

Solving Surface Cure Challenges by Combining UVA and UVC LED in UV Curable Waterborne PUD or 100% Solid Systems

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Abstract

Insufficient surface cure is a known issue for thin coatings cured by UVA LED, namely 395 nm. In this study, UVC LED is used in combination with UVA LED to improve surface cure of thin coatings. Various classes of photoinitiators (PI) are tested in waterborne UV curable polyurethane dispersions (PUD) or 100% solids over print varnish (OPV) formulations. The $\sim 5 \mu\text{m}$ thick coatings are cured under UVA LED, then followed by UVC LED. The minimum energy density required to achieve a mar free surface, yellowing and chemical resistance are reported when cured under UVA LED alone or in combination with UVC LED post cure. The impact of photoinitiator type on curing (both surface and through cure) by UVA+UVC LED will also be presented.

Introduction

UV LED cure is becoming a trend in the UV coating industries because it offers several advantages such as instant on and off, long life time, less heat generation and no ozone production. The biggest challenge associated with LED is poor surface cure, which is caused by oxygen inhibition. The coating surface is exposed to air which contains 21% oxygen. Oxygen molecules can quench the triplet state of the photoinitiators, or scavenge the carbon-based free radicals to become unreactive peroxide radicals to slow down the polymerization. Oxygen inhibition is more dominant in LED cure because of the lack of short wavelength radiation. The typical wavelengths of LED are 365, 385, 395 and 405 nm, which are located in UVA range. As illustrated in **Figure 1**, there is a correlation between wavelength and penetration depth. The long wavelength of UVA LED can penetrate deep into the coating, which is good for through cure, but not helpful for surface cure. In addition, the low power output of some LED lamps cannot deliver sufficient energy to the surface to generate enough free radicals to mitigate oxygen inhibition. All of these factors magnify the negative impact of oxygen inhibition, and can result in tacky and uncured surfaces.

UVC LED emits at ~ 280 nm wavelength, which can be beneficial for surface cure. UVC LED is mostly used for sterilization purposes. In recent years, some studies reported using UVA+UVC LED to improve surface cure.^{1, 2, 3} In our work, UVA+UVC LED are used to cure 100% solids UV or waterborne UV PUD OPVs using various photoinitiators. Their cure response to UVA LED has been previously reported.⁴ Based on the previous work, we continue to study surface cure improvements by using UVC LED as a post cure.

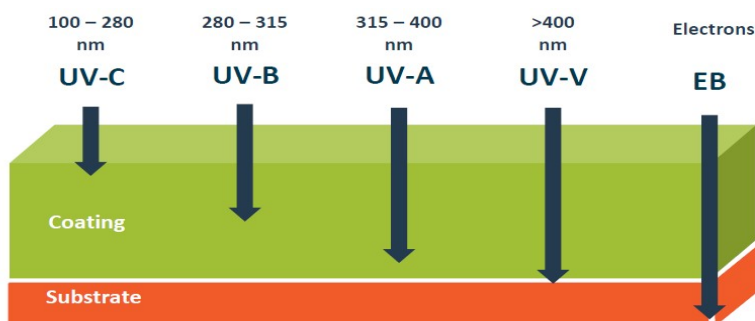


Figure 1. The depth of penetration of different wavelengths

Experimental

Part I. 100% solids UV curable OPV formulations

100% solids formulations were prepared according to **Table 1**. The concentration of epoxy acrylate (bisphenol A diglycidyl ether diacrylate diluted with 40% trimethylolpropane triacrylate) was kept constant, while monomer (trimethylolpropane ethoxy triacrylate) concentration was varied to reach the target viscosity of 500 ± 300 cP at 25°C. LED booster (an amino functional polyester acrylate, 15%) was used in some formulations. Both type I and type II photoinitiators were used. Their properties are given in **Table 2**. A microwave oven was used to gently heat the formulations to 40-45°C in order to fully dissolve the photoinitiators. Then the formulations were mixed at 2400 rpm by speed mixer™ Dac 150 FVZ for 2 minutes. The formulations were coated onto a black and white Leneta chart using a #2 wire rod to achieve ~ 5 μm coating thickness. The coating was first cured under UVA LED (Phoseon Technology, Firejet FJ200, 16W/inch, 395 nm LED), then cured by UVC LED (Phoseon Technology, Fireline 4 W/cm², 278 nm LED). The distance between the lamp and the substrate was 1 cm.

The energy density of UVA LED was measured by an EIT LED cure (LED-R series) L395/40W radiometer. The energy density of UVC LED was measured by an ILT490 belt radiometer. The surface cure was checked by scratch resistance using a wood tongue depressor to gently swipe across the OPV on the black area of the Leneta chart. Through cure was indicated by acetone double rubs. A round head hammer with 1 kg weight was wrapped with 6 layers of cheese cloth. The cheese cloth was soaked with acetone. The surface was rubbed back and forth by the hammer. The numbers of double rubs until the coating was damaged was reported. The color of coating was indicated by b value measured by color guide Cat No 6800.

Table 1. 100% solids OPV formulas

Ingredients	No LED booster	LED booster
Epoxy acrylate in 40 % TMPTA	37	37
Monomer(trimethylolpropane ethoxy triacrylate)	X1	X2
LED booster(amino functional polyester acrylate)	0	15
PI	63-X1	48-X2
Total	100	100

Table 2. Characteristics of photoinitiators

Category	Name	Chemical name	Form	λ_{max} , nm	Type
Phosphine oxides (POs)	PO-1	Ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate	Liquid	274, 290, 370	Norrish Type I
	PO-2	2,4,6-trimethylbenzoyldiphenylphosphine oxide	Powder	267, 298, 380	
	PO-3	Phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide	Powder	281, 365, 395	
	PO-4	Ethyl(3-benzoyl-2,4,6-trimethylbenzoyl)(phenyl) phosphinate	Powder	247, 364	Hybrid Norrish Type I/ Norrish Type II
α -amino ketones (AAKs)	AAK-1	2-Benzyl-2-dimethylamino-4-morpholinobutyrophenone	Powder	321	Norrish Type I
	AAK-2	2-methyl-1-[4-(methylthio)phenyl]2-morpholinopropan-1-one	Powder	306	
α -Hydroxy Ketones (AHKs)	AHK-1	1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propane-1-one	Powder	219, 275	Norrish Type I
	AHK-2	A mixture of 1-hydroxycyclohexyl phenyl ketone and benzophenone	Liquid	249	Hybrid Norrish Type I/ Norrish Type II
Benzophenones (BPs)	BP-1	Benzophenone	Powder	252	Norrish Type II
	BP-2	4-benzoyl-4'-methyl-diphenyl sulphide	Powder	246, 315	
Phenyl Glyoxylate (PG)	PG	Methylbenzoylformate	Liquid	244	
Thioxanthenes (TXs)	TX-1	2-Isopropylthioxanthone	Powder	259, 383	
	TX-2	2,4-Diethylthioxanthone	Powder	261, 291, 386	
	TX-3	1-chloro-4-propoxythioxanthone	Powder	257, 314, 389	

Part II. Waterborne UV PUD based OPVs

Three types of waterborne UV PUDs (**PUD 1, 2 and 6**) and four types of photoinitiators (**PI-A, PI-B, PO-1 and PI-D**) were used in this study, and their properties are given in **Table 3** and **Table 4**. The photoinitiator was first mixed with the surfactants in water by the speed mixer at 2400 rpm for 1 minute to form a uniform emulsion (**Table 5**). Then the PI emulsion was added into the UV PUD together with the other ingredients, and mixed at 2400 rpm by speed mixer for 1 minute (**Table 6**). The formulation was coated on a black and white Leneta chart with a #5 wire rod. The coating was dried at 80°C for 2 minutes to evaporate the water completely, then cured under UVA LED. The coated Leneta chart was then heated on a 90°C hot plate for 1 minute, then immediately cured under UVC LED. It is recommended to cure UV PUD coatings immediately after the drying step, while the coating is still warm, in order to maintain mobility and achieve the best curing. The cured coating thickness was approximately 5 μm .

The degree of surface cure was indicated by double bond conversion as measured by FTIR-ATR technique. The depth of measurement is 1.6 μm . The absorbance at 765 cm^{-1} was used as a reference. The absorbance at 810 cm^{-1} referred to the acrylate double bond. The double bond conversion was calculated as below:

$$\text{Double bond conversion} = 100 \times (1 - R_c/R_l)$$

R_c : ratio of absorbance 810/765 of cured sample

R_l : ratio of absorbance 810/765 of liquid sample

Table 3. Characteristics of waterborne UV PUDs

Type	% Solid	Viscosity cP @ 25°C	pH	Average particle size (nm)	Surface tension (mN/m)	Tacky or tack free after drying
PUD-1	38	15	6.7	90	35	Tacky
PUD-2	38	200	7.3	80	35	Tacky
PUD-6	35	10	6.7	75	32	Tacky

Table 4. Characteristics of Photoinitiators

Name	Chemical name	Form	λ_{max} , nm	Type
PI-A	A blend of 2-hydroxy-2-methyl-1-phenylpropanone, Phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide, Ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate	Liquid	243, 280	Norrish Type I
PI-B	A blend of 2-hydroxy-2-methyl-1-phenylpropanone and 2,4,6-trimethylbenzoyldiphenylphosphine oxide	Liquid	240, 273, 380	Norrish Type I
PO-1	Ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate	Liquid	274, 290, 370	Norrish Type I
PI-D	A blend of Ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate and Phenyl bis(2,4,6-trimethylbenzoyl)-phosphine oxide	Liquid	228, 272, 368	Norrish Type I

Table 5. Photoinitiator emulsions

Ingredients	PI-A	PI-B	PO-1	PI-D
Water	45.5	45.5	45.5	45.5
Surfactant-1	4.5	4.5	4.5	4.5
Surfactant-2	4.5	4.5	4.5	4.5
PI-A	45.5			
PI-B		45.5		
PO-1			45.5	
PI-D				45.5
Total	100	100	100	100
Emulsion appearance	OK	OK	OK	OK

Table 6. UV PUD based OPV formulas

Ingredients	Parts
Waterborne UV PUD	94.5
PI emulsion	5.5
Total	100
% PI in formulation (solid in solid)	7

Results and Discussion

Part I. UVA + UVC LED cure of 100% solids UV OPVs

Figure 2 shows the minimum energy density needed to achieve a mar free surface for OPVs containing PO photoinitiators. The orange and blue colors represent UVA LED cure alone, and UVA LED cure followed by UVC LED cure, respectively. The solid bars indicate a mar free surface and the patterned bars indicate a tacky surface. The numbers on the bars indicate the number of acetone double rubs. Since all PO photoinitiators have some absorption near 395 nm wavelength, a mar free surface can be achieved in all OPVs when cured by UVA LED alone, but at a cost of high PI concentrations, which can overcome oxygen inhibition⁵. By using UVC LED post cure, mar free surfaces can be achieved with significantly reduced PI concentrations since the PO photoinitiators also absorb at the shorter wavelengths. With the incorporation of the LED booster in the formula, the PI concentrations can be even further reduced. This is due to the presence of amino groups in the LED booster, which are known to reduce oxygen inhibition⁶. For all the OPVs, through cure is good, which is indicated by high acetone double rub numbers. Since phosphine oxide photoinitiators are usually expensive, reducing the PI concentration has a positive impact on the total cost of the formulations. Lower PI concentration is also beneficial for food packaging applications, because less PI means less possibility of PI migration.

Figure 3 shows the minimum energy density needed to achieve a mar free surface in OPVs containing AAK photoinitiators together with TX photoinitiator as synergist. Neither of the AAK photoinitiators absorb the long wavelengths emitted by the UVA LED lamps, and thus cannot achieve surface cure if used alone or if only cured under UVA LED. By using TX photoinitiator as a synergist that absorbs at long wavelengths, a mar free surface can be achieved with UVA LED alone. Incorporation of the LED booster plus UVC LED post cure, achieves a mar free surface with either low UVA dosage (AAK-1) or low concentration of PI (AAK-2). Through cure is still poor even though the surface cure is improved by UVC LED post cure. TX photoinitiators usually give good through cure because they absorb long wavelengths that can penetrate deep into the coating. However only a small amount of TX is used, and it is not sufficient to achieve good through cure.

Figure 4 shows the minimum energy density required to achieve a mar free surface in OPVs containing AHK photoinitiators. Since AHKs do not absorb the long wavelengths emitted by the UVA LED lamps, mar free surfaces cannot be achieved under UVA LED alone, regardless of energy dosage, PI concentration or incorporation of LED booster. Using UVC LED post cure, a mar free surface can be achieved, but through cure is not improved.

Figure 5 shows the minimum energy density required to achieve a mar free surface in OPVs containing BPs plus LED booster. Because BPs do not absorb long wavelengths (395 nm), mar free surfaces cannot be achieved in OPVs containing BP-1 cured by UVA LED alone regardless of energy dosage, concentration of BP-1 or incorporation of LED booster. Using UVC LED as a post cure, a mar free surface can be achieved at a BP-1 concentration as low as 1%. For BP-2, a mar free surface can be achieved by UVA LED cure alone with a BP-2 concentration about 15%. Using UVC LED as a post cure, a mar free surface can be obtained at a lower BP-2 concentration (10%).

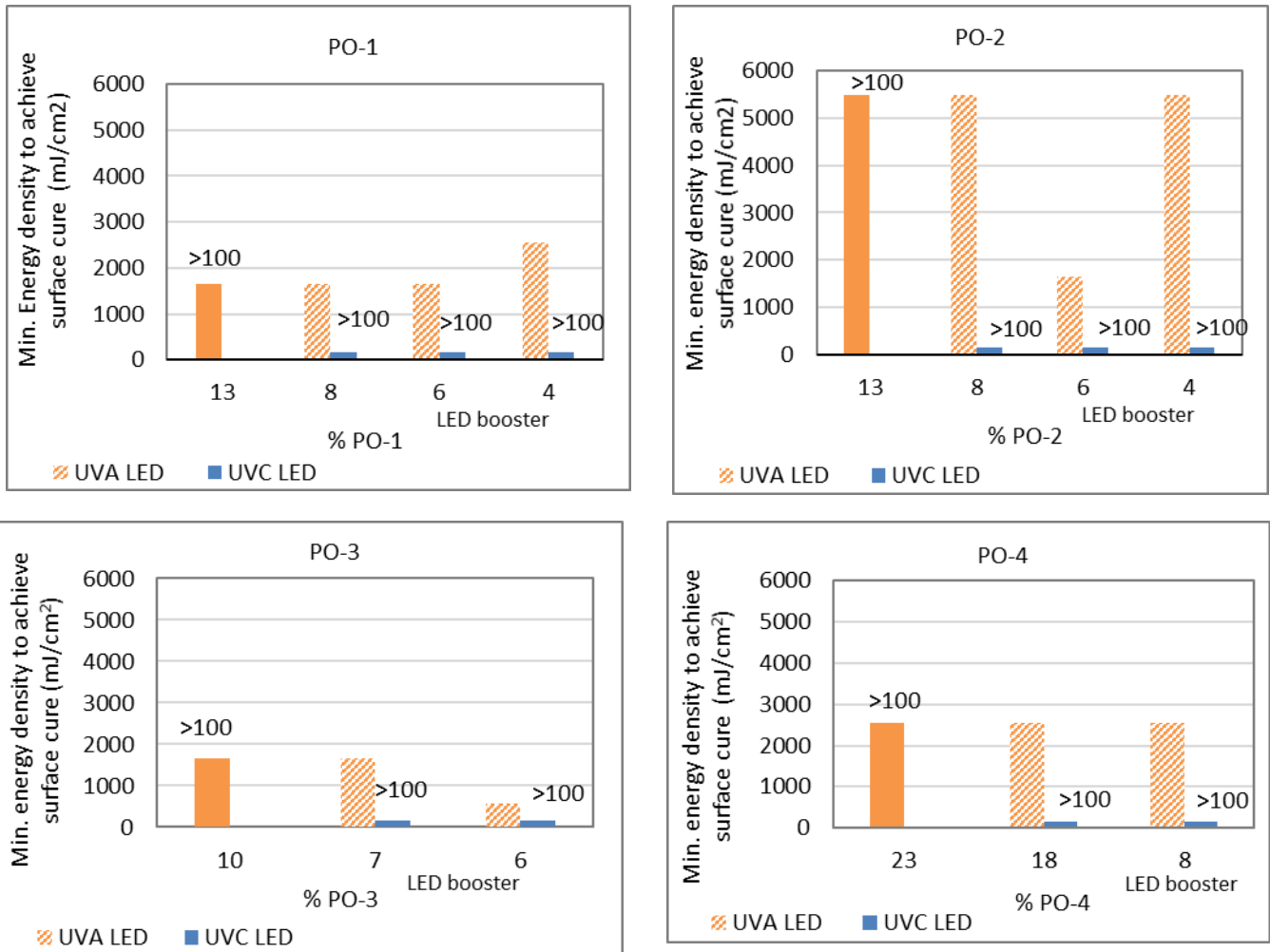


Figure 2. UVA+UVC LED cure of OPVs containing PO Photoinitiators

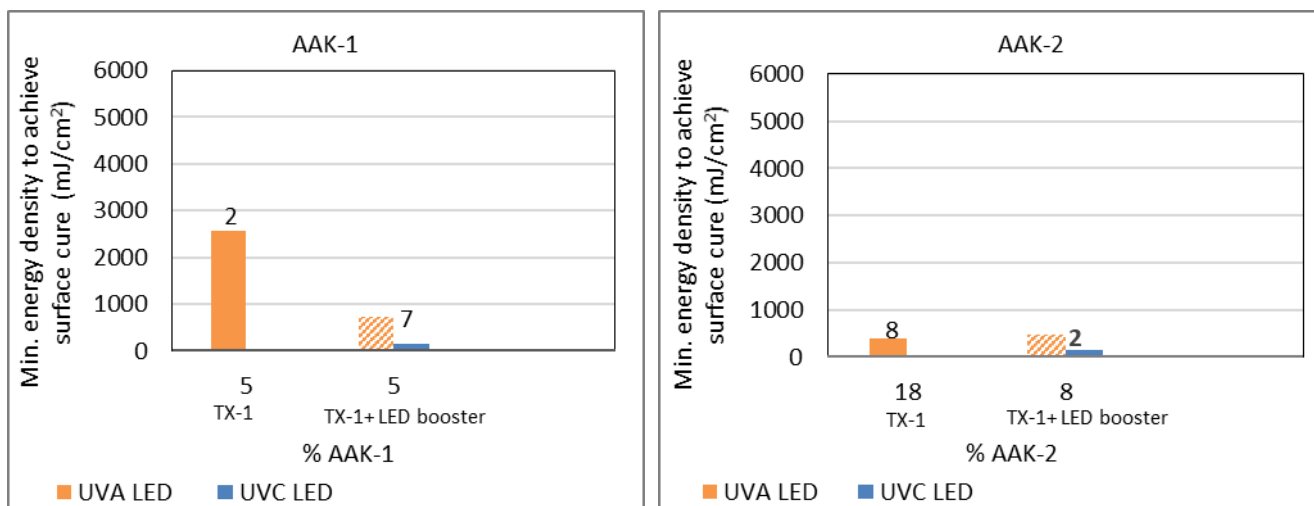


Figure 3. UVA+UVC LED cure of OPVs containing AAK Photoinitiators

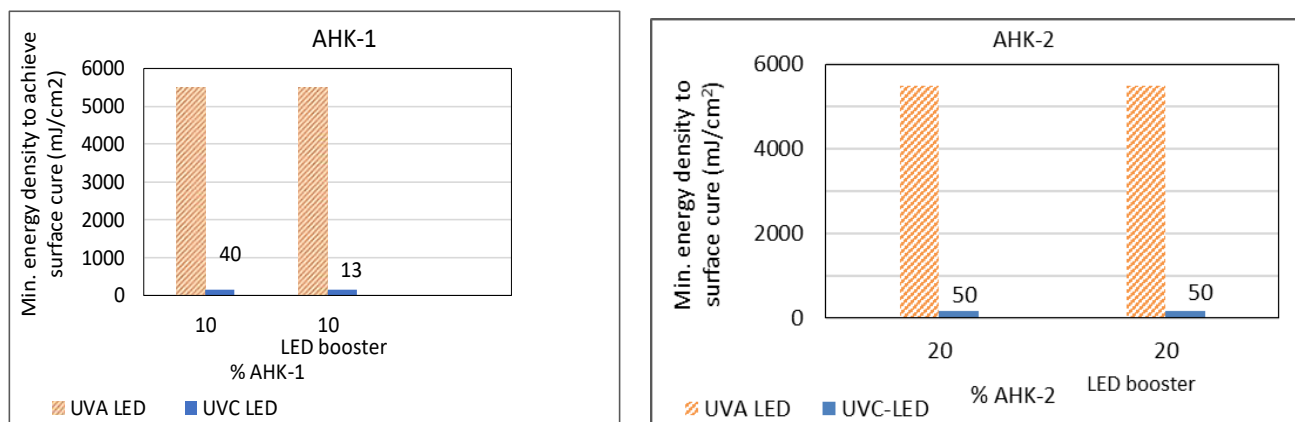


Figure 4. UVA+UVC LED cure of OPVs containing AHK Photoinitiators

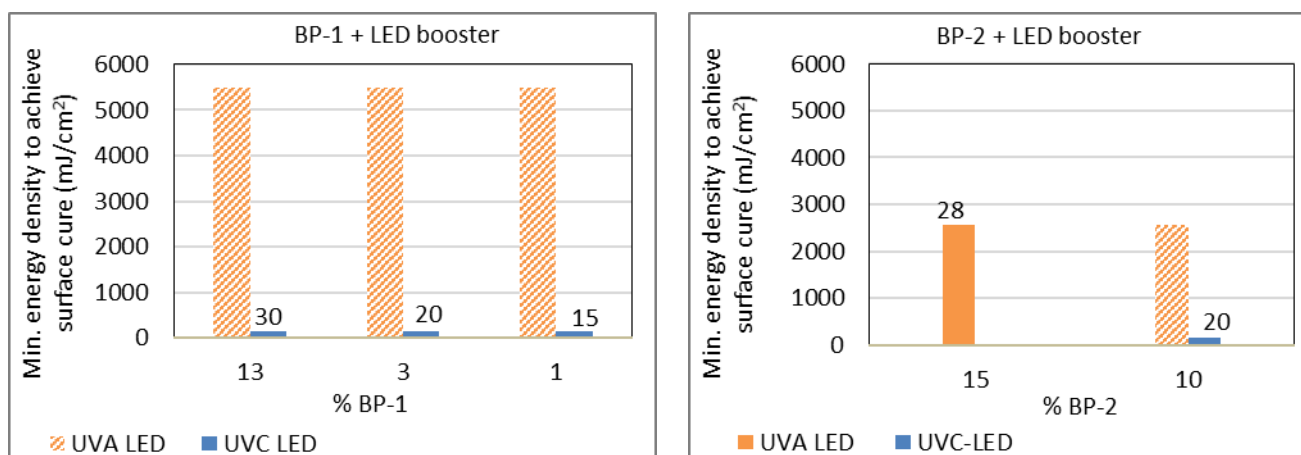


Figure 5. UVA+UVC LED cure of OPVs containing BP Photoinitiators

Figure 6 shows the minimum energy density required to achieve a mar free surface in OPVs containing PG photoinitiator. Since PG only absorbs short wavelengths around 244 nm, a mar free surface cannot be achieved in these OPVs cured by UVA LED alone regardless of energy dosage, concentration of PG, or incorporation of LED booster. Using UVC LED as a post cure, a mar free surface can be achieved with a 5% reduction in PI concentration.

Figure 7 shows the minimum energy density required to achieve a mar free surface in OPVs containing TXs plus LED booster. Since TX photoinitiators absorb long wavelengths and the LED booster mitigates oxygen inhibition, a mar free surface can be achieved at low PI concentrations or low energy dosage even if cured by UVA LED alone. With UVC LED post cure, a mar free surface can be obtained with further reduction of PI concentration. TXs usually impart a yellow color to the coating after cure. Reducing the PI concentration reduces the yellow color. For example, the b value decreases from 6.1 to 5.3 when the TX-2 concentration is reduced from 3 to 1%. Through cure is poor in all OPVs maybe due to insufficient TX concentration.

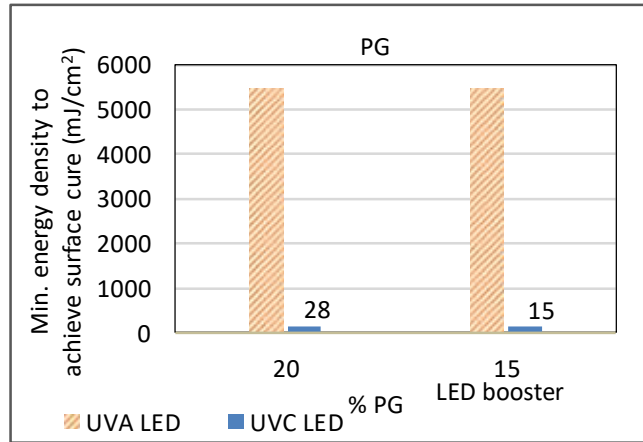


Figure 6. UVA+UVC LED cure of OPVs containing PG Photoinitiator

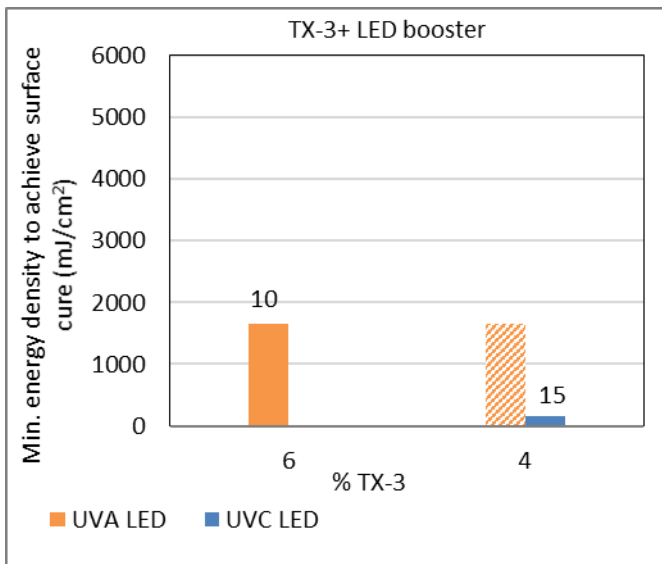
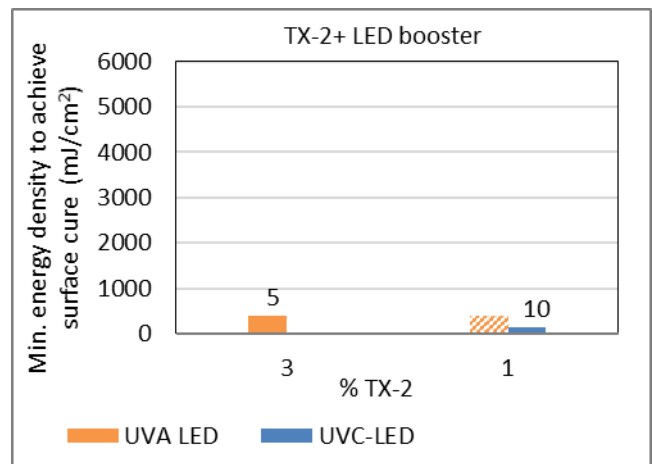
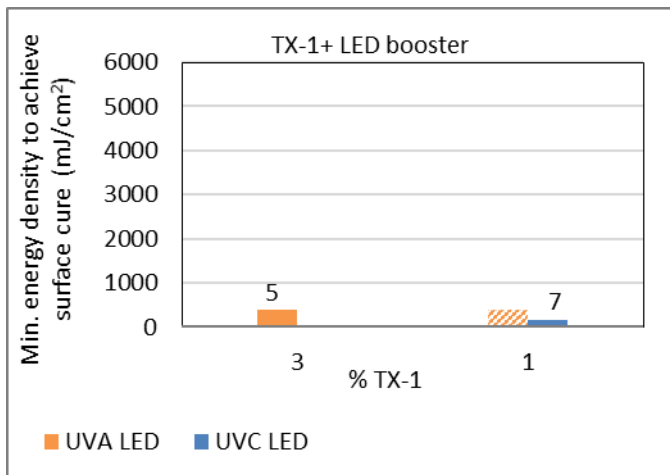


Figure 7. UVA+UVC LED cure of OPVs containing TX Photoinitiators

Part II. UVA + UVC LED cure of UV curable waterborne PUDs

Figure 8 shows the double bond conversion of PUD-1, 2 and 6 with various PIs. Compared to UVA LED cure alone, UVC LED post cure does not improve double bond conversion. For all three PUDs, PO-1 and PI-D have higher double bond conversions than PI-A and PI-B. UV PUDs usually have higher molecular weights than conventional UV resins. When cured under UVA LED, the molecules crosslink with each other, which restricts chain mobility. This lack of mobility inhibits further crosslinking during UVC LED cure, and no additional double bonds are converted.

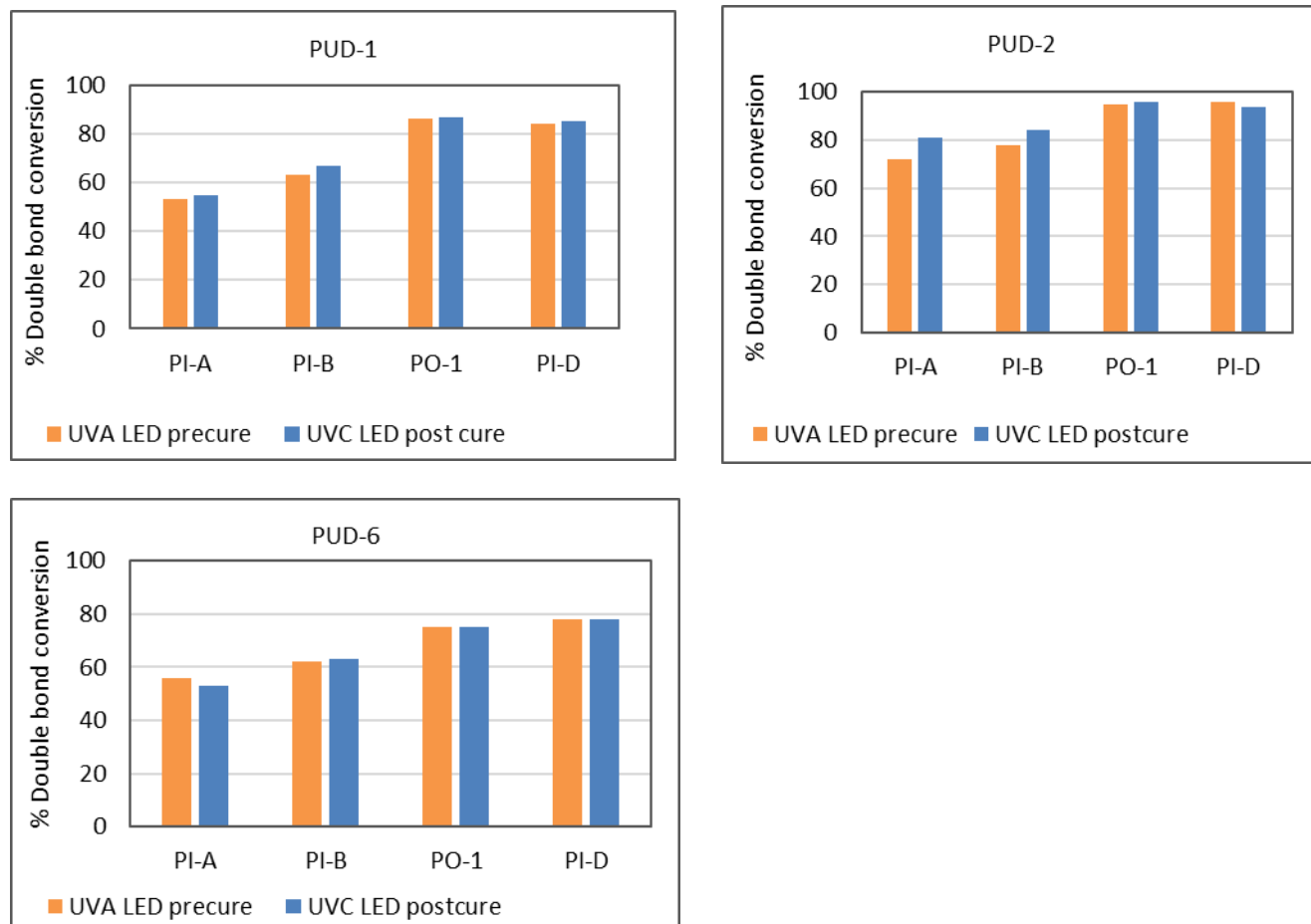


Figure 8. UVA+UVC LED cure of UV PUDs containing various Photoinitiators

Conclusions

UVC LED post cure can help achieve good surface cure in 100% solids UV OPV formulations. For some PIs that absorb both long and short wavelengths, such as PO and TX, UVC LED post cure can achieve mar free surfaces at lower PI concentrations. Incorporation of the LED booster allows further reduction of the PI concentration. The lower PI concentration can lower the cost of the total formulation, reduce the possibility of PI migration in food packaging, and decrease yellowing of the OPV. For those

PIs that absorb short wavelengths, but not long wavelengths, such as AAK, AHK, BP and PG, a mar free surface cannot be achieved when cured under UVA LED alone. With UVC LED post cure, surface cure can be improved at the same or lower PI concentration. Photoinitiator choice is also expanded when UVC LED post cure is utilized. For waterborne UV PUDs, UVC LED does not improve double bond conversion because chain mobility is limited after the UVA LED cure step.

Acknowledgements

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