Formulating for Reactivity

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Introduction

UV curable coatings are typically formulated to meet a variety of performance requirements. Reactivity, or cure speed, is often among the most important of these requirements. UV coatings based on the radical polymerization of acrylates are the most widely used. Such coatings are commonly applied as thin (≤50 μ) clear films to a substrate, and cured in air with medium-pressure mercury vapor lamps ranging in output intensities from ~80 to 240 watts/cm. Under these conditions, abundant UV energy is available to the photoinitiator system for the generation of radicals to polymerize the coating. However, due to the effects of oxygen inhibition on the radical polymerization[(1)], the rate of cure at the surface of the coating trails the rate of cure of the coating at depths where oxygen diffusion is minimal.

In this study, the influence on reactivity of key formulation components such as the type monomer, oligomer and photoinitiator was examined. The effect of the additional variable of curing in air versus curing in nitrogen atmosphere was also tested.

To the extent practical, conditions that would be encountered in commercial UV applications were maintained. The formulations, though simplified, were based on commercially available components at levels within common bounds. Industry standard UV curing equipment was used, and coating thicknesses were typical. A simple but reproducible method was utilized for determining reactivity of the coatings.

Materials

Nineteen commercially available acrylate monomers were selected for testing and are listed in Table 1. The chemical structures[(2)] of these monomers are provided in the appendix.

Oligomers were selected from commercially available epoxy acrylates (EA), polyester acrylates (PEA) and aliphatic urethane acrylates (UA) types. Within each type, three oligomers were selected to reflect differences in equivalent weight/functionality and/or differing backbone structures. Table 2 lists the oligomers along with their equivalent weight, functionality and viscosity. Equivalent weight is inversely related to functionality

Homolytic cleavage and hydrogen abstraction type photoinitiators were compared for their relative effectiveness when curing in air.

Procedures

The coating formulations were applied to the test substrate at a film thickness of 25-50 µ. UV curing in air was performed with one or two 240 watt/cm electrodeless medium pressure mercury vapor lamps at maximum output. UV curing in nitrogen was performed with one or two medium pressure mercury vapor arc lamps at an output of 80 watt/cm. When curing in nitrogen, the oxygen level in the curing chamber was kept below 200 ppm.

The following procedure was used to determine the extent of cure at the coating surface. Four layers of paper cloth were fastened to the curved face of 2-lb. ball-peen hammer. Immediately after UV exposure of the coating, the cloth-covered face was pulled across the coating surface with the hammer handle held parallel to the coating. Care was taken to apply as little downward pressure apart from the weight of the hammer. The surface was then examined for marring. This procedure was repeated until the minimum UV energy level to achieve a non-marring coating surface was identified. This is reported as the energy to cure. The lower the "energy to cure" that is required, the faster the cure speed, or reactivity, of the formulation.

Table 1. Monomers

Monofunctional	Difunctional	Tri & Higher functional
ß-CEA β-carboxyethyl acrylate	**DPGDA** Dipropylene glycol diacrylate	**DTMPTA** Ditrimethylolpropane tetra-acrylate
IBOA Isobornyl acrylate	**HDODA** Hexanediol diacrylate	**GPTA** Glycerol propoxylate triacrylate
ODA Octyl/decyl acrylate	**NPG(PO)$_2$DA** Neopentylglycol propoxylate(2) diacrylate	**PETA (1/1), (1/3)** Pentaerythritol tri/tetra-acrylate
P(EO)$_2$A Phenol ethoxylate (2) acrylate	**TCDA** Tricyclodecanediol diacrylate	**TMPEOTA** Trimethylolpropane ethoxylate triacrylate
2-PEA 2-Phenoxyethyl acrylate	**TRPGDA** Tripropylene glycol diacrylate	**TMPTA** Trimethylolpropane triacrylate
AUA Aliphatic urethane acrylate	**TTEGDA** Tetraethylene glycol diacrylate	**PE(OR)$_x$TA** Pentaerythritol alkoxylate tri/tetra-acrylate

Table 2. Oligomers

	Equivalent weight[(1)]	Functionality[(2)]	Viscosity at 25°C, cP
EA-1	260	2.0	800,000
EA-2	420	2.0	1,600,000
EA-3	740	2.0	200,000
PEA-1	170	4.5	50,000
PEA-2	180	3.3	500
PEA-3	190	3.6	500
UA-1	110	4.7	85,000
UA-2	480	2.0	15,000
UA-3	660	2.0	260,000

Table 3. Photoinitiators

	Designation	Type
1-Hydroxy-cyclohexylphenyl-ketone	CPK	Homolytic cleavage initiator
Benzophenone	BP	Hydrogen abstraction initiator
N-Methyldiethanolamine	MDEA	Synergist

Performance

Monomers

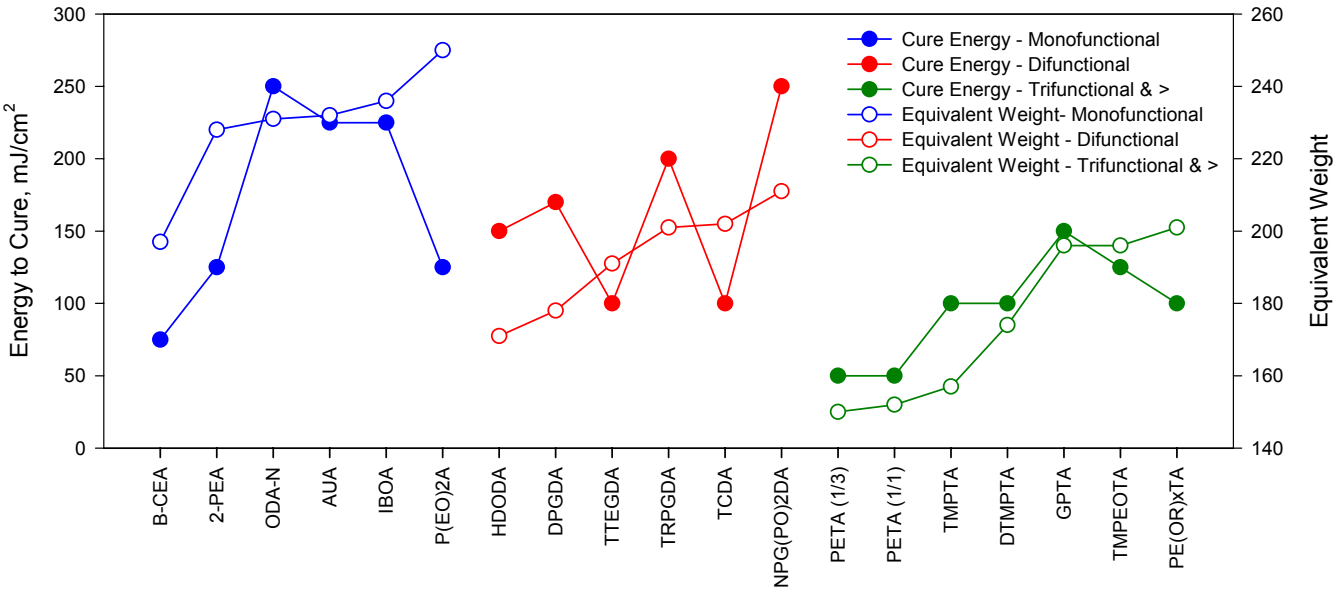
Each monomer was tested in the standard formulation shown in Table 4. EA-1 is an epoxy acrylate oligomer derived from the diglycidylether of bisphenol-A. This oligomer is one of the most commonly used in UV coatings.

Table 4.

Component	%
EA-1	57.7
Monomer	38.5
Photoinitiator (CPK)	3.8

Graph 1 compares the energy to cure with the equivalent weight for each of the formulations. The formulations are grouped by the functionality of the monomer.

Graph 1. Monomers: Cure Energy vs. Equivalent Weight



The data indicate two general trends. First, within each group, as equivalent weight increases, reactivity decreases. Second, as the functionality of the monomers increases, so does the reactivity. However, there are a number of exceptions to these trends. With respect to monomer functionality, the reactivity of the monofunctional ß-CEA exceeds all but the two pentaerythritol tri/tetra-acrylates. Also

the reactivity of 2-PEA and $P(EO)_2A$ is superior to all but two of the difunctional monomers. Similarly, the reactivity of the difunctional TTEGDA and TCDA is equal to or greater than all the tri & higher functional monomers except the two pentaerythritol tri/tetra-acrylates.

The correlation of increasing equivalent weight to decreasing reactivity is weakest among the monofunctional monomers. $P(EO)_2A$ deviates strongly from this trend as, to a lesser extent, do AUA and IBOA. Though ß-CEA and 2-PEA follow the trend, their reactivity is higher than might be expected based on equivalent weight.

Among the difunctional monomers, TTEGDA and TCDA clearly deviate from the trend and DTMPTA, TMPEOTA and $PE(OR)_XTA$ deviate from the trend among the trifunctional & >.

The superior reactivity of 2-PEA, $P(EO)_2A$, TTEGDA, TMPEOTA, and $PE(OR)_XTA$ can be attributed to the presence of the ethylene oxide groups in their structures. These groups may act to mitigate oxygen inhibition through hydrogen abstraction of the alpha hydrogens[4]. Other groups with labile hydrogens such as hydroxyls may also undergo hydrogen abstraction[5]. The presence of hydroxyl groups, in addition to low equivalent weight, may account for the high reactivity of PETA (1/1), (1/3).

Like ethylene oxide, propylene oxide groups contain alpha hydrogens that may undergo hydrogen abstraction. Of the monomers studied, DPGDA, TRPGDA, $NPG(PO)_2DA$ and GPTA contain propylene oxide groups, yet do not deviate from the trend of lower reactivity with increasing equivalent weight. The fewer number of labile hydrogens for propylene oxide compared to ethylene oxide may in part account for this. Also, the corresponding increase in equivalent weight from each propylene oxide group may offset the additional labile hydrogen resulting in no net benefit in reactivity from the propylene oxide groups.

Oligomers

The reactivity of the oligomers was compared by incorporating each into the following test formulation.

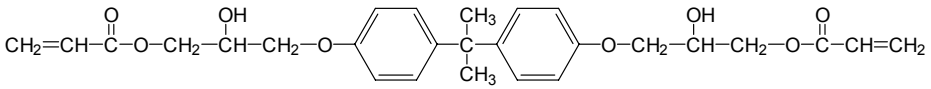
Table 5.

Component	%
Oligomer	57.7
Monomer	38.5
Photoinitiator (CPK)	3.8

Each oligomer was tested in combination with three different monomers: a monofunctional (IBOA), a difunctional (TRPGDA) and a trifunctional (TMPTA) monomer.

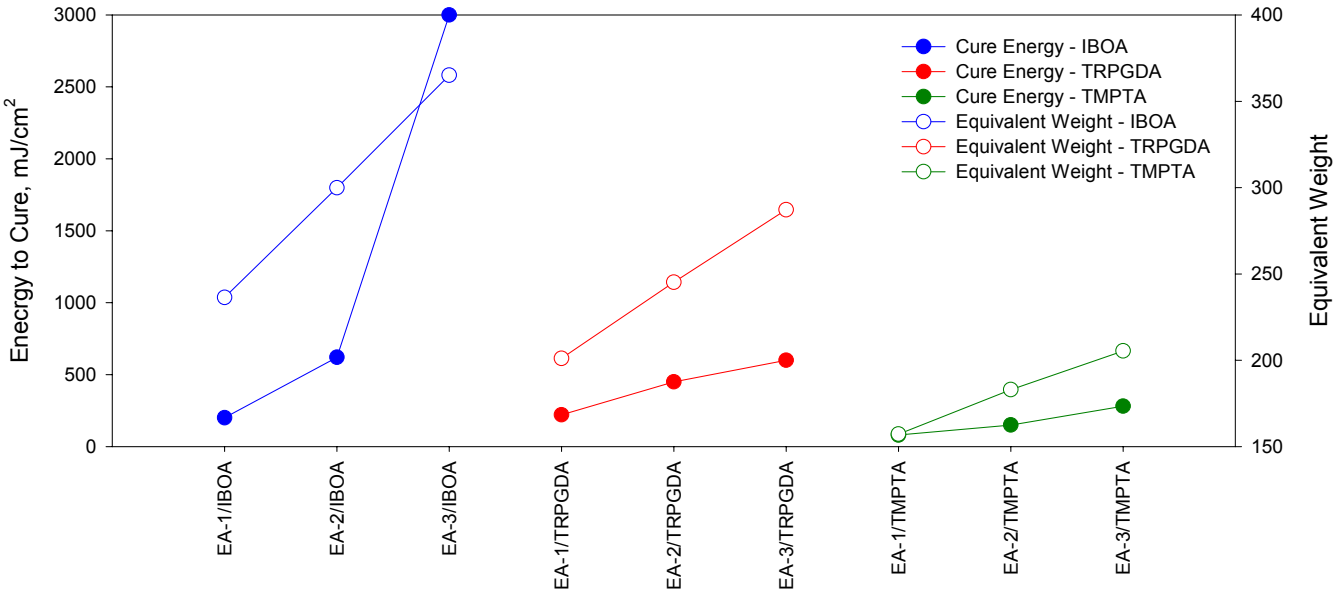
Epoxy Acrylates

Three epoxy acrylate oligomers, EA-1, EA-2 and EA-3 were tested. EA-1 has the following general structure:



EA-2 and EA-3 are chain extensions of this general structure that result in equivalent weights of 420 and 740 respectively, compared to a 260 equivalent weight for EA-1. This equivalent weight applies to both the acrylate and secondary hydroxyl group functionality. Graph 2 compares the energy to cure with the equivalent weight for each of the formulations.

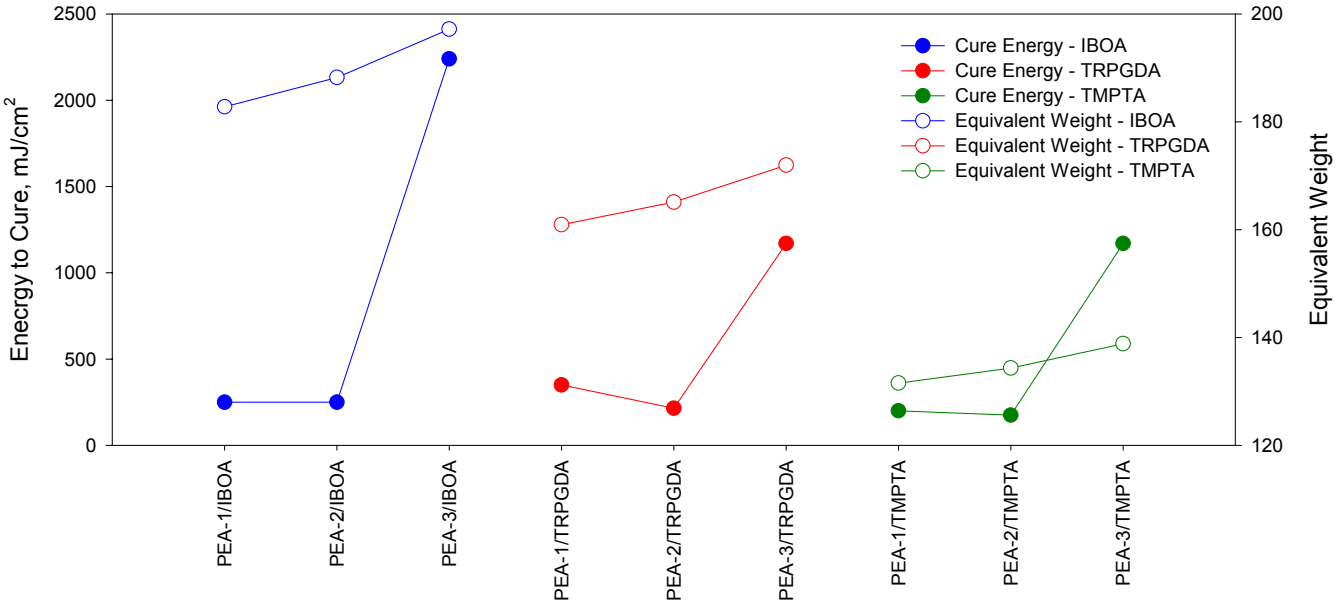
Graph 2. Epoxy Acrylate Oligomers: Cure Energy vs. Equivalent Weight



A clear correlation of equivalent weight with reactivity is seen in the formulations of epoxy acrylates. This is consistent with the method of chain extension used to increase the equivalent weight of EA-2 and EA-3, which does not give rise to an increase in secondary hydroxyls that might further mitigate oxygen inhibition[6].

Polyester Acrylates

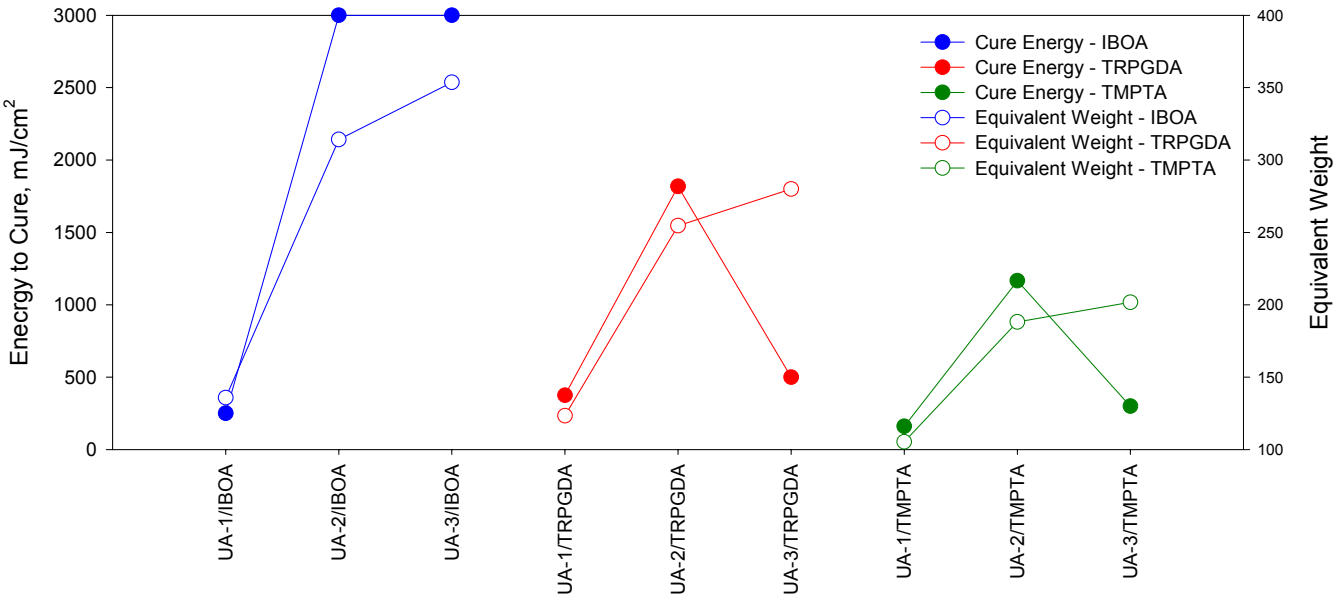
Graph 3. Polyester Acrylate Oligomers: Cure Energy vs. Equivalent Weight



In the case of the polyester acrylate oligomers (Graph 3), the lower reactivity of PEA-3 is notable in each grouping, even though the formulation equivalent weight is only modestly higher. This can be attributed to differences in the structure of the polyester oligomers. PEA-1 contains hydroxyl groups that can undergo hydrogen abstraction and mitigate oxygen inhibition. PEA-2 has an amine modified structure that provides tertiary amine functionality that can reduce oxygen inhibition through oxygen scavenging and hydrogen abstraction[7]. PEA-3 contains no functionality that may mitigate oxygen inhibition and thus has a lesser reactivity than PEA-1 or PEA-2.

Urethane Acrylates

Graph 4. Urethane Acrylate Oligomers: Cure Energy vs. Equivalent Weight



As with the polyester acrylates, deviation from the trend of increasing equivalent weight and decreasing reactivity was observed. The low equivalent weight of the formulations with UA-1 resulted high reactivity in each monomer group. Coatings UA-2/IBOA and UA-3/IBOA did not cure to a non-marring surface which is attributable to the high equivalent of these formulations. It is notable that the three formulations tested that exceeded 300 equivalent weight all failed to achieve a non-marring coating surface.

The energy to cure for UA-2/TRPGDA and UA-2/TMPTA is commensurate with their equivalent weight. UA-3/TRPGDA and UA-3TMPTA deviate from this trend with a decrease in energy to cure despite an increase in equivalent weight. Once again, this can be attributed to the structure of UA-3, which contains ethylene oxide groups.

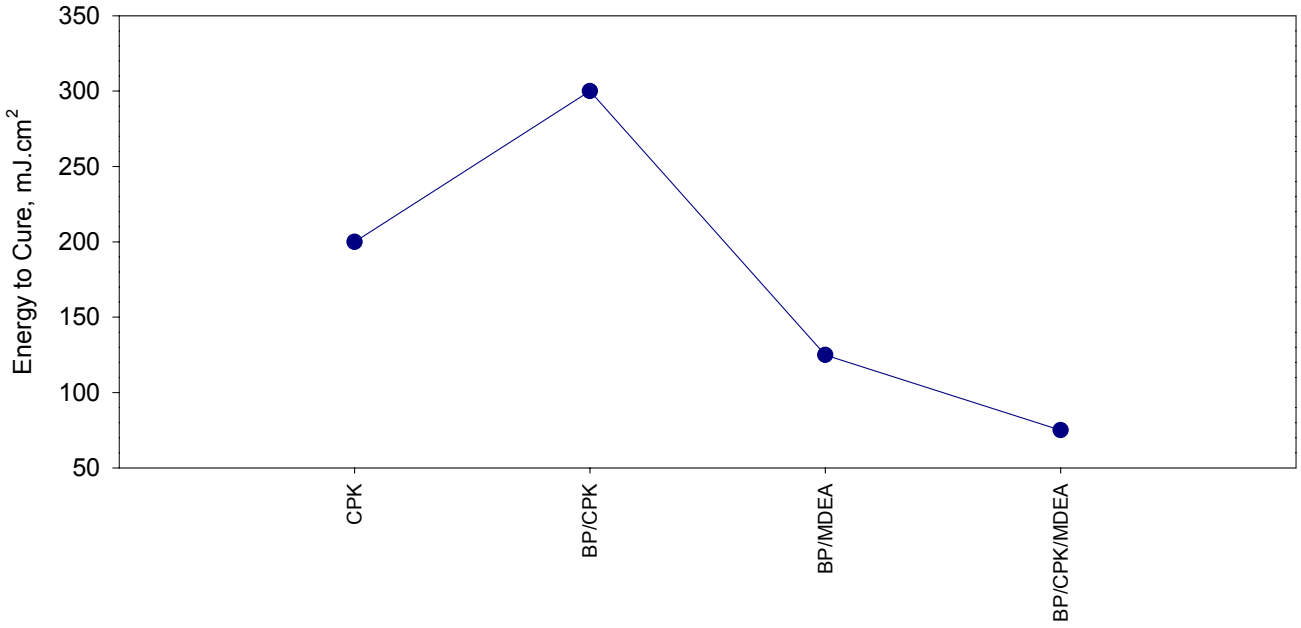
Photoinitiators

Photoinitiator systems that generate radicals through hydrogen abstraction are cited for the ability provide faster surface cure in air by reducing oxygen inhibition[8]. Several formulations were tested comparing homolytic cleavage and hydrogen abstraction photoinitiator systems.

Table 6.

	CPK	BP/CPK	BP/MDEA	BP/CPK/MDEA
EA-1	57.7	57.7	55.6	55.60
TRPGDA	38.5	38.5	37.0	37.00
CPK	3.8	1.9		1.85
BP		1.9	3.7	1.85
MDEA			3.7	3.70

Graph 5. Photoinitiators: Energy to Cure

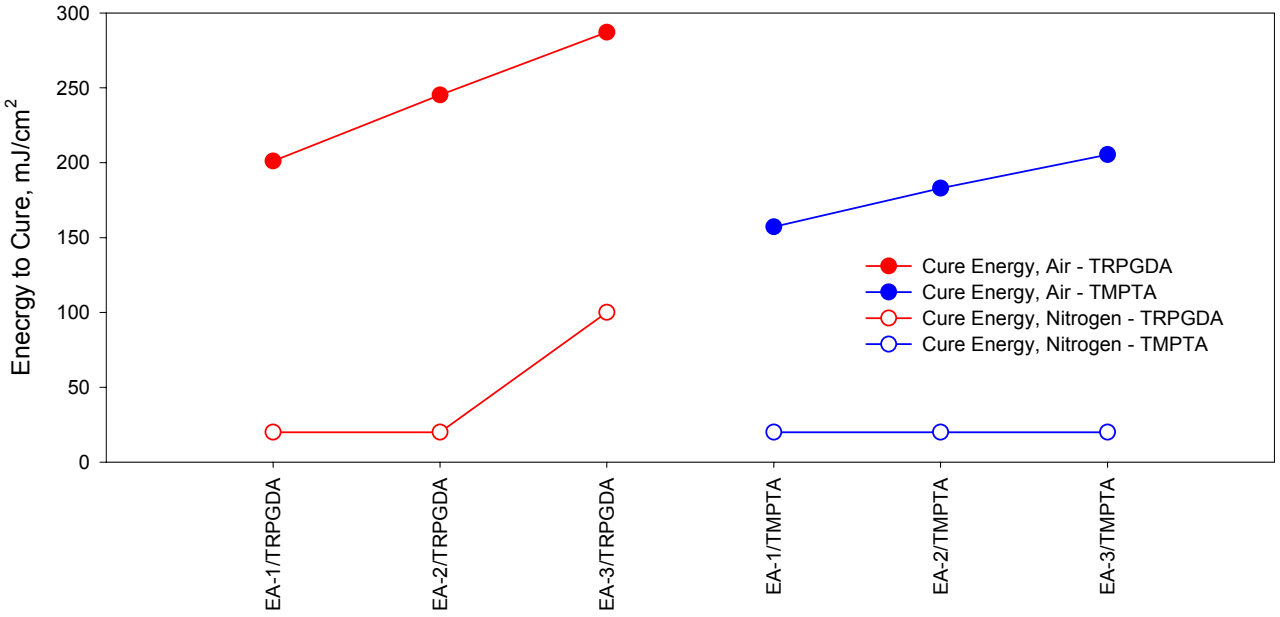


The homolytic cleavage photoinitiator CPK required 200 mJ/cm^2 to cure. Replacing half the CPK with the hydrogen abstraction photoinitiator BP resulted in an increase in the energy to cure. As BP does not directly generate radicals, in the absence of a synergist the replacement of CPK with BP resulted in a reduction in radical generation and a corresponding decrease in reactivity. When BP was combined with the synergist MDEA, significant reduction in energy to cure was observed. The combination of BP and CPK with MDEA provided further reduction in energy to cure, a possible effect of greater radical generation due to broader UV absorption.

Nitrogen Inerting

The UV curing of coatings in a nitrogen atmosphere to eliminate the effects of oxygen inhibition is practiced commercially. To demonstrate the effectiveness of nitrogen inerting, the reactivity of several formulations cure in both air and nitrogen atmospheres was compared.

Graph 6. Energy to Cure in Air vs. Nitrogen



The data clearly demonstrate the effectiveness of nitrogen inerting in reducing the energy to cure. Five of the six formulations cured in nitrogen required only the minimum amount of energy (~20mJ/cm^2) that could be delivered by the curing equipment employed. The actual energy to cure may be less.

Conclusions

Reactivity, as determined by mar resistance of the coating surface upon UV cure of thin clear coatings in air, can be influenced by several factors. The equivalent weight of the coating formulation correlates with reactivity when other factors are absent. In these cases, as equivalent weight increases, reactivity decreases.

In cases where the formulation monomer or oligomer components contain groups such as ethylene oxide, hydroxyl, or tertiary amine that may undergo hydrogen abstraction, oxygen inhibition is reduced and less energy is required to polymerize the coating surface. In these cases, the effect of equivalent weight is minimized, and the correlation between equivalent weight and reactivity is lessened.

The selection of photoinitiator can significantly influence reactivity. A hydrogen abstraction photoinitiator in combination with an amine synergist provides much faster reactivity compared to a homolytic cleavage photoinitiator when curing in air due to the mitigation of oxygen inhibition.

Comparing the reactivity of the same coating formulations cured in air and in nitrogen atmospheres clearly demonstrates the effects of oxygen inhibition. Formulations cured in a nitrogen atmosphere may require less than one tenth the energy needed to cure the same formulation in air.

Acknowledgements

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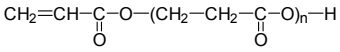
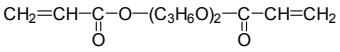
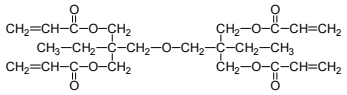
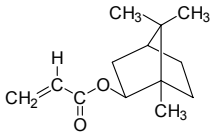
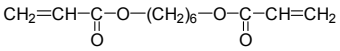
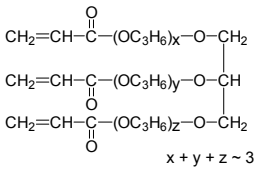
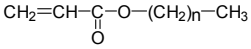
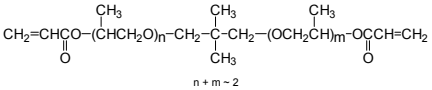
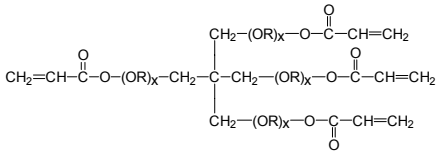
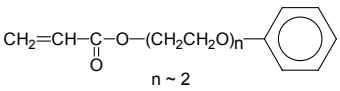
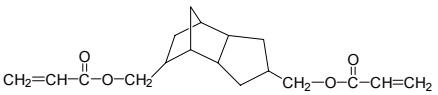
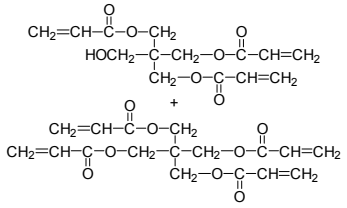
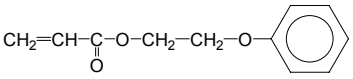
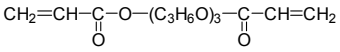
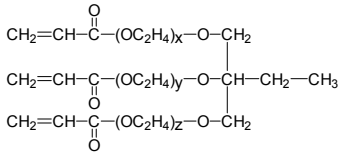
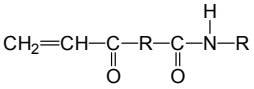
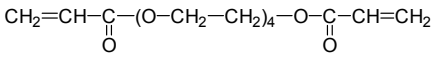
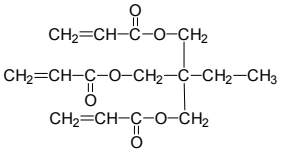
References

(1) Koleske, J., *Radiation Curing of Coatings*, 2002, p. 45
(2) The specific structure of AUA and $PE(OR)_xTA$ is proprietary.
(3) Formulations EA-3/IBOA, UA-2/IBOA, and UA-3/IBOA never reached a non-marring surface. Exposure was stopped at 3000 mJ/cm^2
(4) Hoyle, C. et al., "Photocuring in the Presence of Oxygen – Always a Consideration", *RadTech Report*, Vol. 16, No. 6, November/December 2002, p. 50
(5) Koleske, J., *Radiation Curing of Coatings*, 2002, p. 40
(6) Webster, G. ed., Chemistry & Technology of UV & EB Formulation for Coatings, Inks, & Paints, Vol. II, *Prepolymers & Reactive Diluents*,1997, p. 62
(7) Koleske, J., *Radiation Curing of Coatings*, 2002, p. 46-47
(8) Crivello, J., Dietliker, K., Chemistry & Technology of UV & EB Formulation for Coatings, Inks, & Paints, Vol. III, *Photoinitiators for Free Radical Cationic & Anionic Photopolymerization*, 2nd edition, 1998, p. 85

Appendix

Monofunctional	Difunctional	Trifunctional & >
ß-CEA 	DPGDA 	DTMPTA 
IBOA 	HDODA 	GPTA 
ODA 	NPG(PO)$_2$DA 	PE(OR)$_x$TA 
P(EO)$_2$A 	TCDA 	PETA (1/1), (1/3) 
2-PEA 	TRPGDA 	TMPEOTA 
AUA 	TTEGDA 	TMPTA