Photoinitiator Selection

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DSM Functional Materials
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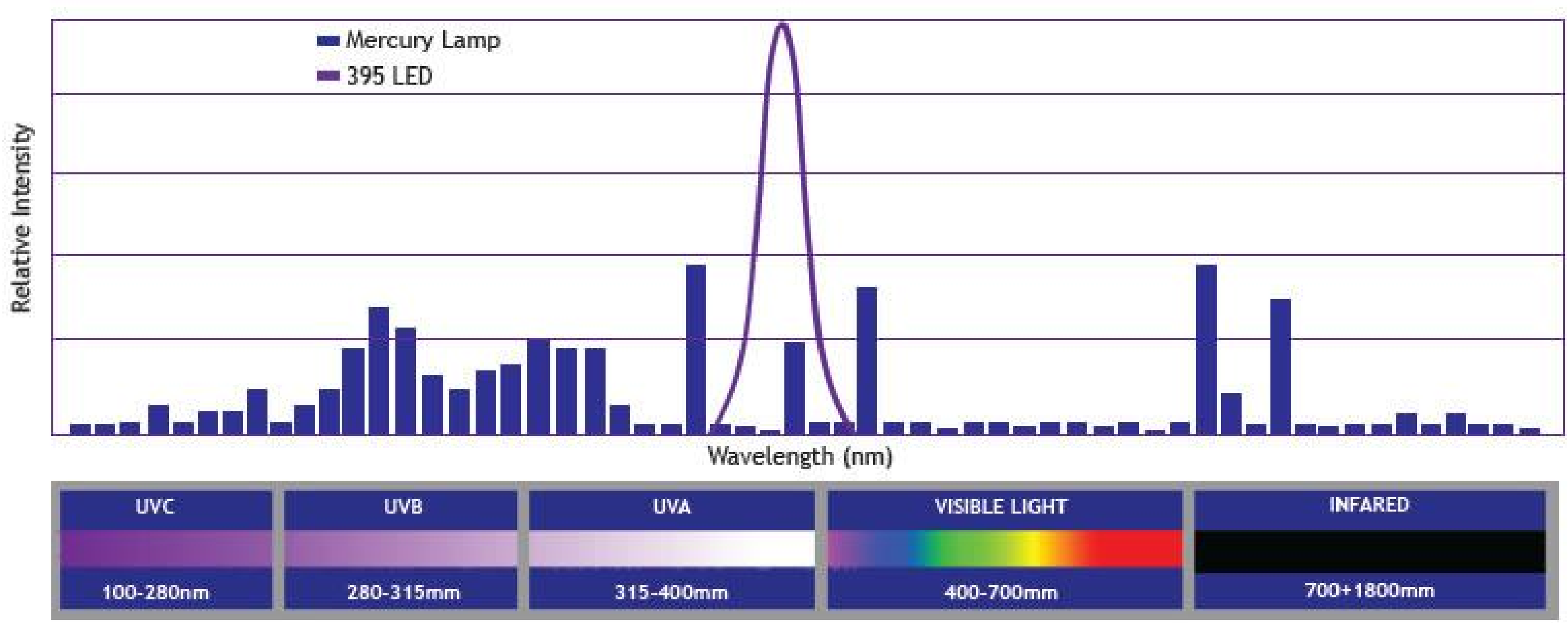
HEALTH · NUTRITION · MATERIALS

Example LED source

Phoseon RX Fireline 395 LED 8W/cm^2
Watercooled with AGT 1.7kW chiller



Information from product brochure and Phoseon website
http://www.phoseon.com/technology/led-uv-wavelength.htm

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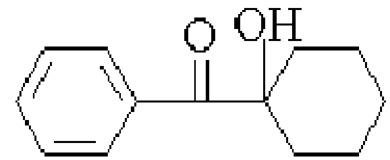
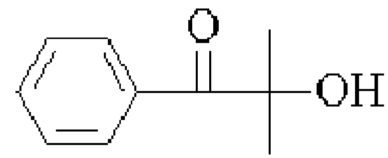
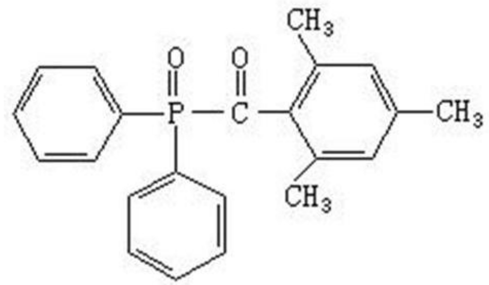
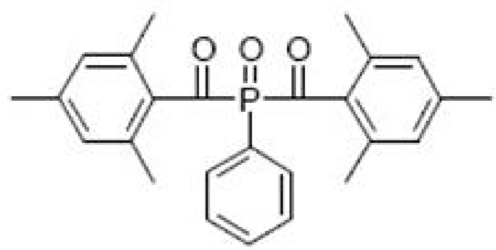
Common Photoinitiators

Abbreviation	Chemical Name	Structure
HCPK	1-hydroxy-cyclohexylphenyl ketone	
HMPP	2-hydroxy-2-methyl-1-phenyl-1-propanone	
TPO	diphenyl (2,4,6-trimethylbenzoyl)-phosphine oxide	
BAPO	phosphine oxide, phenyl bis(2,4,6-trimethylbenzoyl)	

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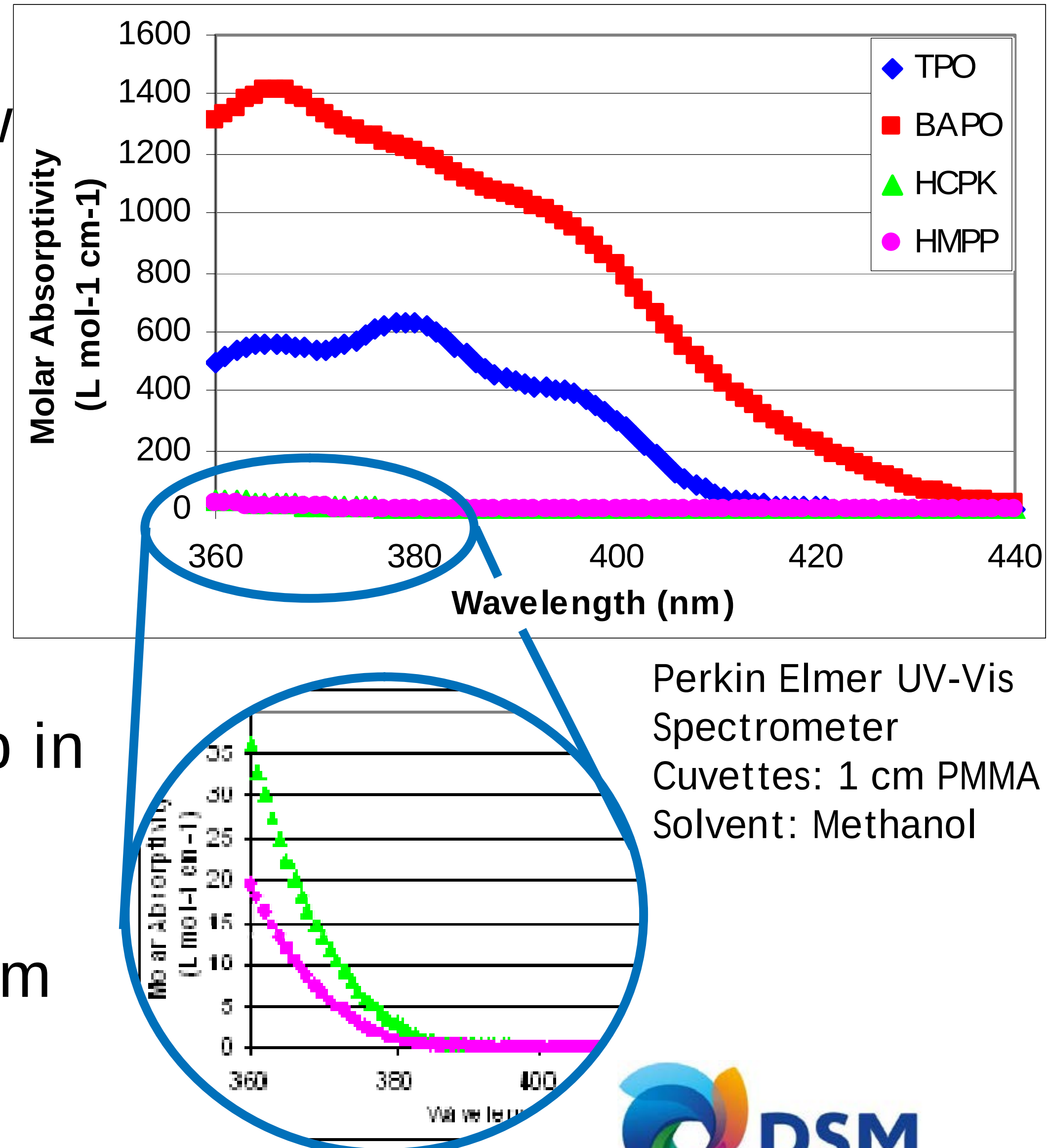
Photoinitiator Spectrum

Molar absorptivity (ε) relates to absorbance by Beer-Lambert law

$$A = \varepsilon\, b\, [c]$$

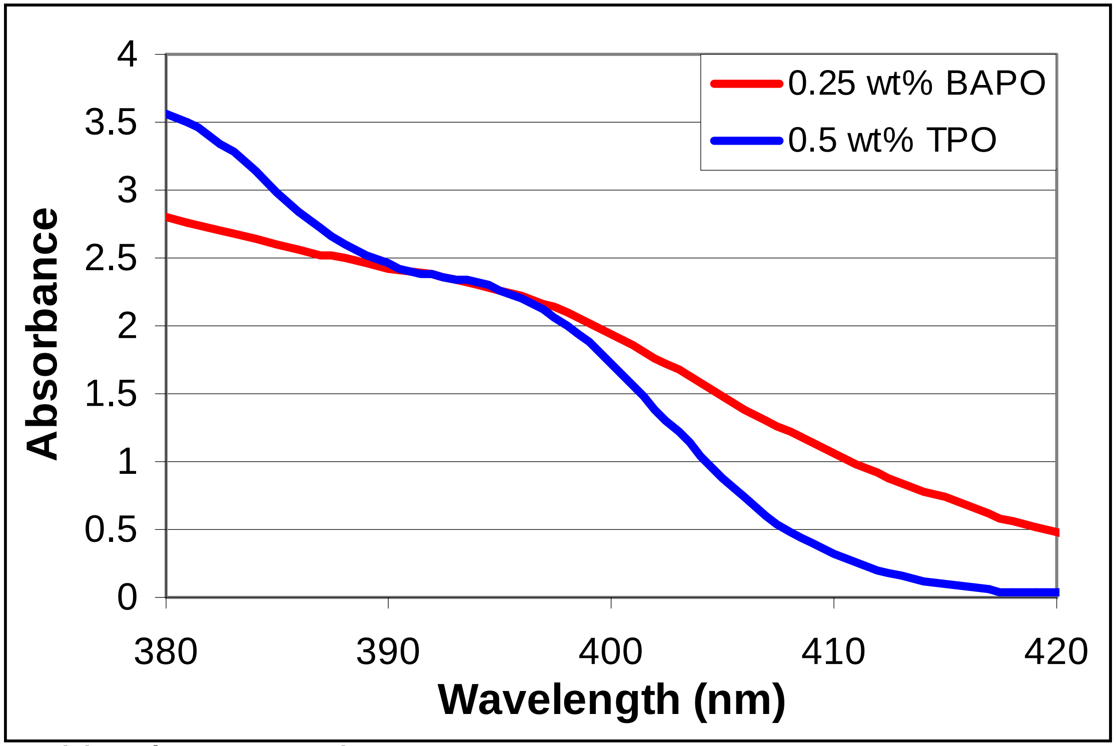
where A is absorbance,
b is path length,
and [c] is concentration

- LED absorbs 380-420nm
- HCPK and HMPP do not absorb in this region
- TPO and BAPO both have high molar absorptivity (ε) at 395nm



Perkin Elmer UV-Vis Spectrometer
Cuvettes: 1 cm PMMA
Solvent: Methanol

More Absorptivity = Less Concentration



Perkin Elmer UV-Vis Spectrometer
Cuvette: 1 cm PMMA
Dilution: 0.5g sample / g Methanol

Conversion

2-phenoxyethyl acrylate cured by 395 LED at low 200 mJ/cm^2 (Intensity 1000mW/cm^2) as measured by FTIR

0.25 wt% BAPO = 56.8%

0.50 wt% TPO = 61.4%

Higher Molar absorptivity means you need less concentration for equal curing

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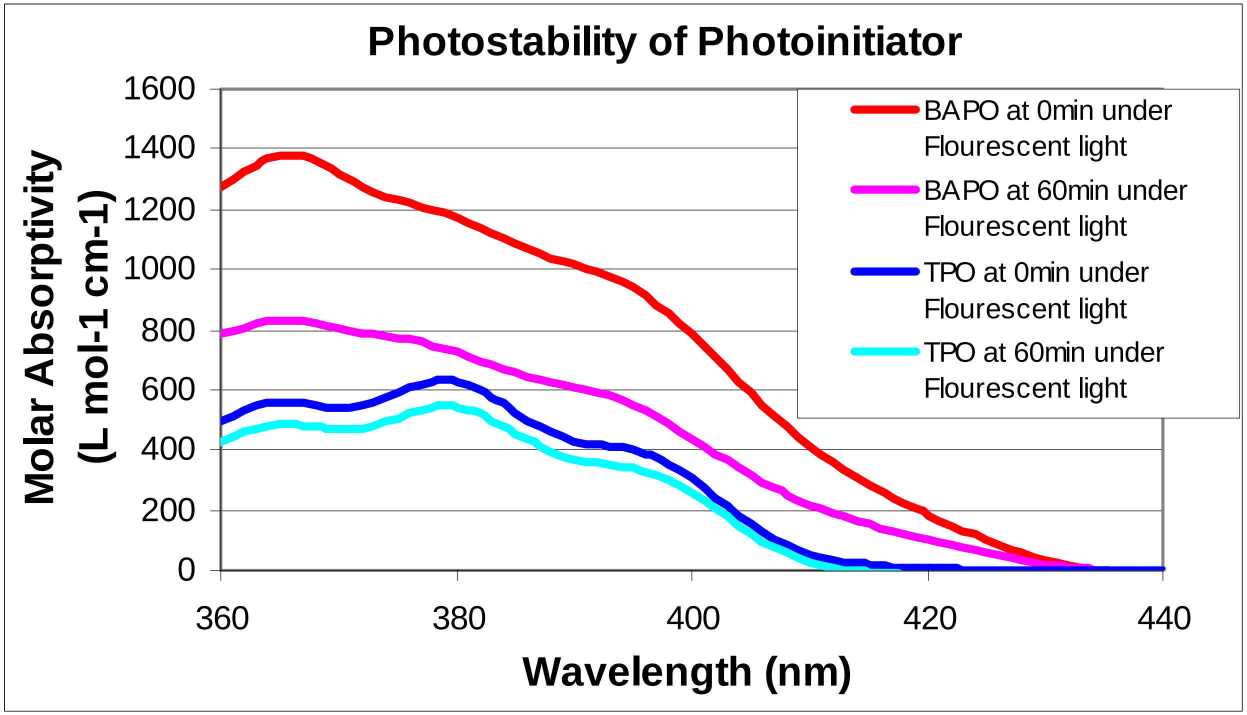
Photostability is important to monitor

LEDs often emit near visible light range meaning photoinitiator will often absorb and react under visible light therefore Photostability is important to include in design.

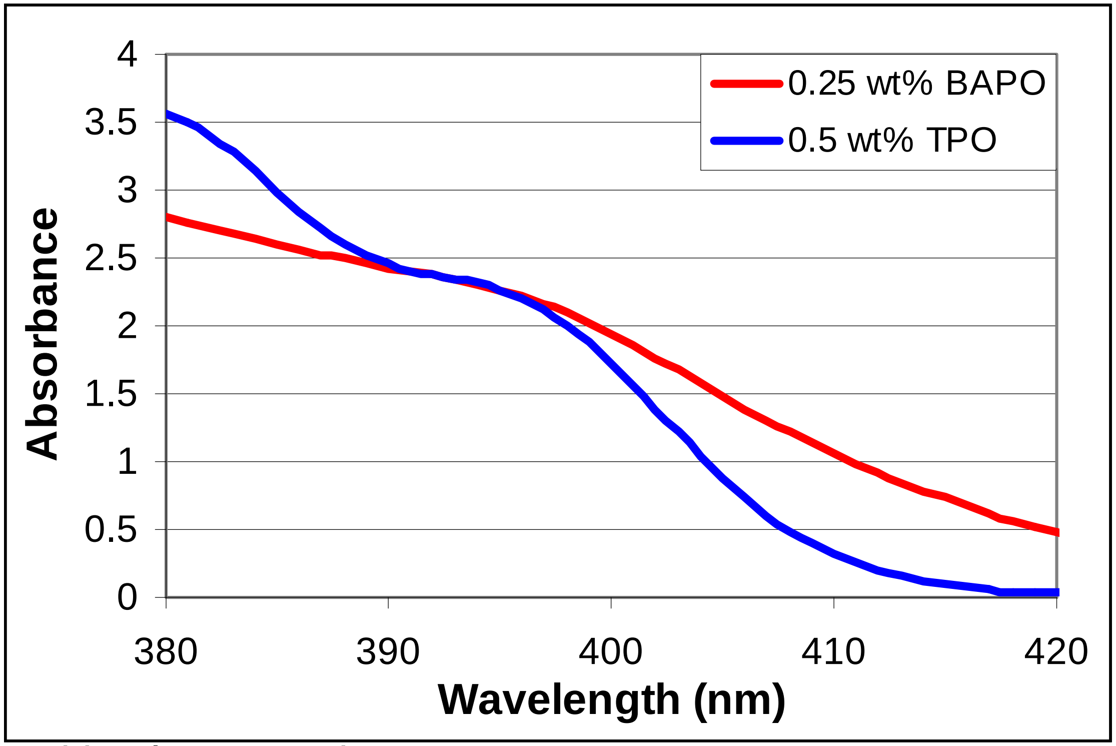


Perkin Elmer UV-Vis Spectrometer
Cuvette: 1 cm PMMA

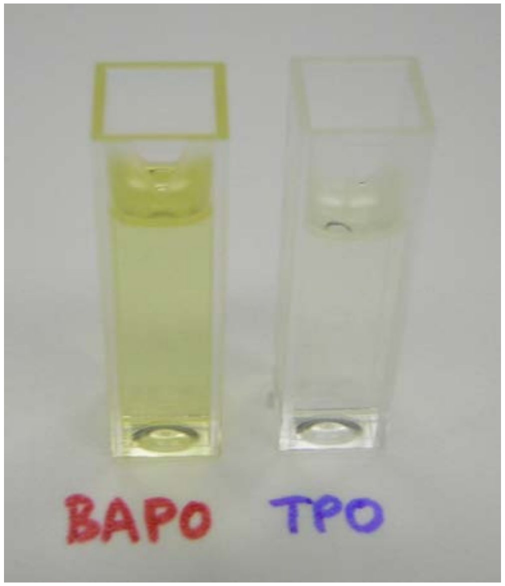
Reacted Photoinitiator
At 395nm under GE F15T8 bulbs (fluorescent light) for 60 min

0.25 wt% BAPO = 42 % Photoinitator Reacted
0.50 wt% TPO = 15 % Photoinitator Reacted

Absorbance in Visible Range = Color



Perkin Elmer UV-Vis Spectrometer
Cuvette: 1 cm PMMA Dilution: 0.5g sample / g Methanol



0.25wt% BAPO
0.5 wt% TPO
in 2-phenoxyethyl acrylate

LEDs often emit near or in visible light range meaning photoinitiator will often absorb somewhere in this range which will give the coating color

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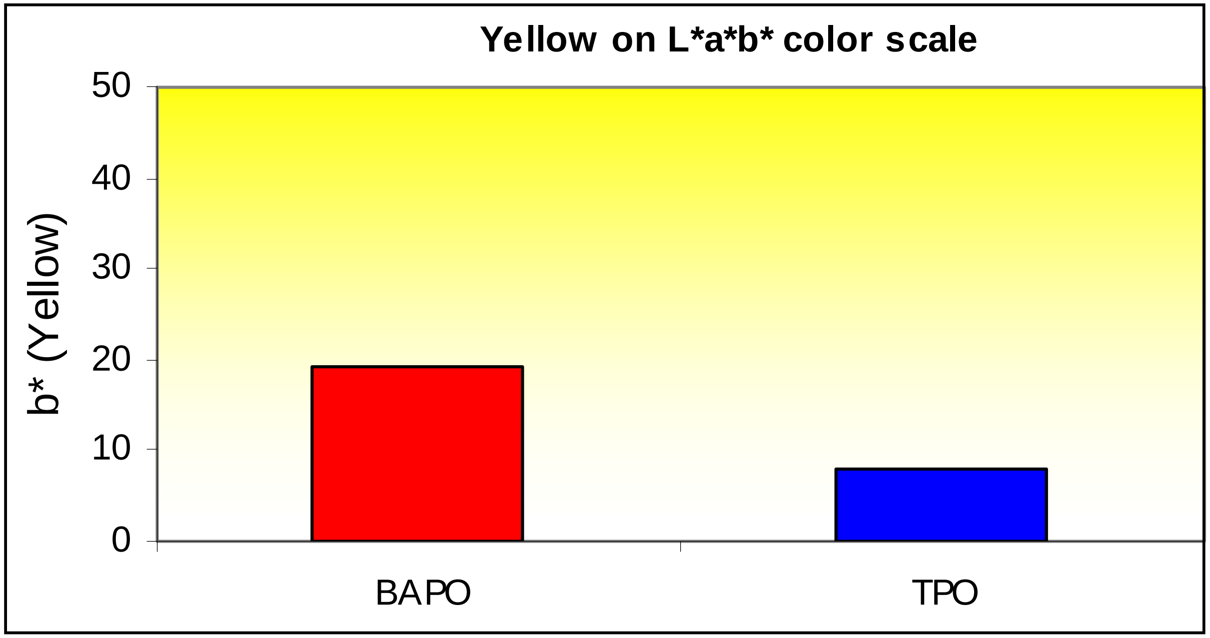
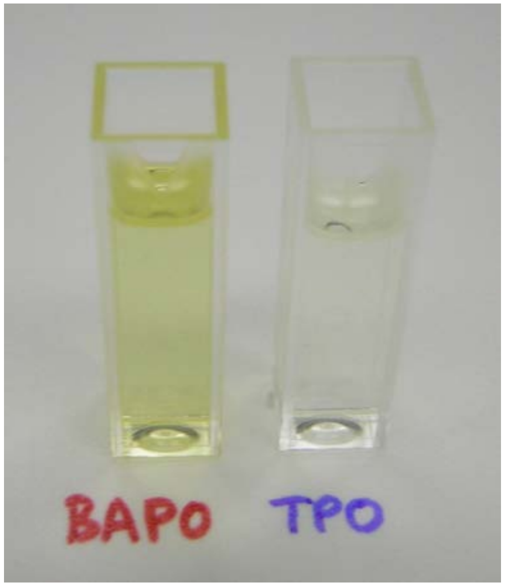
Absorbance in Visible Range = Color



DataColor iQC color inclusively in CIE L*a*b* color space (ILL D65-10° deg. Observer).

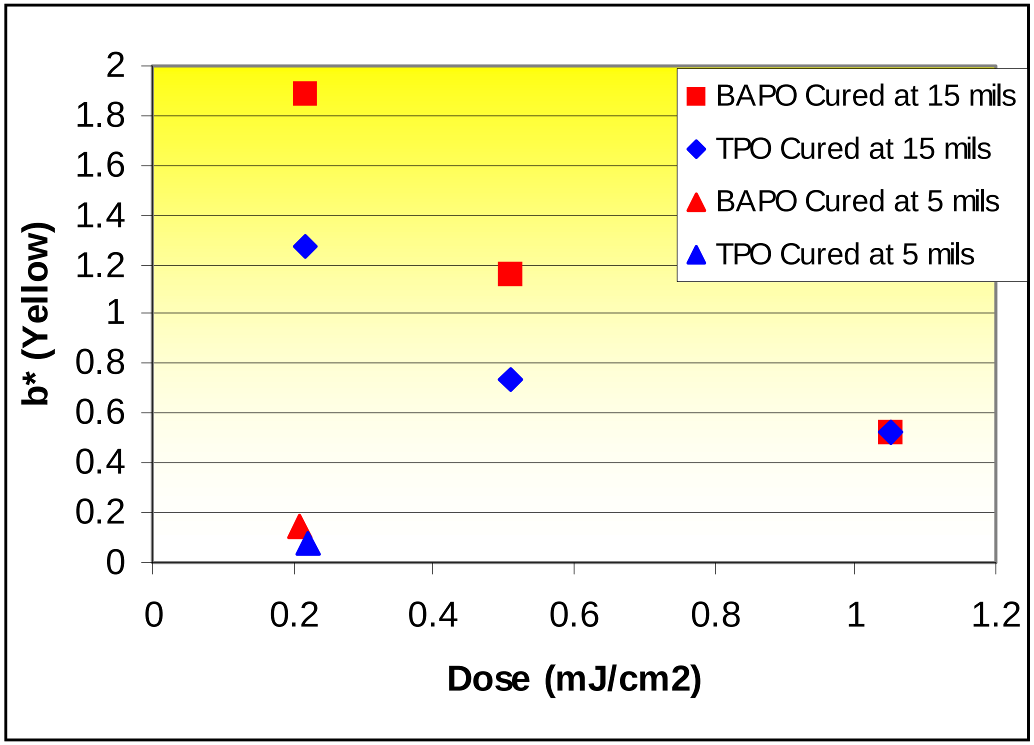


0.25wt% BAPO
0.5 wt% TPO
in 2-phenoxyethyl acrylate

Color strength depends on molar absorptivity in visible range, concentration, and coating sample thickness

Yellow is important consideration

Remember color depend on coating thickness!



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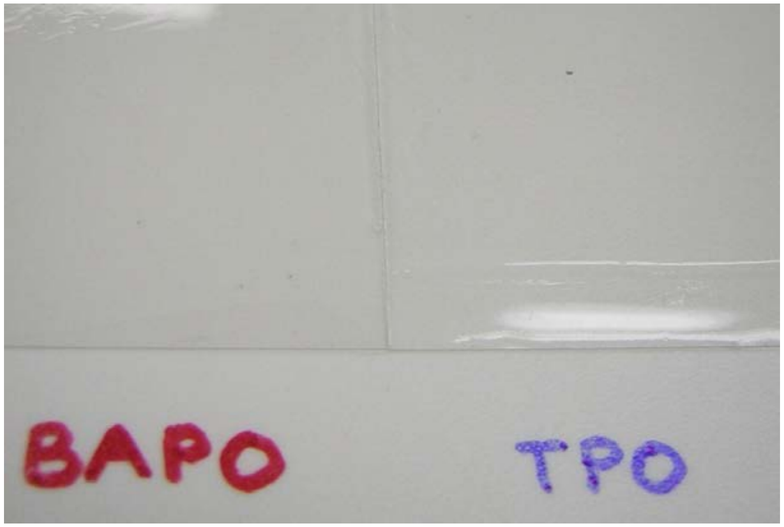

0.25wt% BAPO
0.5 wt% TPO
in 2-phenoxyethyl acrylate
5mils cure at 200mJ/cm2 with 1000mW/cm2

Photoinitiator breaks apart (Photobleaches) as it reacts removing color from sample

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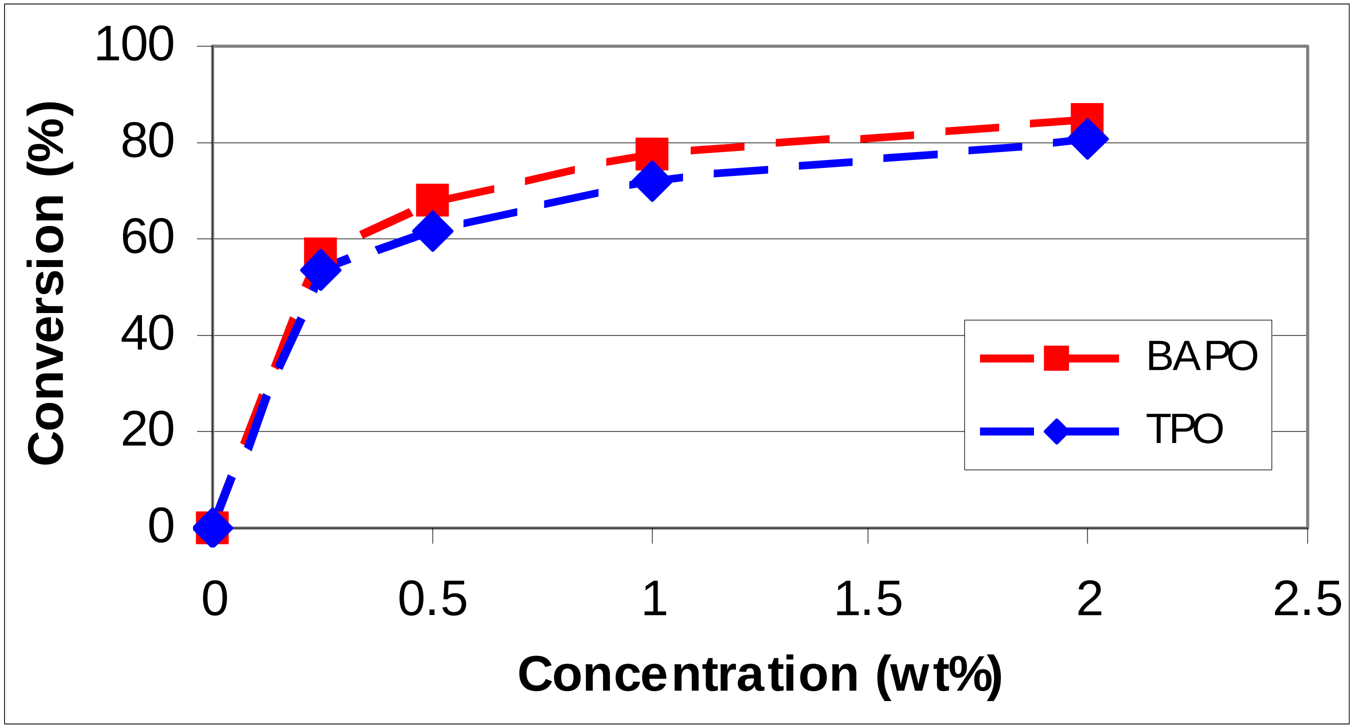
Optimizing the Concentration

Higher photoinitiator concentration will not get you the proper cure if you do not have enough light



20 mil thick films of 2-phenoxyethyl acrylate
Cured by 395 LED at low 200 mJ/cm2 (Intensity 1000mW/cm2)
as measured by Nicolet 8700 FTIR Spectrometer – 810nm peak

More light will not help if there is not enough photoinitiator

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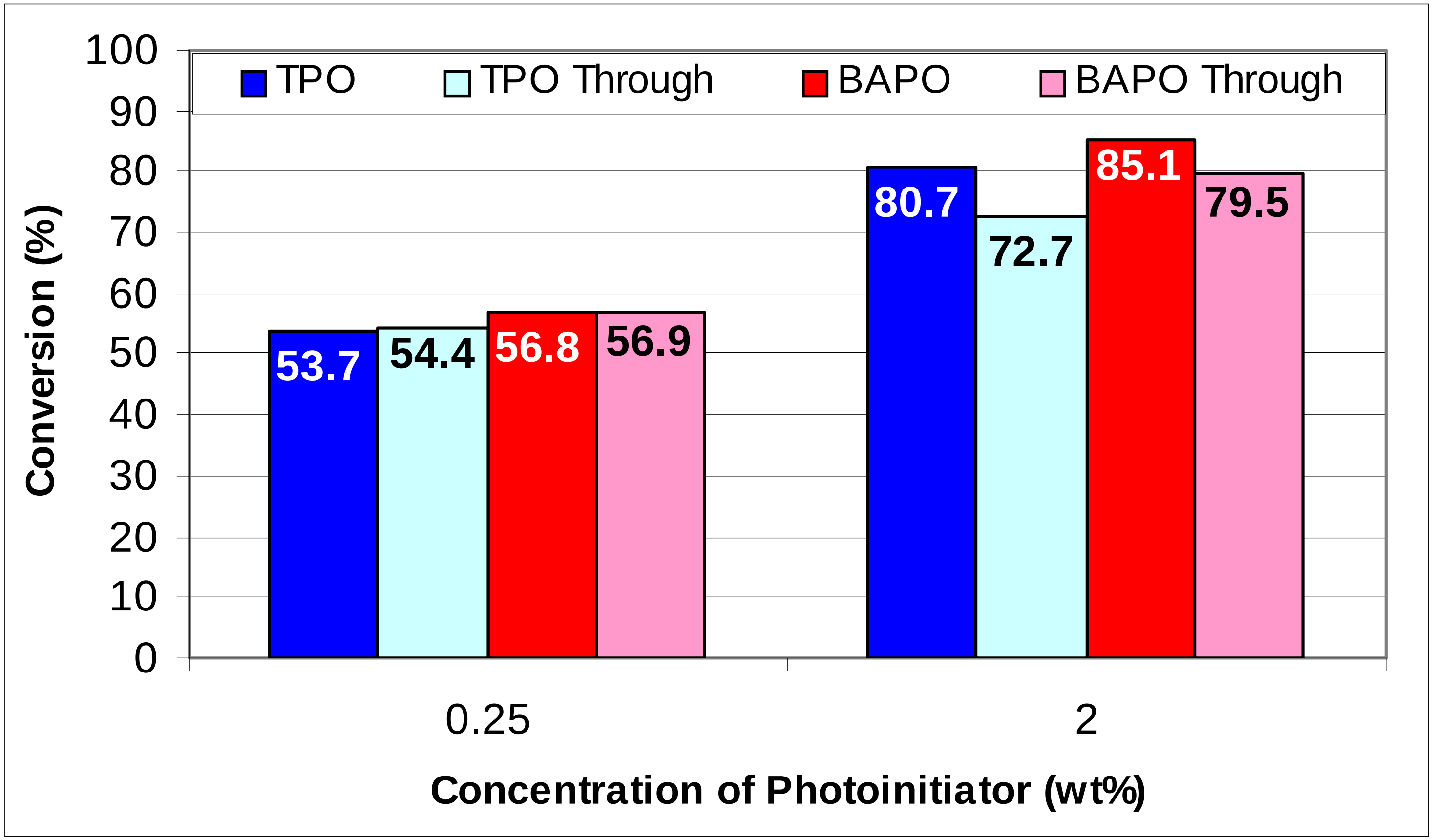
Optimizing the Concentration - Surface vs Through Cure



Nicolet 8700 FTIR Spectrometer – 810nm peak
Cured 20 mil thick films

Higher concentration of photoinitiator will shield the light and create cure gradients

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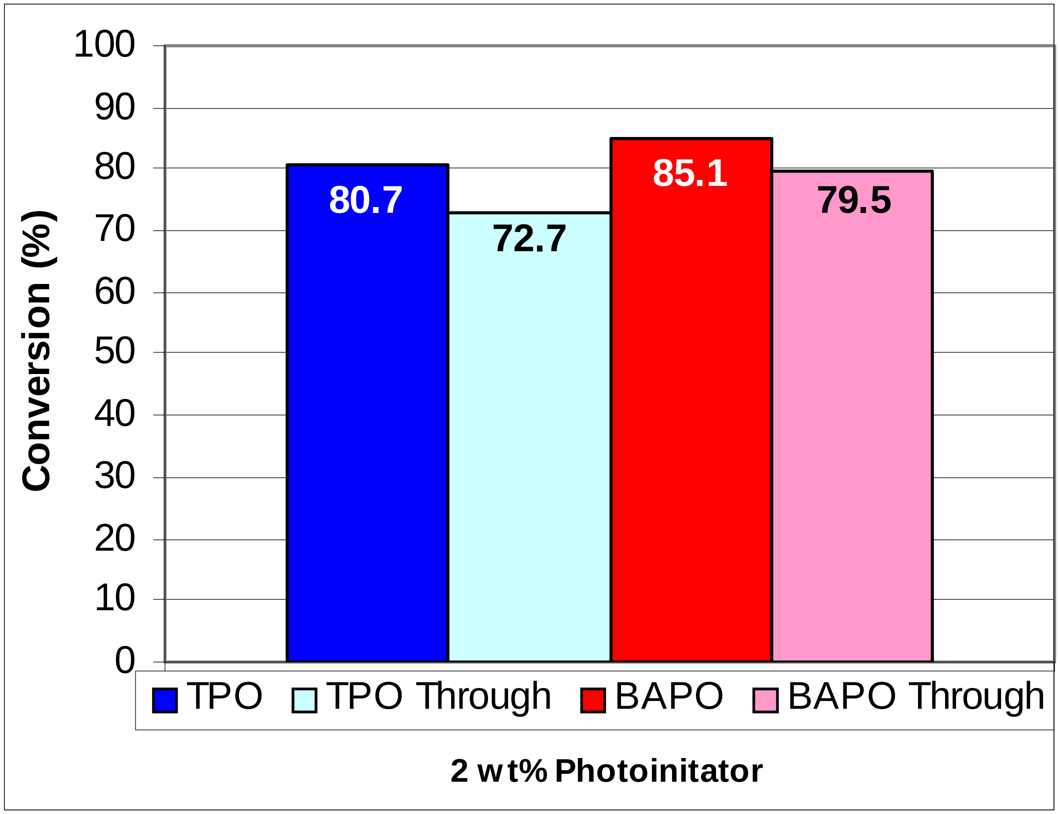
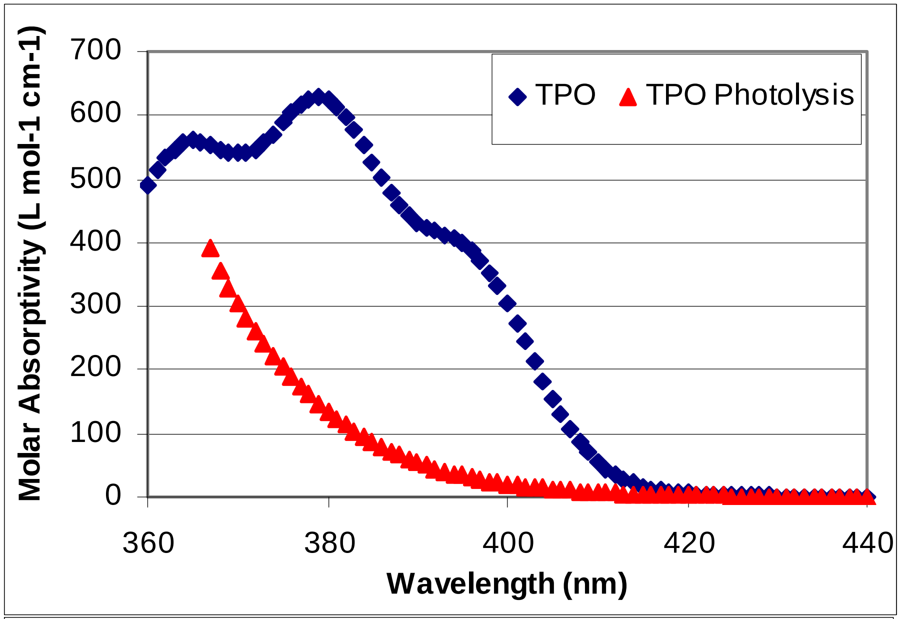
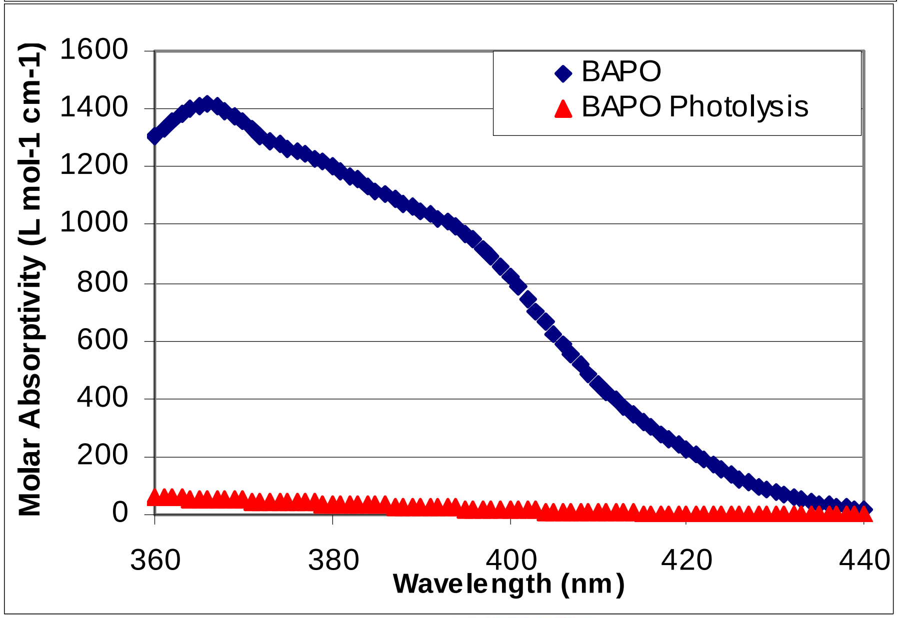
Optimizing the Concentration - Surface vs Through Cure







Photolysis products can have effect on through cure due to shielding

Conclusions

- Photoinitiator must absorb where LED emits
- More molar absorptivity means less concentration is needed for equal curing
- Absorbance in visible range (where many LED emit) results in your photoinitator being colored
- Color depends on molar absorptivity, concentration, thickness and photolysis products
- Absorbance in visible range decrease your photostability
- Proper cure depends on the dose/intensity of light emited as well as photoinitiator concentration
- Higher photoinitiator concentration causes cure gradients in coatings
- Photolysis products can shield depths in coating decreases through cure

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