes in non-polymerised composition over time [26]. These tests prevent the creation of unstable systems during the development phase of new products.

In the course of the work, the color stability of *Kromachem* red pigment dispersions *Red 170* and *Red 48* in urethane acrylate composition based on composition K64 (BDA mixture (*Exothane 26*; *Exothane 8*; *Exothane 10*) in the ratio 2:1:1 in the concentration from 60 % to 65 % depending on the system, photoinitiator TMBFF – 0.8 %, EGDMA – 10 %, HPMA – 25 %, SiO₂ – 1 %, CAB – 2 %) was studied.

Pigment dispersions were tested at four different concentrations – 0.1 %, 0.2 %, 1 % and 5 %. The color stability of the pigmented systems was evaluated at room temperature and at elevated temperature in a 50 °C oven after 2 days, 7 days and 28 days.

The color of the coating to be analyzed was compared with the original color of the standard sample with a spectrophotometer to obtain a measurement of ΔE , which is the total color difference. The obtained data on ΔE are summarized in Figs. 37 A and B.

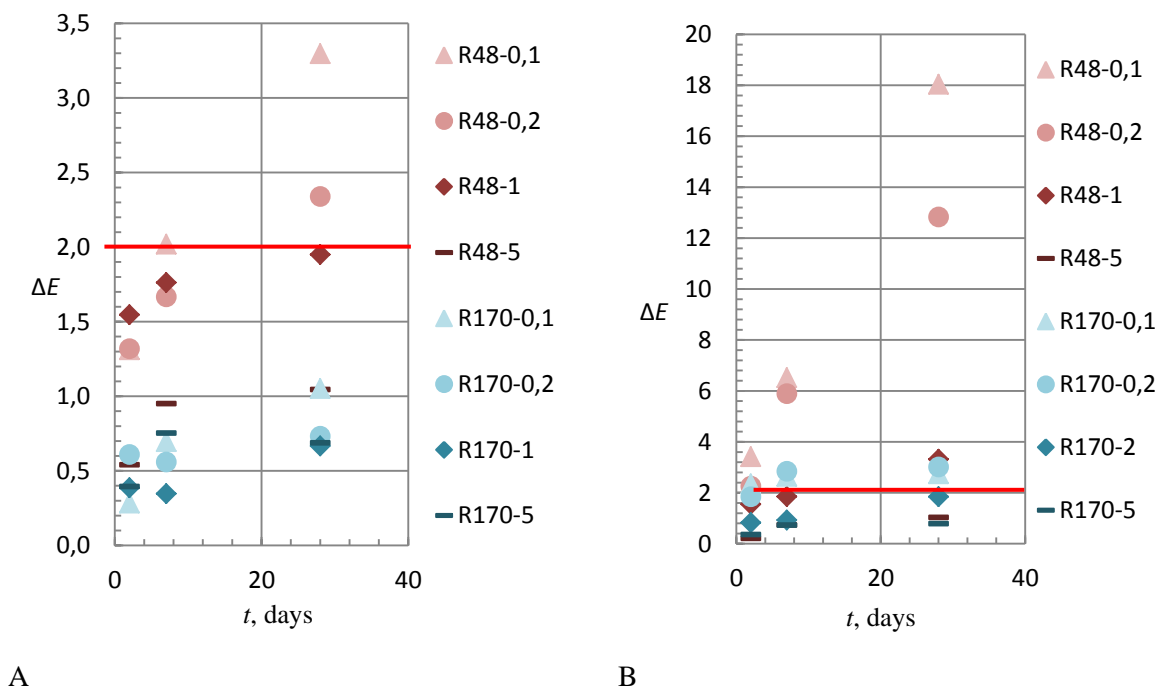


Fig. 37. Change of color difference (ΔE) in the time of composition coating samples with 2 different red pigments: A – coating samples as a function of time exposed at room temperature; B – coating samples as a function of time exposed at 50 °C temperature. Red line indicates acceptable color change.

The color of the composition changes over time as UV light and elevated T cause photo and thermal destruction. The absorption of UV and IR energy causes chemical reactions between the polymer and oxygen and releases free radicals [27]. Chemical reactions of free radicals cause physical changes in the coating: discoloration, loss of gloss and thickness, and cracking of the coating [28].

Figure 37 A shows that ΔE values increase with increasing exposure time. There is also a clear trend – the higher the pigment concentration, the lower is the ΔE value. This is due to the ability of pigments to absorb free radicals, and higher pigment concentrations result in less coating color destruction over time [29].

The lowest ΔE values were obtained for the compositions R170-5.0 (5 % of pigment *Red 170*) and R48-5.0 (5 % of pigment *Red 48*), where $\Delta E \leq 1.2$. According to DIN 55987, the stability of pigmented coatings is considered acceptable and sufficient if $\Delta E \leq 2$. In this test, after 28 days of exposure at room temperature, compositions containing more than 0.2 % of pigment *Red 48* and all compositions containing containing pigment *Red 170* can be considered stable because $\Delta E < 2$.

An increase in ambient temperature significantly increases the ΔE values of all compositions. In particular, the ΔE values for compositions with *Red 48* pigment increase. All compositions with this pigment exceeded the permissible ΔE value in 28 days.

As *Red 48* is an inorganic pigment and *Red 170* is an organic pigment, this would explain the ability of the organic pigment to neutralize free radicals and be more stable over time than the inorganic red pigment.

Examining these two *Kromachem* pigments in the urethane acrylate composition, it can be concluded that only a concentration $>0.2\%$ containing *Red 170* can be used for coatings on natural nails.

These tests also show a correlation between pigment concentration and ΔE : the higher the pigment concentration, the lower the ΔE value.

This test leads to the conclusion that pigmented systems should be tested not only at room temperature but also at elevated temperature.

Figure 37 B shows that all pigmented systems containing *Red 170* had the same ΔE values after 2 days and after 28 days. These results will reduce the color stability test time from 28 days to 2 days in the future.

8. Formula Creation Methodology for Three-Layer Coating

The history of nail coatings dates to the third millennium BC [30].

The world's first water-resistant polymer solution nail polish appeared in the 1930s [30].

Initially, layers containing colored pigments were applied to the nails, mainly to give the nails color.

To prevent the staining of the natural nail and to ensure that the pigmented layer adheres better to the nail, a colorless base layer was applied to the nail before the pigmented layer [31].

Over time, a transparent top layer was applied to the pigmented layer to give the coating an extra shine, as well as to protect it from mechanical damage [31].

The three-layer coating currently is the most popular type of nail coating.

The sequence and thickness of nail coatings are given in Fig. 38.

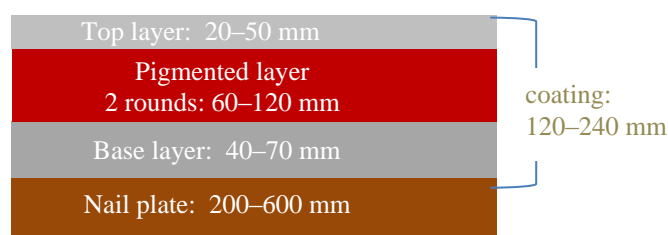


Fig. 38. Traditional nail coating layer scheme.

The application of coatings is as follows:

- Apply the layers with a brush.
- The thickness of the base layers is the largest, because it smooths out the roughness of the nail surface. It is applied in one way.

- Pigmented layers are applied in two rounds, as the total thickness of 60–120 μm and saturation of color must be achieved.
- Lastly, the top layer is applied.
- After application of each layer, it is polymerized under UV radiation (>30 s).

Each layer has its own composition. The basis of the development for these compositions is the basic composition.

The research of the Doctoral Thesis is mainly devoted to the development of the methodology of basic composition.

The compositions for the base layer, the pigmented layer and the top layer are derived from the base composition by adjusting the base diacrylate (BDA) and comonomer (KM) content ratios. The content of the corresponding additives is determined from them.

The desired properties of non-polymerized compositions and corresponding coatings are briefly described further (Tables 9 and 10).

Table 9

Desired Properties of Non-Polymerized Compositions

| Properties | Layer type | | |
|--|--|---|-------------------|
| | Base layer | Pigmented layer | Top layer |
| Viscosity η , Pa·s | $\eta = 4-7$ Pa·s | $\eta = 3-5$ Pa·s | $\eta = 1-3$ Pa·s |
| | η values determined by the viscosity of BDA and KM, the ratio of the content of these components [Chapter 4.1], content of additives [Chapter 5.1] | | |
| Thixotropic properties | Thixotropic properties given by dispersed additives [Chapter 5] | | |
| Polymerization time t_p , s | $t_p < 30$ $T_{MAX} < 70$ t_p and T_{MAX} values are determined by the chemical nature and content of the polymerization initiator [Chapter 3]. Chemical nature and content relations of BDA and KM [Chapter 4] | | |
| Heat effect of polymerization T_{MAX} , °C | | | |
| Color ΔE | Colorless | ΔE ΔE is determined by the nature and content of the pigment color [Chapter 7] | Colorless |
| Stability of the pigmented system | Not decisive | The pigment does not sediment in 3 months at 50 °C | Not decisive |
| | | Achieved by adding special additives [Chapter 5.1] | |

After the development and testing phase of the compositions in laboratory, tests on natural nails are performed by manicure masters for their customers.

The properties of the polymerized coating for all composites are tested on the first and third day after polymerization, as the coatings show a strong post-cure effect [12], [13].

To date, the longest post-polymerization time studied by other authors is 48 h [12], [13], but our studies show that the properties change on the second day and the test readings stabilize on the third day.

Table 10

Desired Properties of Coatings

| Major properties | Layer type | | |
|--|---|-------------------------|---|
| | Base layer | Pigmented layer | Top layer |
| Set of physico-mechanical indicators in tension: σ_B , MPa; ϵ_B , %; E , MPa | $\sigma_B = 10-35$, $E \geq 200$ Pa | | |
| | Compositions σ_B and E determine the values of UV polymerized pure BDA σ_B and E [Chapter 4.1], KM content in the composition [Chapter 4.3], content of additives [Chapter 5.2] | | |
| | $\epsilon_B = 10-70$ % | $\epsilon_B = 40-160$ % | $\epsilon_B = 10-30$ % |
| | lower ϵ_B values correspond to higher E values [chap. 4.3., 5.2.] | | |
| Surface hardness HV , MPa | $HV > 30$ MPa | $HV > 30$ MPa | $HV > 50$ MPa |
| | Higher HV values correspond to higher E values [Chapter 4.3] | | |
| Surface gloss Gl , GU | Not decisive | Not decisive | $Gl \geq 70$ |
| | | | Gl determined by the composition of comonomers and additives [Chapters 4.3 and 5.2] |
| Abrasion resistance: surface gloss value Gl^* after abrasion resistance test, GU | Not decisive | Not decisive | $Gl^* \geq 60$ GU |
| | | | Gl determined by the composition of comonomers and additives [Chapter 5.2] |
| Relationship of coating adhesion strength to nail surface A_S , MPa | $A_S > 2$ | Not decisive | Not decisive |
| | A_S determined by the composition of comonomers and additives [Chapters 4.4 and 5.3] | | |
| Durability of adhesion when removing the coating A_N , min | $A_N \leq 5$ | Not decisive | Not decisive |
| | A_N determined by the composition of comonomers and additives [Chapters 4.4 and 5.3] | | |

This observation has allowed to evaluate both the raw materials entering the coatings and the final formulas more objectively within the company *SIA Kinetics Nail Systems*. This allowed to avoid many customer complaints about the batches produced and find the production batches in a timely manner that do not meet the formula acceptance criteria.

The development methodology of the created formula was the basis for the development of guidelines for creating new formulas, which allows to save a lot of time for creating new products. In the initial period of operation in laboratory (2011–2014), the time spent on the development of each new formula was from 2 to 4 years. Currently (2021) it takes 6–18 months to develop a new formula.

This optimization of the research and development laboratory work allowed *SIA Kinetics Nail Systems* to rank among the top 5 best nail UV coating manufacturers in the world and to export Latvian products over 45 countries around the world.

CONCLUSIONS

1. The developed compositions of urethane diacrylates and monoacrylates, which cure under the conditions of UV-activated copolymerization process, meet the requirements of cosmetic varnishes: UV radiation parameters (spectrum: 370–410 nm, power 36 W), irradiation duration (<30 s), maximum exothermic effect temperature (<70 °C), forms cross-linked structure coatings with high strength-deformation, surface hardness, surface light reflectance, adhesion and other parameters.
2. The selected urethane diacrylates (E8, E10, E26) due to their unacceptably high viscosity (15–80 Pa·s) cannot be used alone to form cosmetic coating systems. By forming urethane diacrylate compositions with significantly lower viscosity (10–20 mPa·s) copolymerizable compounds – monoacrylates (KM): hydroxypropyl methacrylate (HPMA), tert-butylcyclohexyl acrylate (TBCHA), tetrahydrofurfuryl acrylate (THFA) and diacrylate: ethylene glycol dimethacrylate (EGDMA), the systems have been obtained, whose viscosity is within the permissible range (1–5 Pa·s).
3. The selected photoinitiator 2,4,6-trimethylbenzoylphenylphosphate (TMBFF) at a content of 0.8 % by weight in the composition of urethane diacrylates and monoacrylates provides the highest UV- activated copolymerization yield: the highest growth rate of unsaturated bond conversion $K_{C=C}$, the highest value of the achieved temperature, not exceeding the permissible total value of the coating temperature (70 °C).
4. A method for evaluating the flowability of compositions has been developed, which is based on measurements of the droplet diameter D at time t . The correlation of $D_t = \text{const}$ value with the value of composition viscosity η is shown, which allows to use the method of flow assessment instead of the most labor-intensive and material-intensive viscosity measurement.
5. The values of surface tension σ_{AG} of non-polymerized compositions are in the range from 36 mJ/m² to 43 mJ/m². The compositions wet the model surface of the natural nail well (bovine nail): showing an equilibrium wetting angle θ in the range of 31–49°. The values of compositions σ_{AG} and $\cos\theta$ correlate with each other according to the Young equation. As the wetting capacity of the composition increases (the value of θ decreases), the adhesion bond A_S of the polymerized coating to the coated surface increases.
6. At the content of 35 % of the studied KM in the composition, coatings with high values of the tensile elastic modulus E (500–900 MPa) and surface hardness HV (100–230 MPa) of the polymerized layer were obtained. These parameters are mainly determined by the degree of cross-linking of the components achieved in the copolymerization process: density of cross-links ν and average statistical molecular weight of the polymer between the nearest cross-links M_C , calculated from the corresponding E values.

According to the degree of cross-linking reached, KM is similar: THFA < HPMA < TBCHA < EGDMA.

7. All compositions show a post-cross-linking effect in the form of a noticeable increase in the modulus of elasticity E of the coating and the surface hardness HV within 3 days after photopolymerization. The higher the initial crosslink density is achieved, the smaller is the increase in E and HV .
8. There is a direct correlation between the adhesion bond A_S of the coating to the surface to be coated and the loss of adhesion bond t_A when exposed to solvents. Higher A_S values correspond to higher t_A values.
9. In the presence of certain macromolecular additives (1–2 %) in the composition, a specific adhesion relationship is formed between the coating and the nail surface. The coating degrades more easily by exposure to a solvent during the removal of the coating.
10. Disperse silica as an additive (particle size 1–10 μm) imparts pseudoplasticity to non-polymerized compositions in the shear rate range of 5–20 s^{-1} , as well as thixotropic properties in the range of 60–90 s shear duration.

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