Urethane Acrylate oligomers’ sensitivity to the UV light and moisture with and without UV absorbers

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Abstract

Urethane Acrylate oligomers possess exceptional properties such as chemical and water resistance, low yellowing, good adhesion to different substrates and more. Despite of the usage of urethane acrylates for outdoor applications, their performance depends on many different factors to be resistance against weather related phenomena. Product selection with certain properties could prolong the life of outdoor protective coatings. Also, it has been proven that addition of HALS and UV absorbers to the formulation, would help to enhance weatherability of outdoor coatings. In this study, several products are tested to determine their resistance to UV and moisture with and without UV absorber. The comparison will distinguish mechanical and physical degradation of each product under the same condition. Tensile properties, hardness, film appearance, adhesion, impact, and water immersion are tested.

Introduction

The corrosion of metals will change the properties and performance, often leading to failure, when they are exposed to exterior environmental conditions. Coatings are applied to metal substrates in order to protect them from environmental degradation. Metal coatings are expected to grow at >5% CAGR during the forecasted period of 2022 to 2027. Stringent VOC regulation, demand to lower energy consumption and more are the factors driving the market to shift into the more environmentally friendly coatings.

UV technology is an alternative to traditional direct-to-metal (DTM) coating due to low to no VOC emissions, higher production speeds, and lower energy usage. This technology is becoming more and more popular across the globe.

UV cured urethane acrylate-based coatings are one of the alternatives that could protect metal substrates from corrosion. Even though these products are known for great adhesion, non-yellowing and resistance to environmental factors, performance varies from product to product.

In this study, urethane acrylates have been evaluated against polyester and epoxy resins to better understand their values. In addition, a UV absorber and HALS have been added to the study and compare performance of the coating with and without additives.

Materials

The materials used include a standard bis-A type epoxy acrylate oligomer (EA oligomer), a polyester acrylate oligomer (PA oligomer), 5 different urethane acrylate oligomers (UA1, UA2, UA3, UA4, and UA5 oligomer), cyclic trimethylol formal acrylate monomer (CTFA), Butylaminocarbonyloxy ethyl acrylate monomer (BACEA), a hydroxyphenyl-triazine (HPT) UV absorber, and a liquid hindered amine light stabilizer (HALS), an acid functional acrylate monomer, a short wavelength photoinitiator (PI-1 short λ) and a long wavelength photoinitiator (PI-1 long λ).

Oligomers

The EA oligomer was chosen as a reference material as the BADGEDA type of oligomers are generally known in all UV industries and in particular are known to perform poorly under long term UV exposure thus acting as a 'negative' control in the UV exposure testing. The PA oligomer and all UA oligomers were selected for exploration purposes and range properties such as viscosity and cured hardness/Tg. UA1 is a hard oligomer, UA3 is a moderately hard oligomer, with UA2, UA4, and UA5 considered soft oligomers.

Monomers

The CTFA monomer was chosen for its mono-functional structure and moderate Tg. The 'native' cross-link density and cure-induced stress of each oligomer will not be moderated significantly by the addition CTFA in comparison to more commonly used monomers like TMPTA, HDDA, TPGDA, and DPGDA. These multifunctional monomers greatly increase cross-link density and the cure-induced shrinkage stress, both effects would likely limit adhesion and impact performance of the formulas.

Formulas

The materials were combined into formulas with the 'resin' part of the formula consisting of oligomer, monomer, and adhesion promoter. The ratio of oligomer, monomer, and adhesion promoter were generally 65/30/5, unless specified otherwise. The PI concentration is based on parts per hundred (phr) of the resin part with the PI-1 short λ = 2.5 phr and PI-2 long λ = 0.5 phr. Both the UV absorber and the HALS were set to 1 phr of the resin part. Formulas MC01-MC08 do not have any UV absorber or HALS added while MC09-MC12 do. Additionally, MC08 and MC12 differ from the other formulas by replacing part of the oligomer portion of the resin part with a low Tg monomer BACEA. This was done to investigate the role of film hardness in general performance. The film can be made soft by using softer oligomers (UA2, UA4-UA5) or by introducing soft monomers to the resin part (MC08 and MC12 test this strategy).

These materials were combined into 12 unique test formulas, which are shown in table 1 below. The viscosity measurements were made using a Brookfield LV viscometer fit with the small sample adapter and spindle number 34.

Table 1

Component	MC01	MC02	MC03	MC04	MC05	MC06	MC07	MC08	MC09	MC10	MC11	MC12
EA oligomer	65								65			
PA oligomer		65										
UA1 oligomer			65					48.75		65		48.75
UA2 oligomer				65							65	
UA3 oligomer					65							
UA4 oligomer						65						
UA5 oligomer							65					
CTFA	30	30	30	30	30	30	30	30	30	30	30	30
BACEA								32.5				32.5
Adhes. Prom.	10	10	10	10	10	10	10	10	10	10	10	10
PI-1 (short λ)	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PI-2 (long λ)	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
UV absorber									1	1	1	1
HALS									1	1	1	1
Viscosity (cP)	4770	2320	8598	1040	2439	765	5150	2100	4729	8750	1030	2060

Methods

The test formulas were subjected to a variety of tests including pendulum hardness, mandrel flexibility, tensile testing, adhesion to metal, impact resistance and UV exposure. In the following paragraphs descriptions of specimen preparations are given.

Tensile test specimens were prepared by drawing the formula on a release film using a wire wound rod. The film was then cured under a mercury H-bulb lamp at approximately 10 M/min (UVA+UVB = 600 mJ/cm^2). The cured film was approximately 200 microns in thickness. Type IV tensile specimens were then cut from the film using a pneumatic hollow die punch.

6x5 inch 0.25 mm thick steel panels were used for both pendulum hardness and mandrel flexibility tests. 3x5 inch 0.8 mm thick steel panels were used for crosshatch adhesion testing and impact resistance testing. 3x5 inch 0.6 mm thick aluminum panels were used for crosshatch adhesion testing and UV exposure testing in the QUV chamber. All coatings were applied with a #4 wire wound rod resulting in a cured film thickness of 25-30 micron.

Tensile Testing

Tensile bars prepared as described were conditioned at 23 ± 2 °C for 48+ hours prior to testing. Using a 34SC-5 single column Instron tensile tester fit with a video extensometer the specimens were tested until failure by pulling at a rate of 50 mm/min. The elongation was calculated based on a gauge length of one inch. The tensile modulus was determined by the maximum slope of the stress/strain curve at the beginning of the tensile profile (cases of strain hardening during the end of the tensile test were not observed). The tensile strength was determined by the maximum stress measured during the tensile test and the % elongation was determined by the strain observed at break. Ten specimens were used for characterizing the tensile properties of each test formula.

Pendulum Hardness

A TQC pendulum hardness tester was fit with the Koenig pendulum and calibrated against a smooth glass plate prior to testing the coated panels in accordance with ASTM D4366. Test panels were conditioned at 23 ± 2 °C for 48+ hours prior to measuring the pendulum hardness. Each panel was tested in three locations and the average of three panels (nine measurements) was used for assigning the pendulum for a given formula.

Mandrel Flexibility

Coated steel test panels were placed in a TQC cylindrical mandrel bend test apparatus and bent over mandrels of varying diameter, starting from large (29 mm) to small (5 mm). After releasing a panel from the testing apparatus, the panel was inspected for failure in the form or film cracking or delamination. The mandrel one size larger than the mandrel where failure was observed was reported as the mandrel flexibility.

Metal Adhesion

The adhesion to aluminum and steel test panels was evaluated using the cross-cut (crosshatch) method as described in ASTM D3359.

Impact Resistance

The resistance to rapid deformation impact was evaluated according to ASTM D2794 using BYK-Gardner PF-1120 Heavy-Duty Impact Tester. The reported values here were obtained from intrusion (direct) impact testing and represent the inflection point in testing. Below the inflection point most energies do not fracture or delaminate the coating and at energies above the inflection point most energies cause failure in the coating.

UV resistance

A QUV accelerated weathering tester was used to expose the coated aluminum test panels to UV light and condensing humidity. The unit provided 0.62 W/m^2/nm of UV irradiance (roughly 4.5 J/cm^2 per day) and operated at 34 °C while the UV lamps were powered on. A 24-hour cycle consisting of 20 hours of UV exposure and 4 hours of condensation without any UV light was used to accelerate the weathering of the test formulas and was evaluated after 1200 hours of exposure. The coated panels were then tested for yellowness using the X-rite Exact spectrophotometer.

Results and Discussion

Tensile Properties

Property	*MC01*	*MC02*	*MC03*	*MC04*	*MC05*	*MC06*	*MC07*	*MC08*	*MC09*	*MC10*	*MC11*	*MC12*
Tensile Modulus (MPa)	NA	NA	2280	14	897	11	66	2360	2250	2203	15	1970
Tensile Strength (MPa)	NA	NA	57	8	22	5	12	59	34	49	11	50
Elongation (%)	NA	NA	4	54	36	48	52	3.9	1.7	3.1	60	4.8

Most test formulas were amenable to tensile testing, with two exceptions. MC01 is based on a BADGEDA oligomer and made a very brittle film which fractured while cutting test specimens with the pneumatic hollow-die punch. On the other end of the spectrum was MC02 which was primarily composed of PA oligomer and proved to be far too flexible to handle. Though specimens were made it could not be successfully loaded and measured in the tensile tester. The remaining formulas exhibited properties reflective of the primary ingredient, the oligomer. MC04, MC06, MC07, and MC11 used soft UA oligomers and all four formulas show low modulus and tensile strength, but relatively high elongation at break. MC05 is made of a moderately hard oligomer and has middling properties. MC03, MC08, MC09, MC12 are primarily composed of hard UA oligomers, excepting MC09 which is made of the EA oligomer. MC01 and MC09 are very similar formulas differing only by the UV absorber and HALS components being added to MC09. The UV absorber and HALS will interfere with light absorption and therefore have potential to limit the degree of cure, given the curing conditions and PI content are identical. The potential for differential cure responses between these materials may explain why MC01 shattered while preparing specimens and MC09 did not. The slightly lower cure may soften/toughen the formula. Alternatively, the additives may act as plasticizers, enabling specimen preparation and tensile testing.

Pendulum Hardness

	MC01	MC02	MC03	MC04	MC05	MC06	MC07	MC08	MC09	MC10	MC11	MC12
Koenig Hardness (# Swings)	147	16	125	8	52	8	13	41	109	121	12	46

The pendulum hardness results generally correspond with the tensile data. Hard oligomer-based formulas have high Koenig swings, moderate oligomer formulas have middling Koenig swings, and formulas based on soft UA oligomers had low Koenig swings. Comparing the effect of the UV absorbers on coating hardness shows a similar trend as observed in the tensile data. MC01 compared to MC09 shows a drop in ~30 swings, while the other comparatives do not exhibit a significant difference (compare MC03 to MC10, MC04 to MC11, and MC08 to MC12).

Mandrel Flexibility

Mandrel Flexibility	MC01	MC02	MC03	MC04	MC05	MC06	MC07	MC08	MC09	MC10	MC11	MC12
mm	10	5	5	5	5	5	5	5	6	5	5	5

All formulas, except MC01, showed a high degree of flexibility by being bent around the smallest of mandrels (5 and 6 mm).

Metal Adhesion

Substrate	Test #	MC01	MC02	MC03	MC04	MC05	MC06	MC07	MC08	MC09	MC10	MC11	MC12
Steel	1	Fail	Fail	Fail	Pass	Pass	Pass	70%	Fail	Fail	Pass	Fail	Fail
	2	Fail	Fail	Fail	Fail	Pass	Pass	Pass	Fail	Fail	Fail	Fail	Fail
	3	Fail	Fail	Pass	Pass	Pass	80%	Pass	Fail	Fail	Pass	Fail	Fail
Aluminum	1	Fail	Fail	Fail	50%	Fail	Fail	Fail	Fail	Fail	Fail	Fail	Fail
	2	Fail	Fail	Fail	50%	Fail	Fail	70%	Fail	Fail	Fail	Fail	Fail
	3	Fail	Fail	Fail	50%	Fail	Pass	Fail	Fail	Fail	Fail	Fail	Fail

In adhesion testing the aluminum substrate was found to be more challenging than steel. More specifically, the only formulas that performed well under adhesion tests were the 'soft' formulas (MC04-MC07, and MC10). These formulas were based on either the soft or moderate UA oligomers. One exception was found in MC10. This formula is the only formula among those with added UV absorber and HALS additives to show any passing performance in adhesion tests. The oligomer in the MC10 formula is the hard UA1 oligomer. The positive adhesion test results for MC10 may be simply anomalous as all the other formulas with UV absorber and HALS additives were found to perform poorly in adhesion tests.

Impact Resistance

Impact Energy	MC01	MC02	MC03	MC04	MC05	MC06	MC07	MC08	MC09	MC10	MC11	MC12
Inch-lb	24	140	36	160	160	160	160	1	12	26	160	1

The results of impact resistance testing correspond roughly with softer more flexible materials tolerating higher energy impacts and harder materials failing under low energy impacts. The formulas with UV absorber and HALS additives performed more poorly than the corresponding 'additive free' formulas. The exception to this rule is MC11 which performed equal to the MC04 (both formulas did not fail under the highest energy impact of 160 inch-lb). Additionally, the impact resistance for MC08 and MC12 are the lowest of all test formulas. These formulas represent the strategy of softening via addition of low Tg mono-functional monomers. The reduction in crosslink density achieved by monomer addition may have been too great and therefore reduced the cohesive strength of the material to a point which virtually no impact resistance remained.

UV resistance

	MC01	MC02	MC03	MC04	MC05	MC06	MC07	MC08	MC09	MC10	MC11	MC12
1200 hrs Y	0.78	NA	0.64	0.65	0.64	0.62	0.65	0.65	0.73	0.68	0.68	0.67
1200 hrs ΔE	9.95	NA	1.19	0.74	1.68	2.10	2.26	0.88	6.60	1.81	1.03	1.70

As expected, the two formulas based on the BADGEDA type EA oligomer yellowed intensely. The PA oligomer formula, MC02, delaminated prior to 500 hours of exposure. It cannot by determined whether the delamination of MC02 was caused by UV degradation or the condensing water phase of the exposure cycles. All formulas based on UA oligomers showed no yellowing to the naked eye and virtually no yellowing nor discoloration as measured by the spectrophotometer.

Summary

As noted, soft urethane acrylate oligomers showed low tensile strength and modulus, while exhibiting in high elongation. Semi-hard oligomers performance was in the middle, whereas hard oligomers resulted in high tensile strength and modulus with low elongation. The pendulum hardness, which is indicative of surface hardness, is directly related to tensile hardness. As results indicate, systems with high tensile strength and modulus show high pendulum hardness. In terms of flexibility, all showed a high degree of flexibility, except for epoxy system without UV absorber and HALS. Systems with higher flexibility performed better for adhesion and impact resistance. It is observed that UV absorbers and HALS interfere with the cure and as a result, crosslinking of cured film is lower than that of the system that lack of these two. Lower cure will result in more film flexibility. This trend is observed in tensile strength and pendulum hardness