

UV CURABLE CONCRETE COATINGS

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Introduction

Coatings have been UV cured in industrial settings since the 1960s. The graphics industry was one of the first to adopt this technology, with a high gloss coating on cards. Today, there are numerous industrial applications that utilize UV curing as the method of drying or polymerizing their coatings or inks. It is only in the past five years or so that commercial UV curing has moved out of the factory and into the field. Floor coatings are one of the main applications for field applied UV cured coatings. Today, floor coatings for concrete, wood, vinyl and tile are all in some phase of commercialization. This paper will introduce the basics of UV curing, and provide structure property relationships for UV curable materials. Several starting point formulations for UV curable concrete coatings will also be provided.

UV Curing Basics

Advantages

UV curing is also known as radiation curing or energy curing. It utilizes the ultra-violet (UV) portion of the electromagnetic spectrum, 200-400 nanometers (Figure 1), to physically dry or cure coatings. (The coating actually polymerizes or increases in molecular weight during the curing process.) To do this on an industrial scale, lamps that emit UV light replace drying ovens, and the drying takes place in fractions of a second. Fast cure speeds are not the only benefit of UV curing. The physical space and energy requirements for the drying are also greatly reduced versus conventional drying mechanisms. Because UV curable coatings are 100% solids, VOCs and HAPs are also very low, generally less than 5% VOC content. Since solvents are not typically used in UV curable systems, inhalation and flammability hazards are essentially non-existent.

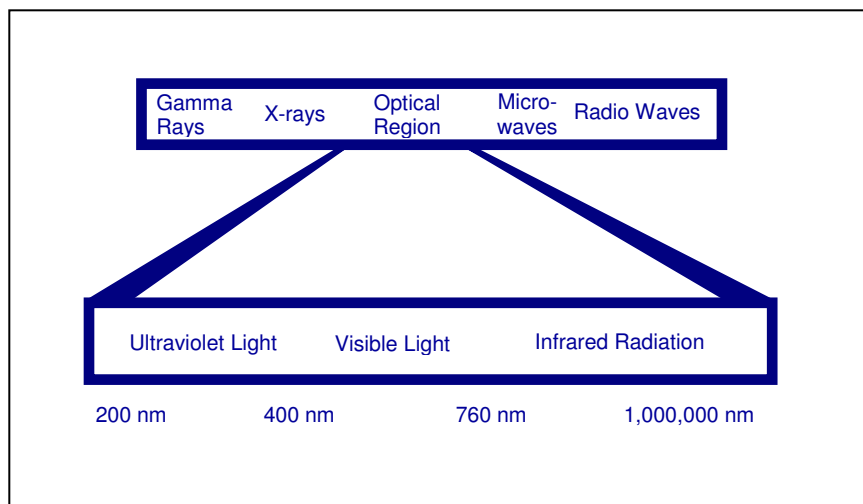


Figure 1. Electromagnetic Spectrum

Free Radical Polymerization

The ultra-violet light ($h\nu$) must be absorbed by the coating in order for curing or polymerization to occur. This step is accomplished by photoinitiators (PI), which react to form free radicals (PI^\cdot). These free radicals then react with the double bonds in the coating (typically acrylate double bonds, Figure 2) to form new free radicals (PIR^\cdot) in an initiation step. The propagation step causes the molecular weight of the coating to increase through chain reactions with additional acrylate double bonds (R_2). As the molecular weight increases, the coating becomes less fluid or mobile, and begins to solidify. The chain transfer step controls the molecular weight increase by terminating one chain reaction, and transferring the free radical to begin a new chain reaction. The termination step ends all reactions and stops molecular weight increase. Figure 3 shows these various steps in the free radical chain polymerization process.

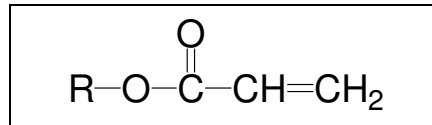


Figure 2. Acrylate Double Bond

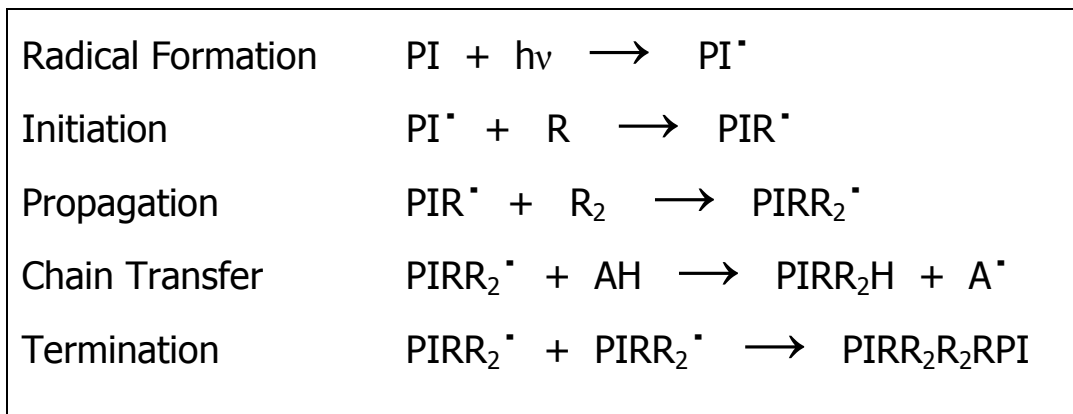


Figure 3. Free Radical Chain Polymerization

Crosslink Density

During the free radical polymerization, the coating becomes crosslinked because the acrylate molecules contain multiple double bonds. The number of acrylate double bonds in a molecule is called its acrylate functionality. For example, if a molecule contains two acrylate double bonds, it is difunctional. The degree of crosslinking of a coating indicates how tightly the polymer network is interconnected. This crosslink density impacts the coating properties. A more highly crosslinked coating will be hard and chemical resistant. A less crosslinked coating will be flexible and soft. The weight per double bond of a coating formulation predicts the crosslink density, and thus the coating properties. Table 1 illustrates this concept. The weight per double bond is calculated by dividing the average molecular weight of the formulation by the average functionality of the coating. (It should be

noted that this is only a predictive tool, and that factors other than crosslink density also affect coating properties.)

Table 1. Effect of Weight per Double Bond on Coating Properties

Low Weight per Double Bond	Property	High Weight per Double Bond
Faster	Cure Speed	Slower
Lower	Flexibility	Higher
Higher	Tensile Strength	Lower
Higher	Shrinkage	Lower
Higher	Chemical Resistance	Lower
Worse	Adhesion	Better

Cure Speed

Cure speed is the line speed at which the desired coating properties are obtained. The desired coating properties can and do vary based on the end use of the coating. For an overprint varnish, this may be 10-20 MEK double rubs. For a wood floor coating, this may be 200+ MEK double rubs and Shore D hardness of 70. For coatings for food packaging, this may be a migration level of less than 50 ppb. In most cases, the acrylate double bonds in a coating are not completely consumed. Consumptions of 80-90% are typical since the vitrification of the coating limits the mobility of the free radicals in the latter stages of the reaction. Since there are multiple acrylate double bonds on most components in the formulation, these consumption rates do not necessarily indicate raw materials that are not part of the polymer network.

As discussed in the previous section, cure speed is impacted by the weight per double bond of the formulation. The lower the weight per double bond (or the more acrylate double bonds per molecule), the higher the cure speed. Cure speed is also affected by a phenomenon known as oxygen inhibition. Molecular oxygen is a very reactive material that can react with the photoinitiator and polymer radicals to form peroxy radicals, which then slow down the free radical chain reaction. Severe oxygen inhibition manifests itself as a thin layer of unpolymerized (liquid) material on top of the coating. Less severe results are reduced coating properties, such as decreased hardness and chemical resistance.

Oxygen inhibition can be mitigated in several ways. The use of inert atmospheres, such as nitrogen, removes oxygen from the curing process. Higher UV lamp intensities and higher levels of photoinitiator increase the concentration of photoinitiator and polymer radicals versus that of the oxygen-based peroxy radicals to reduce the amount of oxygen inhibition. Photoinitiators that absorb at shorter wavelengths are particularly useful. Finally, amine synergists can be added to the formulation to consume oxygen, and thus reduce its effects.

Oxygen inhibition is mainly a surface cure phenomenon, since dissolved oxygen is quickly consumed and not easily replaced. Through or deep cure of a coating is affected by other issues, and is generally manifested by lack of or decreased adhesion and decreased solvent resistance. To mitigate through cure issues, photoinitiators that absorb at longer wavelengths are used. The photoinitiator

concentration should generally be lower for good through cure. (The UV light must not be completely absorbed at the surface of the coating, which may occur at high levels of photoinitiator.)

Cure speed is also affected by ability of the photoinitiator to absorb the UV light emitted by the UV lamp. The UV absorbance of the photoinitiator must closely match some portion of the UV light emitted by the UV lamp in order to get good initiation of the free radical polymerization. Figure 4 illustrates the UV emissions from a medium pressure mercury lamp and a gallium doped medium pressure mercury lamp. The UV absorbance of several photoinitiators is shown in Figure 5. Figure 6 shows an overlay spectrum of UV lamp output and photoinitiator absorbance. Good overlap is seen in the 290-320 nm range for several of the photoinitiators.

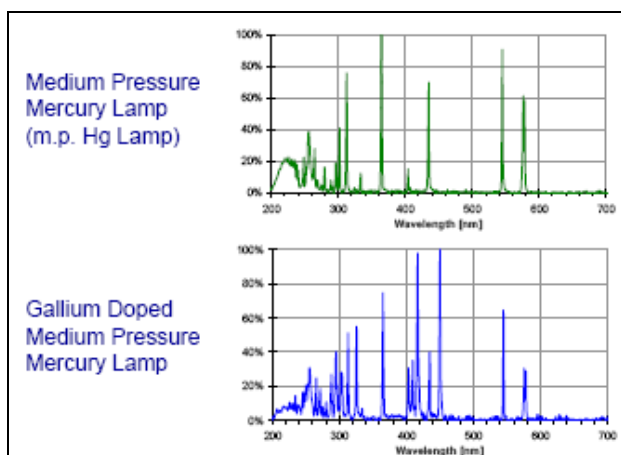


Figure 4. UV Lamp Emissions

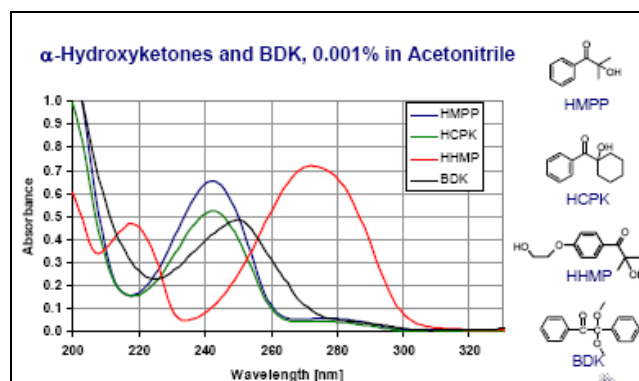


Figure 5. UV Absorbance of Photoinitiators

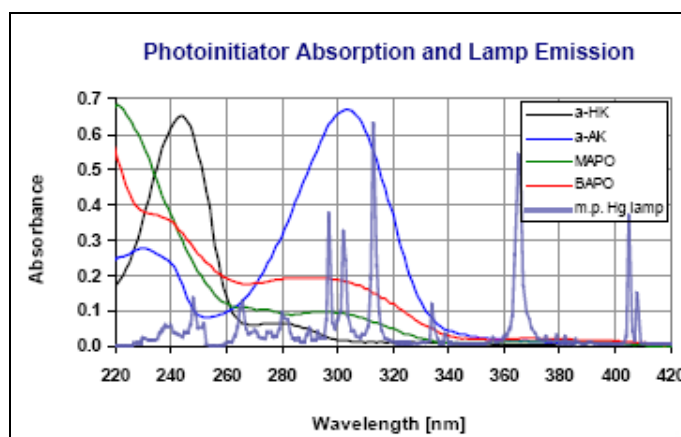


Figure 6. Overlay of UV Lamp Emission and Photoinitiator Absorbance

Other components of the formulation should not absorb at the same wavelength as the photoinitiator (compete for the UV light). This can be very important for pigmented systems, which absorb over broad portions of the UV spectrum. Figure 7 illustrates this by showing the UV absorbance of OPP

foil substrate, an unpigmented formulation, and the same formulation with blue, red, yellow, and black pigment. The substrate and unpigmented formulation have essentially no absorbance in the range of 300-700 nm, and the unpigmented formulation absorbs strongly from 200-300 nm. The blue formulation absorbs strongly from 200-450 nm and 550-700 nm, red from 200-300 nm and 450-600 nm, yellow from 200-300 nm and 350-550 nm, and black from 200-700 nm.

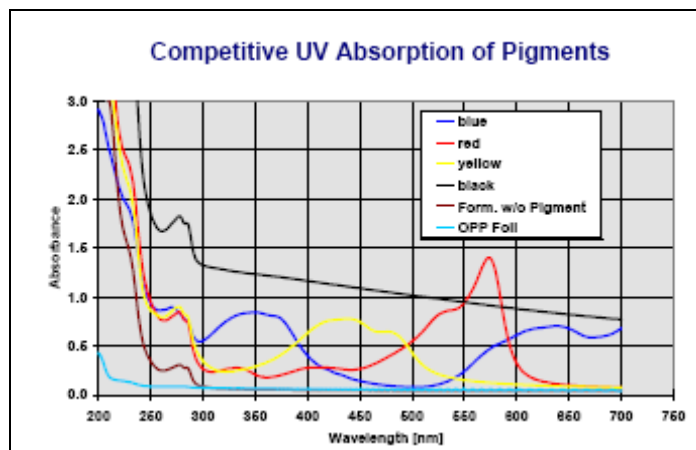


Figure 7. Effect of Pigment on UV Absorbance of Formulations

Combinations of photoinitiators, which absorb at different wavelengths, are often used to overcome many of these pigment absorbance issues. For each formulation, different types and combinations of photoinitiators should be evaluated, and ladder studies for concentration of the photoinitiators should be run to optimize the cure of the coating.

UV Curable Raw Materials

Acrylate Oligomers

There are two main classes of acrylate raw materials: oligomers and monomers. Oligomers are also known as prepolymers, and are generally high in molecular weight (500-5000). They provide much of the overall coating performance. Coating properties such as hardness, abrasion and scratch resistance, chemical and solvent resistance, flexibility, and toughness are greatly impacted by oligomer choice. The number of acrylate double bonds per oligomer molecule (acrylate functionality) varies from 2-6. Oligomers are divided into three main classes by their chemical backbones: epoxy acrylates, urethane acrylates, and polyester acrylates.

Epoxy acrylates provide coatings that are hard, chemical and temperature resistant, glossy, and fast curing. Coatings based on epoxy acrylates do not weather well because of their aromatic character. This oligomer is generally the highest viscosity and the lowest cost. It is almost always difunctional. Figure 8 shows the most commonly used epoxy acrylate.

Urethane acrylates provide coating toughness and abrasion resistance. They can vary in hardness and flexibility, depending on their composition and acrylate functionality (2-6). Urethane acrylates are moderate to high in viscosity and provide coatings with moderate cure speed. Aliphatic urethane acrylates provide coatings with the best weatherability.

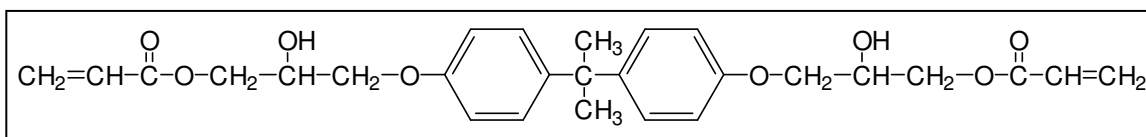


Figure 8. Bisphenol A Based Epoxy Acrylate

Polyester acrylates are low viscosity oligomers that provide moderately hard, high gloss coatings. They generally provide good pigment wetting, and have limited exterior durability. Their acrylate functionality can vary from two to six.

Table 2 summarizes the properties of the different oligomer classes on a relative basis. This is a general summary, and there can be substantial deviations, depending on the specific oligomer.

Table 2. Relative properties by Oligomer Class

	Epoxy Acrylate	Urethane Acrylate	Polyester Acrylate
Weatherability	+	+++++	+++
Toughness	++	+++++	+
Chemical Resistance	+++++	++	+++
Hardness	+++++	+	+++
Flexibility	+	+++++	++
Cure Speed	+++++	+	+++

Acrylate Monomers

Since oligomers are high in molecular weight, they are quite viscous, and generally require monomers as diluents to obtain the desired application viscosity. Monomers are also known as reactive diluents since they contain double bonds and react to become part of the polymer during free radical polymerization. Since monomers become part of the coating, the flexibility or hardness of the coating can be impacted by monomer choice. They are generally low in molecular weight and viscosity. Their acrylate functionality varies from 1-6, and they are generally categorized by their functionality.

Monofunctional monomers contain one acrylate double bond per molecule. They are the lowest viscosity monomers and the best viscosity reducers for oligomers. Monofunctional monomers reduce crosslink density, and result in flexible coatings with better substrate adhesion. Since they only have one acrylate double bond, they reduce the cure speed of formulations, and may result in unreacted monomer that is potentially extractable.

Difunctional monomers contain two acrylate double bonds per molecule (Figure 9). They are good viscosity reducers and can help with adhesion to the substrate. They can also improve solvent resistance of coatings while maintaining flexibility.

Tri- and higher-functionality monomers are typically higher in viscosity, and are not as effective in reducing the viscosity of the oligomers. They increase the cure speed of a coating, but can also impart

brittleness to the coating. Increased crosslink density typically improves hardness, abrasion and scratch resistance, and chemical and solvent resistance.

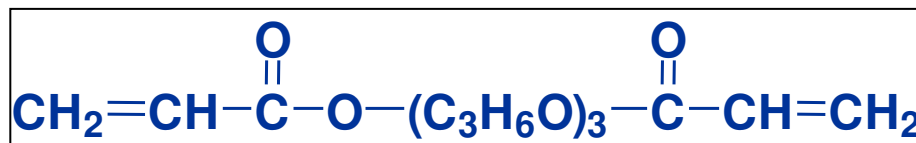


Figure 9. Tripropyleneglycol Diacrylate

Table 3 summarizes the properties of the monomers by functionality on a relative basis. This is a general summary, and there can be substantial deviations, depending on the specific monomer.

Table 3. Relative properties by Monomer Functionality

	Monofunctional	Difunctional	Tri- and higher-functional
Viscosity Reduction	+++++	+++	+
Adhesion	+++++	+++	+
Chemical Resistance	+	+++	+++++
Hardness	+	+++	+++++
Flexibility	+++++	+++	+
Cure Speed	+	+++	+++++

Health & Safety

Acrylate functional raw materials are non-toxic and have very low volatility at room temperature. Therefore, the inhalation hazard is very low, and respiratory protection is generally not necessary. The acrylates may be skin and eye irritants, so eye and skin protection such as safety glasses and gloves are required. Additionally, protection from exposure to the UV light may be required, and is provided by tinted safety glasses and sunscreen for exposed skin areas.

UV Curable Coatings

Coating Basics

A UV curable coating must contain several basic materials in order to undergo effective curing or polymerization. Additional materials are also required to obtain the desired coating aesthetics. The coating pyramid is often used to demonstrate the use of these materials. (Figure 10) Materials at the base of the pyramid generally comprise more of the formulation than materials at the top of the pyramid. The base of the pyramid contains the oligomers, which as discussed earlier, provide the bulk of the coating properties. Next on the pyramid are the monomers, which are primarily used to obtain the desired application viscosity. Additives are used to enhance the coating performance and/or to change the coating appearance. As in conventional coatings, these additives can be flattening agents, fillers, wetting/leveling agents, defoamers, or slip aids. Pigments can also be added to a formulation for color or special effect. Photoinitiators are needed to absorb UV light and form free radicals.

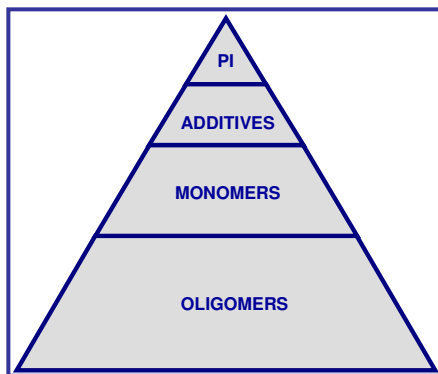


Figure 10. Coating Pyramid

Concrete Coatings

A UV curable concrete coating must be low in viscosity, around 150 cP, to allow air release upon application of 1-7 mils coating thickness. This low viscosity requirement limits the choice and/or concentration of oligomers in a formulation. Monomer choice also becomes more important since the formulation will contain a large amount of diluting monomer. A combination of photoinitiators should be used to insure both surface and through cure. Flow, leveling and wetting agents, and defoamers may be necessary for coating aesthetics. See Table 4 for a generic starting point formulation for a UV curable coating for concrete.

The effect of oligomer choice on concrete coating properties will be evaluated using the actual starting point formulation given in Table 4. Epoxy acrylate (EA), urethane acrylate (UA), and polyester acrylates (PEA 1 and PEA 2) will be evaluated as the oligomer. These oligomers were chosen because of their low viscosity and beneficial properties for concrete coatings. Various coating properties, such as cure speed, gloss, adhesion, hardness, flexibility, chemical resistance, and abrasion resistance will be measured. These coating properties will then be correlated to structural elements of the oligomer.

Experimental Details

Materials

Smooth concrete blocks (4 x 6 x 1 inch) were obtained from Patio Concrete Products, Inc., and were wet wiped and then dry wiped to clean the surface before coating.

Oligomers, monomers, and photoinitiators were obtained from Cytec Industries Inc., and were used as received. Additives were obtained from Ciba Inc. and Air Products and Chemicals, Inc., and were used as received.

The coatings were cured using a laboratory cure unit from HID Ultraviolet, LLC. This laboratory cure unit consists of a mobile curing unit (Bulldog 15-3000) equipped with a 250 watts per inch medium pressure continuous wave xenon lamp. It is mounted on a conveyor system with variable belt speed (Dynamometer) to enable ease of laboratory work. The curing unit was calibrated using a 390 Belt Radiometer from International Light Technologies.

Table 4. Starting Point Formulation for a UV Curable Concrete Coating

PRODUCT	PARTS	
	Generic Formulation	Actual Formulations
Resin System		
Oligomers for Desired Coating Properties	10 - 30	25
Oligomers for Surface Cure	10 - 20	15
Monomers for Properties		
Multi-functional for Crosslinking and Hardness	10 - 30	20
Mono-functional for Adhesion and Viscosity Reduction	0 - 20	0
Monomers for Viscosity Reduction	To obtain viscosity of ~150 cP	29.6 (plus additional as needed)
	PARTS PER HUNDRED RESIN	
PI Package		
Surface Cure	1 - 2	2
Multipurpose	2 - 4	3
Through Cure for Thick Coatings	0.25 - 0.5	0.4
Amine Synergist for Surface Cure	2-5	5
Additives		
Flow and Leveling	0 - 1.0	0
Substrate Wetting	0 - 2.0	0
Defoaming	0 - 1.0	0.3
Coat at 1-7 mils on non-porous concrete*		5-7
Cure at exposure (mJ/cm ²) necessary to get a mar free surface		410 - 1861

* If the concrete is porous, a seal coat should be applied. Waterborne UV-PUDs are recommended as seal coats. These sealers must air dry before UV cure. The UV-PUDs may be used in combination with conventional acrylic emulsion sealers, but at least 10% of the UV-PUD is required for intercoat adhesion. If the sealer is not tack free after dry, an intermediate UV cure step is needed.

Procedures

An Instron model 4467 was used to determine tensile properties on 6-7 mils thick, UV cured films of the oligomer containing 4% 2-hydroxy-2-methyl-1-phenyl-propanone as the photoinitiator.

The coatings were prepared by mixing under agitation all components shown in Table 4, except the oligomer for coating properties and the defoamer. The oligomer, which had been heated overnight at 65° C to reduce viscosity, was then added under agitation, followed by the defoamer. The viscosity of the resulting formulation was measured at 25° C using a Brookfield DV-II + viscometer equipped with a #21 spindle. The viscosity of the UA and PEA 2 formulations was adjusted by adding 7% of the viscosity reduction monomers, and the EA formulation was adjusted by adding 5%. The final viscosities were then measured in the same manner as noted above.

The coatings were applied to the concrete blocks with a #25 Meyer wire wound rod, to obtain a coating thickness of 5-7 mils, as measured with a Gardco wet film gauge.

The coatings were then cured at various exposures (mJ/cm^2), corresponding to various walking speeds (feet per minute, fpm). The minimum exposure required to obtain a mar free surface as determined with a wooden tongue blade was recorded as the cure speed. Coating properties at the cure speed were then determined as shown in Table 5. Additionally, all coatings were cured at $919 \text{ mJ}/\text{cm}^2$ (20 fpm), in order to compare coating properties at the same cure speed.

Table 5. Methods of Measurement of Coating Properties

PROPERTY	METHOD
X-Cut Adhesion	ASTM D 3359-07; Test Method A
Pencil Hardness	ASTM D 3363-05
Chemical Resistance (24 Hour Spot Test)	ASTM D 1308-02
Solvent Resistance (MEK Double Rubs)	ASTM D5402-06 (Method 3; 2 lb. ball peen hammer)
60° Gloss	ASTM D 523
Abrasion Resistance	Steel Wool (0000) Double Rubs with a 2 lb. ball peen hammer; fail = surface scratch
Flexibility by Direct Impact	ASTM D 2794; modified for coating on concrete substrate

Results

The oligomer tensile properties are given in Table 6, and the stress-strain properties for the oligomers are graphed in Figure 11. The coating properties are shown in Table 7.

Table 6. Tensile Properties of Oligomers

	Polyester Acrylate 1	Polyester Acrylate 2	Epoxy Acrylate	Urethane Acrylate
Tensile Strength (psi)	960	4,425	4,825	2,940
Young's Modulus (psi)	8,400	182,100	266,200	35,800
Toughness (psi)	62	102	1135	611
Elongation at Break (%)	12	4	27	31

Discussion

The stress-strain properties shown in Table 6 and Figure 11 indicate that the epoxy acrylate and urethane acrylate are tougher than the two polyester acrylates. The epoxy acrylate has been modified to be more flexible than the standard bisphenol A based epoxy acrylate, and this is reflected in its tensile properties that differ from the typical properties of epoxy acrylates. The urethane acrylate shows toughness expected for its oligomer class. The two polyester acrylates show expected results as well.

Differences in cure speed, adhesion, hardness, and possibly flexibility are noted in Table 7. The other coating properties (abrasion resistance, gloss, and solvent resistance) are the same or essentially the same. As discussed earlier, the weight per double bond of a formulation plays an important role in the determination of coating properties. Table 8 provides data on the molecular weight, functionality, weight per double bond, and viscosity of the oligomers and the formulations. Although the weight per double bond of the oligomers varies from 168 to 392, once formulated the weight per double bond is fairly consistent, varying only from 144 to 166. This lack of variation is due to the low viscosity requirement of the coating, and the large amount of monomer that is needed to obtain this viscosity. This fairly consistent weight per double bond may explain some of the similar coating properties shown in Table 7, along with the fact that only about 25% oligomer is in the formulation because of viscosity constraints.

Table 7. Performance Properties of Concrete Coatings

	Polyester Acrylate 1		Polyester Acrylate 2		Epoxy Acrylate		Urethane Acrylate	
Viscosity (cP @ RT)	135		179		176		177	
Cure Conditions	MAR FREE	EQUAL	MAR FREE	EQUAL	MAR FREE	EQUAL	MAR FREE	EQUAL
Exposure (mJ/cm ²)	410	919	410	919	919	919	1861	919
Speed (fpm)	45	20	45	20	20	20	10	20
X-Cut Adhesion	3A/4A	4A	1A/2A	4A	4A	4A	2A	4A
Steel Wool Double Rubs	1	1	1	1	1	1	1	1
Pencil Hardness	3H	HB	3H	2H	HB	HB	4H	HB
60° Gloss	87	91	90	86	91	91	89	90
Chemical Resistance ¹								
Water	5	--	5	--	5	--	5	--
Formula 409	5	--	5	--	5	--	5	--
Brake Fluid	5	--	5	--	5	--	5	--
Transmission Fluid	5	--	5	--	5	--	5	--
Mustard	4	4	4	4	4	4	4	4
MEK Double Rubs	>200	>200	>200	>200	>200	>200	>200	>200
Direct Impact (in lb)	8	4	4	8	4	4	6	8

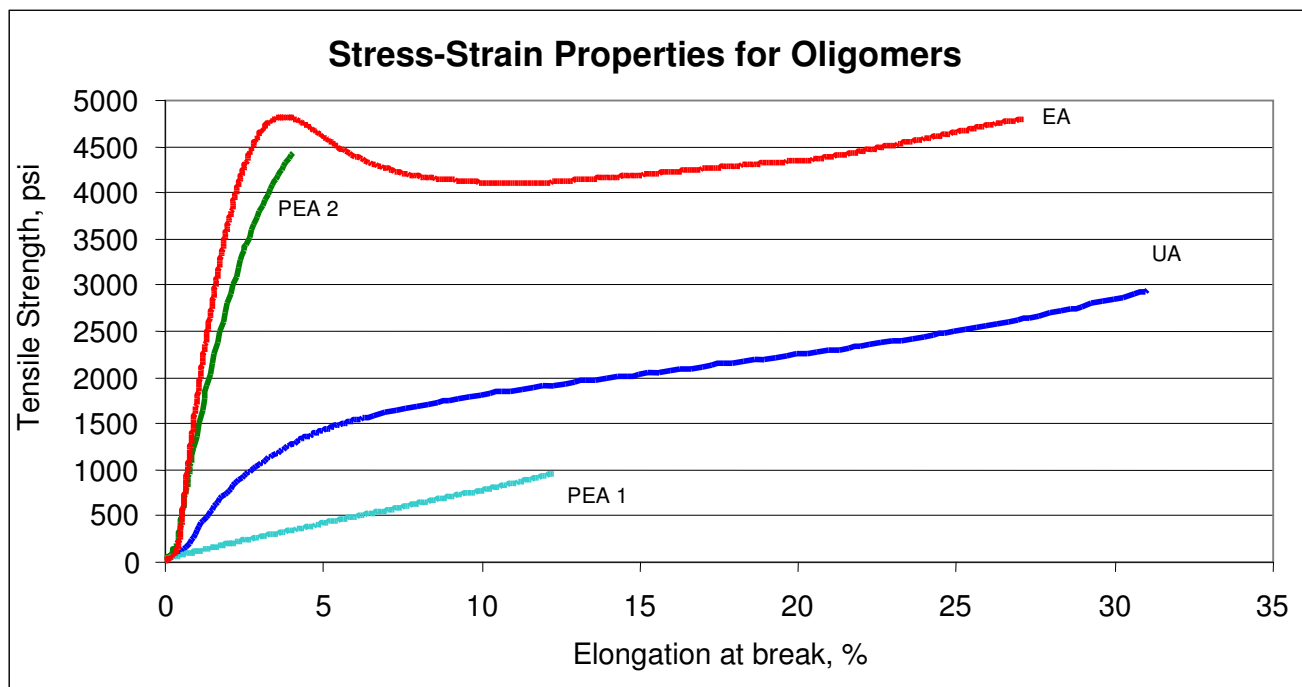
¹ Scale of 0-5. 5 = no stain, no coating deterioration; 4 = slight stain, no coating deterioration

Table 8. Viscosity (Visc; cP @ 25°C), Molecular Weight (MW), Functionality (Func), and Weight per Double Bond (WPDB) of Oligomers and Formulations

	Oligomer				Formulation			
	Visc	MW	Func	WPDB	Visc	MW	Func	WPDB
PEA 1	3,000	862	3.5	246	135	426	2.7	158
PEA 2	50,000	755	4.5	168	179	403	2.8	144
EA	600,000	667	1.7	392	176	399	2.4	166
UA	36,500	829	2.3	360	177	408	2.5	163

Faster cure speeds are seen for PEA 1 and PEA 2. These two oligomers have the lowest weight per double bond, so this result is expected. The fast cure speed of an EA is generally attributed to the labile hydrogens on its backbone, which like those in an amine synergist, mitigate oxygen inhibition. This effect is seen in the results, as the EA cures two times as fast as the UA, although they have essentially the same weight per double bond.

Figure 11. Stress-Strain Properties of Oligomers



At mar free cure speeds, better adhesion is seen for PEA 1 and EA. The EA contains monofunctional monomer, which is known to improve adhesion by increasing the weight per double bond, and decreasing crosslink density. This monofunctional monomer content is also manifested in the lower hardness number for the EA (HB). The weight per double bond does not predict the better adhesion for PEA 1. In this case, the actual composition of PEA 1 may be contributing to the better adhesion. The two PEAs have the same hardness, 3H, and the UA unexpectedly has the highest hardness, 4H.

At equal cure speeds, all oligomers have the same adhesion, however the hardness and flexibility varies with cure speed for all oligomers. (EA was only evaluated at 20 fpm (919 mJ/cm²) because its mar free cure speed was also 20 fpm.) PEA 1, when cured at slower speeds or higher exposure, has about the same adhesion, but lower hardness and lower flexibility. These results suggest overcure at the slower cure speed of 20 fpm, with resulting embrittlement. PEA 2, on the other hand, shows increased adhesion and flexibility at slower cure speeds, and only slightly less hardness. These results may indicate undercure at 45 fpm for PEA 2. The UA shows decreased adhesion, but increased hardness and decreased flexibility at slower cure speeds. Except for adhesion, these results suggest better cure at the slower cure speed of 10 fpm.

The direct impact test was modified for use on concrete substrates. The effect of this modification on results is unknown. The results show a limited variation, from 4 to 8 inch pounds. There is no correlation between results and structure or weight per double bond.

The relative weatherability and cost of the oligomers is shown in Table 9. If the concrete coating will be exposed to sunlight and requires excellent weatherability, the urethane acrylate is the oligomer of choice, although at a higher cost. The two polyester acrylates can be used in areas where the need for weatherability is not extreme, and at a better cost than the urethane acrylate. The epoxy acrylate should only be used in areas where weatherability is not a concern.

Table 9. Relative Weatherability and Cost of Oligomers

	Weatherability	Cost
PEA 1	+++	+++
PEA 2	+++	+++
EA	+	+++++
UA	+++++	+

Conclusion

Three classes of oligomers have been evaluated in coatings for concrete. The low viscosity requirement of the concrete coatings minimizes the effect of oligomer choice on final properties, and all classes of oligomers provide coatings with high gloss and good chemical and solvent resistance. However, the PEAs do provide better hardness at reasonable cure speeds, along with a good compromise on weatherability and cost. PEA 1 provides the best combination of properties: cure speed, adhesion, hardness, weatherability and cost.

General References

Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints, Volumes 1-7. John Wiley & Sons Ltd, Inc., New York, NY. (1998).

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