Broad Permanent UV Light Stabilization for Polyolefin Films & Overview of Hyperchromicity and Plasmonic Mechanism in Extension and Synergism of Light Stabilizers

Stabilization Technologies LLC

Charlotte, NC

Joe R Webster Ph.D

Current Global Technologies

Hindered Amines (HALS)

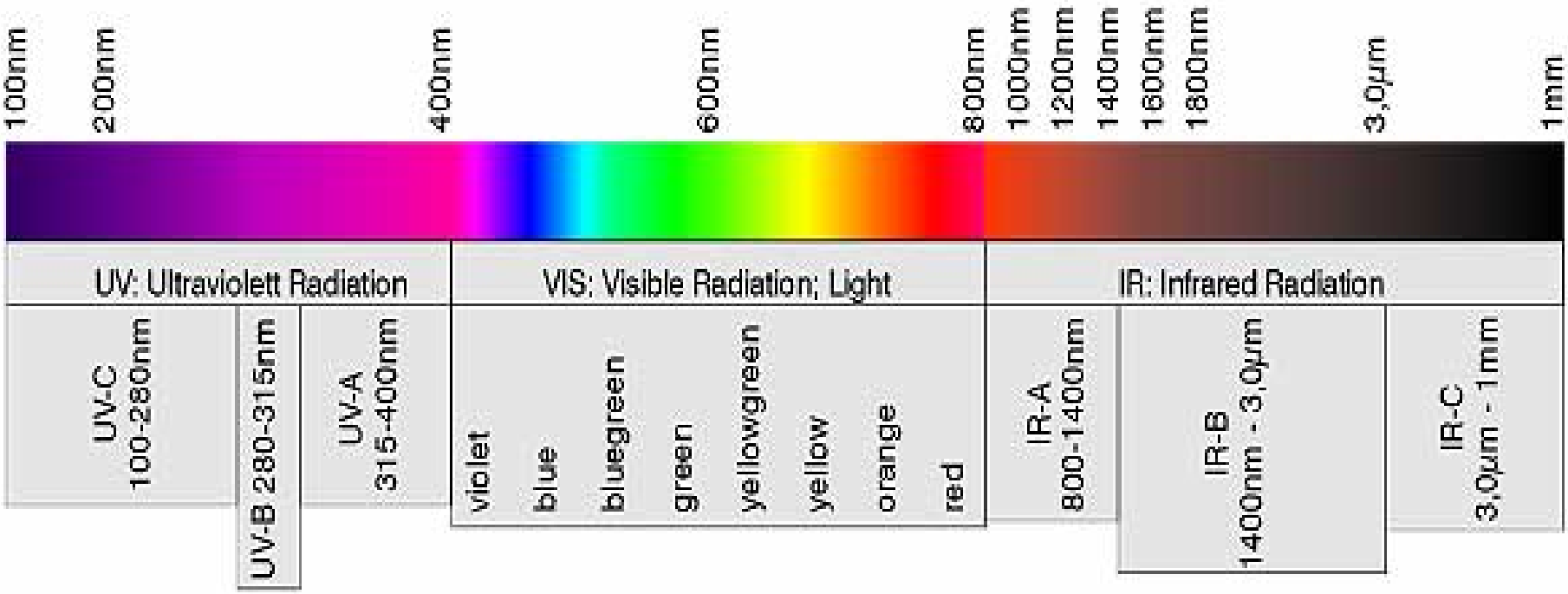
- Low Molecular weight
- High Molecular weight
- Oligomeric HALS
- Mechanism requires in-situ mechanism of nitroxyl conversion through a partially degraded polymer system. Rate of conversion determined by state of the system
- Inhibited by acids and several plastic additives used as stabilizers.
- Major discoloration reactions due to the intrinsic basic nature and residual basic processing chemicals during manufacturing.

UV Light Absorbers

- Main types are all hydroxy substituted benzotriazoles, benzophenones and triazine chemistries. Oxanilides and cyanoacrylates and other minor chemistries are in the mix. Nano oxides reactive and wavelength limited and expensive.
- Reactive, fugitive, limited in wavelength range and absorptivity and system dynamics. Migratory, volatility and in-situ interactions with other additives.
- Cost going up!

Radiation

According to DIN 5031, the term "optical radiation" refers to electromagnetic radiation in the wavelength range between 100 nm and 1 mm. The terms "light" and "visible radiation" (VIS) refer to the wavelength range between 400 nm and 800 nm, which can be perceived by the human eye. Optical radiation with wavelengths shorter than 400 nm is called ultraviolet (UV) radiation and is further subdivided in UV-A, UV-B and UV-C ranges. Similarly, infrared (IR) radiation covers the wavelength range above 800 nm and is subdivided in IR-A, IR-B and IR-C ranges (DIN 5031, part 7).



Terms and Definitions

INFRARED is invisible radiant energy, electromagnetic radiation with longer wavelengths than those of visible light, extending from the nominal red edge of the visible spectrum at 700 nanometers (frequency 428.27 THz; 1.77 eV) to 1 mm (300 GHz; 1.24 meV), (although people can see infrared up to at least 1050 nm in experiments).

PLASMON In physics, a plasmon is a quantum of plasma oscillation. As light consists of photons, the plasma oscillation consists of plasmons. The plasmon can be considered a quasiparticle since it arises from the quantization of plasma oscillations, just like phonons are quantizations of mechanical vibrations. Thus, plasmons are collective (a discrete number) oscillations of the free electron gas density, for example, at optical frequencies. Plasmons can couple with a photon to create another quasiparticle called a plasma polariton.

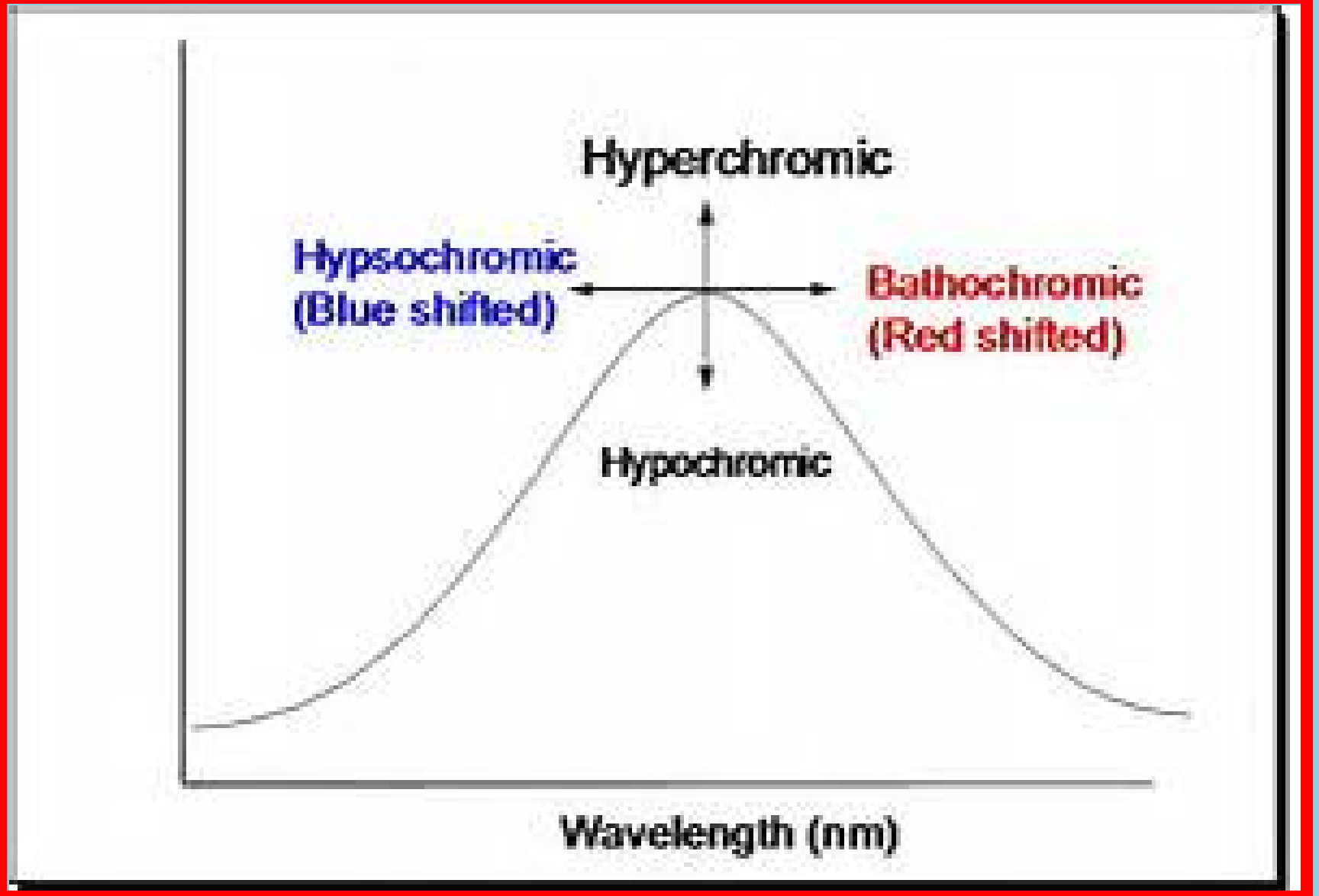
Terms and Definitions

BATHOCHROMIC SHIFT is a change of spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a longer wavelength (lower frequency). Because the red color in the visible spectrum has a longer wavelength than most other colors, this effect is also commonly called a ***red shift***.

HYPOCHROMICITY is the decreasing ability of a material to absorb light.
HYPERCHROMICITY is the increasing ability of a material to absorb light.

HYPSOCHROMIC SHIFT is a change of spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a shorter wavelength (higher frequency). Because the blue color in the visible spectrum has a shorter wavelength than most other colors, this effect is also commonly called a ***blue shift***.

UV Absorbance



Beer-Lambert Law of Absorbers

SPECTROMETRY NOMENCLATURE

A = Absorbance (Optical Density)
a = Absorptivity
b = Cell Length in cm
c = Concentration in g/Liter
C = Concentration in Moles/Liter
E = Molar Absorptivity (Extinction Coef.)
T = Transmittance

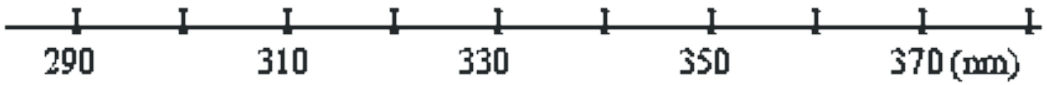
$$a = \frac{A}{b\ c} \qquad E = \frac{A}{b\ C}$$

$$a = \frac{E}{\text{Mol. Wgt.}}$$

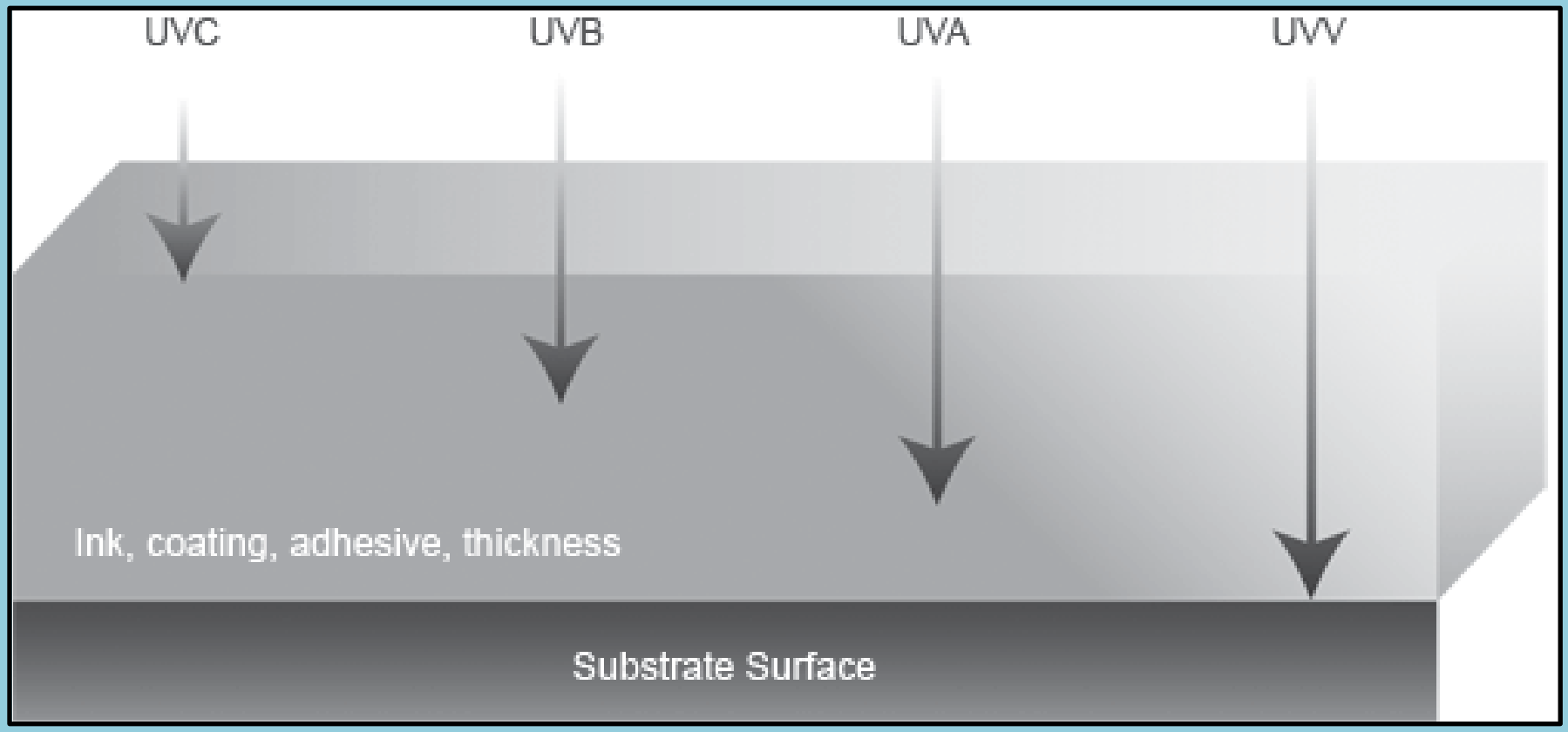
$$A = \log \frac{1}{T}$$

Radiation Damage by Wavelength

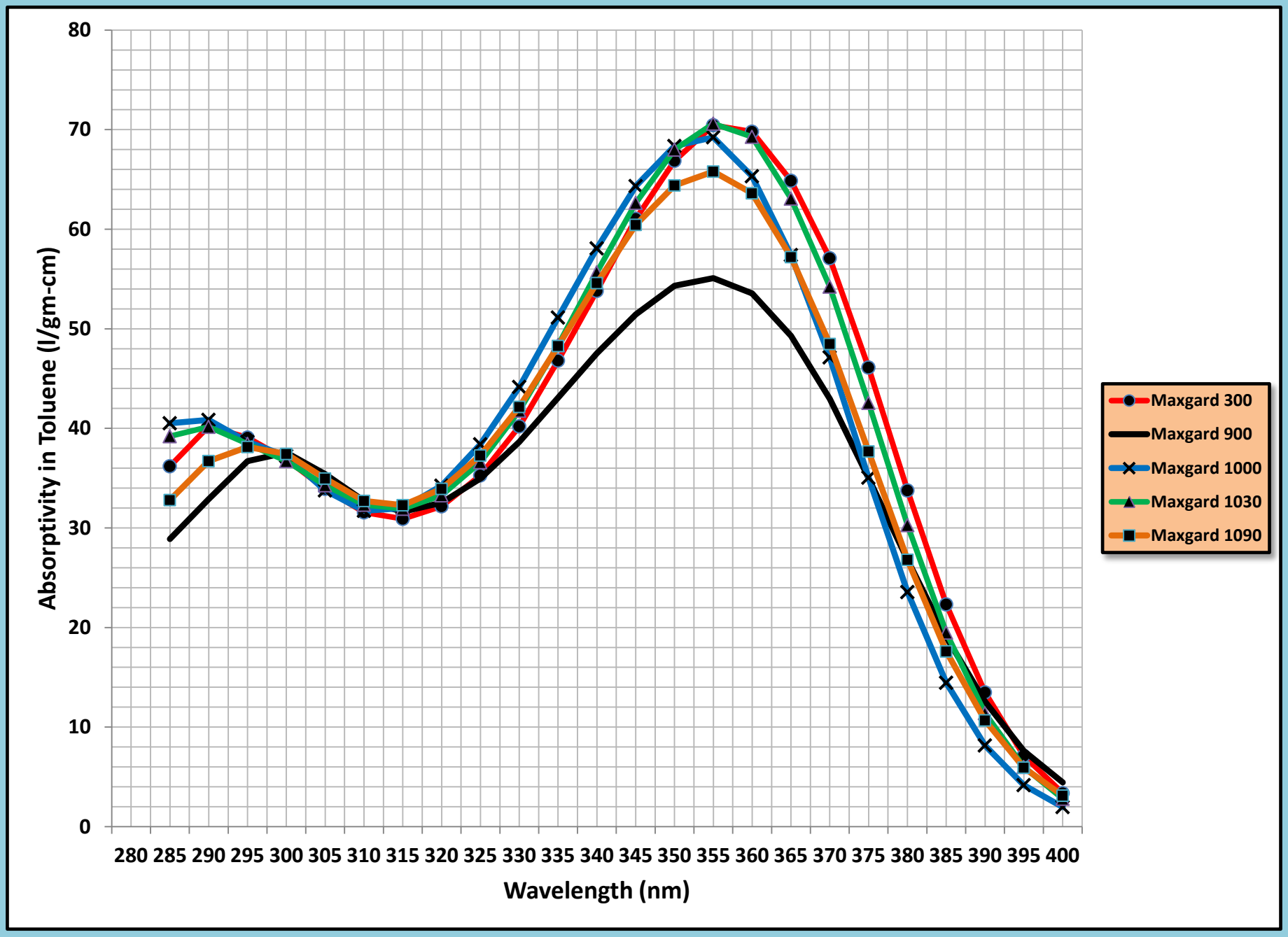
	Wavelength region showing highest activity	Polymer	Damage
14		Nylon	Spectroscopy
13		ECO film	Extensibility
12		Polyethylene film	Extensibility
11		Polyethylene (molded)	Extensibility
10		Polyethylene	Spectroscopy
9		Polypropylene	Extensibility
8		Polypropylene	Spectroscopy
7		Polystyrene foam	Yellowing
6		PC (stabilized)	Yellowing
5		PC (unstabilized)	Yellowing
4		PVC (Rigid (0% TiO_2)	Yellowing
3		Wool	Yellowing
2		Newsprint	Brightness
1		Newsprint	Yellowing

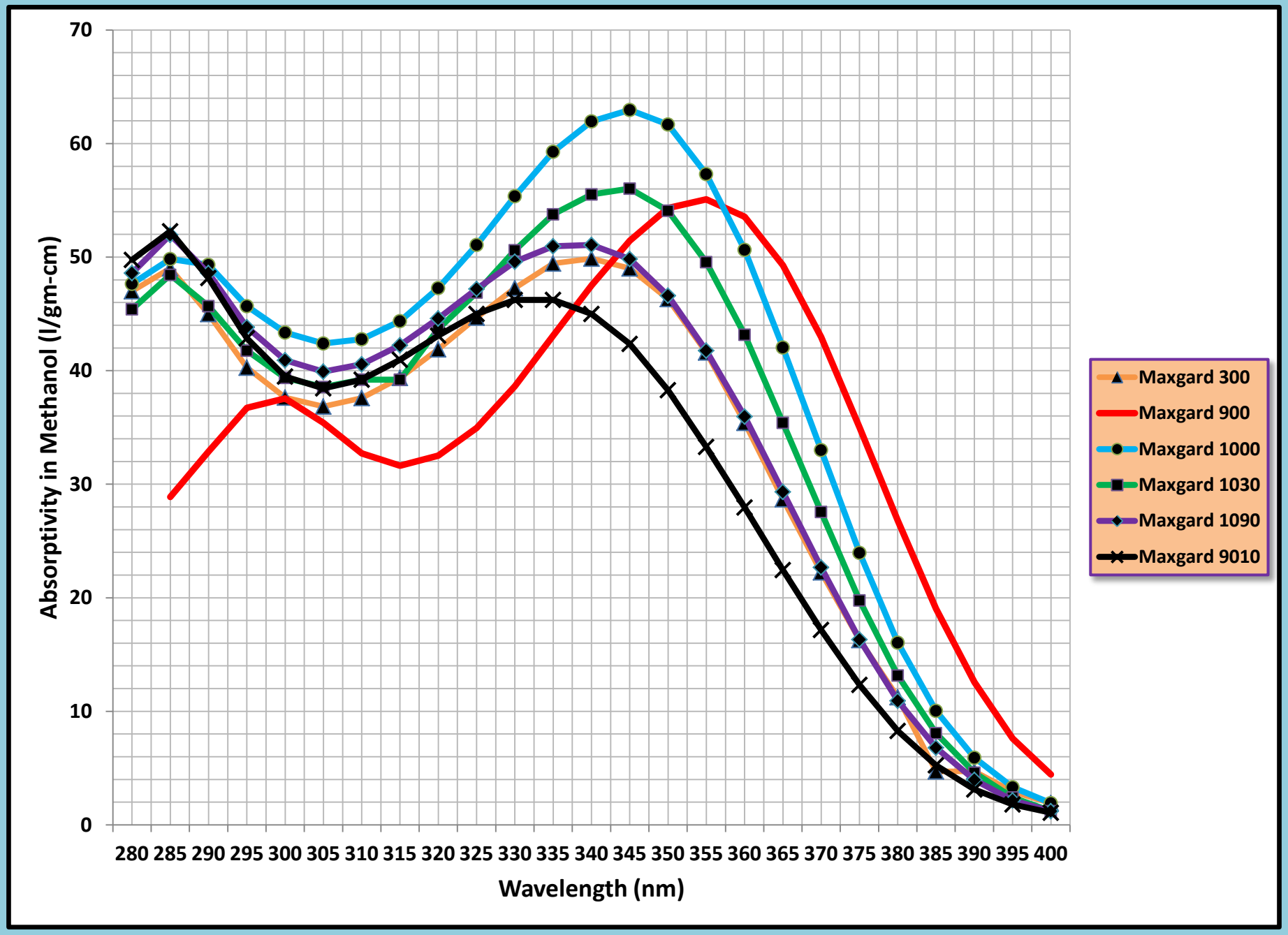


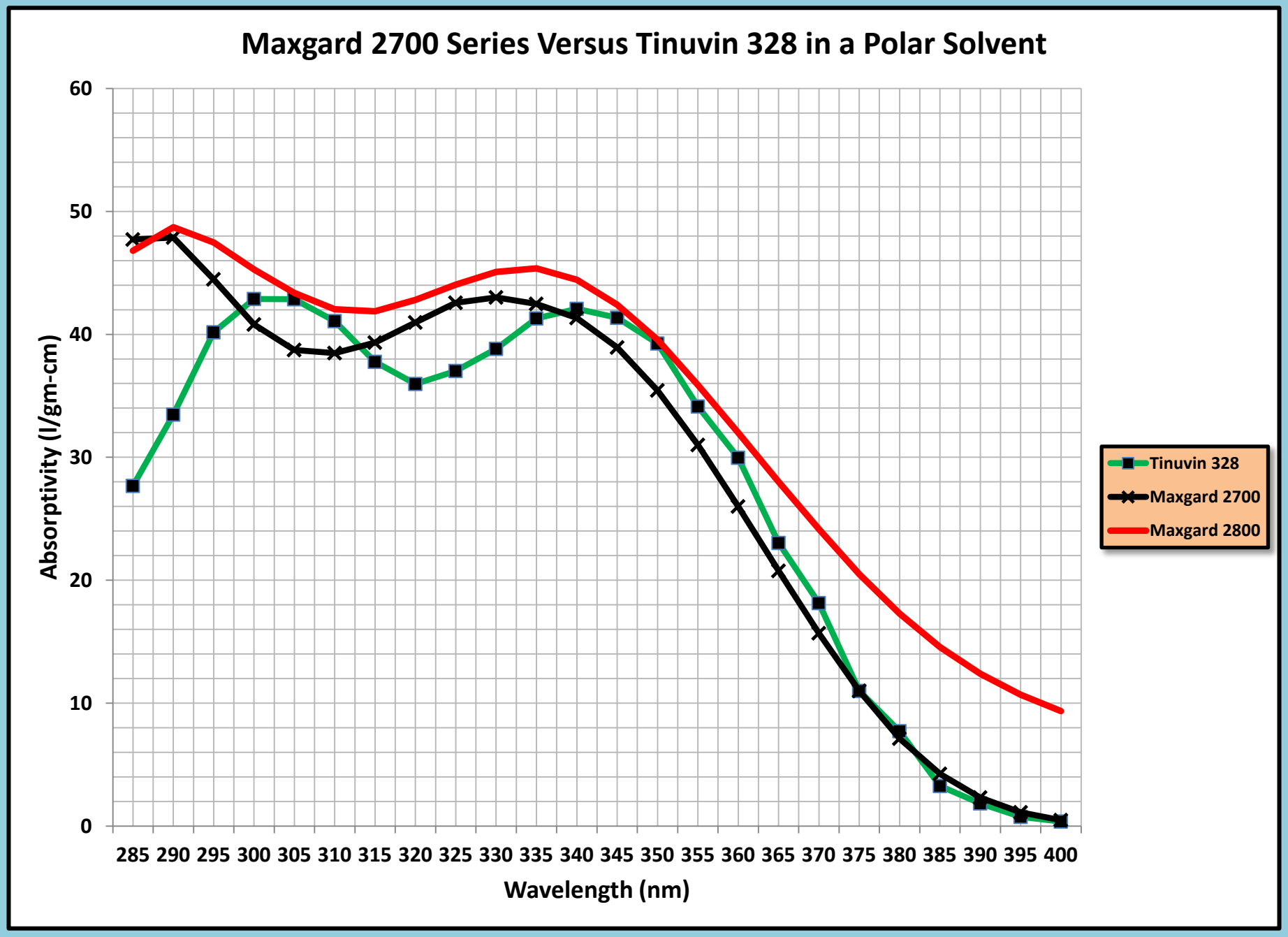
Penetration of Wavelengths



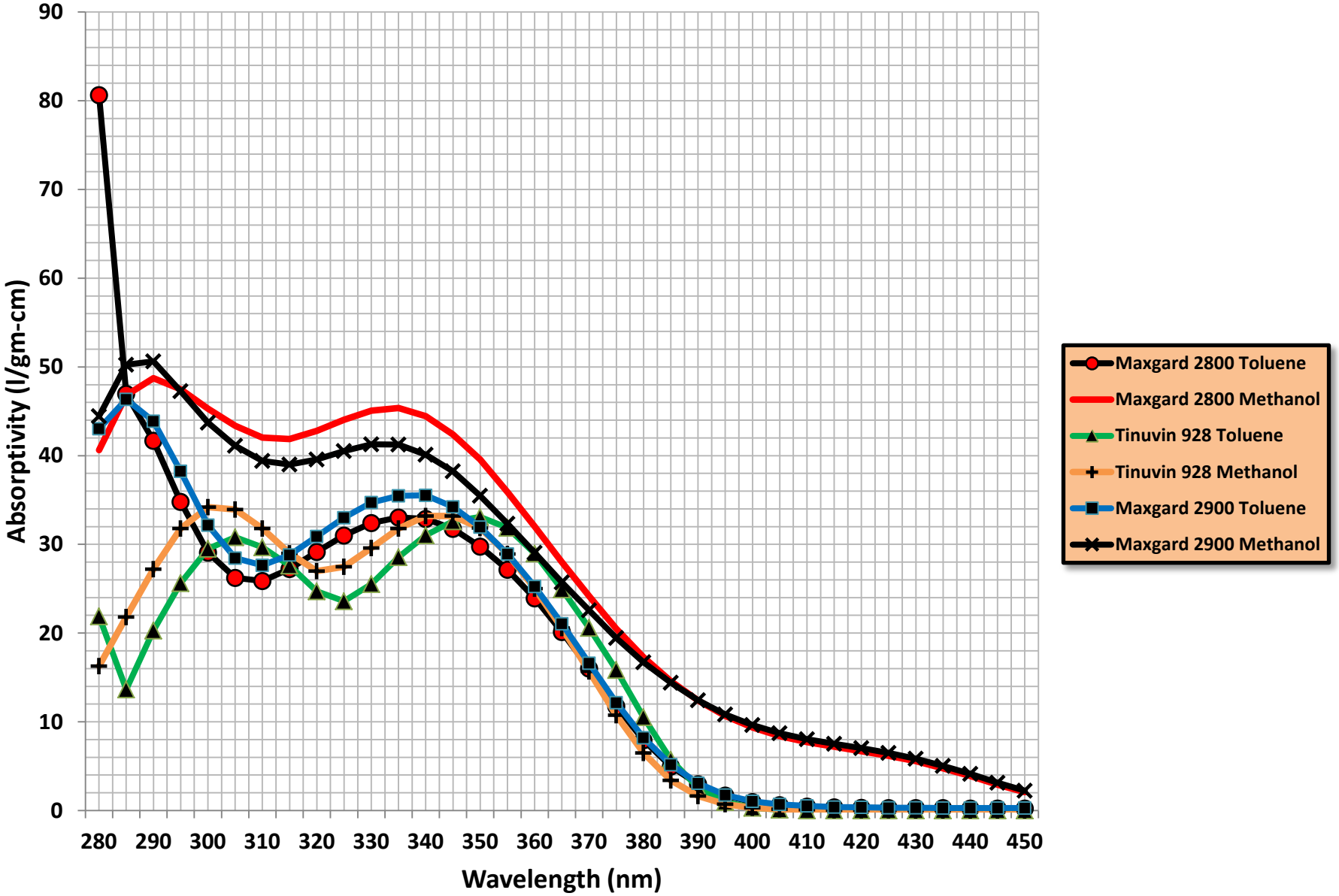
The Photo Physics of UV Absorbers limits them typically to thick section for UV protection while in thin films, fibers and coatings the UVA provides substrate protection and that protection is fugitive over time.


Absorptivity in Toluene (l/gm-cm)
80
70
60
50
40
30
20
10
0
280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400
Wavelength (nm)
Maxgard 300
Maxgard 900
Maxgard 1000
Maxgard 1030
Maxgard 1090

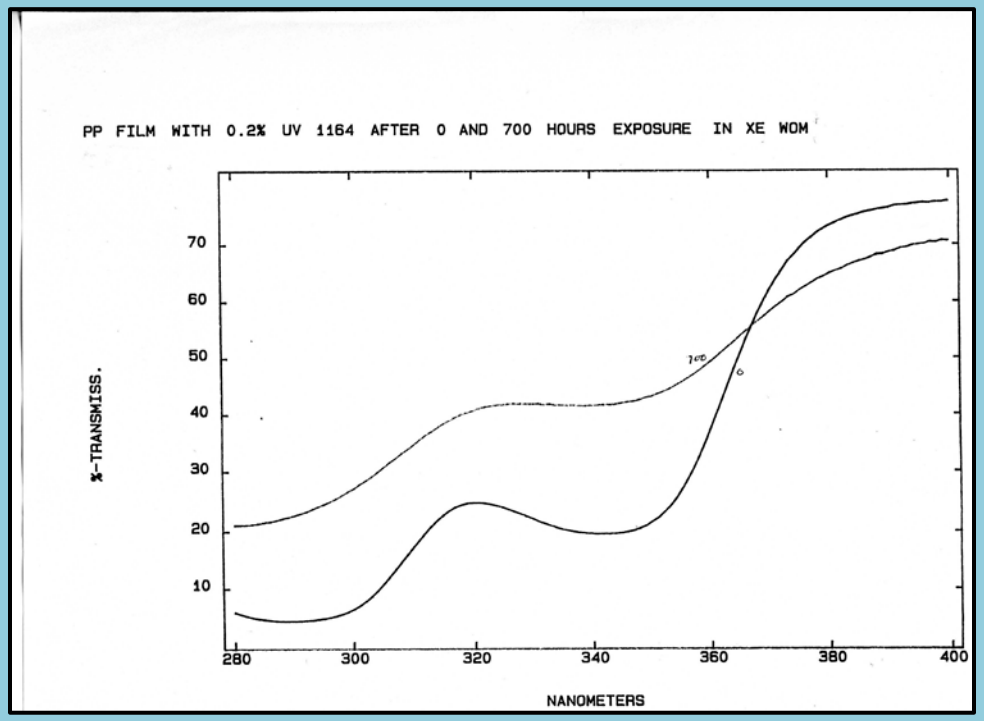

Absorptivity in Methanol (l/gm-cm)
70
60
50
40
30
20
10
0
280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400
Wavelength (nm)
Maxgard 300
Maxgard 900
Maxgard 1000
Maxgard 1030
Maxgard 1090
Maxgard 9010


Maxgard 2700 Series Versus Tinuvin 328 in a Polar Solvent
Absorptivity (l/gm-cm)
60
50
40
30
20
10
0
285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400
Wavelength (nm)
Tinuvin 328
Maxgard 2700
Maxgard 2800

Maxgard 2800 & 2900 Versus Tinuvin 928 in Polar and Non Polar Solvents

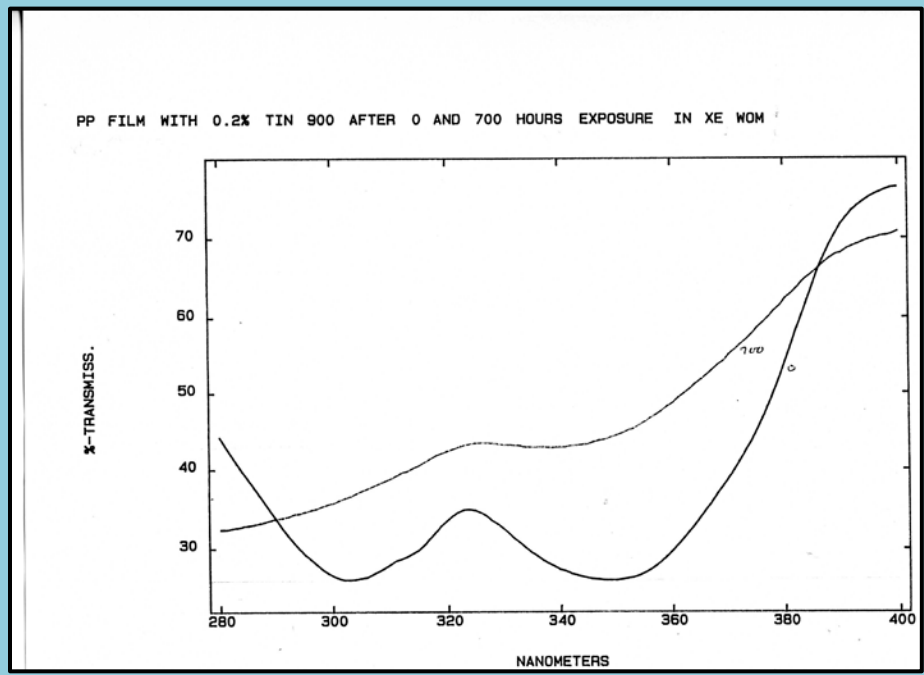


Fugitive Nature of UVA In-Situ Conversion



2-[4,6-Bis(2,4-dimethylphenyl)- 1,3,5-triazin-2-yl]-5-(octyloxy) phenol

Hydroxy substituted benzotriazole



Film Trends in the Global Market

- Higher processing temperatures.
- Longer Residence times
- Thinner Gauge
- Multiple Layers
- Higher performance
- Lower cost
- Sustainable and recycled use.
- Global temperatures increasing.

Better compatibility of plastic additives with greater performance.

Multipurpose additives that provide broader utility.

Longer durability of plastic additive systems.

New Innovations in additive technologies that expand market penetration.

Sustainable additives for higher temperature environments !

UVITA SME & Plasmonics

Uvita SME™ plasmonics technology provides permanent and broad sustainable UV protection, with no migration or extraction from 200 to 800 nm and into the near to far IR.
Uvita SME™ is highly synergistic with other UV light stabilizers, including hindered amine light stabilizers (HALS).
Uvita SME™ provides plasmonic UV protection and stabilization for all plastics and coatings, without the common restrictions of red and blue shifts and hypsochromicity.
Uvita SME™ produces a consistent hyperchromic shift with other UV light stabilizers, never before seen in the history of light stabilizers.
With Uvita SME™ there is an electromagnetic transfer of excited electrons from the surface of the particle to form a plasmon cloud over the particle, and transference of that energy to the conductive band of the organic UV absorbers

SPECTRAL ENHANCERS/MODIFIERS

Control of Absorbance (Absorptivity)

Permanence without blooming and extraction, non volatile

Permanent UV Absorbance for the Life of the Plastic Film or Coating.

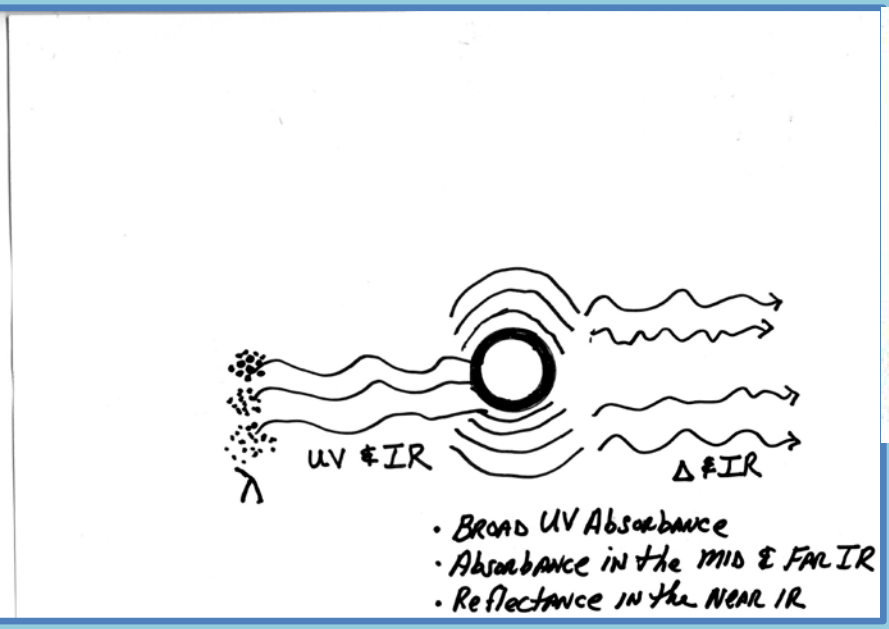
Synergism with Organic UVA and Hindered Amines!!!

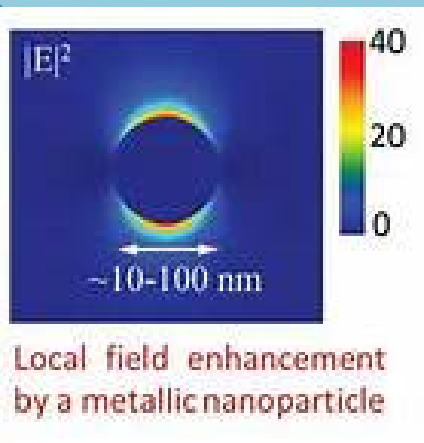
Post Modification for Antimicrobial, Antifungal, Anti counterfeiting; coloration, and extending expensive fluorescent and phosphorescent dyes and infrared absorbers.

Plasmonics

- The field has grown in the last five years more specifically in the optics area with No applications in Plastics and Coatings until now.
- The practical end use applications are limited and expensive and for the most part novel in nature.
- The key is to exploit the mechanism and end use application cheaply and with sustainable green chemistry. The applicability must be broad and flexible to changes for other end use applications and without the limitation of other organic chemistries known to the art.

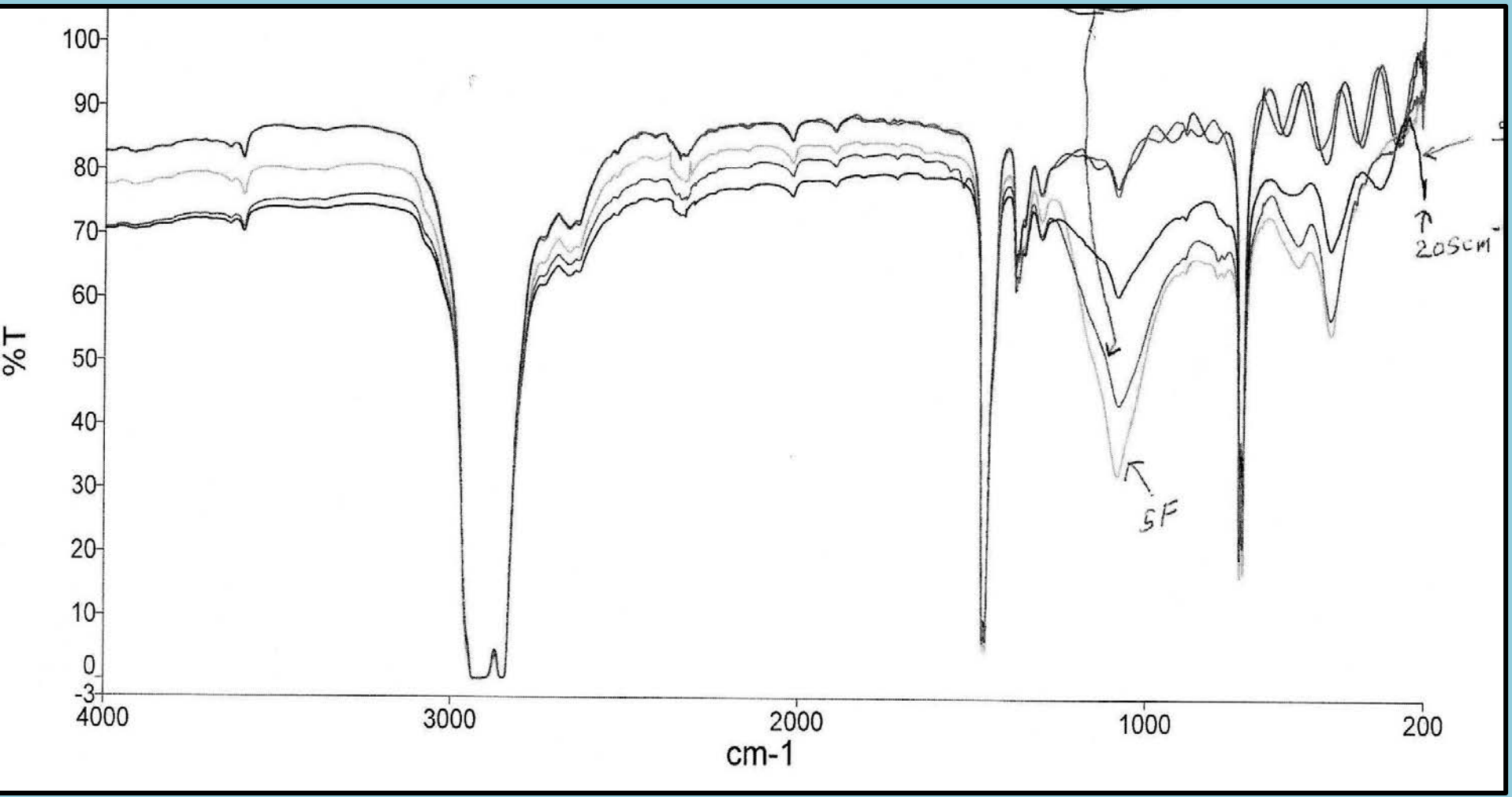
Spectral Modifier & Enhancer





A insulative non conductive core is key and the band gap of the nano coating must be above 3.7.
The existing nano coating is fused and fixed and not mobile but has a reactive surface towards select chemistry.

Enhanced Spectral Modifiers



UVITA SME 3811
Doped and Undoped
10 micron upper cut (mean 4 microns)

UVITA SME 3811 vs Organics

UVITA SME 3811

- No Migration
- No Blooming Non Extractable
- Thermally Stable
- No Chemical Reactivity
- Synergisms
- Minimum color to system
- Broad Wavelength absorbance
- Permanence over time
- Hyperchromic with HALS and Organic UVA

Organic UVA (BZT;BZ;Triazine)

- Migration and surface haze
- Blooming and Extractable
- Volatile and Thermally unstable
- Chemically Reactive
- Synergisms
- Highly Colored to System
- Highly selective Absorbance and wavelengths
- Limited performance over time
- No Hyperchromic behavior mostly Hypochromic !

Uvita SME™ products work well alone or especially well in combination with organic ultraviolet absorbers, and with their counterparts in hindered amine light stabilizers (HALS). They are highly suitable for use in hot climates and high humidity environments, and have no restrictions in their maximum wavelength absorption (lambda maxima).

Uvita SME™ products are the result of green chemistry derived from sustainable resources. They complement all organic UVA and HALS synergistically, by increasing the absorbance of the UVA and HALS in the polymer system, while showing hyperchromicity and bathochromic shifts to higher wavelengths.

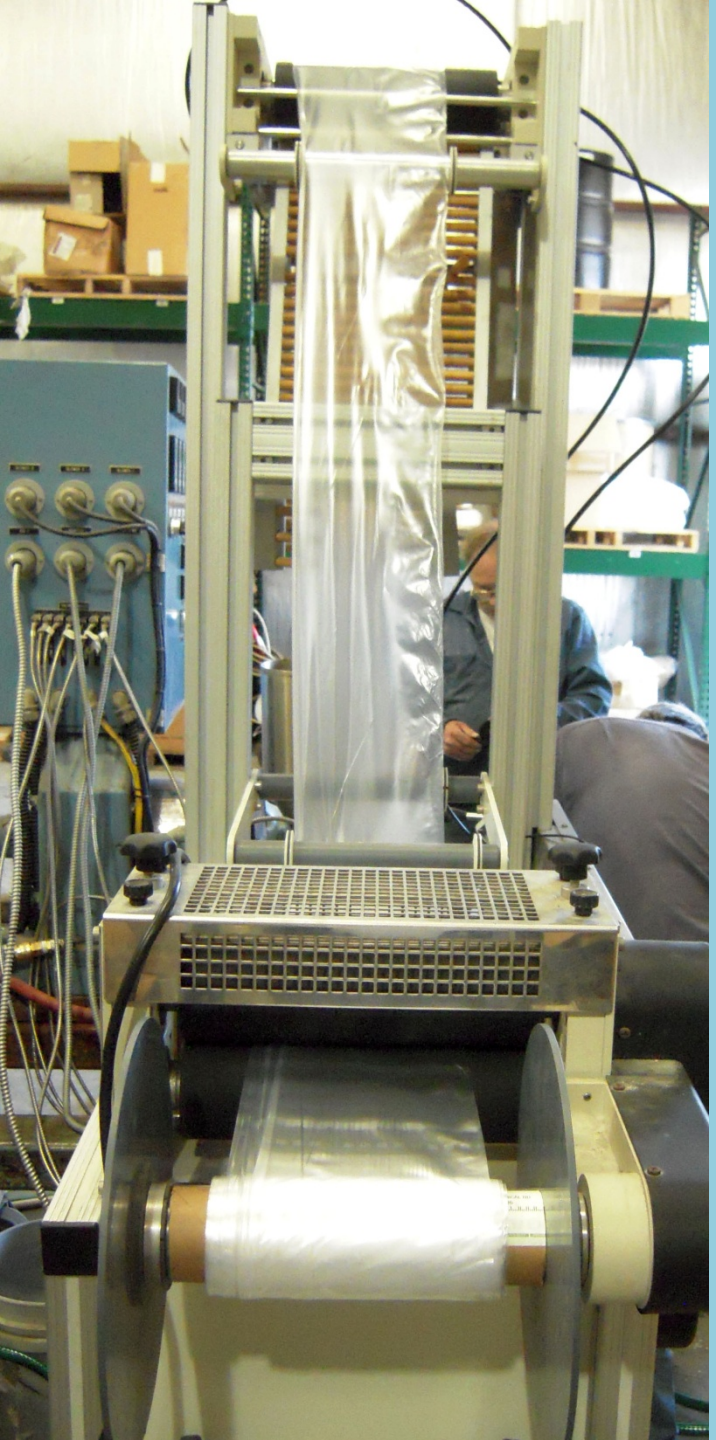
UVITA SME™ in combination with HALS and organic UVA, also slows down in-situ consumption when exposed to UV radiation.

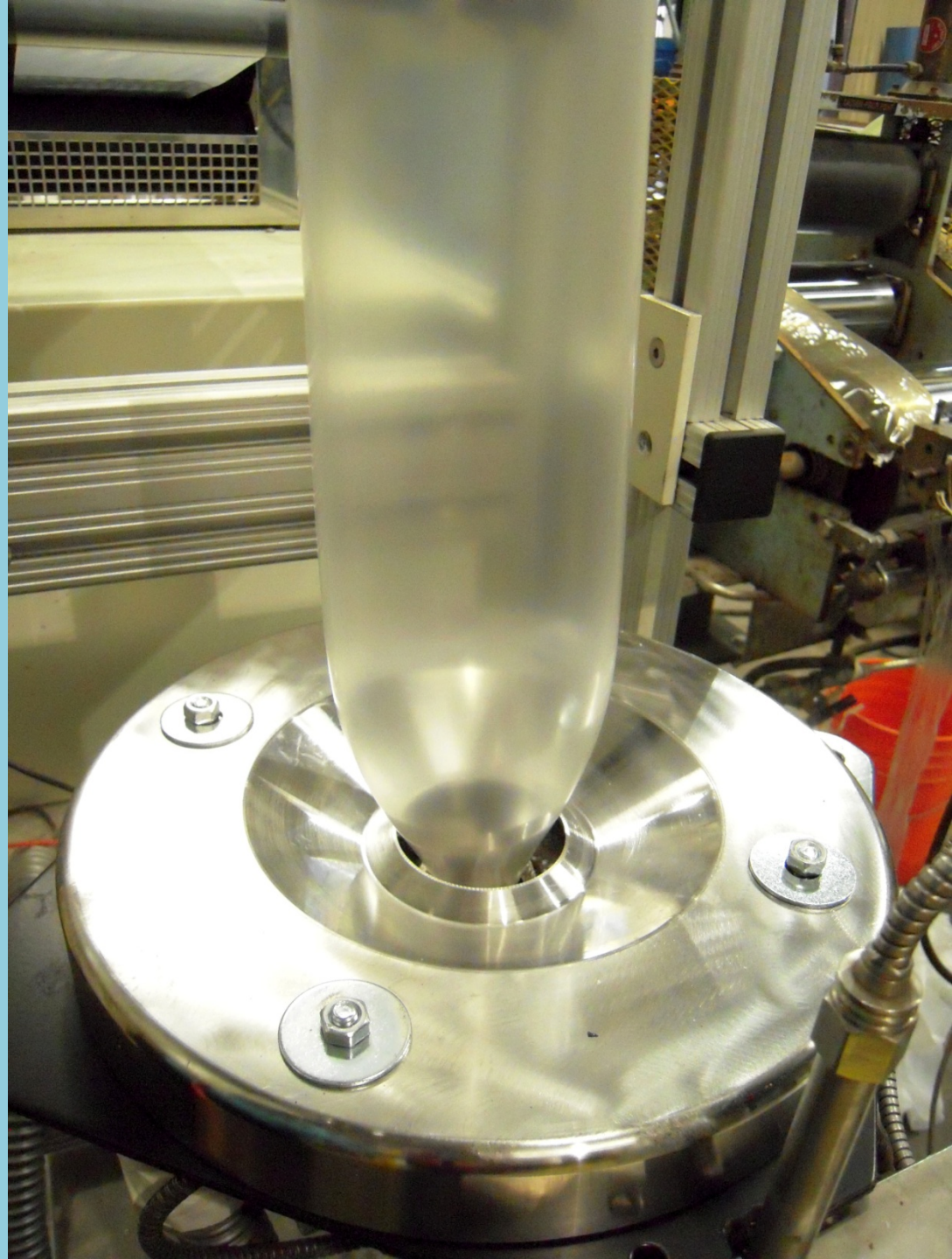
They are very cost-effective and highly efficient in applications such as:

- CONTROL OF POST-HARVEST FOOD PACKAGED IN PLASTICS.
- INSECT VECTOR CONTROL DURING CROP PRODUCTION.
- LAMINATED THERMOPLASTIC FILMS OVER PIGMENTED PLASTIC.
- DECKING AND ROOFING, AND SIMILAR APPLICATIONS.
- PROTECTION OF FOOD PACKAGING AND OILS BEYOND THE 400 NM RANGE.

Very long term to permanent broad UV protection is the key to superior performance. Uvita™ SME technology to achieve this is available today.

There are no known limitations for the use of this technology, which has been tested in condensation polymers, PET fibers, cast films and PETG, with no adverse effects.





3% BATCH #1 SF/ 0.32944

FIG. 1A

FIG. 1B

3% PERMINIX W/ 0.32944

FIG. 1A

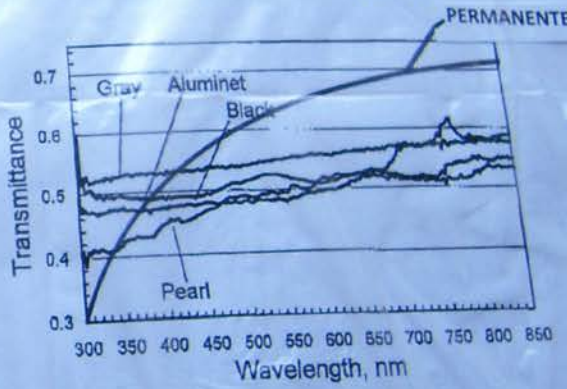
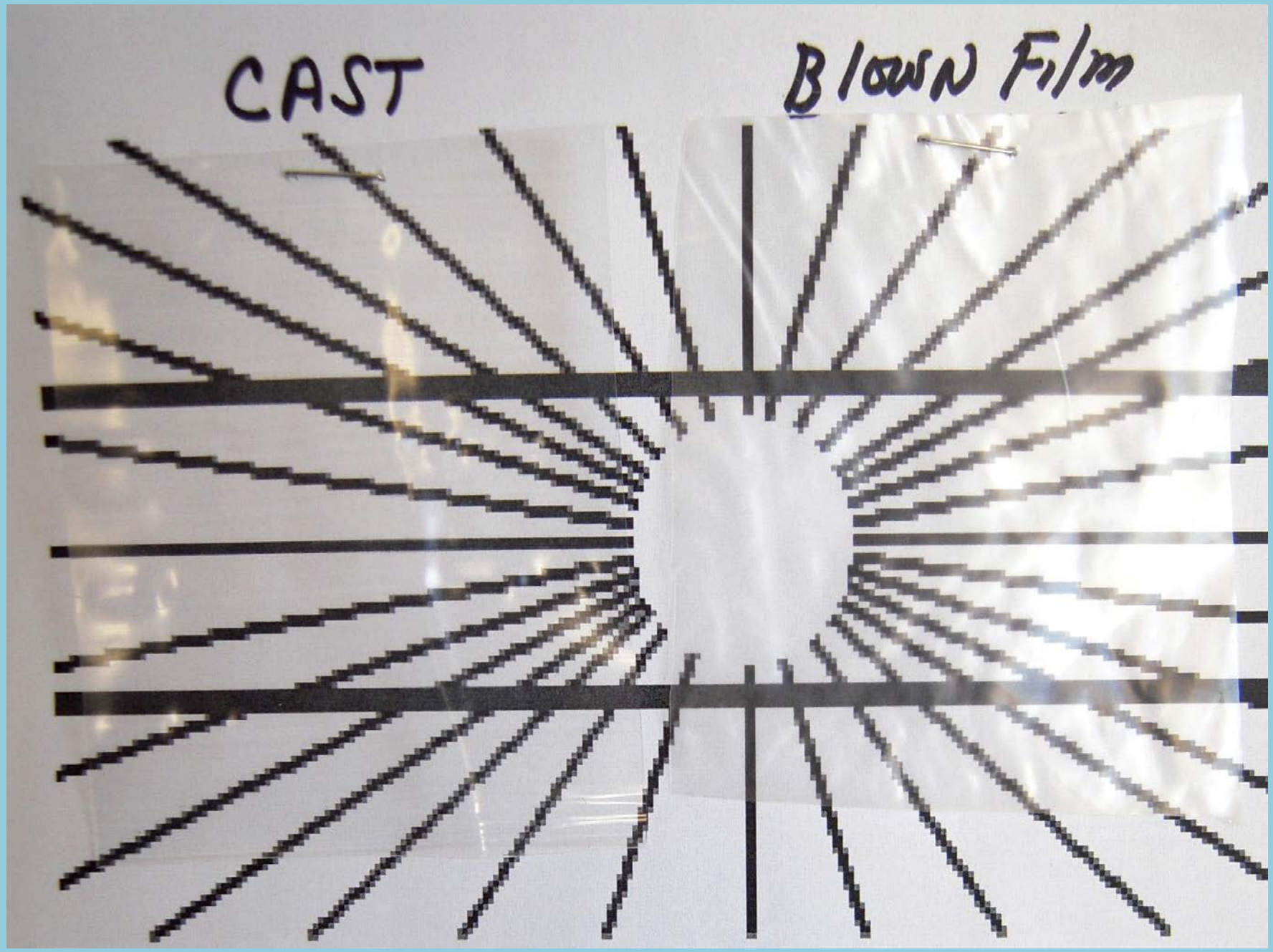
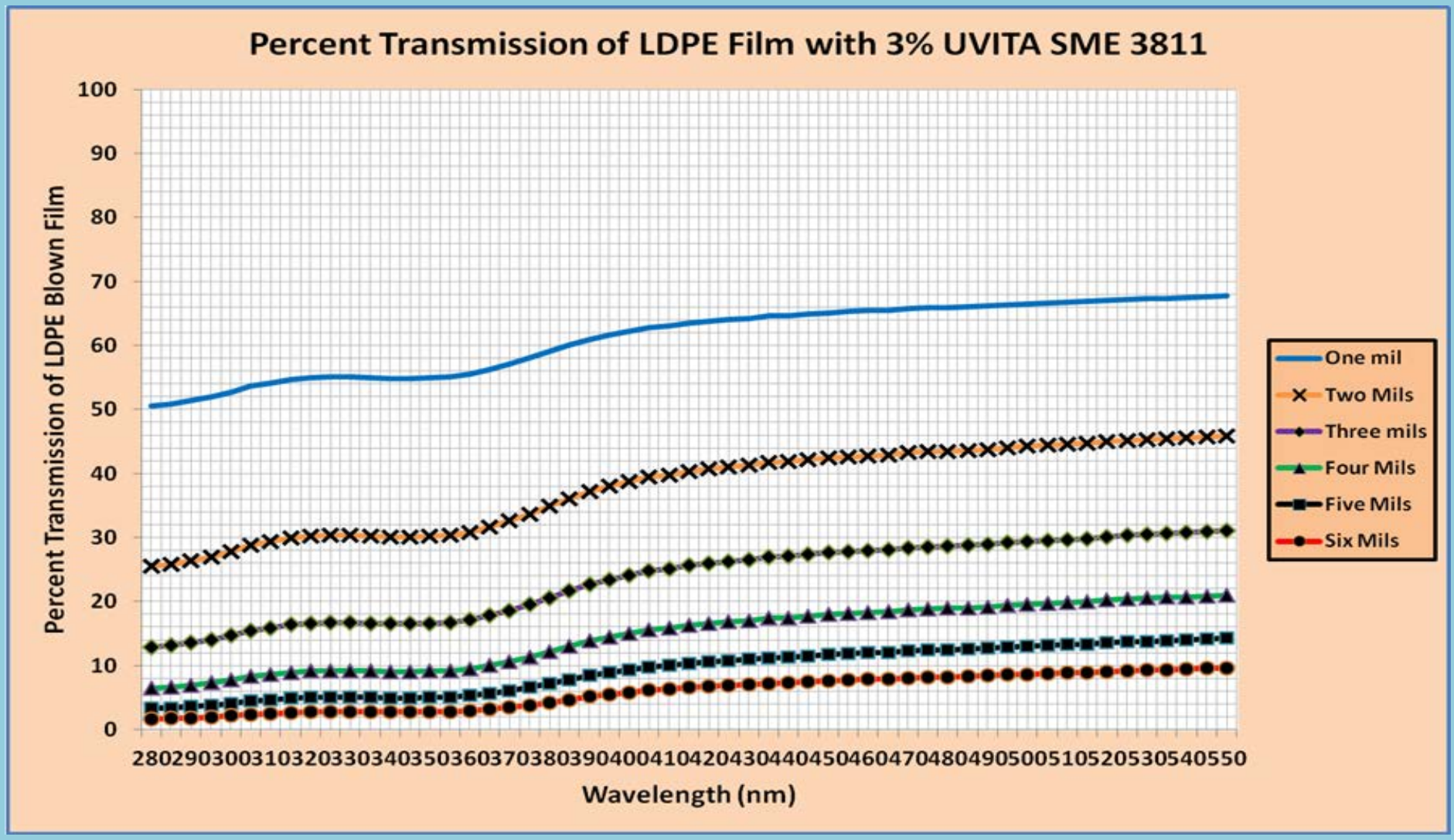


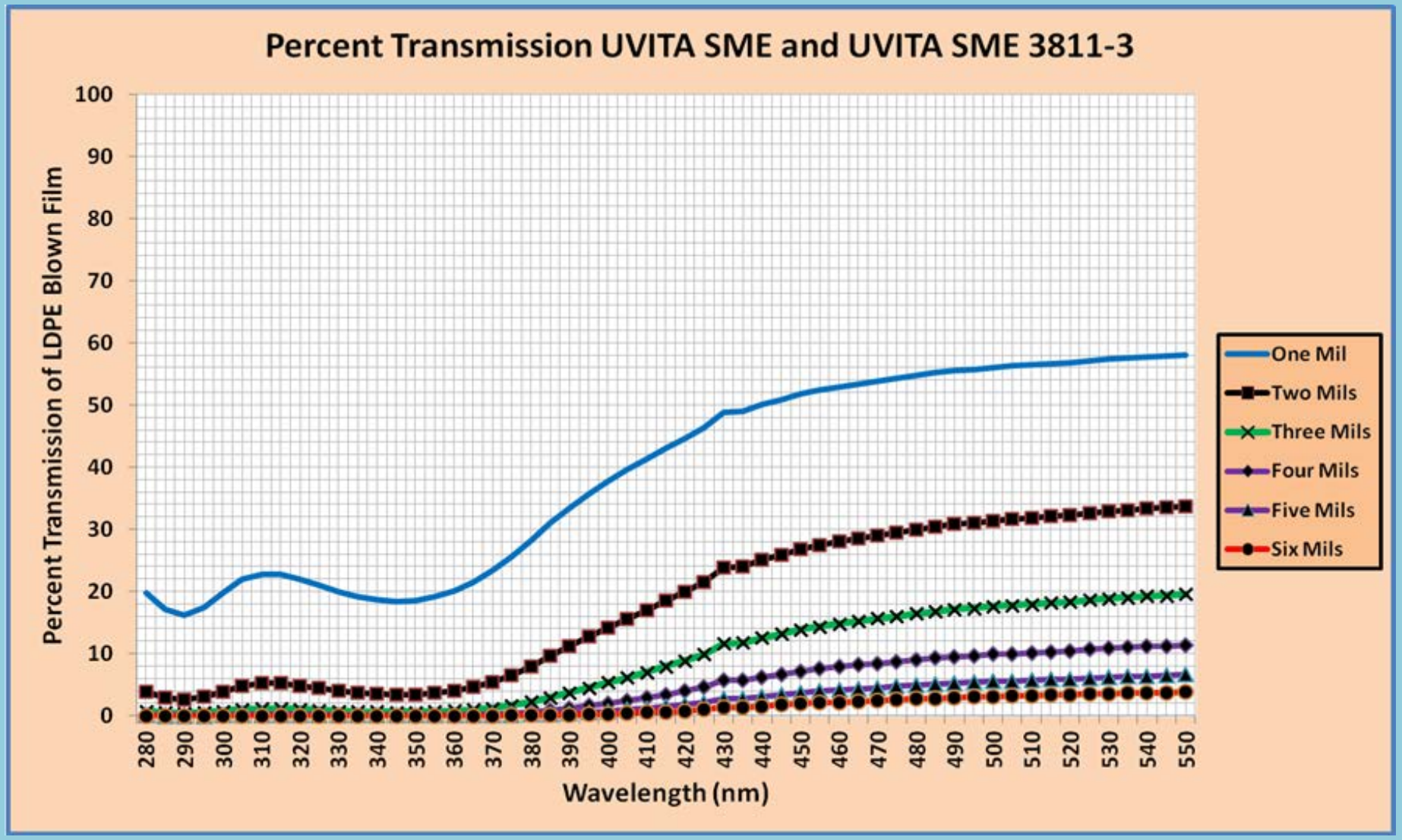
FIG. 1B


CAST
BLOWN Film

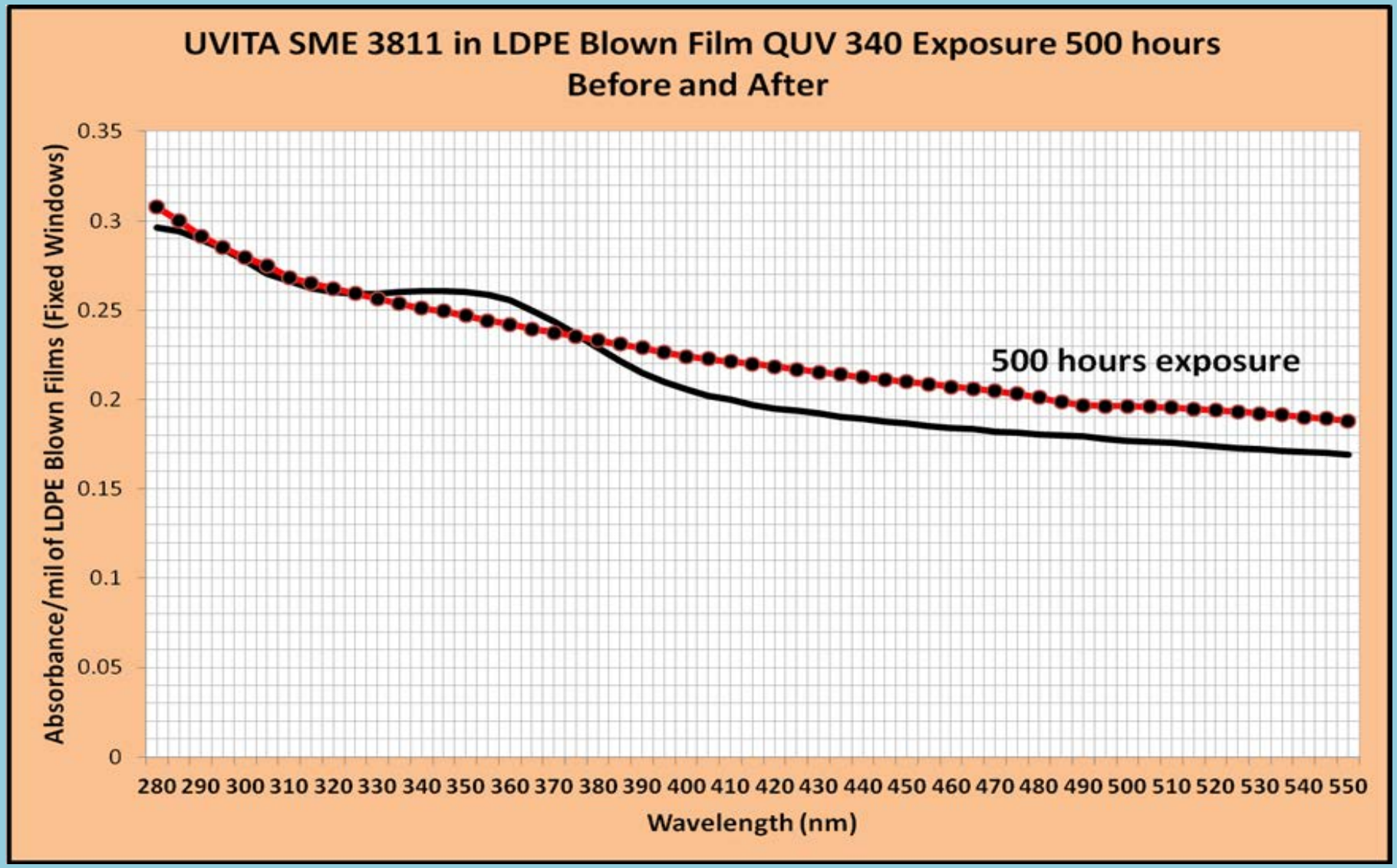
UVITA SME 3811 Spectra modifier and Broad Permanent UVA



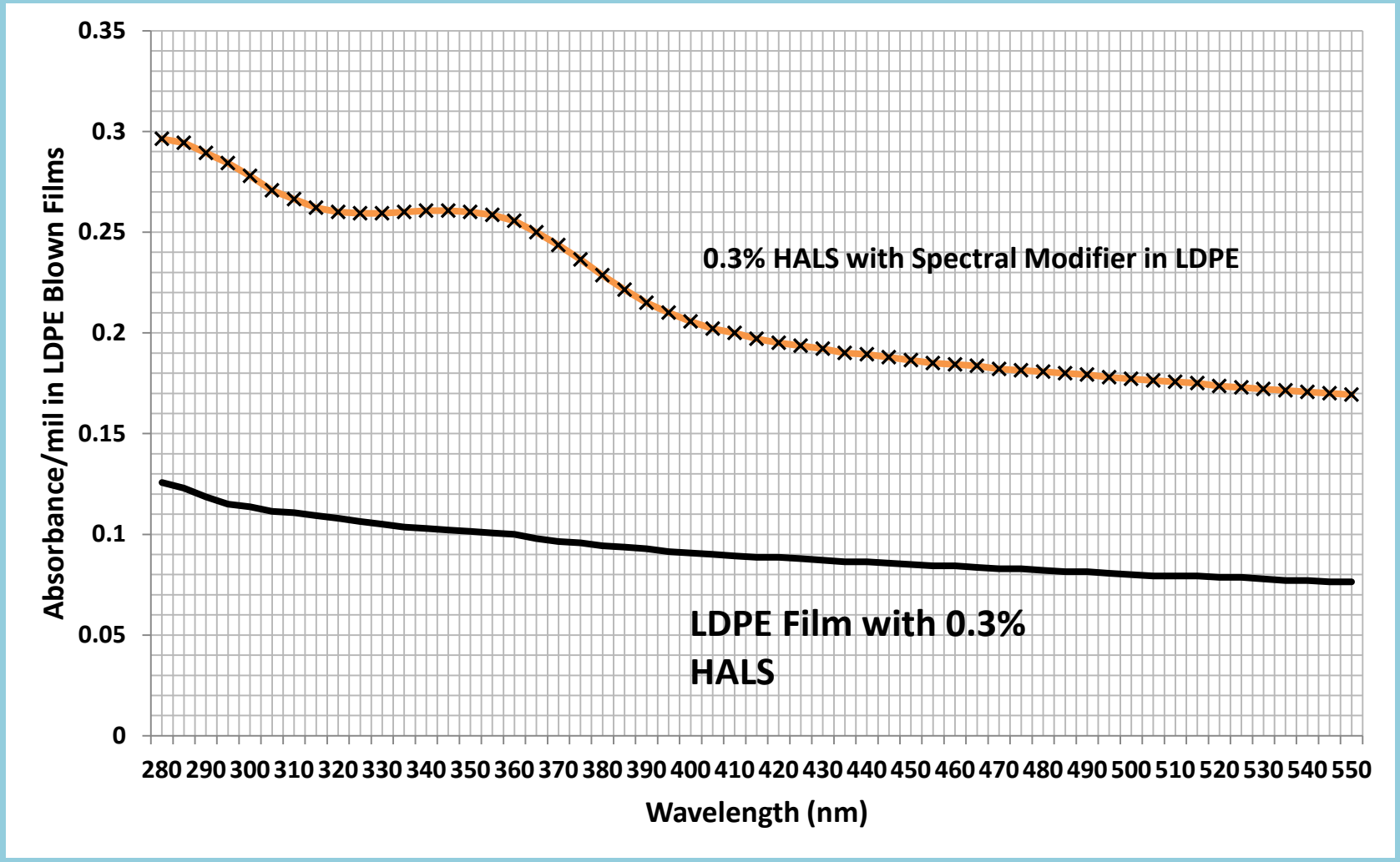
UVITA SME 3811-3 Synergism



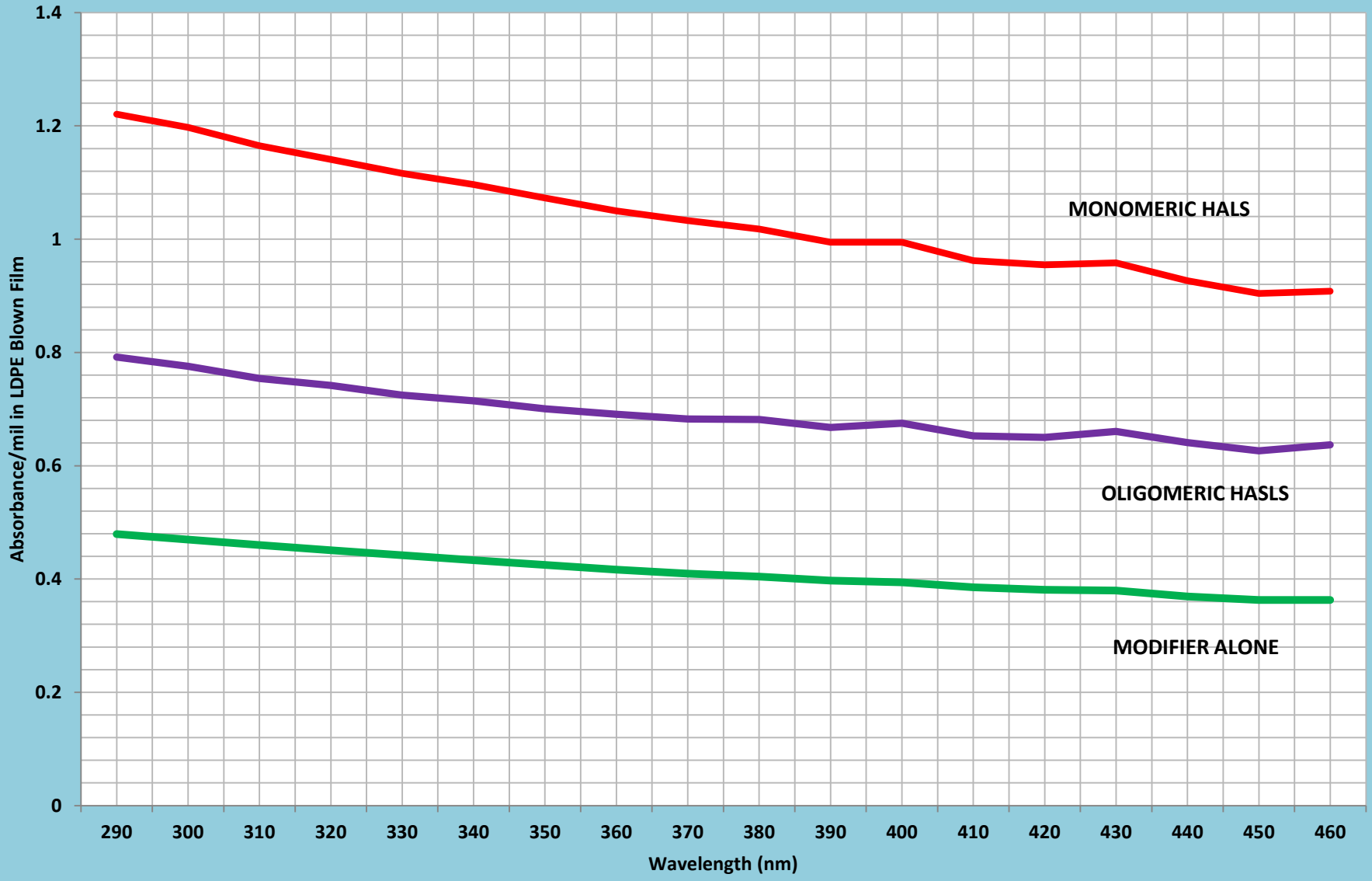
Effect of UV Exposure on Absorbance



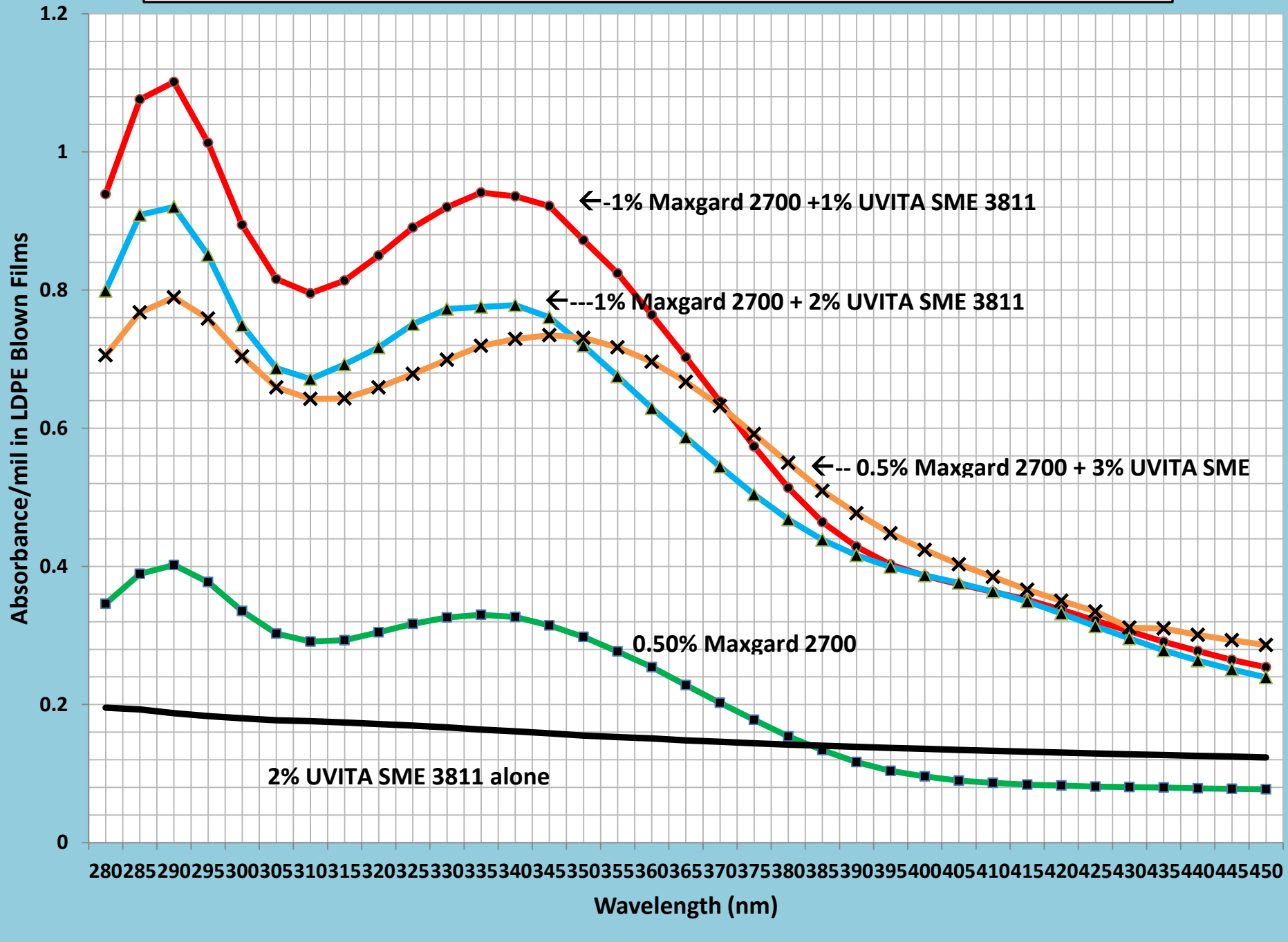
Synergisms with Monomeric and Oligomeric HALS !



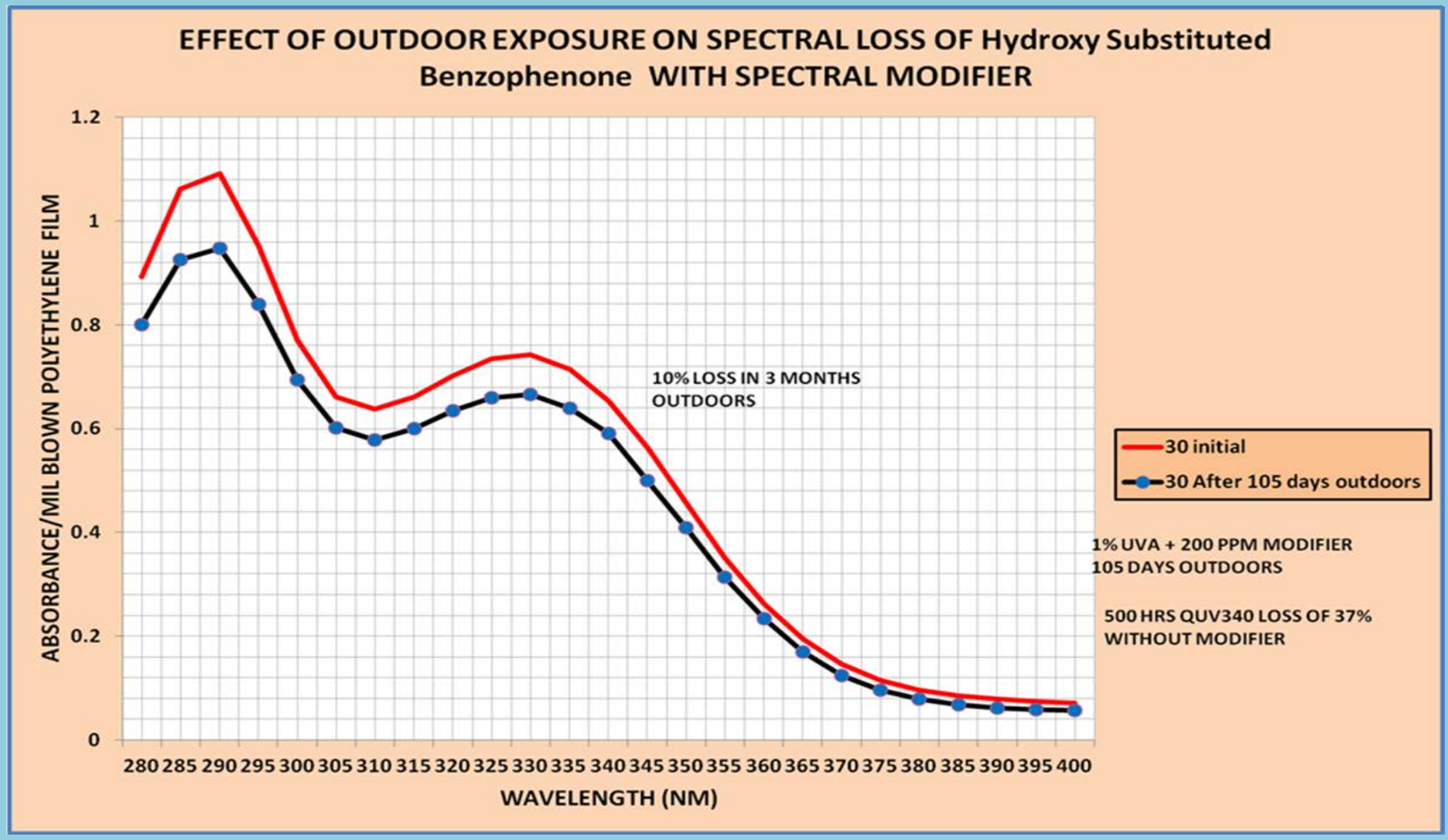
Hyperchromic Shift in the UV in LDPE Blown Film by Oligomeric and Monomeric HALS and Spectral Modifier



ONE Mil LOW DENSITY POLYETHYLENE FILMS



Spectral Modifier Reduces In-Situ Conversion of Conventional Organic UVA



UV Exposure LDPE Blown Films
QUV-340 Exposure: 500 hrs. at Lambda Maxima

- No Spectral Modifier
- Tinuvin 328 (0.5%):43% loss.
- Tinuvin 328 (1%): 42% loss
- Maxgard 700 (0.5%)37% loss
- Maxgard 1000 (0.5%): 79% loss
- Maxgard 300 (0.5%):75%
- Loss
- Maxgard 900 (0.5%):85% loss

- Spectral Modifier Used
- Tinuvin 328 (0.5%):28% loss
- Tinuvin 328 (1%) not done
- Maxgard 700(0.5%):25% loss
- Maxgard 1000 (0.5%): 34% average two films.
- Maxgard 300 (0.5%):19% average two films
- Maxgard 900 (0.5%):54% loss

UV Exposure 500 hours continued:

No Spectral Modifier

Tinuvin P (0.5% wt.): 61% loss in LDPE film.

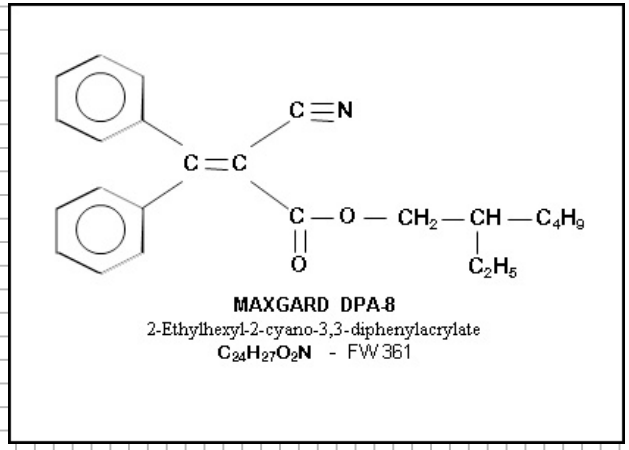
Maxgard 2700 (1%):57% loss in LDPE film

- With Spectral Modifier
- Tinuvin P (0.5% wt.): 41% loss in LDPE Film
- Maxgard 2700 (1%):38% loss in LDPE film

3% UVITA SME 3811 in PET 1 dpf fiber


CONTROL
0.20% 944
0.15% UVHA SME
0.20% 944
25

Polypropylene Homopolymer Injection Molded Plaques



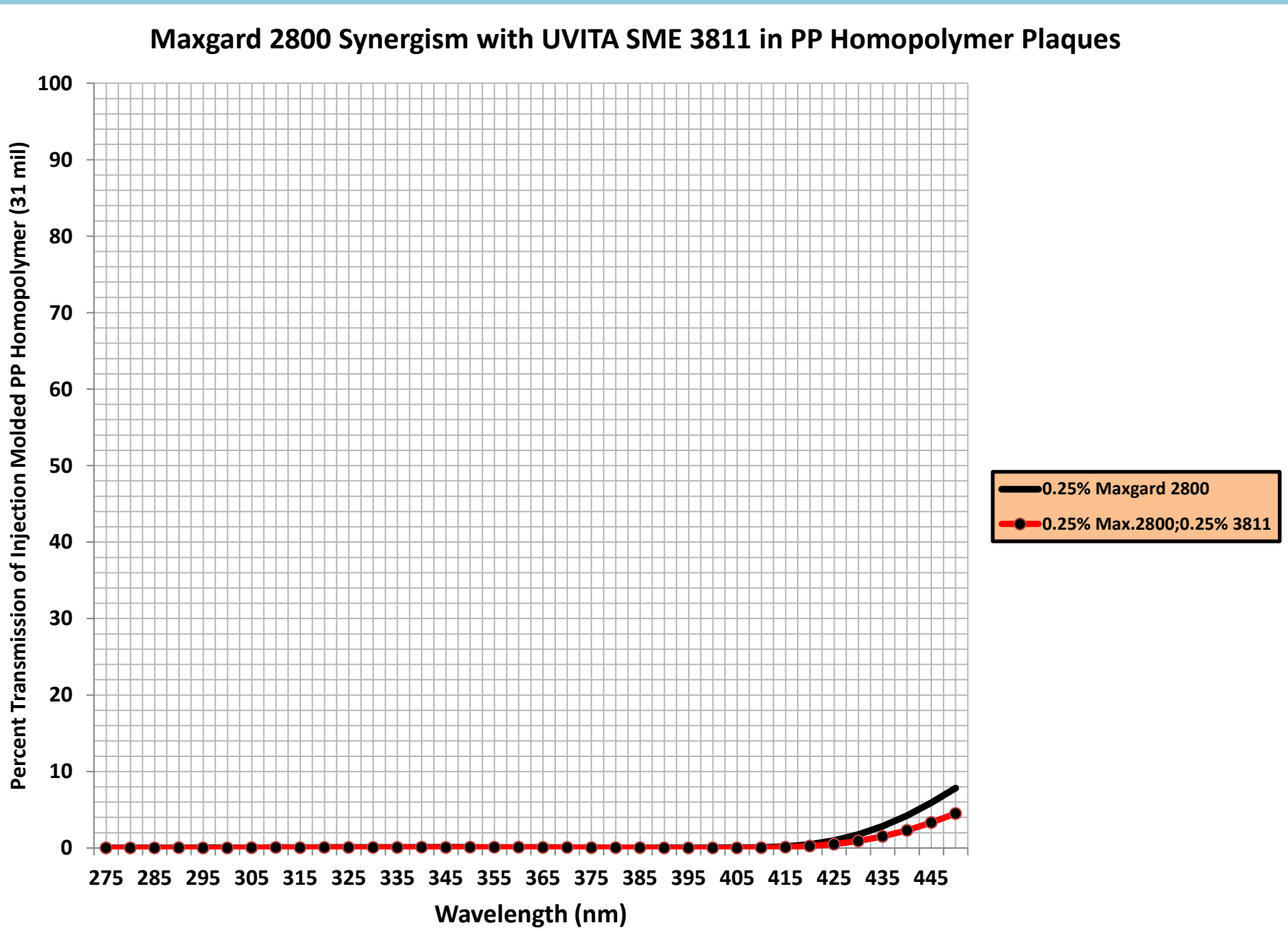
Percent Transmission of Injection Molded Plaques (31 mils)

100
90
80
70
60
50
40
30
20
10
0

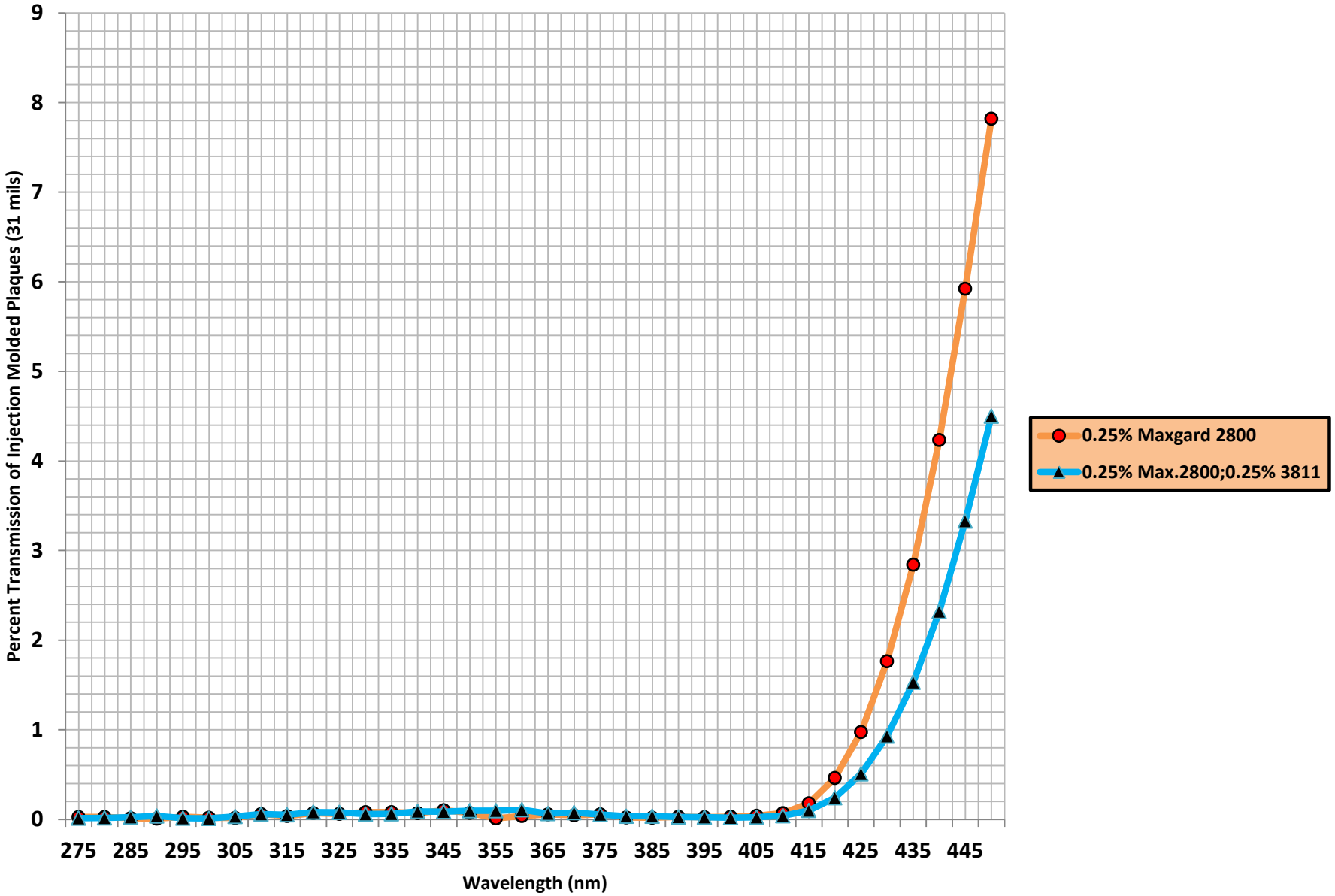
275 285 295 305 315 325 335 345 355 365 375 385 395 405 415 425 435 445

Wavelength (nm)

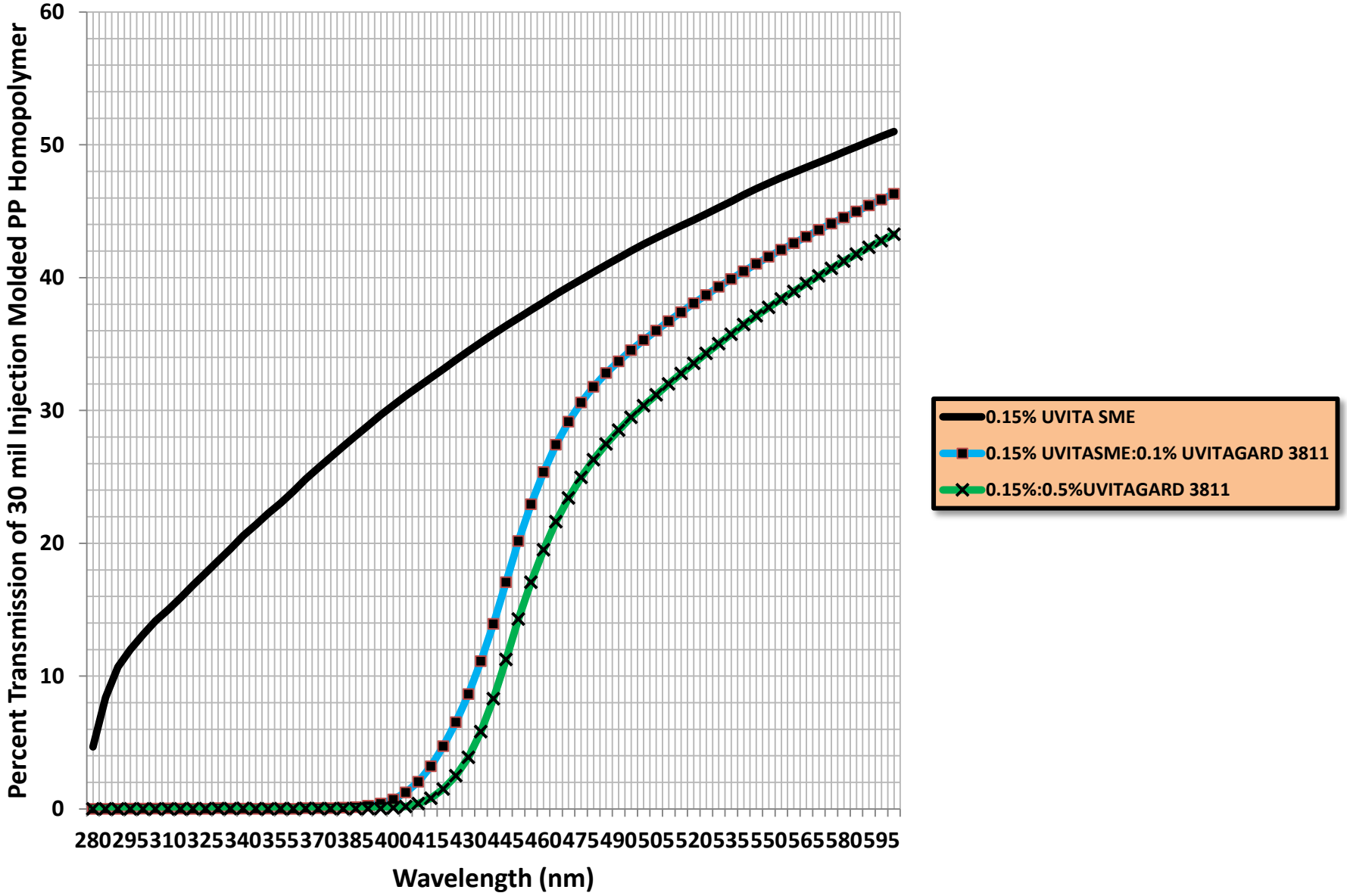
- 0.25% DPA8
- 1% DPA8
- 0.25% DPA8,0.1% 3811
- 0.25% DPA8,0.25% 3811


Maxgard 2800 Synergism with UVITA SME 3811 in PP Homopolymer Plaques
Percent Transmission of Injection Molded PP Homopolymer (31 mil)
100
90
80
70
60
50
40
30
20
10
0
275 285 295 305 315 325 335 345 355 365 375 385 395 405 415 425 435 445
Wavelength (nm)
0.25% Maxgard 2800
0.25% Max.2800;0.25% 3811

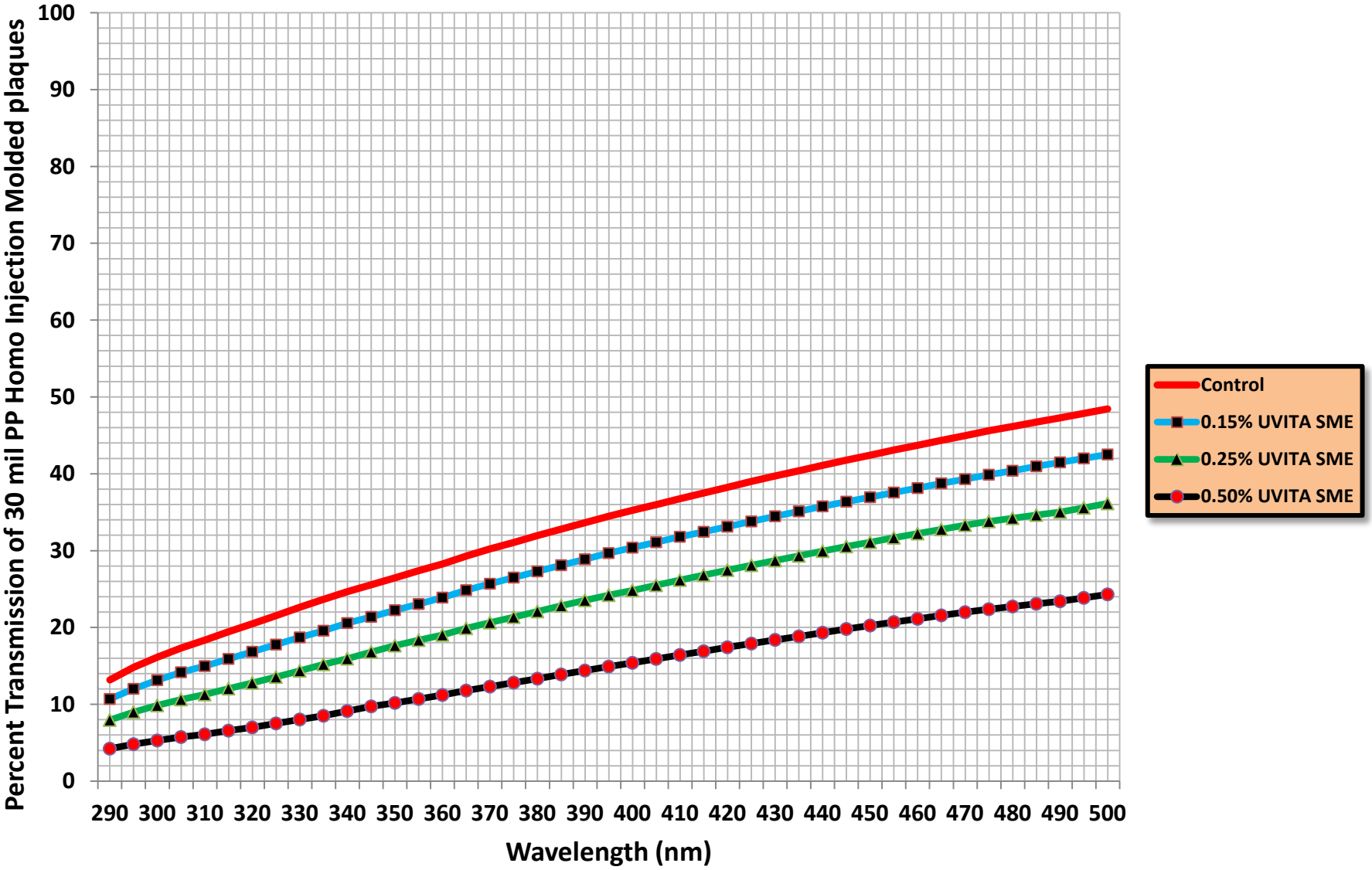
Polypropylene Homopolymer Injection Molding Plaques with Maxgard 2800

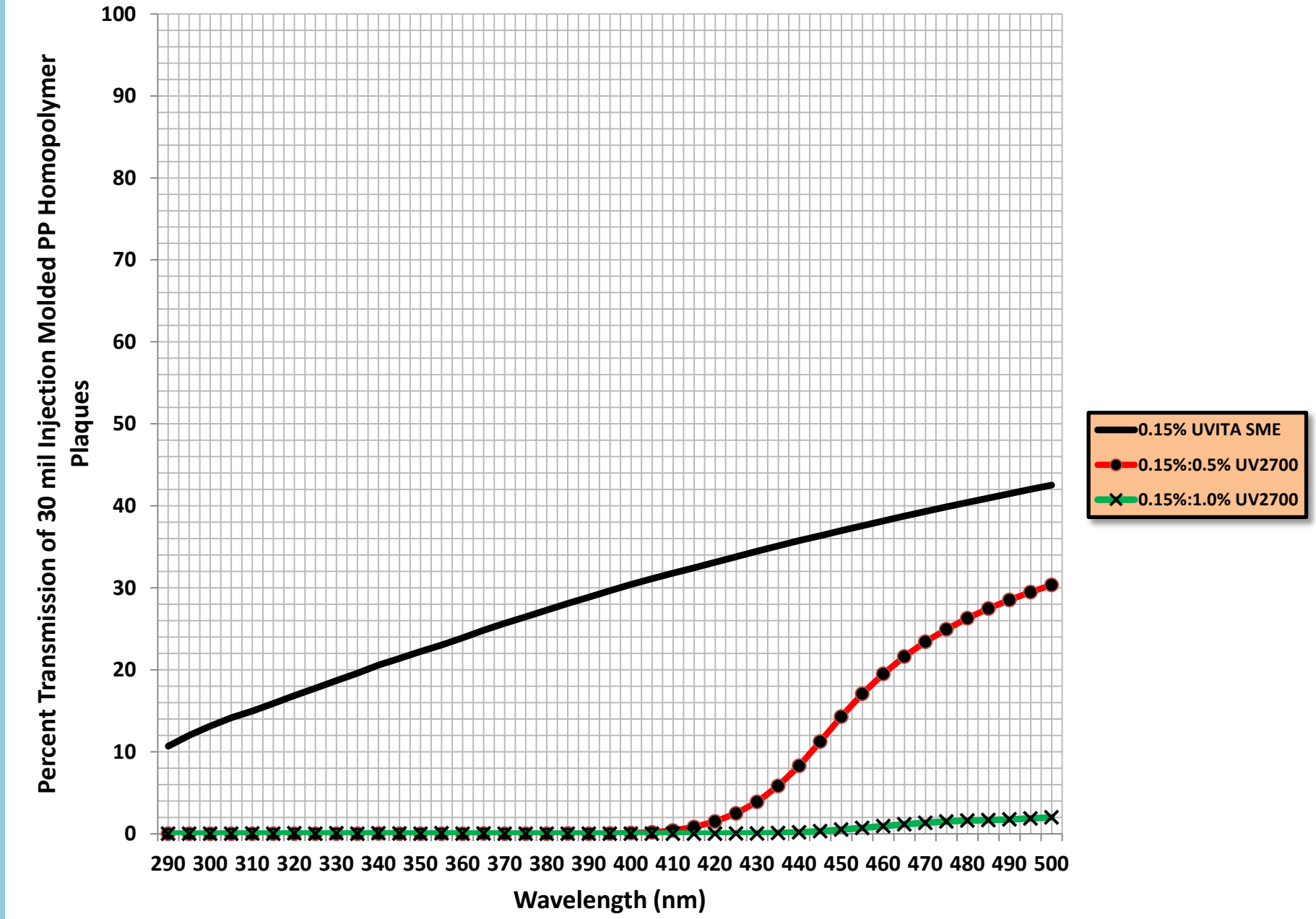


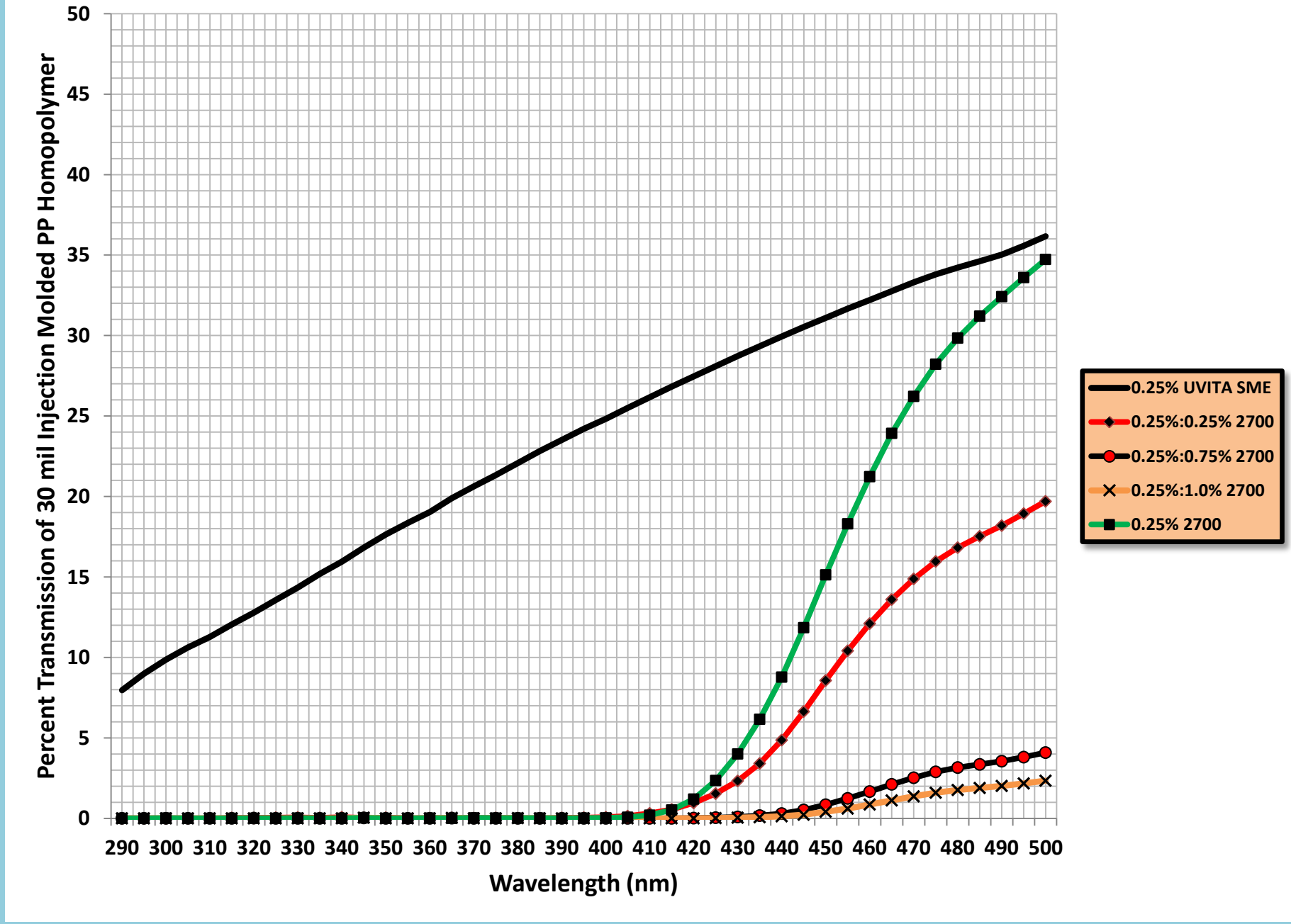
Broad UV Coverage of UVITAGARD 3811

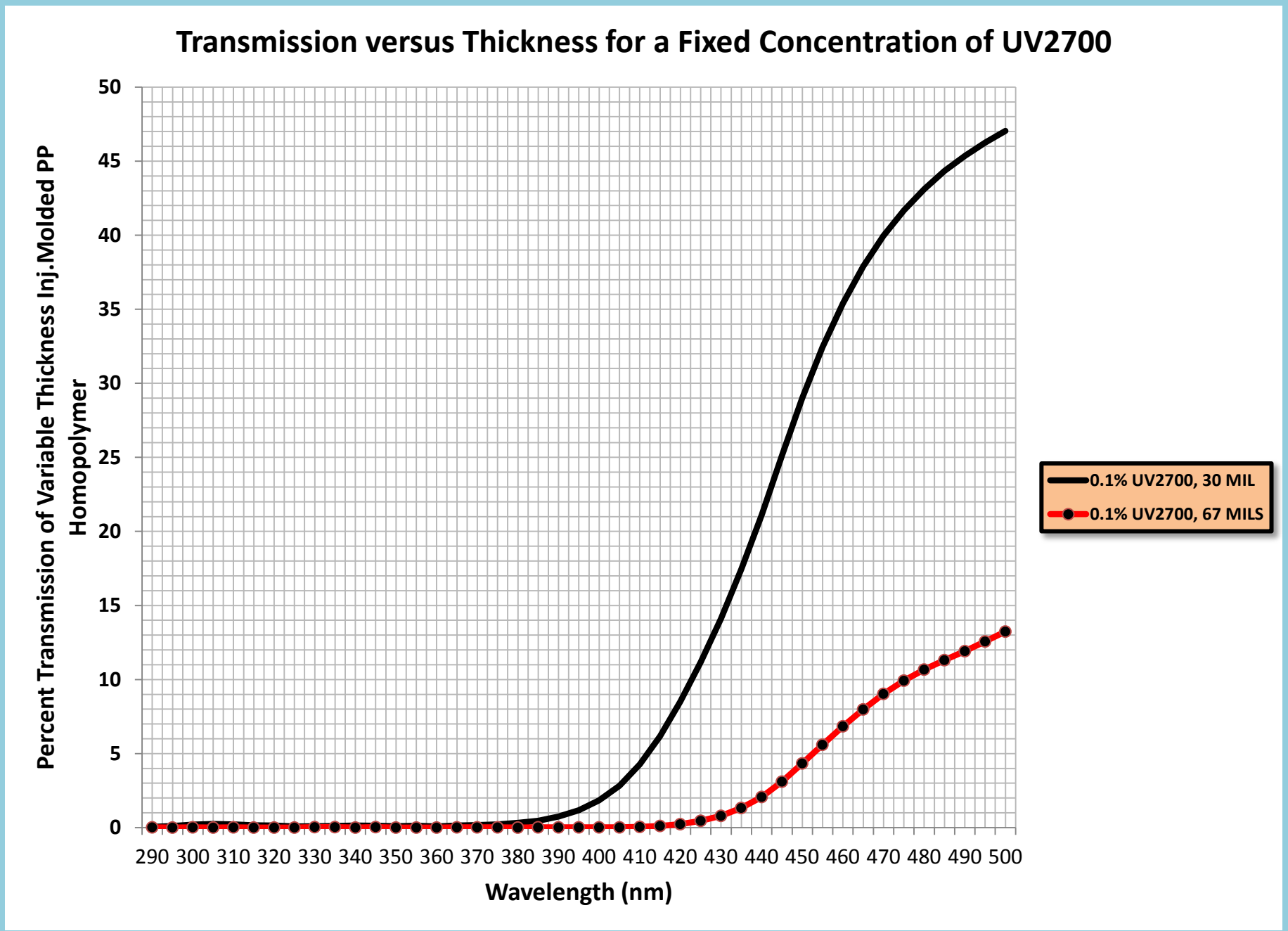


EFFECT OF UVITA SME CONCENTRATION ON 30 MIL INJECTION MOLDED PP HOMOPOLYMER PLAQUES

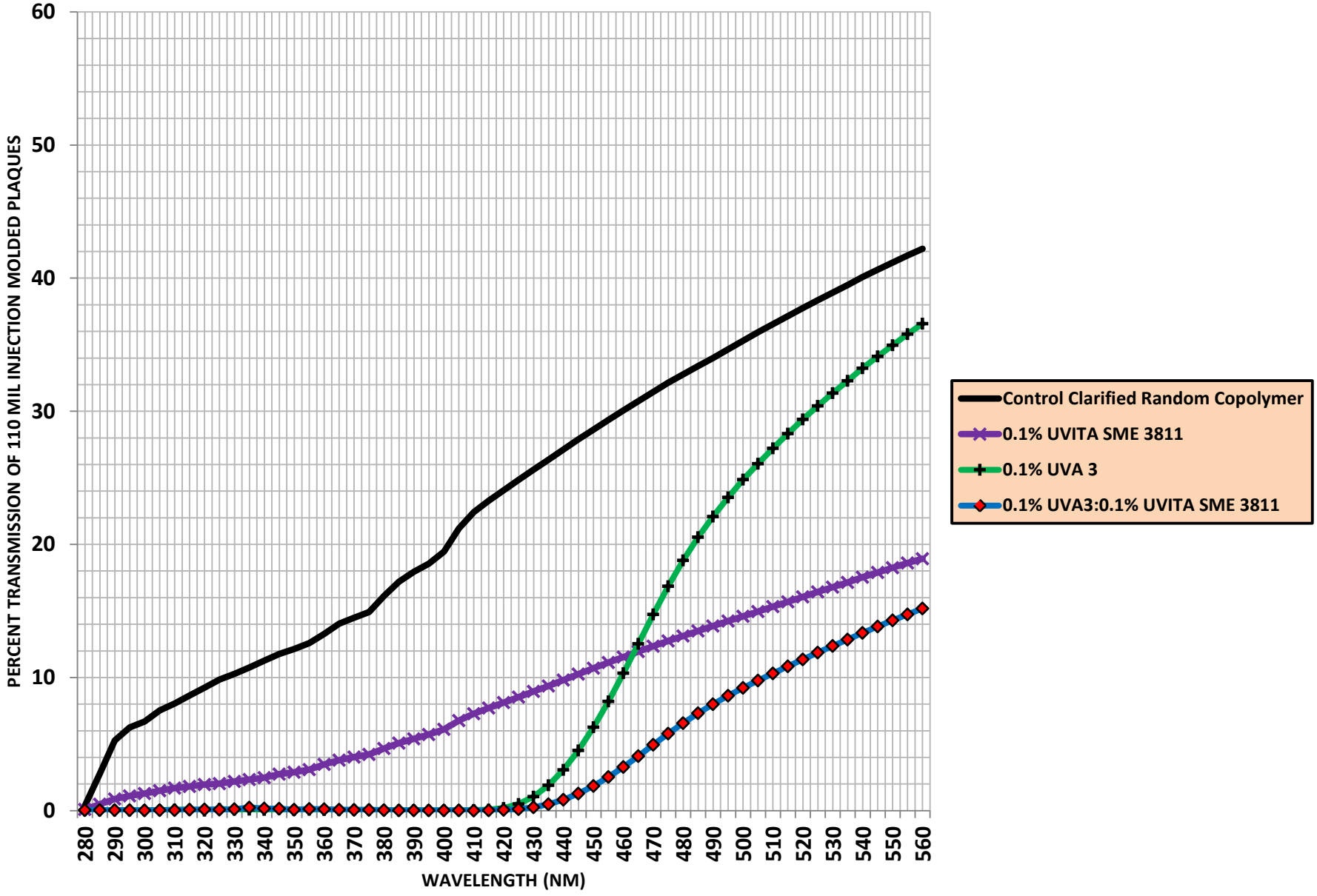



Percent Transmission of 30 mil Injection Molded PP Homopolymer Plaques
100
90
80
70
60
50
40
30
20
10
0
290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500
Wavelength (nm)
0.15% UVITA SME
0.15%:0.5% UV2700
0.15%:1.0% UV2700

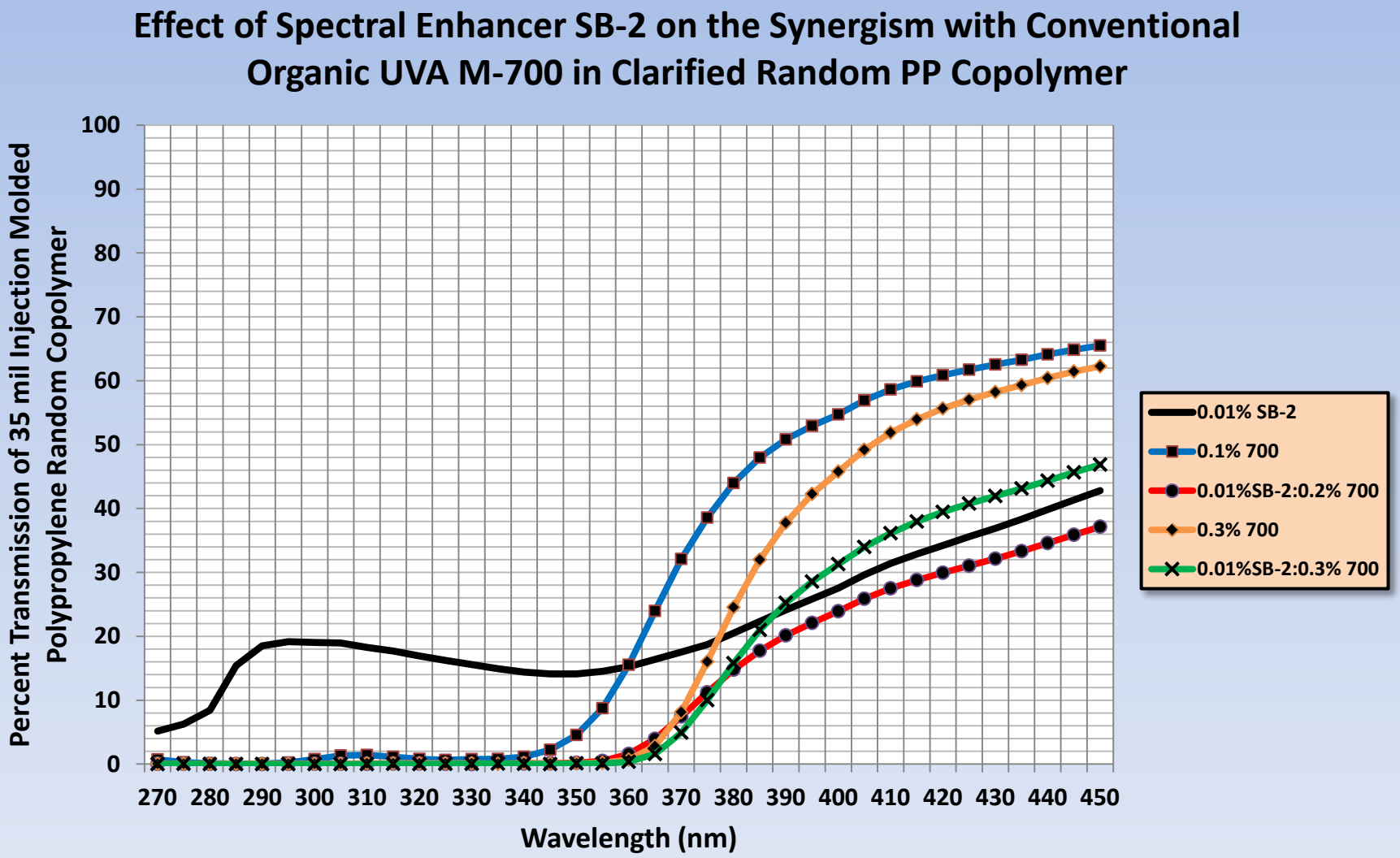

Percent Transmission of 30 mil Injection Molded PP Homopolymer
50
45
40
35
30
25
20
15
10
5
0
290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500
Wavelength (nm)
0.25% UVITA SME
0.25%:0.25% 2700
0.25%:0.75% 2700
0.25%:1.0% 2700
0.25% 2700


Transmission versus Thickness for a Fixed Concentration of UV2700
Percent Transmission of Variable Thickness Inj.Molded PP Homopolymer
50
45
40
35
30
25
20
15
10
5
0
290 300 310 320 330 340 350 360 370 380 390 400 410 420 430 440 450 460 470 480 490 500
Wavelength (nm)
0.1% UV2700, 30 MIL
0.1% UV2700, 67 MILS

ULTRAVIOLET SPECTRA OF THICK SECTION CLARIFIED POLYPROPYLENE RANDOM COPOLYMER



New Spectral Enhancer



Conclusions

- Broad Sustainable Permanent UV Absorbance with multiple synergistic qualities is now possible.
- Alone or in combination with other organic UV light stabilizers today we can extend performance with better economics. **The key is ratio of HALs or Conventional Organic UVA and the Spectral Enhancer!**
- Light Stabilization in more hostile **higher temperature environments is now possible.**
- Greater flexibility in designing new light stabilizer systems. Greater Initial Absorbance for the same level.
- New Spectral Enhancers appear to exist more broadly than expected based on their chemistries.

Acknowledgements

- Lycus Ltd. El Dorado, Arkansas a domestic manufacturer of hydroxy substituted benzophenones and cyanoacrylates for plastics and coatings. John Sinclair and Tasha Sinclair operating officers.
- Endex International, Ajax Ontario Canada the distributer for UVITA SME 3811 and their affiliated branches globally.