

Effect of Additives on UV-Activated Urethane Acrylate Polymerization Composite Coatings

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An increased demand for new and improved coating systems, for environmental & health & safety and performance reasons, have appeared during the recent decades. Currently, there is new interest in preparation of thin UV curable urethane acrylate (UA) composite coatings with short-term properties. Cellulose based additives: nitrocellulose, cellulose acetate butyrate, sucrose benzoate and silica were evaluated to determine their influence on unreacted composite characteristics (viscosity, pigment suspension stability) and characteristics of cured film (ultimate tensile strength, elongation at break, surface gloss, surface scratch resistance and film adhesion loss time). The most suitable additive content was found to provide required viscosity. All additives increase surface scratch resistance, but cellulose based additives increase surface gloss values and decrease the time of adhesion loss. Silica has great effect on the interaction between linear and hyperbranched urethane acrylates, which has crucial influence on the stability of uncured pigmented mixture samples.

Keywords: UV-curable, coatings, photopolymerization, urethane acrylate.

1. INTRODUCTION

Light induced curing in polymer coating systems has been intensively studied because of its association with environmental protection, lower energy consumption and rapid curing even at the room temperature [1]. Compared to thermally cured coatings, the use of UV-radiation curable coatings offers advantages, such as instant drying, broad formulating range, reduced energy consumption and coating of heat sensitive substrate [2]. Therefore, UV-curing technology has been considered as an alternative to traditional solvent-borne coatings, because of its eco-compatible manufacturing process and excellent properties, such as high hardness, gloss, scratch and chemical resistance [1]. The main components of UV curable photopolymer compositions are monomers, oligomers, and photoinitiators. Most commercially used UV curable compositions are based on acrylic functional monomers and oligomers [3]. Their properties are influenced by their functionality, the type of isocyanate, and the type and molecular weight of polyol used in the synthesis. The higher functionality gives greater reactivity and harder cured films with good scratch and chemical resistance, but at the same time causes increase of resin viscosity [4]. The monomer is used to control formulation viscosity (reactive diluent) but it affects both the cure speed and the extent of polymerization, and the properties of the cured film. Some of the commonly used acrylic monomers (especially the multifunctional acrylic monomers) have a strong odor, and are skin and eye irritants. Due to their low molecular weight, additional

problems may arise as there could be a high amount of extractables and considerable shrinkage could occur. This causes poor adhesion to substrate [5]. The chemical structure of the monomers and oligomers determines the physical properties of the formulation before and after curing [6]. Photoinitiation is one of the most efficient methods for achieving quasi-instantaneous polymerization as it transforms a liquid molecule into a solid polymer material in less than 1s [7]. The high reactivity of acrylate monomers and oligomers means that radical-type polymerization can be initiated with only a small amount of photoinitiators (Fig. 1) [3].

Increased demands for new and improved coating systems, for both environmental and performance reasons, have appeared during recent decades. Techniques such as low temperature curing systems, and high-solids have gained increased interest and obtained significant market shares. Although improved in many aspects, for technical reasons, these systems still have limited use in certain applications [8]. Efficient way to improve the properties of uncured system as thixotropy, anti-sedimentation, pigment wetting is supplementing the composite material with different additives [9, 10, 11]. Coating additives belong to a broad and diffuse category of key components used in a coating formulation. The function of any additive is very specific in nature and provides a range of properties to a coating [12]. There are few articles in the scientific literature about additives for UV curing coatings, although they are widely used in the industry. The most reported additive is nano-silica, which has been widely used in coating industries to decrease pigment particle sedimentation and surface leveling [13] because interfacial interactions [9, 14].

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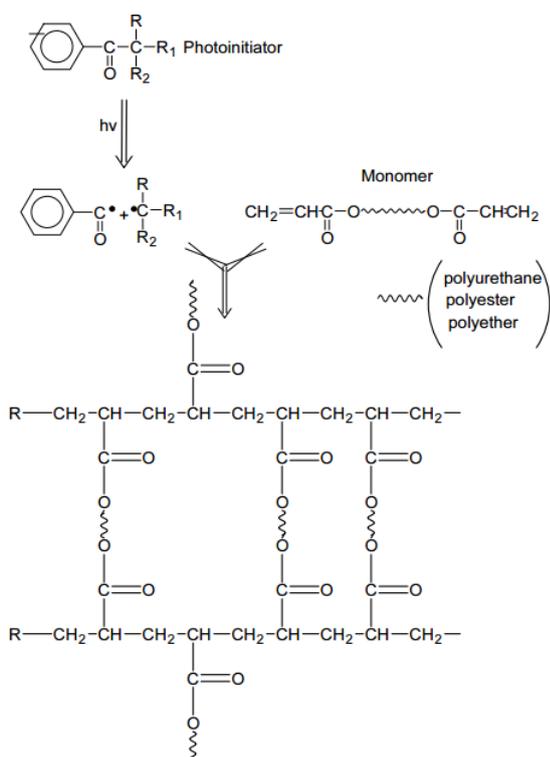


Fig. 1. UV-induced radical polymerization of a diacrylate monomer leading to a photo cross-linked polyacrylate network [3]

All previous studies have focused on creating coatings with long-term properties, but in recent years the coating industry has devoted much research in the direction of making eco-friendly coating material [2]. Cellulose derivatives [10], chitosan and other biopolymers [15] are of interest in improving the composite eco-profile [16, 17], especially when these applications are designed for medicine, dentistry and cosmetics [12, 15, 17].

In the last decade new market space for coating applications with short-term requirements has appeared. The market space includes medicine and cosmetics such as natural nail coatings [18, 19]. Short-term coating applications haven't been reported yet, only some patent applications have been submitted [20, 21, 22]. The formulation of appropriate coatings is critical to achieve not only adhesion loss from substrate (within 5–30 min after treatment by cosmetically permitted solvent acetone) but also pigment suspension stability, reduced viscosity (3000–4500 mPas), increased deformability (tensile strain 40–150 %), degree of conversion (50–90 %) and high surface gloss (> 70 GU). Novel additives have been searched to ensure the required characteristics and easy removability from the substrate after loss of functionality. The aim of this study was to improve specific coating application characteristics and to optimize the composition of a system composed of urethane acrylate oligomers, monomer, photoinitiator by addition of different supplements.

2. EXPERIMENTAL

2.1. Materials

Different formulations of the UV curable coating consisting of urethane acrylate oligomers, monomer and

photoinitiator were studied. Hydroxypropylmethacrylate (HPMA) (Esstech, USA) was used as a monomer (Fig. 2) (Purity > 97 %, Inhibitor MeHQ 225 ppm). Photoinitiator ethyl 2,4,6-Trimethylbenzoylphenylphosphine (Lucirin TPO_L) (BASF, Germany) was applied for the initiation of radical photopolymerization reactions. Its chemical structure (Fig. 3) and absorbance spectrum (Fig. 4) are shown below. Three different commercially available difunctional urethane acrylate oligomers were used for film forming: Exothane 8, Exothane 10 and Exothane 26 (Esstech, USA). Their main properties are shown in Table 1. Cured oligomers are characterized by rather high deformability (elongation at break 40–80 %).

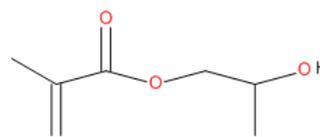


Fig. 2. Chemical structure of HPMA

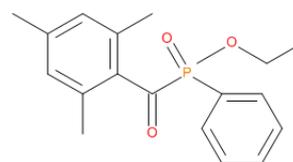


Fig. 3. Chemical structure of Lucirin TPO_L

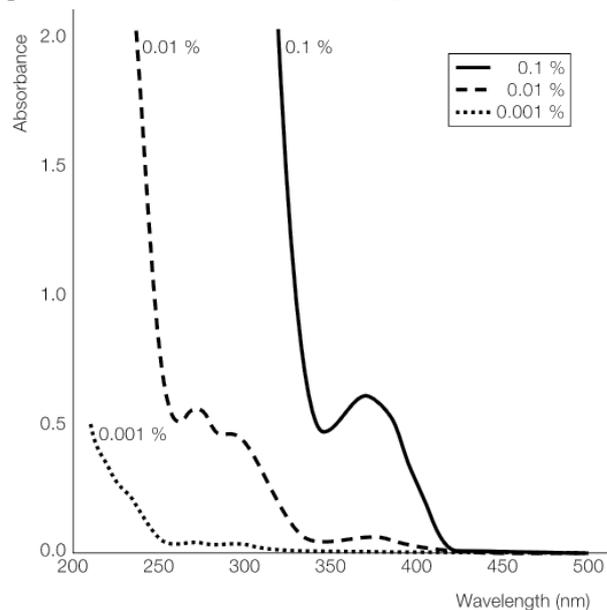


Fig. 4. Absorbance spectrum of Lucirin TPO-L in Ethanol

Four different additives were evaluated. Nitrocellulose E400 (NC) (DOW Europe, Switzerland) (molecular weight 400, film elongation at break 5–10 %, tear resistance 59–69 N/mm²) and cellulose acetate butyrate (CAB) (CAB-551-0.2) (Eastman, The Netherlands) (molecular weight 30000, melting point 130–140 °C, glass transition T = 101 °C) were selected as film former additives. Both of these additives were chosen to ensure the easier coating removability. Sucrose benzoate (SB) Miramer SB (Miwon, Corea) was chosen due to their excellent UV stability, unusual clarity and low solution viscosity [20, 21]. Fumed silica HDK H15 (Wacker, Germany) (BET surface area 175–225 m²/g, refraction index at 20 °C 1.46) was chosen

to reduce pigment particle sedimentation and to improve surface leveling.

Table 1. Major properties of base oligomers Exothane 8, Exothane 10 and Exothane 26 [AH1]

Property	Exothane 8	Exothane 26	Exothane 10
uncured			
Molecular weight	600–1300	700–1400	400–1000
Inhibitors	MeHQ* – 8 ppm	MeHQ – 22 ppm	MeHQ – 29 ppm
	BHT** – 584 ppm	BHT – 586 ppm	BHT – 3730 ppm
Viscosity (PaS)	30 110	15 510	70 000
cured			
Ultimate stress (MPa)	345	125	607
Tensile strength (MPa)	17	6	29
Tensile elastic modulus (GPa)	76.1	17	345
Elongation at break (%)	79	46	64
MeHQ* – Mono Methyl Ether of Hydroquinone BHT** – Butylated Hydroxytoluene			

2.2. Sample preparation

To avoid premature polymerization, each composition was mixed in a round bottom flask in yellow (570–590 nm) light. Preliminary tests were performed to find the best technology to bring the additive into the mixture and to evaluate the optimal concentration of each additive. All additives in the concentration range 0.5–3.0 wt.% (as % of total mixture) were mixed by mechanical stirring (100–3000 rpm) in monomer, at temperature 50 °C for 5–60 min to achieve a fully dispersed premix. Microscope Model DC5-420TH was used for visual inspections to evaluate mixture homogeneity. After premix, prepared definite content (26 wt.%) of each oligomer, monomer (20 wt.%) and photoinitiator (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, mixed gel was used for stability tests or was applied on 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 by use of Bykdrive applicator from BYK Gardner with the rate 10mm/s to reach film thickness 200 µm. The coating 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. Initiation of polymerization requires precise matching of photoinitiator and UV light source [1]. To avoid oxygen inhibition activity on the curing in coating surface, it was coated with transparent PE film with thickness 50µm. After curing PE film was removed.

2.4. Design of the experiments

Evidently additives will influence all characteristics of both the uncured mixture and the cured coating. Therefore in this work firstly viscosity and pigment suspension stability tests were performed to determine the optimal additive concentration. Based on the test results the best compositions were chosen for further tests, which are shown in Table 2: performed tests for uncured mixture and cured coating.

Table 2. Characteristics and relevant evaluation methods

Mixture	
Characteristic	Method
Pigment suspension stability	Stability test at 40°C
Viscosity	Brookfield viscosity
Degree of conversion	Gel fraction determination
Coating	
Characteristic	Method
Adhesion loss	Soak off in acetone
Scratch resistance	SAM
Strength deformation	Tensile tests

2.5. Test methods

To evaluate additive effect on pigment suspension sedimentation stability, tests on pigmented uncured mixtures were performed with 2 % white pigment TiO₂ (Durlin, France) and 0.01 % red pigment (RED 403, Kromachem, Germany) 40 °C for 4 weeks. After each 7 day period pigment sedimentation was evaluated optically. The test was considered to be passed if after 4 weeks there was no difference in the color of the mixture and pigment sedimentation wasn't observed.

Coating adhesion loss was evaluated using 95 % acetone solution in water. 200 µm of uncured mixture was applied on aluminum sheets (on area 3 cm x 3 cm), and cured under UV lamp for 30 s. Cured coatings were wrapped in paper pads impregnated with acetone, coated in aluminum foil (100 µm thickness) to avoid solvent evaporation and kept for 5–30 minutes. Adhesion of coating on the substrate was measured with SAM (Scratch Adhesion and Mar Tester) device S.A.M PA-5050 (Gardco, USA) where the Hoffman tester concept is used [24]. After each 2.5 minutes period, coating adhesion to the substrate was evaluated using 5 SAM scratches (with distance 5 mm, force 250 g) longitudinal and transversely. Effective soak-off time was detected when 100 % adhesion loss between substrate and coating is ascertained.

Additive effect on uncured urethane acrylate viscosity was determined by Brookfield viscometer DV-II+ Pro (Brookfield Engineering Laboratories, USA). Needle was used according to the composition tested. Three parallel measurements for each composition were made at 100 rpm, measuring for 3 minutes and recording results with a time interval of 30 seconds. Average result from the measurements was taken.

Scratch resistance to evaluate the additive influence on coating surface was measured with SAM device S.A.M PA-5050 (Gardco, USA). The trolley is pulled across the test sample and the effect, if any, of the “blade” is observed. SAM was used in the lower range of up to

250 grams and the imprint was measured on a 20-point scale marked on the SAM device according to STP 500, 5.1.2.5, Paint Testing Manual, published by the ASTM [24].

The mechanical properties of UV-cured films were determined by standard tensile stress-strain tests to measure ultimate tensile strength (σ_{max}) and elongation at break (ϵ_b). Standard tensile stress-strain experiments were performed at room temperature on Tensile tester BDO FBO20TN (Zwick Roell, Germany) according to requirements [25, 26] (sample shape: double blade films; the speed of the upper cross-head: 10 mm/min). The results present the mean values of five independent measurements.

The gloss measurements were carried out using the Novo Gloss Lite Gloss Meter (Rhopoint Instruments Ltd., Great Britain) at an angle of 60°.

Gel fraction was used as characteristic of degree of conversion in polymerization reaction. The gel fraction is measured by Soxhlet-type extraction in acetone for 8 hours and by drying the extracted gel until it has a constant weight in vacuum. The gel fraction is then calculated as a ratio of the weight of the acetone-insoluble part and the feed monomer and oligomer [27, 26].

3. RESULTS AND DISCUSSION

At the beginning of the experiments the best incorporation technology for additives was found using visual inspections with the microscope. It was found that additives such as NC, CAB and SB can be mixed in monomer with low shear rate stirring (100–300 rpm) and for shorter periods of time (10 min), but silica needs to be dispersed in monomer with high shear rotation (3000 rpm) for 30 min to achieve full dispersity of silica particles in acrylate gel.

Secondly suitable additive concentrations were determined. Uncured composition should prevent pigment particle sedimentation and viscosity should be less than 4500 mPas. NC and CAB in concentrations 2% can efficiently prevent the pigment particle sedimentation.

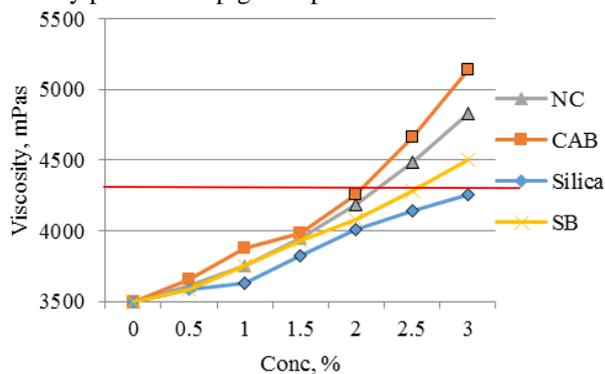


Fig. 5. The influence of additive content on UA base viscosity and pigment suspension stability. Stable concentrations are marked with black line around the point. Red line indicates the highest possible viscosity [AH2]

As higher concentrations of these additives strongly increase system viscosity (Fig. 5), 2% was chosen as appropriate additive concentration. Silica already at 1% can prevent the pigment particle sedimentation. This system also has the smallest viscosity, what makes the

coating application more convenient, therefore suitable concentration for it is found to be 1%. Silica already previously have been described as effective gelling agent for pigmented systems [11, 13]. Compositions with additive SB in concentration range 0–3% cannot prevent the particle sedimentation, therefore test concentration was chosen using viscosity data and effective soak off time, were the compromise between them is for the systems with 2% SB.

Further adhesion loss from the substrate was studied. Pure base needs 25 min in acetone medium to lose the adhesion from the substrate. All additives decrease the soak off time. NC and CAB gave the highest influence on adhesion loss after solvent treatment, decreasing the destruction time from 25 min to 15 min (2% of additives) (Fig. 6 a). All additives improve surface scratch resistance data compared to pure urethane acrylate base (Fig. 6 b).

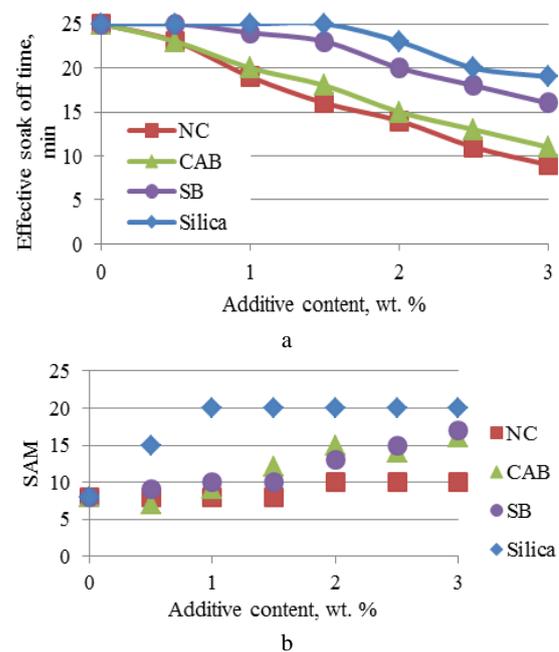


Fig. 6. Additive content influence on coating soak off time (a) and surface abrasion resistance (b)

The highest impact on surface scratch resistance was shown by silica (increase 2.5 times). Due to smaller particle size silica can fill free space between polymer molecules and behave as a surface additive. CAB and SB can be considered as potential additives for surface coating, as increasing amount of them increases surface scratch resistance.

Degree of conversion was determined by evaluation of gel fraction values. These data can explain the adhesion loss results, showing correlation between degree of conversion and effective soak off time (Fig. 7 a). Compositions with NC and CAB have the smallest gel fraction values, therefore additives promote faster adhesion loss. The stress (σ)–strain (ϵ) curves of the UV cured samples were taken. Initial elastic modulus $E = \lim(d\sigma/d\epsilon)|_{\epsilon \rightarrow 0}$, characterizes the resistance of the initial structure of the polymer at low unit strain values, when structure transformations nearly have not yet occurred [4]. There is a significant drop of E values with addition of various additives (Table 3).

Table 3. Additive influence on film modulus of elasticity, elongation at break and surface gloss at 60°

Additive	E , MPa	ε_b , %	σ_{max} , MPa	Surface gloss, GU
No	484	52	31	54
Silica	475	24	31	51
NC	250	9	19	68
CAB	350	46	21	84
SB	277	40	24	86

They strongly reduce the value of σ_{max} and the value of ε_{break} . There is also correlation between values of σ_{max} and degree of conversion (Fig. 7 b).

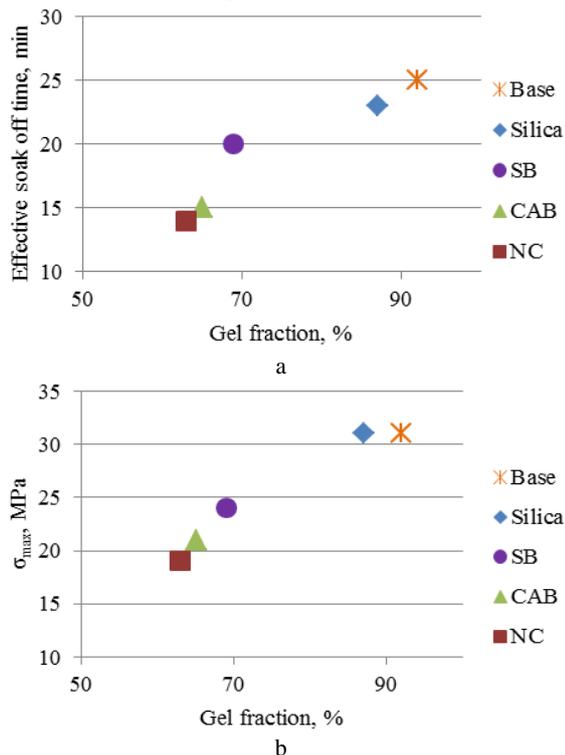


Fig. 7. Gel fraction data correlation with effective soak off time (a) and Ultimate strength (b) for compositions with 1 % of silica, 2 % of SB, CAB and NC comparing with pure base

Gloss is a measure of the ability of a coating surface to reflect a beam light at a particular angle without scattering. This is an important property of the coating, which is especially used for aesthetic and decorative purposes [1]. The final gloss of the cured samples is dependent on the UV light intensity used and cure time. Using a lamp with luminous intensity 130 mw and radiation spectrum area ($\lambda = 405$ nm) optimal cure time was found to be 30 s. Samples without additives and with 1 % of silica and 2 % of NC showed medium gloss values 10–70 GU (gloss units) (Table 4), but samples with 2 % of CAB and 2 % of SB reached high gloss values > 70 GU. The increase of the gloss is more intense for the additives that are primarily film formers: SB and CAB.

4. CONCLUSIONS

Using obtained data, optimal additive concentration has been found. 1 % of silica and 2 % of CAB and NC can provide stability of the suspension, were 2 % TiO₂ and 0.01 % red pigment is used. Compositions with 1 % silica

and 2 % CAB, SB and NC conform the requested initial viscosity (3000–4500 mPa). Degree of conversion is the most important parameter, which correlates with adhesion loss of the coating and film mechanical characteristics. All additives decrease degree of conversion, ultimate strength and effective soak off time in acetone. Biggest impact on pure base characteristics is obtained by 2 % of NC and 2 % of CAB, which decrease effective soak off time on 60 % and meet the requirements for coating removability (10 min).

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