Additives in UV-activated urethane acrylate polymerization composite coatings

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Abstract. Thin UV curable coating systems is an important research field from the industrial perspective due to the improved environmental profile and wide varieties of characteristics. When used for short-term applications as coatings on natural nail for esthetical and medical reasons, the system may be manipulated to attain various properties, either desired or required by the manufacturer e.g. ensuring both excellent long-term properties (deformability, toughness, and good adhesion) and short-term properties (ability to be destroyed quickly after use). Performance of thin UV curable urethane acrylate composite coatings was investigated depending on the content of the additive. Nitrocellulose (NC), cellulose acetate butyrate (CAB), sucrose benzoate (SB), and silica were evaluated to determine their influence on unreacted composite characteristics (viscosity, suspension pigment stability) and reacted film characteristics (ultimate strength, elongation at break, surface gloss, surface micro hardness, and film adhesion loss). According to the tests performed all additives increase the modulus of elasticity. CAB and NC increase the elongation at break values, and strongly increase the uncured gel viscosity, what makes it inconvenient for application.

Key words: UV-curable coatings, urethane acrylate, silica, nitrocellulose, cellulose acetate butyrate, sucrose benzoate.

1. INTRODUCTION

Light induced curable polymer coating systems have many industrial applications because of their excellent mechanical properties, low energy consumption, reduced VOC emissions, and rapid curing even at room temperature [1]. Acrylic coating systems are among the most broadly used ones in various industrial applications [2]. The current research has mainly focused on the long-term properties, necessary for coating industry (wood, metal, etc.) and dentistry with good physical–mechanical properties and excellent adhesion [3–5]. New coating applications for specific purposes need good long-term properties of the coating and also short-term functionality – the ability to be destroyed after a period of use; for example, for nail coatings [6,7]. Such short-term properties have been studied mainly for the biopolymers and their application for biodegradable items (packaging etc.) [8–10].

Mechanical and other properties of the acrylic coating system depend on the composition, created by acrylic functional monomers and oligomers, photo initiators, and other additives [1,2,6]. Supplementing the polymer system with various additives including biopolymer fillers, one can impart short-term functionality (good destruction in solvent media) for the coating but also change mechanical and other properties. In addition, the choice of biopolymers can reduce impact to health and environment due to low toxicity and renewable origin [6–10].

Compared to other coatings, the nail coatings industry occupies a very small niche; therefore only some patents have been issued [7] and the scientific literature is rather scarce.

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In order to achieve ideal compatibility, the nail coating system has to resemble the properties of the natural nail, which are: strength, hardness, flexibility toughness, and wear resistance, which is the ability to resist abrasion [11]. Additional important parameters for nail coating systems are suspension pigment stability, rheological properties (viscosity), and surface gloss. Such properties can be influenced by modifying the composition with different filler systems [1,8–10,12–14].

Assuming that good mechanical and rheological properties of the acrylic system can be maintained, but short-term properties are allocated by the use of specific fillers, we examined a novel composition: an acrylic base modified with silica of mineral origin or various organic renewables, nitrocellulose (NC), cellulose acetate butyrate (CAB), and sucrose benzoate (SB) with the aim to find the optimal system for maintaining necessary long-term mechanical and adhesion properties, and obtaining short-term properties needed for fast destruction after the usage period.

Nitrocellulose and CAB are known as film forming polymers [8–10]. Sucrose benzoate is known for its good compatibility with the acrylic system [7] used in forming high quality coating films. Silica builds a molecular network that stabilizes the emulsion in the presence of insoluble compounds, e.g. pigments, as well as creates thixotropy. Silica also has positive impact on mechanical properties [12–14].

The performance of various compositions, consisting of a simple varnish system (urethane acrylate oligomers, monomer, photo-initiator) and different additives (silica, SB, CAN, nitrocellulose) was tested to explore additive effects on long-term and short-term characteristics of the coatings.

2. EXPERIMENTAL

2.1. Materials

Materials were selected to ensure two different goals: long-term mechanical properties (good adhesion) and short-term properties (quick destruction in the solvent media). The main composite ingredients (oligomers, monomer, photoiniciator) were selected as follows. The base consisted of three different commercially available bifunctional urethane acrylate oligomers: Exothane 8, Exothane 10, and Exothane 26 (Esstech, USA). Uncured oligomers are characterized by medium viscosity (10 000–70 000 mPa·s), while cured oligomers have high elasticity (elongation at break 40–80%). As a monomer, hydroxypropylmethacrylate (HPMA) (Esstech, USA) was used.

For the initiation of radical photopolymerization reactions ethyl-2,4,6-Trimethylbenzoylphenylphosphinate (Lucirin TPO_L) (BASF, Germany) photoiniciator was applied [6].

Four different additives were evaluated to ensure necessary long-term mechanical properties. Two cellulose based additives were chosen: Nitrocellulose E400 (DOW Europe, Switzerland) and cellulose acetate butyrate (CAB-551-0.2) (Eastman, The Netherlands). Sucrose benzoate with the commercial name Miramer SB (Miwon, Corea) was chosen for examination after a patent study [7]. Fumed silica HDK H15 (Wacker, Germany) was chosen to improve secondary composite properties: to reduce pigment particle sedimentation and improve surface levelling [12–14].

2.2. Sample preparation

To avoid untimely polymerization, each composition was mixed in yellow light (570–590 nm). The optimal content of each additive was previously determined [6]. All additives at optimal concentrations, depending on the additive, were mixed by mechanical stirring (100 rpm for NC, CAB, SB and 3000 rpm for silica) in a monomer, at temperature 50 °C for 5 min (for NC, CAB, SB) or 60 min (for silica) to achieve a fully dispersed premix. Microscope Model DC5-420TH was used for visual inspections to evaluate mixture homogeneity. After premix, the prepared definite content (23 wt%) of each oligomer, monomer (29 wt%), and photoiniciator (2 wt%) were added and blends were further stirred at 100 rpm at ambient temperature for 30 min. After preparation, systems were stored at 40 °C for 12 h to lose air inclusions. Further, the mixed gel was used for stability tests or was applied on the substrate, cured and films were obtained.

2.3. Coating formation

The coating was formed on the surface of acetone treated teflon sheets or aluminum sheets with Bykodrive from BYK Gardner applicator with 10 mm/s. The coating of 200 μm was cured under UV lamp (KP800LED, luminous intensity 130 mw, $\lambda = 405$ nm) (YI Liang Electron Technology Co, China) for 30 s. The curing time of photopolymers is dependent upon the dose intensity and wavelength of the UV light, which is found before. Initiation of polymerization requires precise matching of the photoiniciator and the UV light source [15]. To avoid oxygen inhibition activity on the coating surface, it was coated with transparent PE film with thickness 50 μ. After curing, PE film was removed from the substrate.

2.4. Test methods

Natural nail has a complicated porous structure and may have different types (oily, dry) and conditions (brittle, thin, normal). Human habits and lifestyle affect the nail structure [11], therefore there is no close material to

natural nail to test the adhesion. Based on previous experience [3–6] we put forward the hypothesis that adhesion is dependent on the elasticity and toughness of the coating as the coating should be as flexible as substrate and as tough as substrate to ensure crack resistance. To evaluate these primary characteristics, a tensile strength test was performed. To ensure coating short-term functionality, additive influence on destruction ability was studied. Other characteristics such as mixture viscosity, pigment stability in the suspension, coating surface gloss, and coating structure by gel fraction determination were also explored.

The mechanical properties of UV-cured films were determined by standard tensile stress–strain tests to measure ultimate tensile strength (σ) and elongation at break (ε). Standard tensile stress–strain experiments were performed at room temperature on tensile tester BDO FB020TN (Zwick Roell, Germany) according to the requirements of LVS EN ISO 527-3:2000 [16] and [2,6,17] (sample shape: double blade films; the speed of the upper cross-head: 10 mm/min). Samples were placed in a universal testing facility holder and deformed at a rate of 25 mm/min. The results are the mean values of 5–7 independent measurements.

Coating degradability was evaluated using 95% acetone solution in water; 200 μm of uncured mixture was applied on aluminium sheets (on an area of 5 cm × 5 cm), and cured under UV lamp for 30 s. Coatings were left for 72 h to assure complete polymerization, and afterwards coatings destructivity was evaluated. Coatings were wrapped in paper pads impregnated with acetone, coated in aluminium foil (100 μm thickness) to avoid solvent evaporation, and kept for 1–5 min. After each 30 s period, coating adhesion to the substrate was evaluated using 5 SAM (scratch adhesion and mar tester) scratches (with distance 5 mm, force 250 g) horizontally and vertically. Adhesion of the coating on the substrate was measured with the SAM device S.A.M PA-5050 (Gardco, USA) where the Hoffman testing concept is used [18]. When the 100% adhesion loss between the substrate and coating appears, effective soak-off time was detected.

Additive effect of the urethane acrylate mixture viscosity was determined by Brookfield viscometer DV-II + Pro (Brookfield Engineering Laboratories, USA). The needle was chosen according to the composition tested. Three parallel measurements for each composition were made at a speed of 100 or 60 rpm, measuring for 3 min and recording the results every 30 s. The average result from the measurements was taken.

To evaluate the additive effect on the pigment sedimentation stability, tests on pigmented uncured mixtures were performed with 2% white pigment TiO_2 (Durlin, France) and 0.01% red pigment (RED 6, Durlin, France) in a thermostatically controlled environment at the temperature of 50 °C for 4 weeks. After each

7 day period, the pigment sedimentation was evaluated optically. The test was considered to be passed (or the pigment system was regarded as stable) if after 4 weeks there was no difference in the colour of the mixture and pigment sedimentation had not been observed.

Gloss measurements were carried out using the Novo Gloss Lite Gloss Meter (Rhopoint Instruments Ltd., Great Britain) on black substrate at an angle of 60°. The average from 10 parallel samples was taken.

Micro hardness experiments were chosen to evaluate coating surface abrasion resistance. The data were obtained using Vickers microscope M41 at 200 g statistic force.

The measurements of the structural properties and of the curing rate were performed by the evaluation of the gel fraction of cured films. The gel fraction was measured by Soxhlet-type extraction in an acetone vapour environment for 40 h (2 parallel samples) until a constant weight. The gel fraction was then calculated [19,20].

3. RESULTS AND DISCUSSION

3.1. Mechanical characteristics

The tensile stress–strain (σ–ε) curves of the UV cured films up to the break point were determined. The following parameters were determined from these curves: initial elastic modulus $E = \lim(d\sigma/d\varepsilon)|_{\varepsilon \to 0}$, which characterizes the resistance of the initial structure of the polymer at low strain values when structure transformations have not yet occurred [17], tensile stress σ_y and elongation ε_y at the yield point, and the tensile strength σ_B and elongation at break ε_B. The data obtained are represented in Figs 1, 2, and 3.

Evaluating the modulus of elasticity E for the composite with different additives, it was found that all additives, to a greater or lesser extent, caused an increase in E. The greatest impact on the E increase had addition of NC (21% increase) and SB (7% increase) compared to the pure film (384 MPa). Composite films, containing these additives, also showed the highest
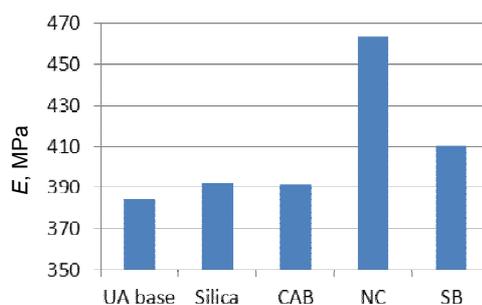

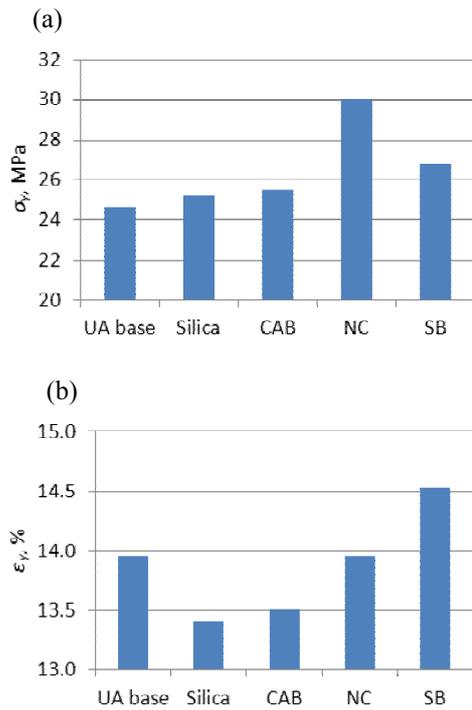**Fig. 1.** The effect of the additive on the modulus of elasticity of the film.

(a)

(b)

Fig. 2. The effect of the additive on the elongation (a) and tensile strength (b) at the yield point.
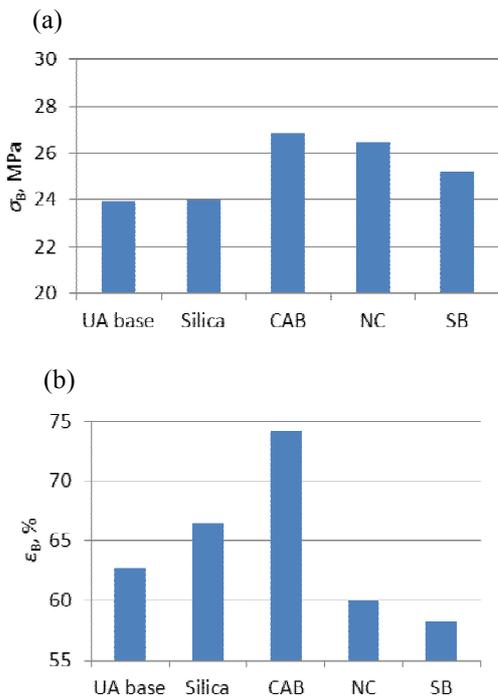

(a)

(b)

Fig. 3. The effect of the additive on the elongation (a) and tensile strength (b) at the break point.

yield stress σ_Y and to some extent higher break σ_B values. The equally high value of σ_B (27 MPa) of CAB containing composites is likely explained by the fact

that these composites showed the most pronounced orientation during the deformation process, largely due to the best deformability of these systems, i.e., the greatest deformation at break ε_B values (74%), which were 18% higher than of the base composition (63%).

The highest value of the stress at the yield point σ_Y was reached for systems with NC, increasing pure film strength by 20%. Evaluating mechanical test results, they showed compatibility effect between synthetic urethane acrylate polymers and 3 biopolymers; also inorganic silica showed good compatibility with the urethane acrylate system. Evaluating coating tensile strength and deformability, CAB and NC seemed to be the most appropriate additives for nail coating applications.

3.2. Coating degradability

By evaluating coating degradation ability in solvent media, nitrocellulose showed the highest influence on the adhesion loss. After solvent treatment (Table 1), the coating with nitrocellulose degraded in acetone media in 1 min, while film without any additives needed 2 min and 30 s to degrade. Compared to the pure film, CAB and silica decrease degradation time by 1 min, while SB had the lowest impact on film solubility. NC and CAB have higher particle size and they can interrupt and impair the urethane acrylate network. Because of the highly dispersed silica particles, cured film can also be more easily destroyed. The particles prevent the occurrence of high quality oligomer and monomer polymerization; the cured network is not as dense as the network without additives and solvent influence on adhesion loss can be higher. To understand the adhesion loss process in solvent medium more deeply, more detailed experimental data, especially microscopic observations, are necessary.

3.3. Mixture viscosity

All additives increase viscosity of the uncured gel mixture (Table 2) while silica and SB, due to their smallest particle size, had the smallest impact on that. Addition of 2% NC almost doubled viscosity of the clear base while CAB increased it by 70%. Silica and SB has the smallest impact on the viscosity increase.

Table 1. Additive influence on UA coating properties

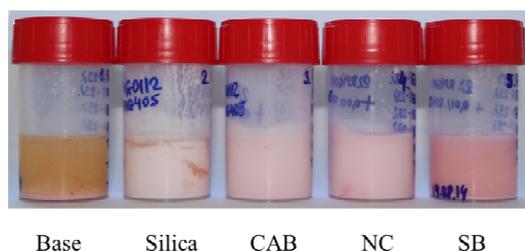| Additive	GF, %	HV, MPa	Gloss at 60°, GU	Adhesion loss time, min
UA base	96	50	86	2:30
Silica	98	64	53	1:30
CAB	96	58	58	1:30
NC	97	54	52	1:00
SB	95	50	67	2:00

Table 2. Additive influence on UA mixture viscosity and suspension pigment stability

Additive	wt%	Stability of suspension	Initial viscosity	
			mPas	rpm
UA base	0	No	4973	100
Silica	1	Insufficient	5890	60
CAB	2	Stable	8453	60
NC	2	Stable	9700	60
SB	2	No	5397	100

Additive concentration 2% is too high to ensure required gel viscosity. Highly increased viscosity is an inconvenience when applying the coating; the lower the viscosity, the easier the application. Therefore a compromise between mechanical characteristics, adhesion and viscosity should be found by decreasing the additive concentration in the content or mixing different additives with different concentrations.

3.4. Pigment stability

One of the most important coloured coating characteristics is pigment distribution and stability. When adding pigments to a urethane acrylate base system, pigment stability in this suspension should be ensured. Pure base without any additives does not provide this function. From previous experience it is well known that silica can build a network in UA gels, preventing pigment and other bigger particle sedimentation [12–14]. Results of the test performed are shown in Fig. 4 and demonstrate that at these mixture viscosities polymeric additives such as CAB and NC can also provide pigment stability function. These additives can make a gel. Increased viscosity and internal forces between the particles, provided by OH groups, means that stability can be ensured. Tests at 50 °C on silica after 4 weeks did not show the best result, as some clear base areas are found. This can be explained as inefficient sample preparation, where not all silica particles were fully dispersed in the system. Sucrose benzoate cannot provide the stability of the pigmented suspension and cannot be used as additive for pigment stabilization in the gel.

Fig. 4. Additive effect on pigment stability of pigmented suspensions after 4 weeks at 50 °C.

3.5. Coating microhardness and gloss

Gloss is a measure of the ability of a coating surface to reflect a light beam in a particular angle without scattering. This is an important property of the coatings, especially of those used for aesthetic and decorative purposes [1]. The final gloss of the cured samples is mainly dependent on the used UV light intensity and photoiniciator amount. The amount of additives also considerably affects final gloss of the coating (Table 1). Surface gloss can be evaluated together with microhardness as both of these characteristics describe the surface properties. The highest gloss values were reached for a clear base, while all of the additives decreased the surface gloss. Sucrose benzoate had the smallest negative impact on the surface gloss, decreasing the initial value by 22%.

All additives except SB increased coating surface microhardness, therefore, abrasion increased. The highest hardness values were reached in the case of the SiO_2 containing composite, which increased it by almost 30%. Increment in microhardness was observed in comparison to clear coating.

3.6. Structure

Structural studies by gel fraction extraction showed that both the base composition and all composites containing additives had the same high degree of crosslinking. Depending on the additive, the degree of crosslinking varies within a narrow range of 95–98%. Additive concentration is too small to show considerable effect on the formation of the urethane acrylate network. Higher concentration effect should be studied to evaluate the additive effect on cured coating of urethane acrylates.

4. CONCLUSIONS

In this work four different additives were evaluated to find their influence on short- and long-term properties of the urethane acrylate coating systems.

The best mechanical properties were found with NC, which increased film toughness (Young modulus growth 21%) and CAB, increasing film elasticity (elongation at break growth 18%).

Evaluating short-term functionality of the coatings, we found that all additives decreased the destruction time, but the most efficient was NC, with CAB and silica following. Characteristics such as mixture viscosity, pigment stability in the suspension, coating surface gloss, microhardness and coating structure by gel fraction determination were also explored. All additives increased uncured mixture viscosity, especially CAB and NC, therefore from a coating application perspective the concentration of these additives should be reduced. Applications of CAB and NC ensured pigment stability function.

Sucrose benzoate showed the highest surface gloss values compared to other additives. Silica improved cured film surface microhardness. There was no effect of additives observed on gel fraction data, therefore further studies should be done, diversifying additive amount, testing structure optically to find the correlation between cured coating structure and adhesion loss.

REFERENCES

1. Jančovičová, V., Mikula, M., Havlinova, B., and Jakubikova, Z. Influence of UV-curing conditions on polymerization kinetics and gloss of urethane acrylate coatings. *Progr. Org. Coat.*, 2013, **76**, 432–438.
2. Milinavičiūtė, A., Jankauskaitė, V., and Narmontas, P. Properties of UV-Curable Hyperbranched Urethane-Acrylate Modified Acrylic Monomer Coatings. *Mater. Sci. (Medžiagotyra)*, 2011, **17**(4), 378–383.
3. Yaldiz, C. E., Veinthal, R., Gregor, A., and Georgiadis, K. Mechanical properties of thin hard coatings on TiC-NiMo substrates. *Estonian J. Eng.*, 2009, **15**, 329–339.
4. Harry, E., Rouzaud, A., Ignat, M., and Juliet, P. Mechanical properties of W and W(C) thin films: Young's modulus, fracture toughness and adhesion. *Thin Solid Films*, 1998, **332**, 195–201.
5. Atanacio, A. J., Latella, B. A., Barbé, C. J., and Swain, M. V. Mechanical properties and adhesion characteristics of hybrid sol–gel thin films. *Surf. Coat. Tech.*, 2005, **192**, 354–364.
6. Grigale-Sorocina, Z. et al. UV-activated polymerization composites. *Mater. Sci. (Medžiagotyra)*. Forthcoming.
7. Koschar, M. Easily removable nail polish composition. Germany Patent DE102011102661 A1, 29 November 2012.
8. Misbah, S., Khalid, M. Z., Haq N. B., Tahir, J., Rizwan, H., and Zuber, M. Modification of cellulosic fiber with polyurethane acrylate copolymers. Part I: physicochemical properties. *Carbohyd. Polym.*, 2012, **87**, 397–404.
9. Gällstedt, M., Törnqvist, J., and Hedenqvist, M. S. Properties of nitrocellulose-coated and polyethylene-laminated chitosan and whey films. *J. Polym. Sci. Polym. Phys.*, 2001, **39**, 985–992.
10. El-Shafee, E., Saad, G. R., and Fahmy, S. M. Miscibility, crystallization and phase structure of poly(3-hydroxybutyrate)/cellulose acetate butyrate blends. *Eur. Polym. J.*, 2001, **37**, 2091–2104.
11. Schoon, D. D. *Nail Structure and Product Chemistry*. Cengage Learning, Milady, 2nd ed., 2005.
12. Zamani, Y., Lahijania, K., Mohseni, M., and Bastani, S. Characterization of mechanical behavior of UV cured urethane acrylate nanocomposite films loaded with silane treated nanosilica by the aid of nanoindentation and nanoscratch experiments. *Tribol. Int.*, 2014, **69**, 10–18.
13. *There's a Secret to Perfect Coatings and Inks: Hdk® Pyrogenic Silica*. Wacker Silicones, Munich, 2006.
14. Horacio, E. B. and Roberts, O. W. *Colloidal Silica: Fundamentals and Applications*. CRC Press, Taylor & Francis Group, U.S.A., 2006.
15. Džunuzović, E. S., Tasić, S. V., Božić, B. R., Džunuzović, J. V., Dunjić, B. M., and Jeremić, K. B. Mechanical and thermal properties of UV cured mixtures of linear and hyperbranched urethane acrylates. *Progr. Org. Coat.*, 2012, **74**, 158–164.
16. [ISO] International Organization for Standardization. 1995. Plastics – Determination of tensile properties – Part 3: Test conditions for films and sheets. BS EN ISO 527-3: 2000th Plastic (in Latvian).
17. Gonçalves, F., Boaro, L. C., Ferracane, J. L., and Braga, R. R. A comparative evaluation of polymerization stress data obtained with four different mechanical testing systems. *Dent. Mater.*, 2012, **28**, 680–686.
18. Koleske, J. V. *Paint and Coating Testing Manual*. American Society for Testing and Materials, Philadelphia, 1995.
19. Marzocca, A. J., Garazza, R.-L., and Mansilla, M. A. Evaluation of the polymer–solvent interaction parameter χ for the system cured polybutadiene rubber and toluene. *Polym. Test.*, 2010, **29**, 119–126.
20. Salamone, J. C. *Polymeric Materials Encyclopedia*. Twelve Volume Set, CRC Press, USA, 1996.

Lisandid UV-kiirgusega polümerisatsiooni käigus tekitatud komposiitkatetes

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Antud töös uuriti nelja erineva lisandi mõju õhukese kile katete lühikese ja pikaajalise toimega omadustele. Lisanditena kasutati ränidioksiidi, nitrotselluloosi (NC), tselluloosi atsetaat-butüraati (CAB) ja sahharoosi bensoaati (SB) ning mõõdeti mehaanilised omadused ja struktuuri karakteristikud. Parim tulemus saavutati nitrotselluloosiga, mis suurendas kile sitkust, ja CAB suurendas kile elastsust. Katsetulemused näitasid, et kõik lisandid vähendavad lagundamise aega, kuid kõige efektiivsemateks olid NC ja CAB, neile järgnes ränidioksiid. Uuriti ka lisandite mõju sellistele omadustele, nagu segu viskoossus, pigmendi stabiilsus suspensioonis, katte pindläige, mikrokõvadus ja katte struktuur. Läbiviidud testide tulemuste järgi saab öelda, et kõik valitud lisandid parandavad komposiidi mõnd omadust, kuid pole võimalik valida ainult üht.