Oligomer Solutions for UV Curable Inkjet and 3D Printing Applications

Jo Ann Arceneaux, Ph.D.
Allnex USA Inc.
*Alpharetta, GA, USA*

INTRODUCTION

Many of the diluting monomers currently used in UV curable inkjet and 3D printing applications are under increased regulatory constraints due to new labeling requirements. It is very difficult to find regulation friendly replacements for these monomers that have equal diluency characteristics. The result is an unacceptable increase in formulation viscosity as these monomers are replaced.   An alternative solution is to use lower viscosity oligomers in the formulation. In addition to low viscosity, the oligomers must provide the performance properties of the formulation. One of these properties is the ability to cure under low energy conditions, such as long wavelength LED lamps.   This paper will explore various classes of low viscosity oligomers, and their cure response to low energy, long wavelength lamps.

DILUTING MONOMERS

Due to the very low viscosity requirements of inkjet inks and some 3D printing applications, monofunctional acrylate monomers are used because of their excellent diluency characteristics. Some typical monomers are CTFA (cyclic trimethylolpropane formal acrylate), THFA (tetrahydrofurfuryl acrylate), and IBOA (isobornyl acrylate). As REACH and other regulations are implemented, more toxicity data on these products are generated, frequently causing changes in their classification and labeling. These changes may then limit the use of these monomers in certain end applications. Food packaging is an especially regulated application. Extractables must be minimized or eliminated, thus monofunctional materials find little use in food packaging applications.

Difunctional monomers with good diluency are also used to reduce viscosity, but suffer from some of the same regulatory constraints as new SHE data is generated. For food packaging applications, the Nestle Exclusion List (BDDA (butanediol diacrylate), DEGDA (diethyleneglycol diacrylate)) and Nestle Minimize List (DPGDA (dipropyleneglycol diacrylate), HDDA (hexanediol diacrylate), TTEGDA (tetraethyleneglycol diacrylate)) reference many of the difunctional monomers with good diluency.

Multi-functional monomers generally have better labeling characteristics, but worse diluency. The Nestle Minimize List for food packaging contains TMPTA (trimethylolpropane triacrylate), and PETIA/PETA (pentaerythritol tri/tetra acrylate). Figure 1 illustrates the structures of some of the diluting monomers.

Figure 1. Diluting Monomers
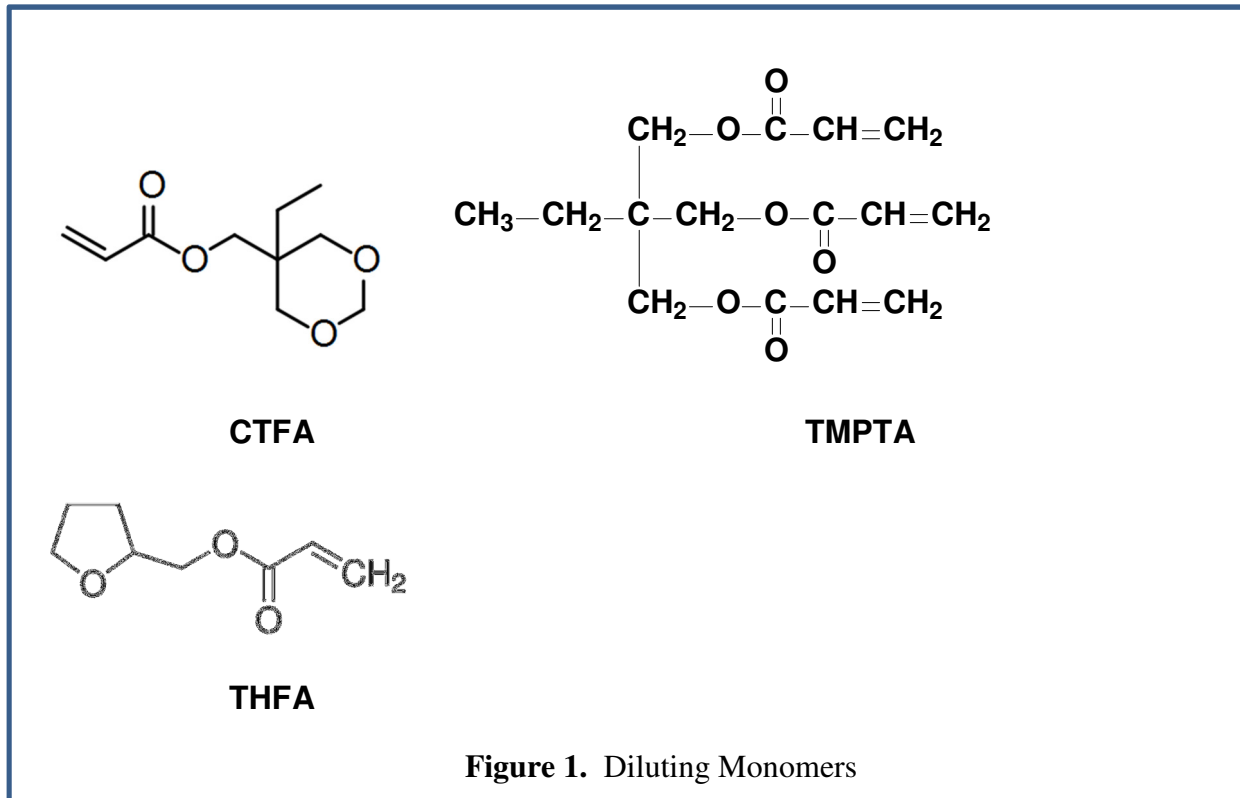
OLIGOMERS

Oligomers are, by definition, higher molecular weight than monomers. The higher molecular weight generally provides better toxicity characteristics, but also higher viscosity. The oligomers also provide the majority of the ink/coating properties, so increasing the amount of oligomer in a formulation generally results in better properties. Thus, it follows that lower viscosity oligomers can provide formulations with higher oligomer content, better properties, and better toxicity characteristics, all at lower or similar viscosities.

**Oligomer Classes and Chemistry**

There are three main classes of UV curable oligomers, epoxy acrylates, polyester acrylates, and urethane acrylates. The epoxy acrylates are mainly based on bisphenol A type structures. (See Figure 2.) While low in molecular weight, hydrogen bonding in their structures results in very high viscosities. Typical properties are high hardness, reactivity, and chemical resistance. Restrictions on bisphenol A (BPA) have recently been limiting the use of epoxy acrylates.

Polyester acrylates are based on polyesters made from multifunctional alcohols and acids. (See Figure 3.) They can vary greatly in molecular weight, functionality, viscosity, cure speed, and cured film properties. Polyester backbones may be aromatic, aliphatic, alicyclic, and/or combinations of these. Amine and thiol modification of polyester acrylates provides fast cure, and some of these are low in viscosity.
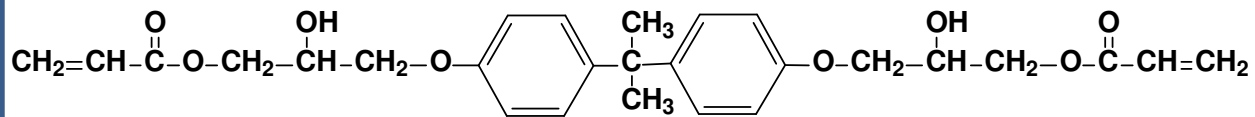
Figure 2. Bisphenol A Epoxy Diacrylate

Urethane acrylates are formed by the reaction of isocyanates with acrylate functional alcohols and optionally, polyols. (See Figure 4.) There are multitudes of possible structures, with varying molecular weights, viscosities, cure speeds, and cured film properties. Urethane acrylates that contain polyethers or thiols are highly reactive. Low weight per double bond oligomers are also fast curing. Cyclic and allophanate structures also provide fast cure characteristics to the urethane acrylates. Depending on their structure, urethane acrylates can be low in viscosity.
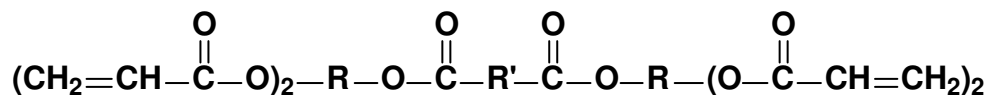
**Figure 3.** Polyester Tetra-acrylate (R = polyol; R´ = diacid)
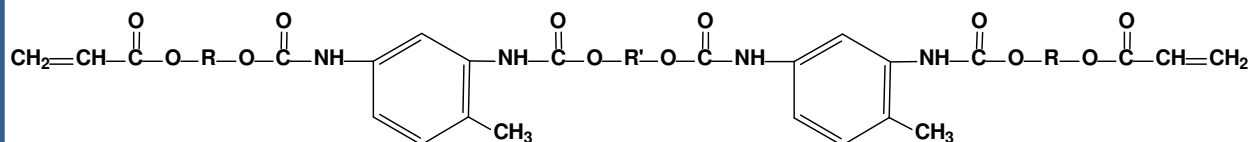
Figure 4. Urethane Diacrylate Based on Toluene Diisocyanate (R´ = diol)

OXYGEN INHIBITION AND MITIGATION

Generally, decreasing the viscosity of a coating increases the oxygen diffusion into the coating, and decreases surface cure due to oxygen inhibition.[1] However, at equal viscosity, formulations with the following characteristics will have better surface cure (less oxygen inhibition): 1) increased acrylate functionality or double bond concentration 2) ether, amine, thiol, and/or other special structural component in the backbone.[2]

Oxygen inhibition of surface cure is due to both quenching and scavenging reactions during free radical polymerization, as shown in Figure 5. The end result is less polymer

formation and/or lower molecular weight polymer chains. In either case, the reaction with oxygen may give a range of results, from reduced coating properties to uncured, liquid surfaces on the coating.

Figure 5. Reactions of Oxygen in UV Initiated Free Radical Polymerization
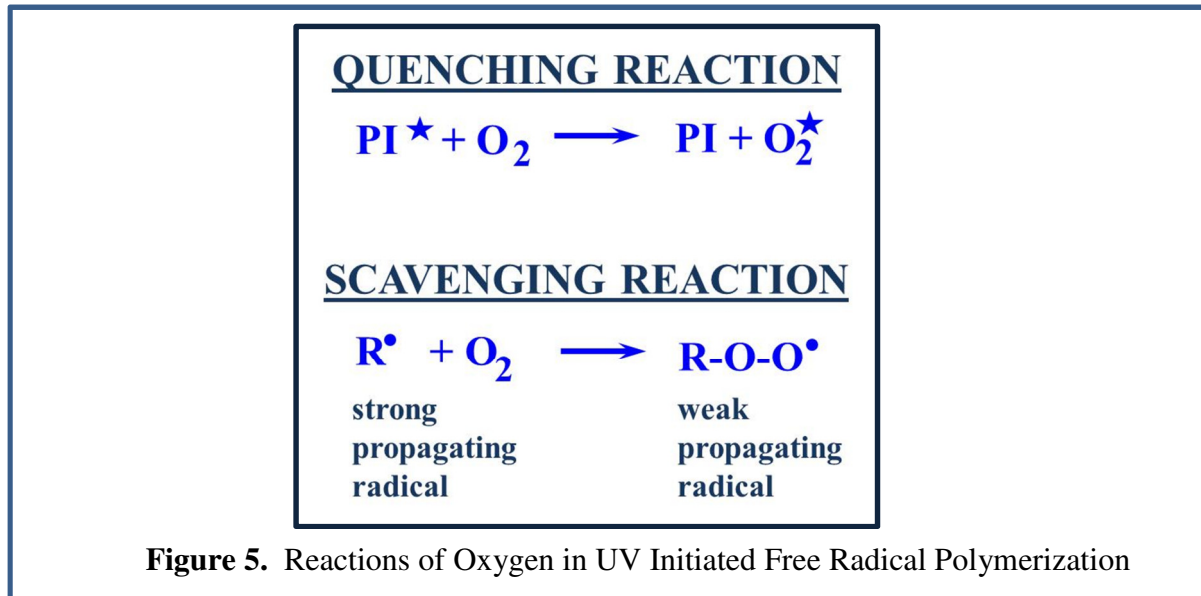
There are known physical and chemical ways to reduce oxygen inhibition and improve surface cure, and these have previously been discussed.[2] A summary of this topic is shown in Table 1. Also, thicker coatings suffer less from oxygen inhibition due to the bulk polymerization reaction, which increases viscosity and significantly reduces oxygen diffusion.[3] Decreasing the distance from the lamp to the substrate increases the irradiance delivered to the substrate, and improves surface cure. Increasing the exposure time, via slower cure speeds or multiple lamps, also generally increases the extent of cure.[2]

The use of reactive chemicals is the most commonly implemented solution to mitigate oxygen inhibition. The chemicals that react with peroxy radicals contain easily abstractable hydrogen atoms. These abstractable hydrogen atoms are found in compounds containing specific structural elements, sulfur (thiols), nitrogen (amines), or oxygen (ethers). The hydrogens on the carbon atoms alpha to the sulfur, nitrogen, or oxygen are those that are easily abstractable, and there are many of these in each molecule. The efficacy of these compounds, for the same equivalency, is thiols > amines > ethers. Improvements in performance are noted when the thiols, amines, and polyethers are acrylated.   The acrylate functionality insures that the materials become part of the polymer backbone, and cannot migrate or bloom to the surface. A reduction in odor may also be obtained through acrylation.

LOW ENERGY CURE MARKETS

UV LED curing is becoming more and more prevalent in several converting areas. UV curable inkjet has used UV LED cure for pinning for many years. Generally a mercury lamp was used at the end of the operation to fully cure the inkjet ink. Today, UV LED cure is being used for the entire inkjet ink converting operation. Flexo presses are being sold or retrofitted to fully

use UV LED lamps. These presses include four-color process inks, plus white inks and clear coats. UV LED lamps are being tested on litho presses, and several wood coating lines are equipped with UV LED cure stations. Other than litho inks, these applications generally require low viscosity formulations. All of the applications require fast cure.

DLP (digital light processing) is a type of 3D printing that uses low energy, high wavelength lamps to manufacture parts from (meth)acrylate based formulations. Another 3D printing type is SLA (stereolithography), which uses long wavelength lasers to manufacture its parts. Both of these 3D printing applications need low viscosity formulations, and fast cure is an advantage.

Table 1. Methods to Mitigate Oxygen Inhibition, with Advantages and Disadvantages

| Method	Advantages	Disadvantages
Inert Gas	Does not adversely affect coating properties	Expensive; difficult to implement
Waxes	Inexpensive	Affects final coating properties; time needed for migration
Films	Good solution when film becomes part of product	Cost/disposal of film when not part of product
Increase PI Concentration	Easy to implement	Increased residuals/by-products; reduced coating properties
Increase Light Intensity	May not affect coating properties	Part of existing equipment; cost
REACTIVE CHEMICALS:		
Thiols	Improved thermal resistance; reduced moisture absorption; improved adhesion	Odor
Amines	Inexpensive; possible improved adhesion	Yellowing upon or after cure; residual odor; moisture sensitivity
Ethers	Can be used in large quantities	Affects coating properties; reduced temperature resistance; possible reduced water resistance
Structural Elements	Can provide good coating properties	Availability; cost; undesired properties

LOW ENERGY CURE SYSTEMS

In the past, UV curing systems have typically consisted of one or two medium pressure mercury bulbs, with broad spectral emissions, and with the wattage steadily increasing over the years from 200 to 600 watts per inch. (See Figure 6.) These systems were generally designed to obtain the fastest cure speed possible, with productivity gains the ultimate goal. Today, curing systems are being designed with other goals also in mind. Safety and environmental concerns, cure temperature, energy consumption, and maintenance schedules are all influencing the design of these new curing systems. As a result, some of the newer cure systems deliver less energy to the coating, and eliminate shorter wavelength UV. Both of these factors tend to increase the impact of oxygen inhibition on UV cure.

Increasing the irradiance increases the concentration of free radicals, and higher concentrations of free radicals consume more oxygen.   Conversely, low energy cure systems,

with lower irradiance, result in lower concentrations of free radicals and more oxygen inhibition. The irradiance should be measured at the substrate, to determine the delivered energy, because delivered energy decreases with distance from the lamp to the substrate.

There is also a wavelength dependence on absorption of UV. UV curable materials exhibit a higher absorbance to short wavelength energy (UVC) than to longer wavelength energy. As a result, short wavelength energy does not penetrate much beyond the surface, and longer wavelength energy (UVB and UVA) survives to penetrate deeper into the material. (See Figure 6 for wavelength nomenclature.) Some of the newer energy cure systems do not emit UVC wavelengths, resulting in increased oxygen inhibition at the surface of the coating.

UVA lamps, by definition, primarily emit wavelengths in the UVA range. Blacklights also have primary emission in the UVA range, and most LED lamps emit at 395 nm, also in the UVA range. LED lamps with 385 nm and 405 nm emissions are also used, and lamps with 365 nm emission are available, but at lower intensity. (See Figure 6.) The LED lamps have seen a steady increase in peak irradiance, from 1.1 watts/cm^2 to 16 watts/cm^2. Improvements in the optics of UV LEDs have also led to an increase in the irradiance that is delivered to the substrate surface.

*courtesy of Phoseon Technology
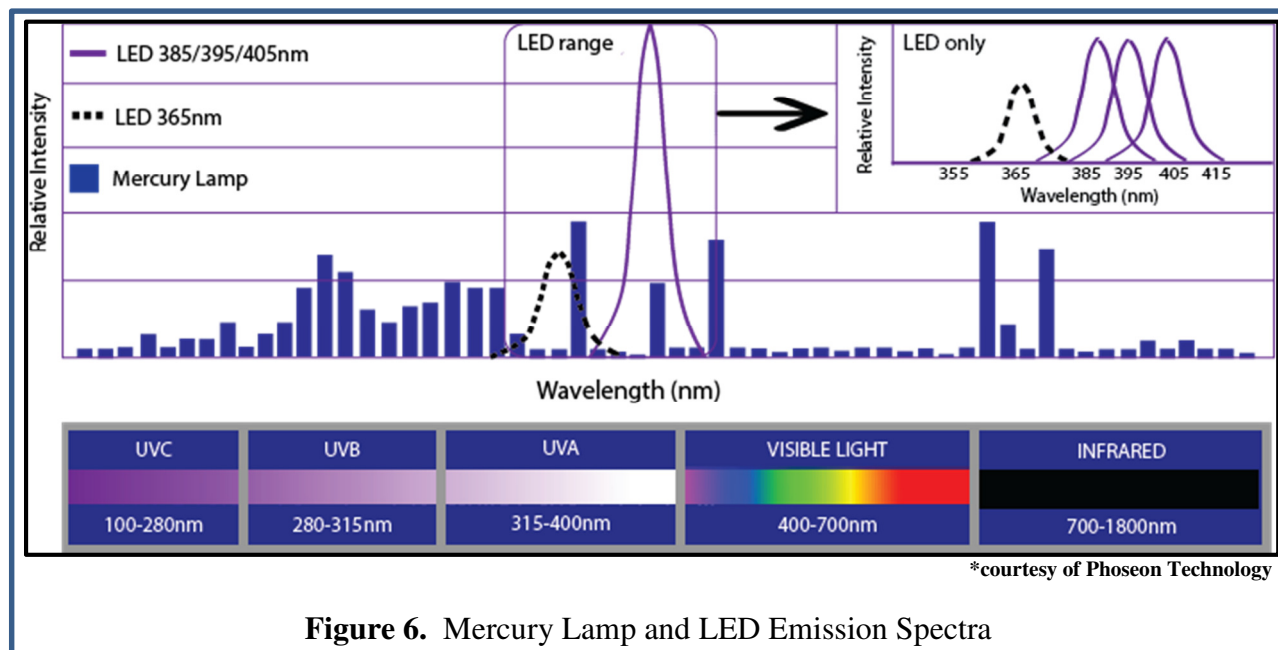
Figure 6. Mercury Lamp and LED Emission Spectra

EXPERIMENTAL DETAILS
Materials
Oligomers, monomers, and mercapto modified resins were obtained from Allnex USA Inc. Photoinitiators were obtained from BASF. All were used as supplied.

Four types of UV cure equipment were used:
1. Fusion UV Systems, Inc. with conveyor system; equipped with 1 or 2 x 600 watts/inch mercury H bulbs
2. HS Autoshot equipped with UVA-400 bulb
3. T12, 40 watt blacklight fluorescent bulbs in homemade cure unit
4. Phoseon FireJet UV LED; 395 nm, 12 Watts/cm^2; 150 mm width; Fusion conveyor system

An ILT 390 Belt Radiometer (International Light Technologies) was used to measure lamp output.

Substrates were aluminum Q-panels, type A, 3x6 inches (Q-Lab), and Mylar D or Melinex 516 type (5 mil, clear, untreated PET film).

Procedures
Formulations were mixed by hand in small glass jars, and then placed in 60° C oven as needed to assist with PI dissolution. Viscosities were measured at 25° C with a Brookfield DV-II+ viscometer equipped with a small cell adapter (#21 spindle).

Tensile properties (tensile strength and modulus, elongation) were measured on UV cured homopolymer films using an Instron, model 4467. Glass transition temperatures (Tg) were measured on UV cured homopolymer films via Dynamic Mechanical Analysis (DMA).

Formulations were drawn down on substrates using wire wound bars, to give approximately 1.5 mils (38 microns) or 0.6 mils (15 microns) coatings. Coatings were cured by exposure to several different UV sources (identified in the Materials section). Either exposure time or conveyor speed was varied during the cure study. Reactivity was assessed via surface cure using a tongue blade to test scratch resistance. Through cure was assessed by solvent resistance (MEK (methyl ethyl ketone) double rubs): ASTM D5402-06 (Method 3; 2 lb. ball peen hammer).

EXPERIMENTAL RESULTS & DISCUSSION
Eleven urethane acrylates (UA) and two polyester acrylates (PEA) were evaluated during this study. As shown in Table 2, the urethane acrylates varied in weight per double bond (146-882), and their backbones were either polyether or polyester. In addition, UA 6 contained an allophanate structure, and UA 10 was a modified polyether. The two PEAs were based on a proprietary structure, with weights per double bond of 127 and 255. As a reminder, materials with lower weights per double bond will generally cure faster than materials with higher weights per double bond. Also, certain structural elements and polyethers can mitigate oxygen inhibition, and result in better surface cure.

In Table 3, the oligomers are arranged in order of increasing viscosity. About half of the oligomers have viscosities less than 5000 cP. The viscosities of all but UA 6 are less than 15,000 cP. UA 6 is high in viscosity (60,000 cP at 23 C), and was included as a negative control. It also has a low weight per double bond (200).

Table 2. Oligomer Descriptions

Product	Weight per Double Bond	Description
UA 1	475	polyester
UA 2	466	polyester
UA 3	458	polyether
UA 4	542	polyether
UA 5	225	polyester
UA 6	200	polyester; allophanate
UA 7	882	polyether
UA 8	869	polyether
UA 9	520	polyether
UA 10	530	polyether; modified
UA 11	146	polyester
PEA 1	127	proprietary
PEA 2	255	proprietary

Table 3 also shows the tensile properties and glass transition temperatures of the oligomers. A wide variety of properties are available with the use of these oligomers. Blends of the oligomers should allow an even greater span of properties.

Table 3. Oligomer Properties

Product	Viscosity (cP, 25°C)	Tensile Strength (psi)	Tensile Modulus (psi)	Tensile Elongation (%)	Tg (°C)
PEA 1	450	1740	456750	<1	162
UA 9	800 (23°C)	5800	210011	13	86
UA 10	1500 (23°C)	2934	92012	6.3	67
UA 11	3746	6400	379000	2	68
UA 3	3846	370	2270	16.1	4
UA 4	4960	207	1335	15.8	-6
PEA 2	5000	2392	288550	0.9	84
UA 8	6000 (23°C)	870	6694	15	9
UA 2	6000	470	2122	24.3	18
UA 5	7170	5700	268000	3.5	54
UA 7	8000 (23°C)	870	6309	15	12
UA 1	14830	3300	14000	90	14
UA 6	60000 (23°C)	9425	194895	4	65

The reactivity of the oligomers with several different UV sources is evaluated in Figure 7. Coatings were prepared from oligomer with 4 parts of photoinitiator (2-hydroxy-2-methyl-1-phenyl-1-propanone), and applied at 37 microns (1.5 mils) on aluminum Q-panels. The

oligomers are listed on the x axis in order of increasing viscosity. The blue bars give the time needed in minutes to cure the oligomers under blacklights. Cure time in minutes with an HS AutoShot UVA-400 lamp is shown by the red bars. The green line is reactivity under Fusion H lamps, in mJ/cm^2. More details on the cure lamps are shown in Table 4. In all cases, higher reactivity is indicated by smaller numbers.
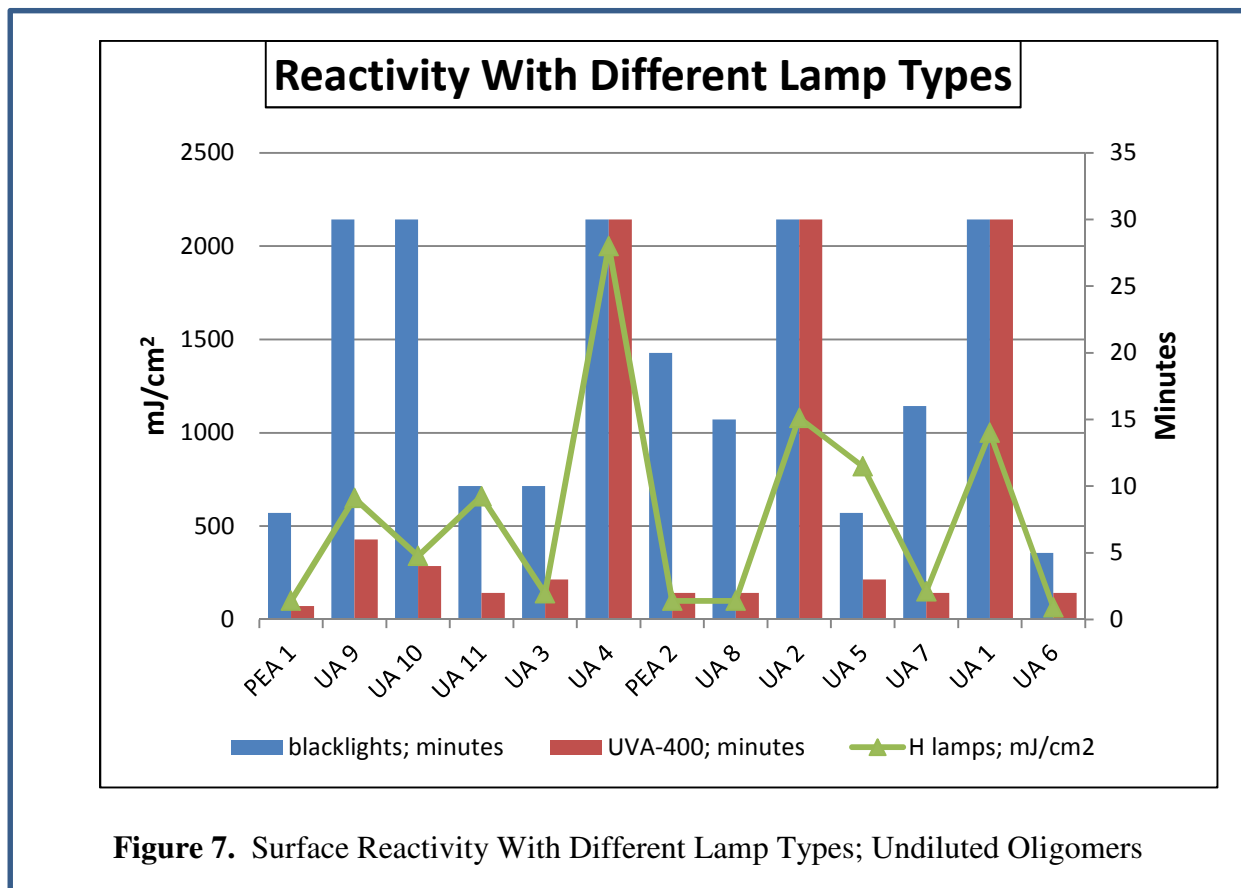
Figure 7. Surface Reactivity With Different Lamp Types; Undiluted Oligomers

The lowest (PEA 1) and highest (UA 6) viscosity oligomers have the best reactivity under all three types of cure. As mentioned earlier, higher viscosity coatings will surface cure faster than lower viscosity coatings because of less oxygen diffusion into the coating. Thus, it is notable that PEA 1, with a RT viscosity of 450 cP cures about as fast as UA 6, with a RT viscosity of 60,000 cP. PEA 1 contains a proprietary structural element that contributes to fast cure through mitigation of oxygen inhibition, and overcomes the effect of additional oxygen diffusion into the low viscosity coating. PEA 1 could then be used to formulate low viscosity, high reactivity coatings without the use of large amounts of diluting monomers. Other low viscosity oligomers with overall good reactivity include PEA 2, UA 3, UA 6, UA 7, UA 8, and UA 11. These oligomers will be further discussed below.

Table 5 more closely investigates blacklight cure. The top four oligomers for fast cure (UA 6, PEA 1, UA 5, UA 11) are also the oligomers with the lowest weights per double bond. Cure speed does not follow weight per double bond after the top four, however. UA 3, UA 7,

and UA 8 are notable for their fast cure with higher weights per double bond. All three are based on polyether structures, which can mitigate oxygen inhibition of cure.

Table 4. Lamp Descriptions

Cure Source	Wavelength Emission	Lamp Type	Distance (lamp to substrate)	Energy at Substrate (one minute of exposure)
Blacklights	UVA (368 nm)	9 watts (T12)	3-4 in	143 mJ/cm^2
UVA-400 Lamp	UVA	400 watts	8-10 in	2136 mJ/cm^2
Hg Lamps	UVC; UVB; UVA	600 watts per inch	6 in	na
UV LED Lamps	UVA (395 nm)	12 watts per cm^2	6-8 mm	na

Table 5. Surface Reactivity with Blacklights

Product	Cure Time; minutes	Weight per Double Bond
UA 6	5	200
PEA 1	8	127
UA 5	8	225
UA 11	10	146
UA 3	10	458
UA 8	15	869
UA 7	16	882
PEA 2	20	255
UA 1	30	475
UA 10	30	530
UA 2	30	466
UA 4	30	542
UA 9	30	520

UVA cure is more closely investigated in Table 6. Once again, UA 3, UA 7, and UA 8 outperform some of the oligomers with lower weights per double bond due to their polyether structures. PEA 1, UA 11, PEA 2, and UA 6 are other top performers with UVA cure. They all have low weights per double bond. PEA 2 also contains a proprietary structural element that contributes to fast cure.

Finally, high intensity, broad spectrum mercury lamp cure is investigated more closely in Table 7. UA 3, UA 7, and UA 8 again perform better than their weights per double bond would predict. Also showing fast reactivity are UA 6, PEA 1, and PEA 2. Demonstrating unexpectedly poor reactivity are UA 11 and UA 5, even though they have low weights per double bond. However, these are both polyester based oligomers.

Table 6. Surface Reactivity with UVA-400 Lamp

Product	Cure Time; minutes	Weight per Double Bond
PEA 1	1	127
UA 11	2	146
PEA 2	2	255
UA 8	2	869
UA 7	2	882
UA 6	2	200
UA 3	3	458
UA 5	3	225
UA 10	4	530
UA 9	6	520
UA 4	30	542
UA 2	30	466
UA 1	30	475

Table 7. Surface Reactivity with Mercury H Lamps

Product	Cure Dose; mJ/cm^2	Weight per Double Bond
UA 6	65	200
PEA 1	100	127
PEA 2	100	255
UA 8	100	869
UA 3	140	458
UA 7	150	882
UA 10	340	530
UA 9	650	520
UA 11	660	146
UA 5	820	225
UA 1	1000	475
UA 2	1080	466
UA 4	2000	542

Table 8 provides an assessment of through cure, as measured by solvent resistance (MEK double rubs). Of the fast surface curing oligomers, only UA 3 cured with blacklights did not demonstrate good through cure. However, it did have good through cure when cured using the UVA-400 lamp. The data in Table 8 demonstrates that low viscosity oligomers can provide both surface cure and through cure when cured under low intensity, high wavelength conditions.

**Table 8.** Through Cure with Blacklights and UVA-400 Lamp

Product	Blacklights; MEK DRs	UVA-400 Lamp ; MEK DRs
PEA 1	50	50
UA 9	1	15
UA 10	3	>50
UA 11	50	>50
UA 3	15	50
UA 4	15	11
PEA 2	>50	50
UA 8	40	>50
UA 2	10	>50
UA 5	>50	>50
UA 7	40	>50
UA 1	6	50
UA 6	>50	>50

The previous studies all evaluated the cure of neat oligomers with photoinitiator. The following studies will investigate diluted oligomer systems. Table 9 shows the amount of monomer (TMPEOTA, ethoxylated trimethylolpropane triacrylate) needed to produce formulations with viscosities of approximately 470 cP. The formulations also contained 25% mercapto modified resin (PEA 1 contained 20%). PEA 1 needed no monomer dilution, as its neat viscosity is 450 cP. In general, 20-30% of TMPEOTA is needed to achieve the target viscosity when diluting the other oligomers. The exceptions are the two lowest and two highest viscosity urethane acrylates. The viscosity of TMPEOTA is about 70 cP at 25° C, and its weight per double bond is 143.

Table 9. Monomer Dilutions For Equal Viscosity Formulations

Product	Neat Oligomer Viscosity (cP, 25℃)	TMPEOTA (%) Target Viscosity of 470 cP @ 25℃
PEA 1	450	0
UA 9	800 (23℃)	6.6
UA 10	1500 (23℃)	16.9
UA 11	3746	20.2
UA 3	3846	24.6
UA 4	4960	Not Tested
PEA 2	5000	25.8
UA 8	6000 (23℃)	28.8
UA 2	6000	25.8
UA 5	7170	25.8
UA 7	8000 (23℃)	30
UA 1	14830	35
UA 6	60000 (23℃)	38.5

The TMPEOTA based formulations are evaluated for LED surface cure in Figure 8. In addition to TMPEOTA, the formulations contained 25% mercapto modified resin (PEA 1 contained 20%), and 5% photoinitiator (phenylbis(2,4,6-trimethylbenzoyl)phosphineoxide). The coatings were applied at 15 microns (0.6 mils) thickness on PET film. The oligomers are shown on the x axis in order of decreasing oligomer content. Since all of the formulations are approximately 470 cP in viscosity, there are no surface cure differences due to oxygen diffusion into the coating. Only surface cure differences due to weights per double bond of the formulations, and to mitigation of oxygen inhibition by structural elements should be present.
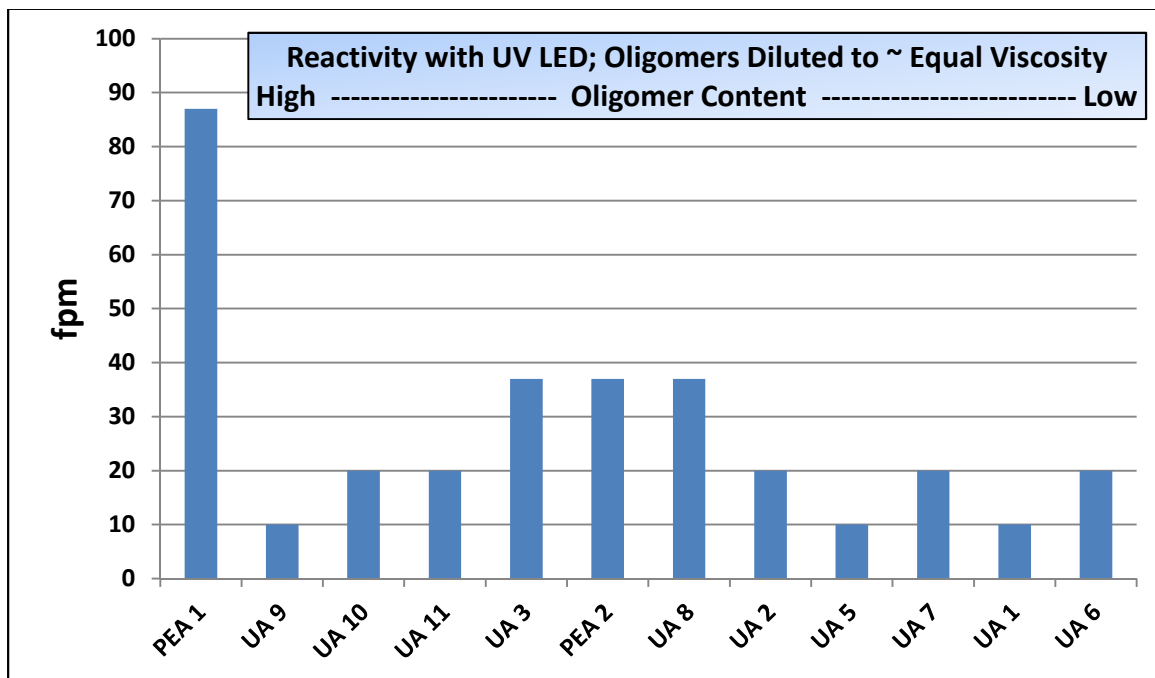
Figure 8. Surface Reactivity with LED Lamps; Oligomers Diluted to ~ Equal Viscosity

PEA 1 has the lowest weight per double bond in the formulation, and continues to give fast cure, more than double the cure speed of the next fastest oligomers (UA 3, PEA 2, and UA 8). As mentioned many times before, PEA 1 is also very low in viscosity (450 cP). The formulation based on PEA 1 thus contains the most oligomer, 75%. This oligomer also has structural elements that provide for fast surface cure. Table 10 provides the oligomer contents, the weights per double bond, and the LED cure speeds of the TMPEOTA diluted formulations. The weights per double bond of the neat oligomers are also included for reference.

PEA 2, UA 3, UA 8, and UA 7 continue to show fast cure of their formulations, outperforming other formulations with lower weights per double bond. PEA 2 has the same structural element as PEA 1, and UA 3, UA 8, and UA 7 have polyether structures, all of which lead to fast surface cure.

Showing slow LED cure speed is UA 6, the high viscosity UA.   Its formulation contains the least amount of oligomer, 31.5%. Although UA 6 showed fast cure in its neat form, once diluted in a formulation, its fast cure speed was lost. This indicates that its fast cure may have been based on its high undiluted viscosity, which limited oxygen diffusion into the coating.

Table 10. Surface Reactivity with UV LED Lamps; Oligomers Diluted to Equal Viscosity in TMPEOTA (Formulation also contains 25% Mercapto Modified Resin (PEA 1 contains 20%) and 5% PI)

Product	Oligomer (%)	Oligomer Weight per Double Bond	Formulation Weight per Double Bond	Formulation Cure Speed (fpm)
PEA 1	75	127	138	87
PEA 2	44.2	255	204	37
UA 3	45.4	458	251	37
UA 8	41.2	869	269	37
UA 7	40	882	265	20
UA 11	49.8	146	158	20
UA 6	31.5	200	176	20
UA 2	44.2	466	248	20
UA 10	53.1	530	290	20
UA 5	44.2	225	194	10
UA 1	35	475	224	10
UA 9	63.4	520	340	10

CONCLUSIONS

Twelve low viscosity oligomers (<15,000 cP) and one high viscosity oligomer (60,000 cP) as a negative control were evaluated for surface cure speed under various cure conditions (blacklights, UVA-400 lamp, mercury lamp, and UV LED lamps). The oligomers were evaluated both neat and diluted to an equal formulation viscosity. Several low viscosity oligomers exhibited excellent surface cure speed under all of the cure conditions and viscosities. Notable for fast cure were PEA 1, PEA 2, UA 3, UA 7, and UA 8. The fast cure is attributed to the mitigation of oxygen inhibition by proprietary structural elements in PEA 1 and PEA 2 and by polyether structures in UA 3, UA 7, and UA 8. The fast curing oligomers have a variety of properties and weights per double bond that would allow the formulation of coatings and inks with a variety of properties.

This study shows that low energy, high wavelength cure is possible for low viscosity oligomers with certain structural elements.   Since these oligomers have low viscosity, their formulations can eliminate or minimize the use of highly diluting monomers, resulting in better regulatory labeling for the formulations.

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