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Optimizing Surface Cure of Acrylic Coatings Cured in Air using LEDs

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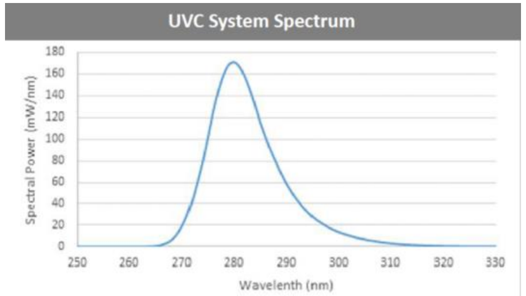
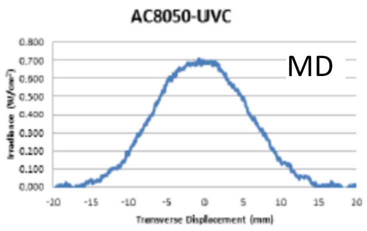
Background

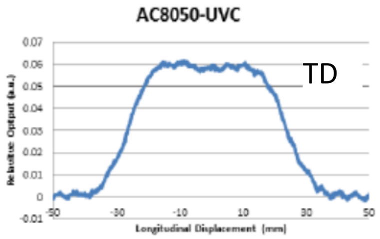
From RadTech “UV/EB Big Ideas” Conference, Redondo Beach, March 2019

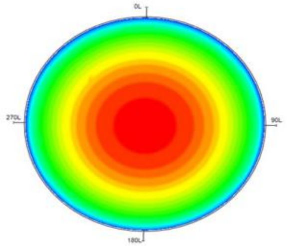
1. Mike Kay and Guomao Yang (Excelitas) reported that combining UVV/UVA with UVC LEDs (285 or 278 nm) improved cure speed and surface cure in air of several commercial acrylic coatings
    a) PI’s included Irg 651 and TPO; most PI’s were unavailable from SDS’s

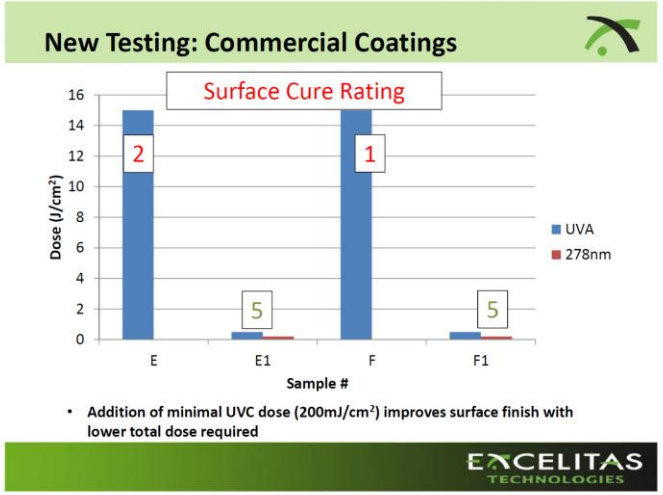
nominal 25 x 50mm window











2. I presented “UVC LEDs - A Reality Check” claiming
    a) that a 255 nm LED array to mimic the UVC output of MP Hg lamps was unlikely to be commercially viable in the near-future due to the high demand for LEDs for germicidal applications where λ=265 nm is optimal, and
    b) calculations indicated that the optimal α-cleavage PI for achieving surface cure using a 278 nm LED array is Irg 2959 because of its much higher extinction coefficient

Reality Check #1

MARKET Research Engine
Trusted by fortune 500 companies

PRESS RELEASE

Ultraviolet Disinfection Equipment Market share to touch USD 5 billion by 2024

Published: Feb 28, 2019 10:40 a.m. ET

Aa

Feb 28, 2019 (Heraldkeeper via COMTEX) -- New York, February 28, 2019: The report covers detailed competitive outlook including the market share and company profiles of the key participants operating in the global market. Key players profiled in the report include The Aquionics, Atlantic Ultraviolet Corporation, Calgon Carbon Corporation, Trojan Technologies (Danaher Corporation), Koninklijke Philips N.V., Xylem Inc., Severn Trent Services, Xenex Disinfection Services LLC and American Ultraviolet, Inc.Company profile includes assign such as company summary, financial summary, business strategy and planning, SWOT analysis and current developments.

The global Ultraviolet disinfection equipment market is expected to exceed more than **USD 5 billion** by 2024 at a CAGR of 14% during the period 2018-2024.

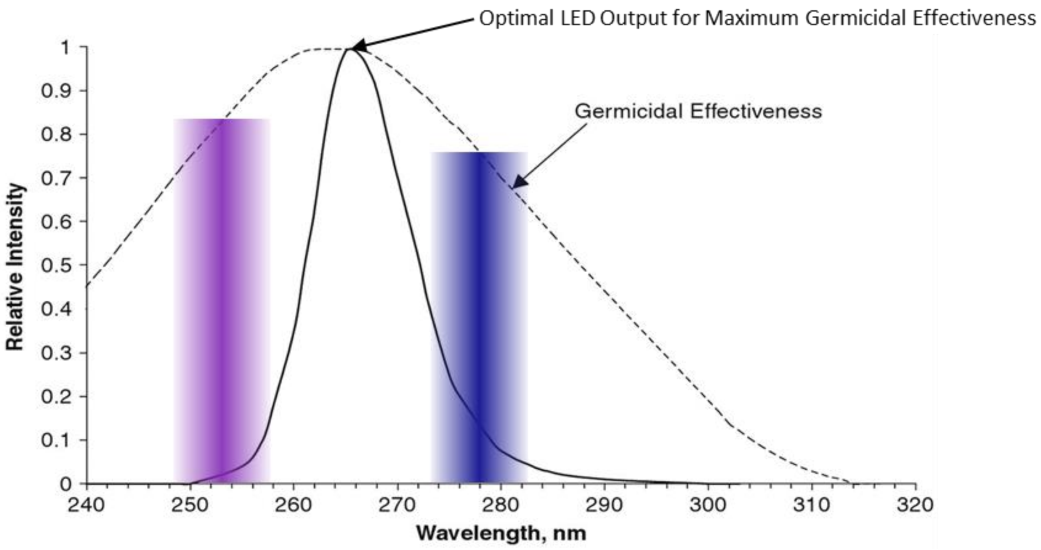
Reality Check #2

Online product literature (Spring 2019)

Name	Wavelength, nm	Max Power (mW)
Klaran WD Series (Crystal IS)	260-275	40, 50, 60
Klaran GD Series (Crystal IS)	260-275, 270-280	20, 25, 30
Nikkiso Giken UV-LED 265	260-270	not specified
Nikkiso UV-C LEDs	265, 280, 285, 300	45 (@285 nm)
Nikkiso UV-C LED array	285	80 @10 mm
SETi (Seoul Viosys)	275, 285, 295, 310	varies
QPhotonics (SETi), single LED	255	0.3 mW
Nichia	280	10 (under development)
DOWA	265, 275, 280, 310	75
LGInnotek	275	100

Reality Check #3

- Axiom: long wavelengths (low ε) are important for through cure, short wavelengths (high ε) provide cure surface
- Low-pressure mercury arc lamps (germicidal bulbs) with a single λ_{max} at 254 nm were introduced in the 1930's
  - These bulbs are used today in many municipal water treatment plants as well as hospital surface sterilizers and residential air sterilization/disinfection units. They contain low amounts of mercury and are unlikely to go away anytime soon.
  - A single bulb has a peak irradiance of 1-3 mW/cm^2 and ca. 8000-hour lifetime; multi-bulb arrays can achieve ~10 mW/cm^2
    - A plurality of germicidal bulbs (electrical power of 1-2 W/in) can cure silicone acrylate release coatings under N_2 at 1000 fpm (US Patent No. 6,244,949 to Wright and Vesley, 3M, 2001) using ~5% of the electrical power required by 3-4 banks of 600 W/in microwave lamps
- If 265 nm LED sources become viable in terms of lifetime and cost, what is the driver for chip makers to develop a more costly 255 nm LED source that would have to compete with germicidal lamps?

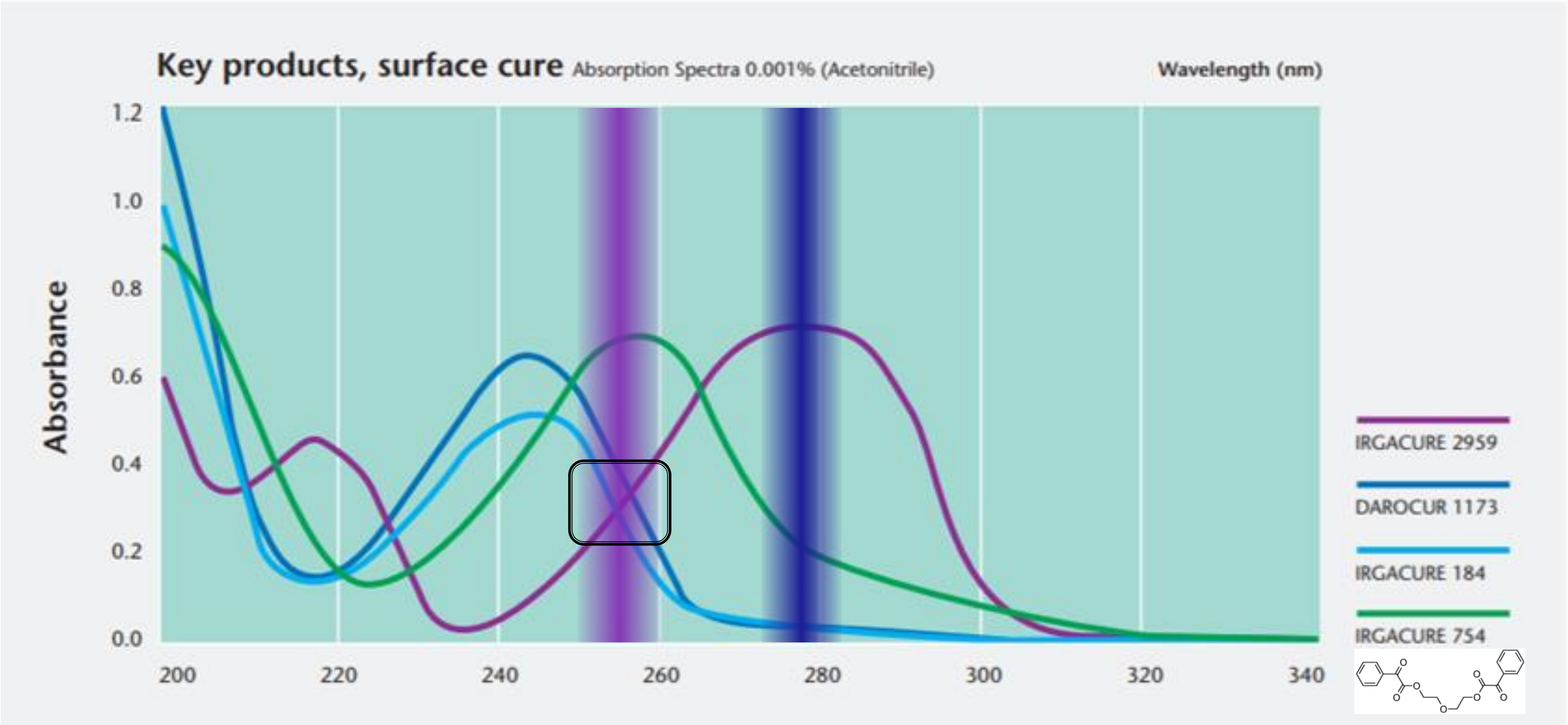


Extinction Coefficients for Common Photoinitiators

Spectra obtained from "Industrial Photoinitiators" by W. Arthur Green (CRC Press, 2010)

Calculations of ε_{255} and ε_{275}			
PI	ε_{255}	ε_{275}	%Change ($\varepsilon_{275}/\varepsilon_{255}$)
184	5054	812	16.1
651	15758	2945	18.7
1173	7599	983	12.9
2959	8236	15673	190.3
DEAP	9664	1272	13.2
Esa ONE	14629	5361	36.6
369 (UVB)	2652	3781	142.6
907 (UVB)	792	2556	322.8
819 (UVV)	7071	6375	90.1
TPO (UVA/UVV)	3733	2610	69.9

Overlap of Photoinitiators with 255/278 nm LED Outputs

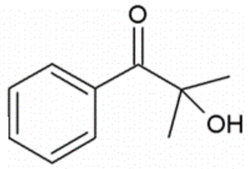
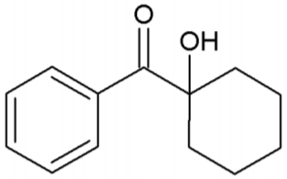
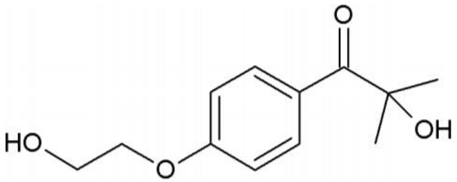


Photoinitiators for UV Curing, Ciba Specialty Chemicals 2003

Premise: 2959 is Superior for Surface Curing at 278 nm

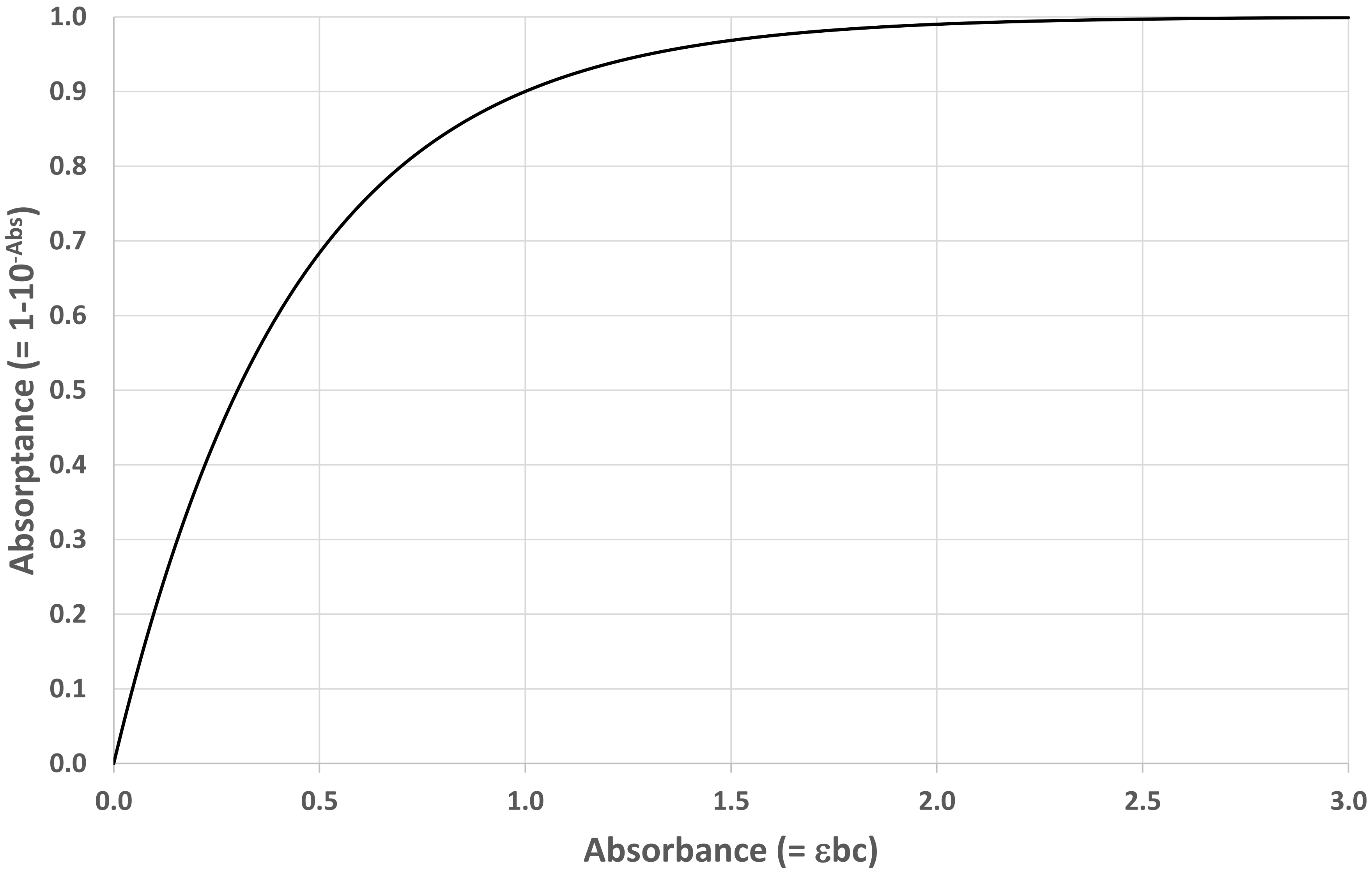
Test solutions provided by Gabrielle Meehan, Sartomer

- Selected test formulation was a clear acrylic blend comprising 50% aliphatic urethane acrylate, 30% isobornyl acrylate (IBOA), and 20% trimethylolpropane triacrylate (TMPTA)

Photoinitiators	Structures	λ_{max}, nm	ε_{max}, $M^{-1}cm^{-1}$
Irgacure 1173		244	10500
Speedcure 84		243	8400
Speedcure 2959		273	15700

Plot of Absorptance versus Absorbance

(assumes scatter and reflectance are negligible)



Plot of Absorptance versus Absorbance

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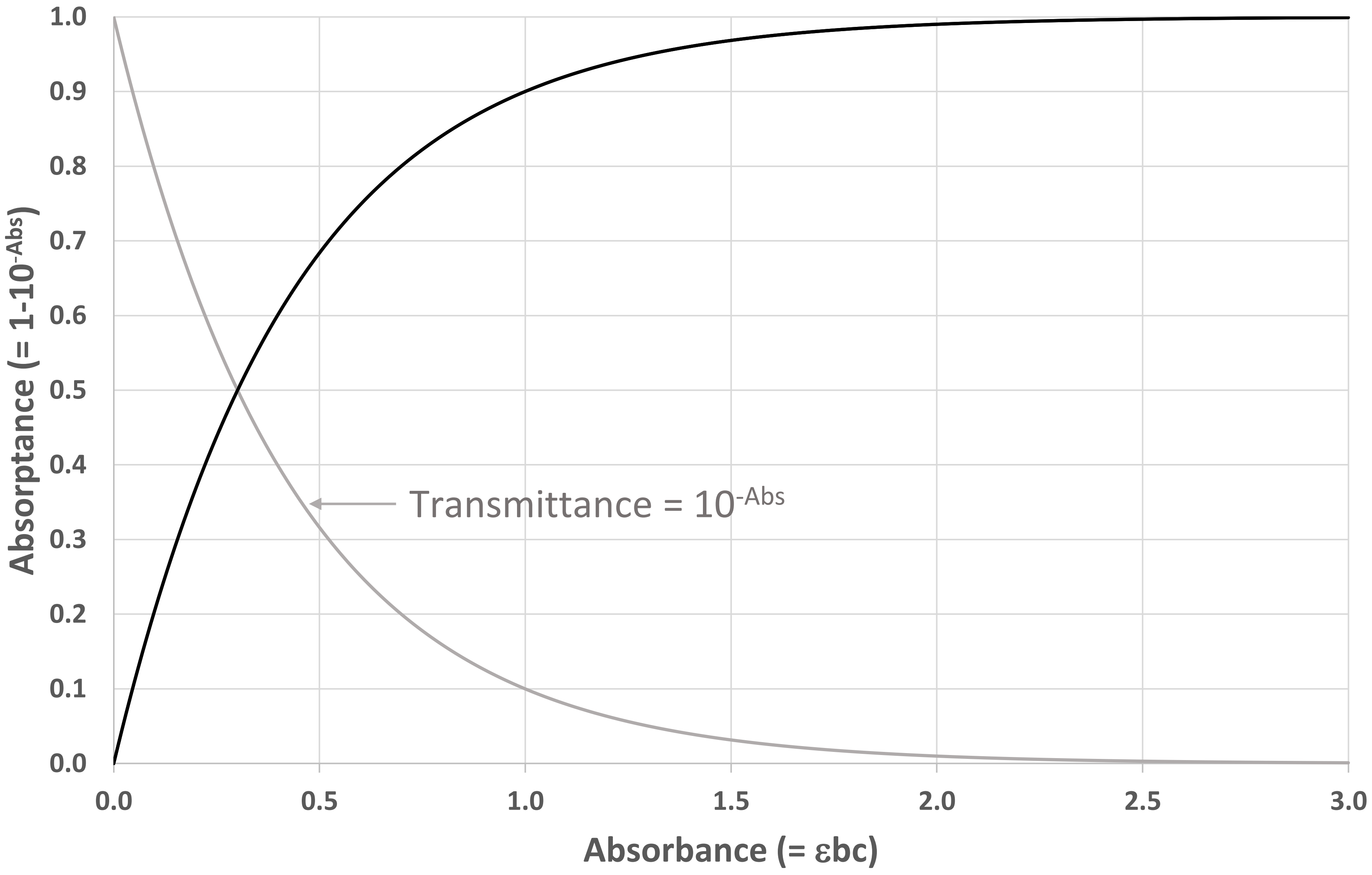


Plot of Absorbance vs. Fraction of Light Absorbed

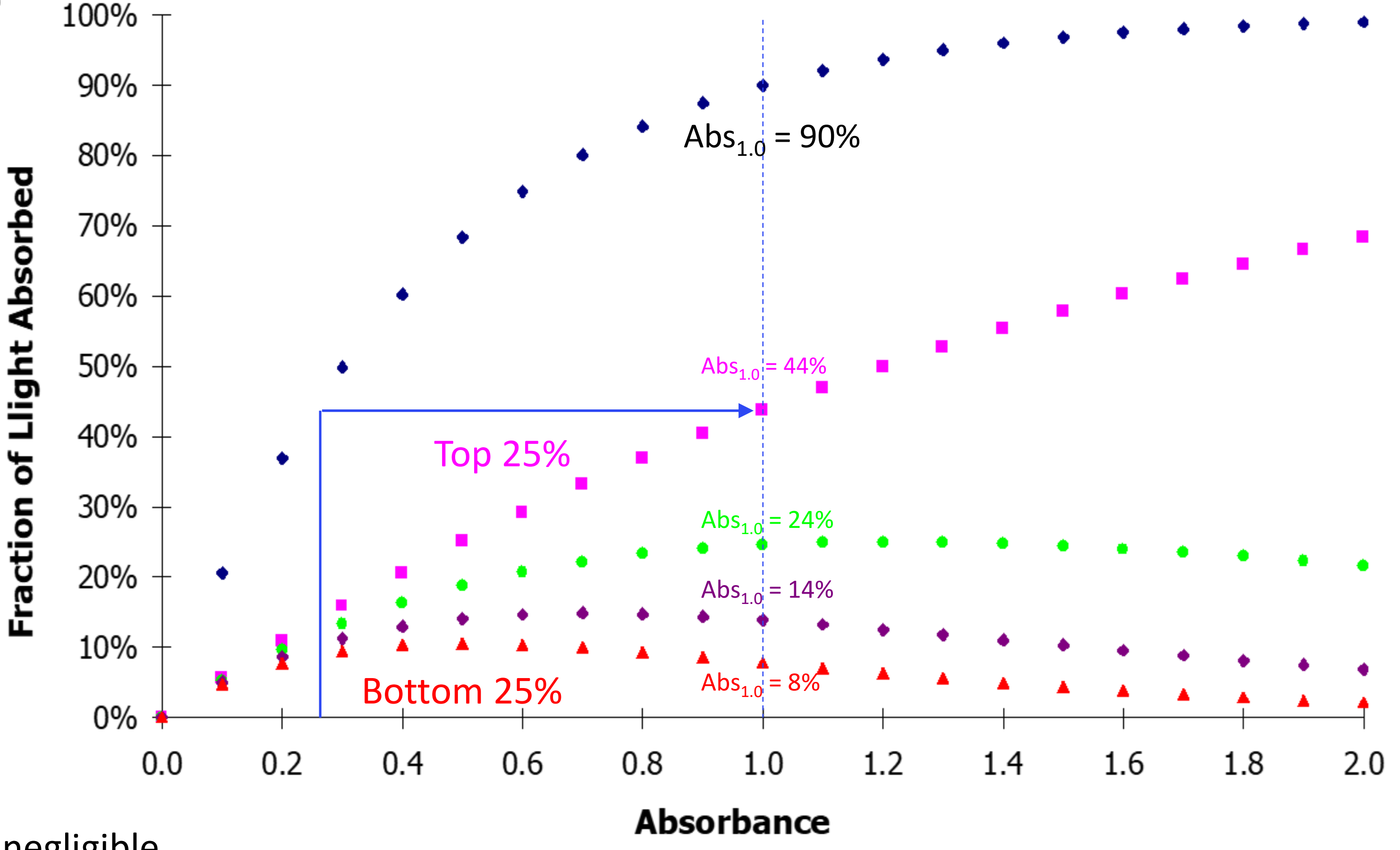
$Abs_\lambda = \varepsilon_\lambda bc$

ε = extinction coefficient ($M^{-1}cm^{-1}$)

b = thickness (cm)

c = molar concentration (M)

$f_{Abs} = 1\text{-}10^{-Abs}$



Assumes scatter and reflection are negligible

Calculated Absorption Data

Assumes scatter and reflectance are negligible

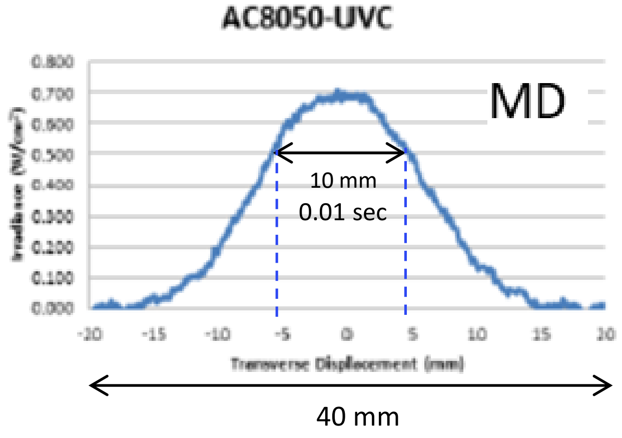
PI	Speedcure 84				Irgacure 1173				Speedcure 2959			
ε_{275}, $M^{-1}cm^{-1}$ (calc)	812				983				15673			
MW, g/mole	204.3				164.2				224.3			
Thickness, μ	25.4				25.4				25.4			
Wt%	1.0	3.0	5.0	10.0	1.0	3.0	5.0	10.0	1.0	3.0	5.0	10.0
[M], moles/L	0.04895	0.14684	0.24474	0.48948	0.06090	0.18270	0.30451	0.60901	0.04458	0.13375	0.22292	0.44583
Abs_{275}	0.1010	0.3029	0.5048	1.0095	0.1521	0.4562	0.7603	1.5206	1.7748	5.3245	8.8741	17.7483
$1\text{-}10^{-Abs}$	20.7%	50.2%	68.7%	90.2%	29.5%	65.0%	82.6%	97.0%	98.3%	100.0%	100.0%	100.0%
Abs_{275}/μ	0.00397	0.01192	0.01987	0.03975	0.00599	0.01796	0.02993	0.05987	0.06988	0.20963	0.34938	0.69875
$1\text{-}10^{-Abs}$	0.9%	2.7%	4.5%	8.7%	1.4%	4.1%	6.7%	12.9%	14.9%	38.3%	55.3%	80.0%

Exposure Conditions

Run by Guomao Yang, Excelitas

Exposure	LED	λ_{max}	W/cm^2	J/cm^2
1	UVA	365	2.9	0.68
2	UVC	278	0.4	0.23

Sample exposure: 2 passes at 0.1 m/sec (= 100 mm/sec)



Test Result using 5% Speedcure 84

Cotton-tipped Applicator Rub Test

	1%	3%	5%	10%
Speedcure 84	worse than 1% 2959	worse than 3% 2959		
Irgacure 1173	worse than 1% 2959	worse than 3% 2959		
Speedcure 2959				

Conclusions

- Summary of qualitative cotton-tipped applicator results
  - Speedcure 2959 samples were superior at all levels
  - Speedcure 84 and Irgacure 1173 were comparable at all levels
- More quantitative test methods are available but larger arrays would be needed to generate larger samples
- Biggest surprise – 1% 2959 should have been comparable to 10% Speedcure 84 and Irgacure 1173 based on calculated surface absorption in the top micron – Why wasn't it???

PI	Speedcure 84				Irgacure 1173				Speedcure 2959			
Abs_{275}/μ	0.00397	0.01192	0.01987	0.03975	0.00599	0.01796	0.02993	0.05987	0.06988	0.20963	0.34938	0.69875
$1\text{-}10^{-Abs}$	0.9%	2.7%	4.5%	8.7%	1.4%	4.1%	6.7%	12.9%	14.9%	38.3%	55.3%	80.0%
	$\Phi = 0.21$				$\Phi = 0.28$				$\Phi = 0.29$			