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Advancements in UV LED Technology and its Impact on UV Curing Applications

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Agenda

- Overview
- Experimental set up
- Clear Coat chemistries
  - % TPO dependence
  - Peak Irradiance vs. Total Dose
    - LED vs. Broadband
    - LED vs. ‘Long-wavelength’ Broadband
  - TPO decomposition
  - TPO with co-PhIs and synergists
- Results and discussions
- Summary/Conclusion

Overview/Background

- UV Curing has been used for many diverse applications
- Until recently, Hg based UV lamps have primarily been utilized
- Key Advantages of Hg based lamps:
  - Mature technology
  - Fast process speed (higher UV output)
  - Low cost of ownership
- Drawbacks:
  - High electrical power consumption
  - Ozone formation
  - Presence of “Hg”

Status of UV LED Technology

- White light LED manufacturing technology has been making steady progress
- Associated manufacturing technology for UV LEDs have benefited
- Some key benefits of LED technology are:
  - Instant on-off
  - Hg free
  - Longer life
  - Possible lower cost of ownership
- UV LEDs has shown significant potential for UV curing applications
- Though some progress has been made, substantial gaps still remain

Basis of Current Research - I

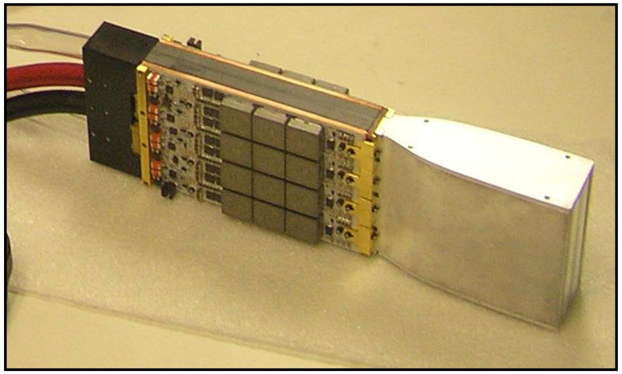
- UVLED systems with *higher output* and *flexible working distance* are beginning to emerge in the market
- Until now, most existing formulations are optimized for broad band illumination
- Since broad band LED sources are not imminent, special formulations, optimized for LED output needs to be developed

Basis of Current Research - II

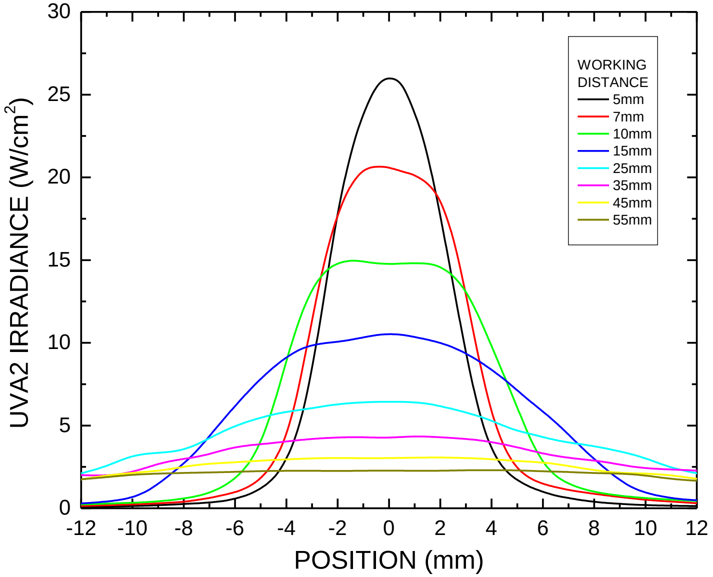
- Additionally, exact interactions between LED wavelength, intensity, total dose, formulation’s photo-absorption property, curing speed etc. need to be carefully considered for optimum performance
- In this paper, we would present the curing effect as a function of:
  - (i) LED intensity
  - (ii) process speed
  - (iii) total dose
  - (iv) PI concentration etc.

Experimental Set Up - LED Lamp

- Additionally, exact interactions between LED wavelength, Custom LED lamp
  - 395 nm
  - High efficiency thermal management
  - High density LED packaging
  - High peak irradiance (> 25 W/cm^2)
  - Flexible optics
  - Longer working distance



LED LAMP OUTPUT IRRADIANCE



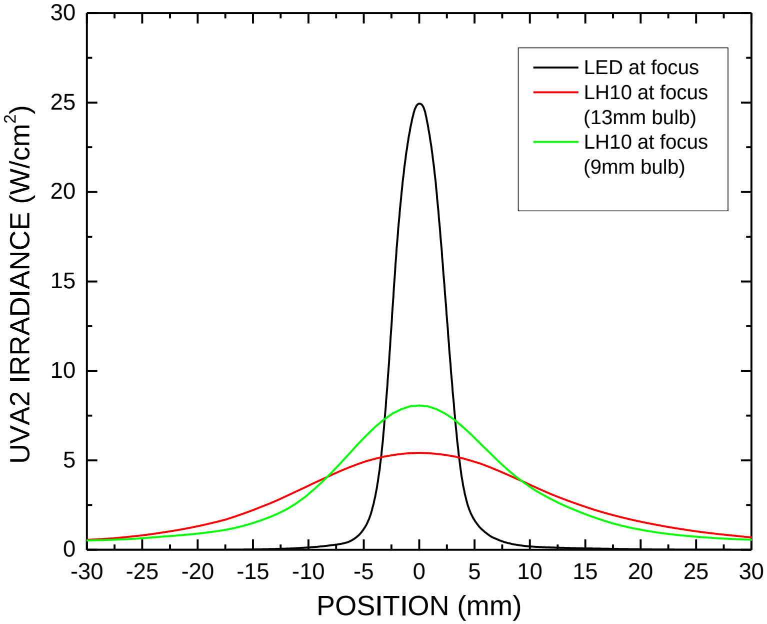
Experimental Set Up - Hg based Lamp

- Broadband source (LightHammer® 6)
  - Microwave driven electrode-less
  - Standard D bulb
  - Cold reflector (dichroic)
  - 4 - 6 W/cm^2

- Standard conveyor (NO N_2 inerting)

Experimental Set Up - Lamps

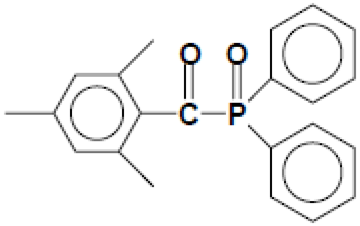
- Comparison of custom LED lamp to high power microwave lamp (LightHammer® 6)
  - LED: higher peak irradiance over smaller area
  - Microwave lamp: broader spatial distribution



Experimental Set Up – Clear Coat Chemistry

9029	HDDA	DESIGNATION
100	0	100/0
80	20	80/20
70	30	70/30
60	40	60/40

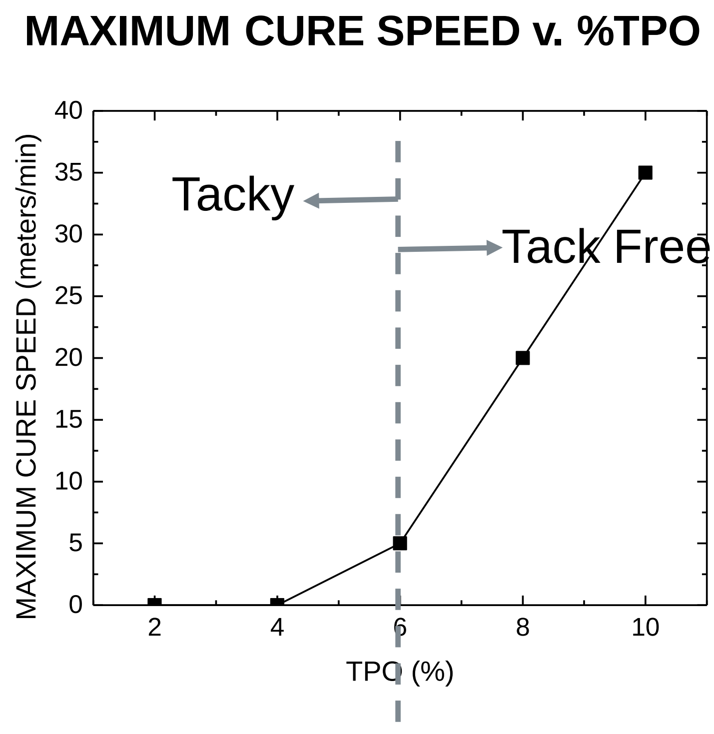
- Urethane acrylates (BASF Laromer®)
  - LR 9029
  - LR 9029 + 20% HDDA
  - LR 8987 (LR 9029 + 30% HDDA)
  - LR 9029 + 40% HDDA
  - Variable viscosity with HDDA addition
  - All solvents evaporated before UV exposure
- Photoinitiator
  - BASF Lucerin® TPO (1-10%)
  - Co-initiator: ITX
  - Synergist: EDB



- 12 micron films on white cards

Maximum cure speed – LED at various % TPO

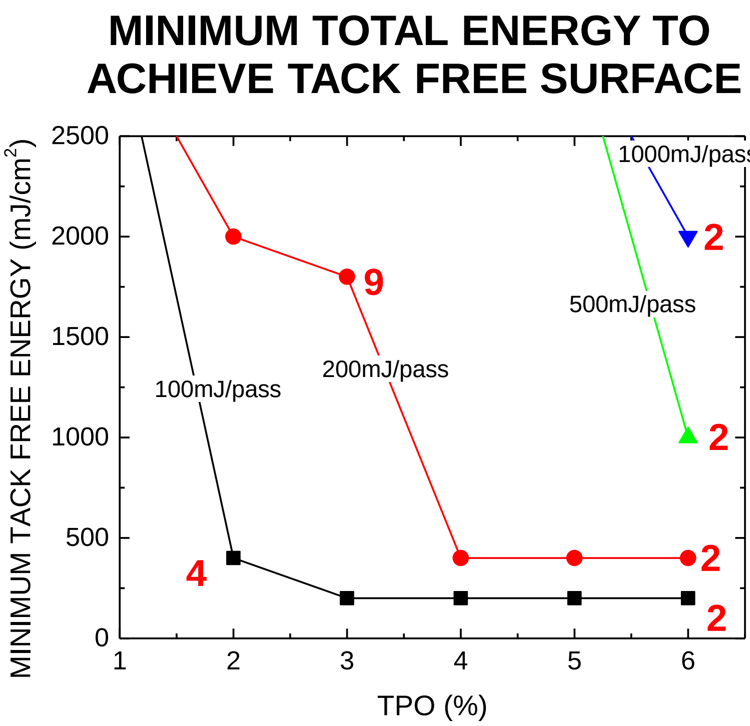
- Maximum cure speed determined by presence of surface tack.
  - LED lamp at 25 W/cm^2
  - 60/40 mixture with %TPO varied
  - Rapid increase in cure speed above 6% TPO
  - NO tack free surface below 6 %TPO



<u>Choice of 'cure' criterion:</u>
Double bond conversion (via FTIR) showed NO correlation with the physical surface tack and therefore only surface tack was considered as a measure of final cure.

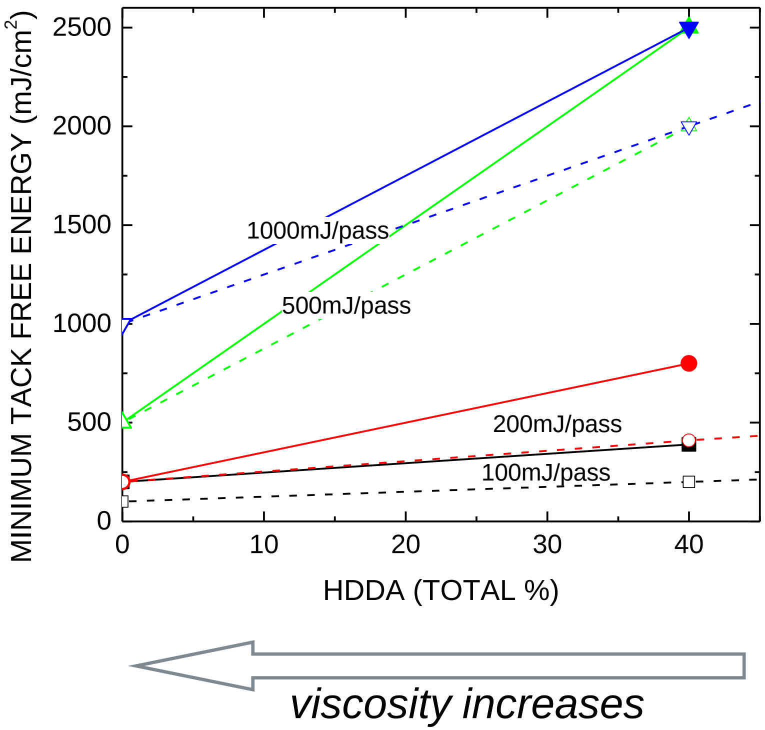
Peak Irradiance vs Dose: @ lower TPO levels

- Previously, negligible curing below 6% TPO
- Focusing on the ‘cure initiation’ seen in previous data (60/40 & low %TPO)
- High peak intensity constant (25 W/cm^2)
- Pass sample under lamp at constant speeds
  - Multiple passes
  - Accumulate total energy (dose)
- Less total energy required with multiple passes
  - Higher speeds achievable
  - Lower % TPO possible



Dose vs Formulation Viscosity at 5% TPO (LED vs. Broadband)

- LED Data (similar to previous page)
  - Lower total energy with increasing formulation viscosity
- Broadband source data
  - Similar trend to LED, but higher energies with lower viscosity
- Difference presumed to be due to higher peak intensity



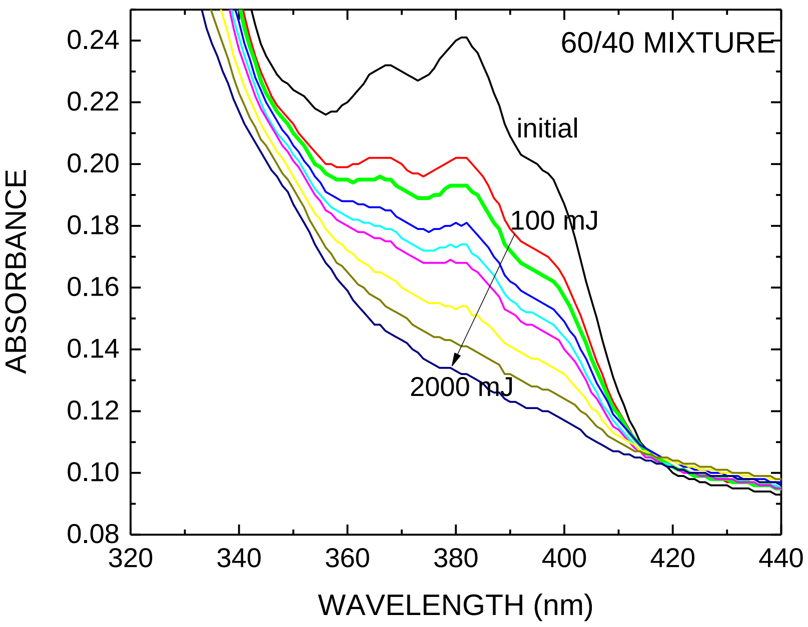
Peak Intensity (LED) = 25 W/cm^2

Peak Intensity (Microwave) = 6 W/cm^2

Consumption of TPO: 60/40/4% TPO (LED irradiation)

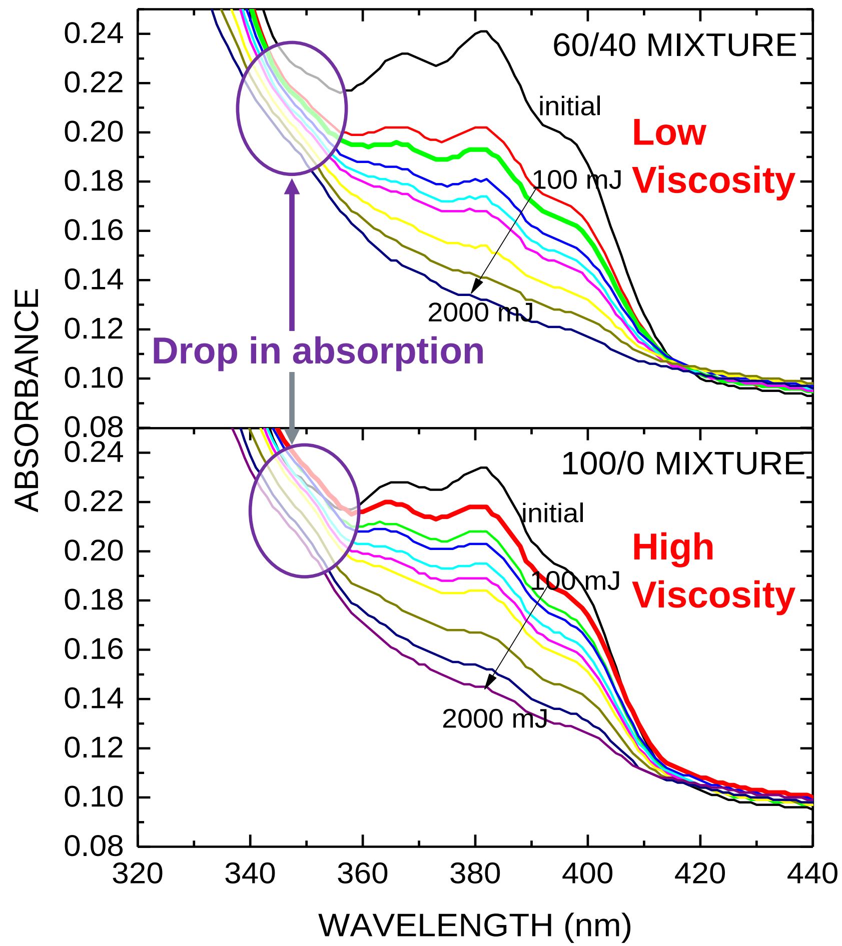
- TPO absorption from UV-VIS spectroscopy between each successive 100 mJ/cm^2 pass
  - Rapid drop after first pass
  - Successive passes more consistent
  - Bold line show tack free surface (from previous graph)

TPO ABSORPTION AFTER EACH PASS



Consumption of TPO: Various viscosity mixtures (LED irradiation)

- 4% TPO in 60/40 and 100/0 mixtures.
- UV-VIS spectroscopy between each successive 100 mJ/cm^2 pass
- Comparison of formulation composition/viscosity
  - Definite change in TPO consumption at initial exposure.
  - Much less TPO was initially consumed with 100% resin formulation
- Bold line show tack free surface (from previous graph)



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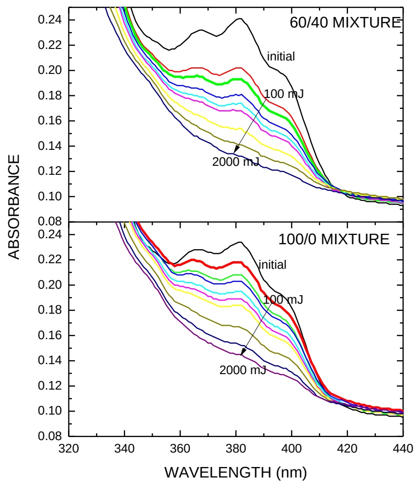
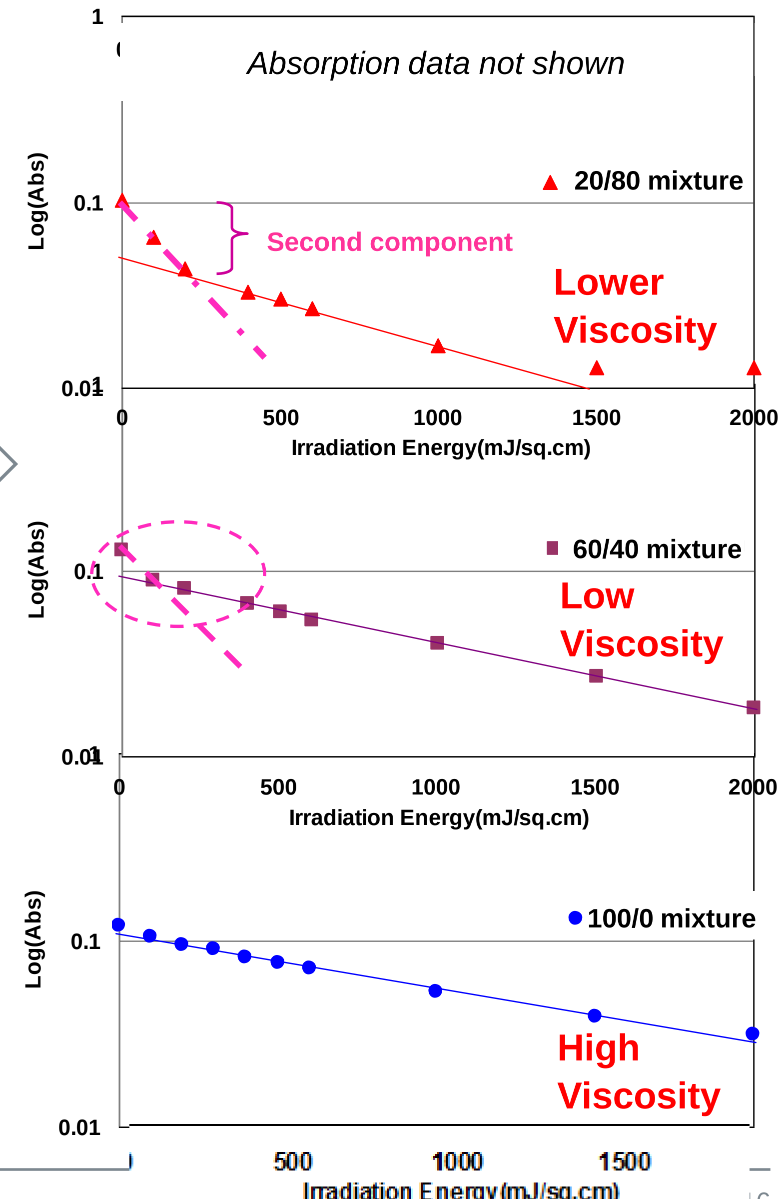
Consumption of TPO: 'Arrhenius' plots

(Previous absorption data)



PLOT: log (total absorption) vs total irradiation energy

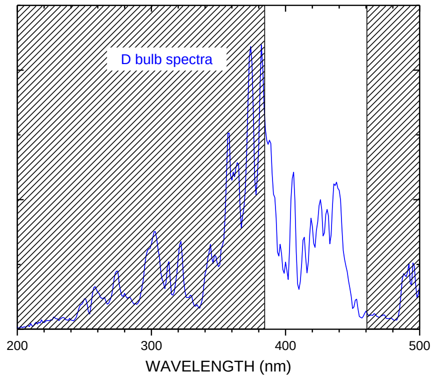


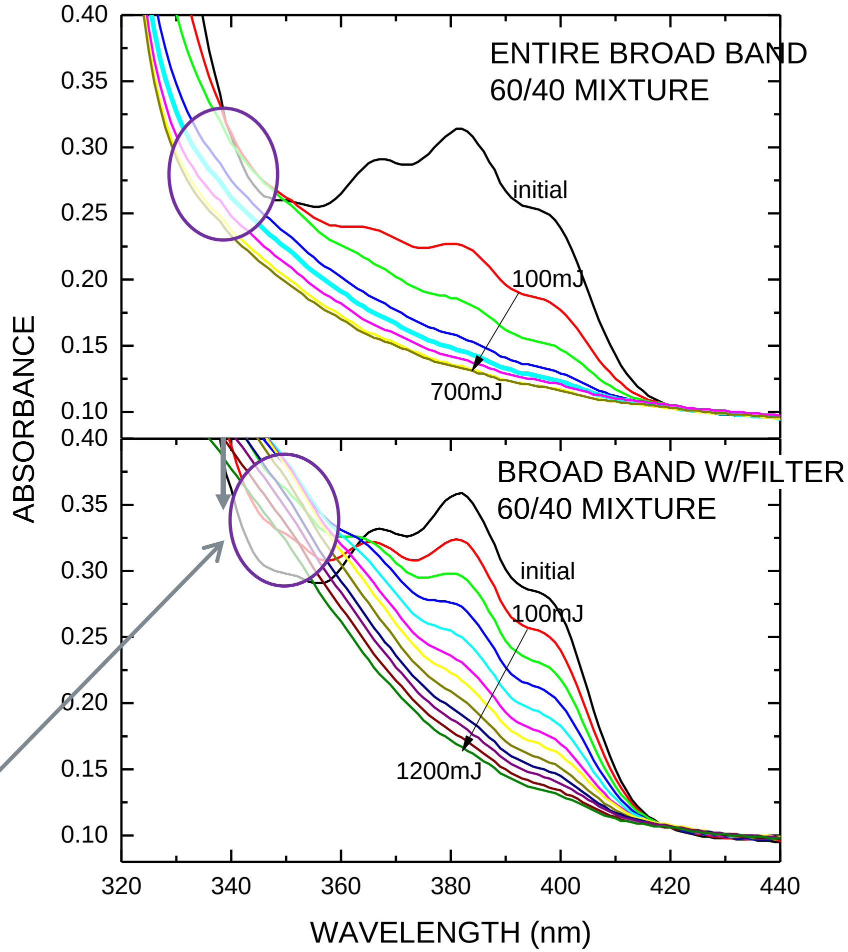
- Second component evolution prevalent in lower viscosity mixtures
- Main component (100/0) very linear

Two different kinetics

Consumption of TPO: Various viscosity mixtures (BB irradiation)

- Similar non-linear consumption of TPO in 60/40/4% TPO mixture with entire BB spectrum
- With only longer wavelengths (385-460nm)
- Second component fraction decreased (consistent TPO reduction)

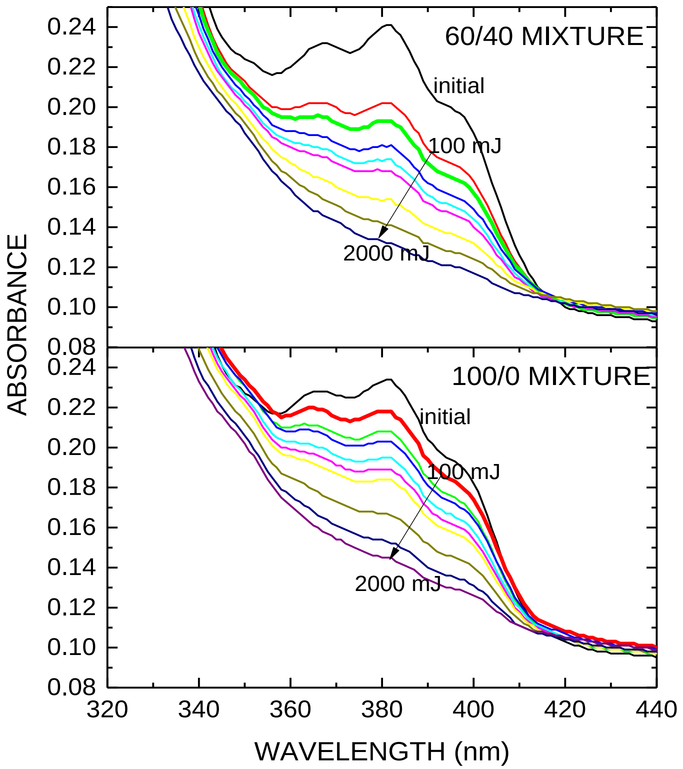


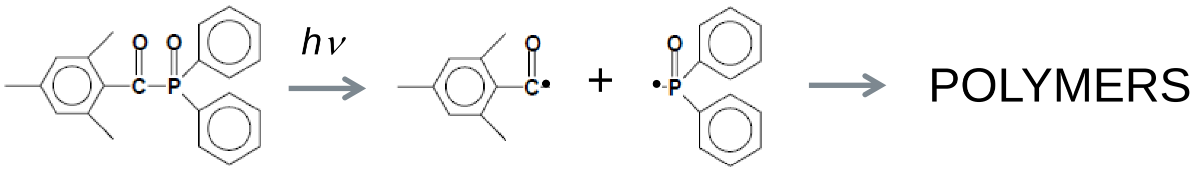


Absorption at shorter wavelengths increased

Consumption of TPO: Summary

- Two different mechanisms:
- Mechanism 1
- TPO consumption rate inconsistent
  - At lower viscosities, increased diffusion and monomer (LED and BB irradiation)
  - Alleviated by increased viscosity OR additional long wavelengths
- Competing reactions decrease TPO photo-polymerization efficiency



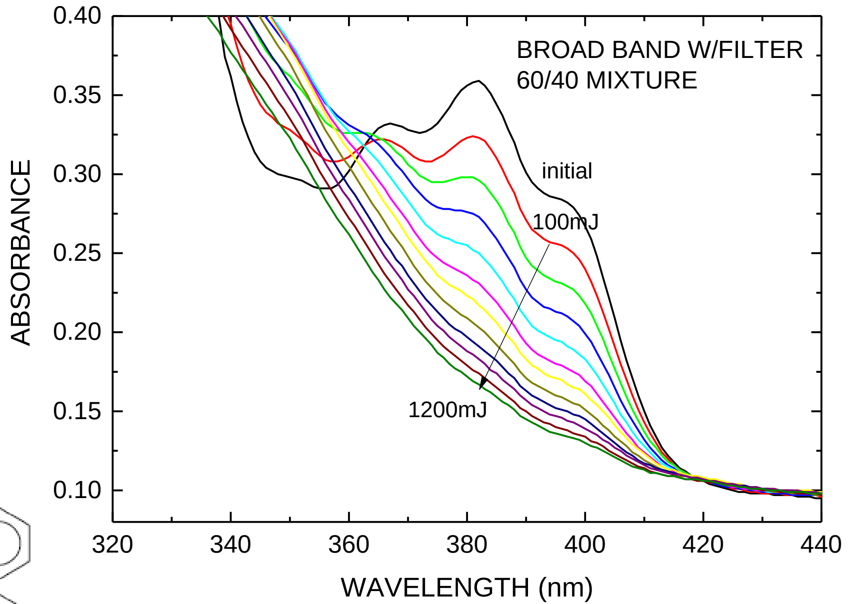


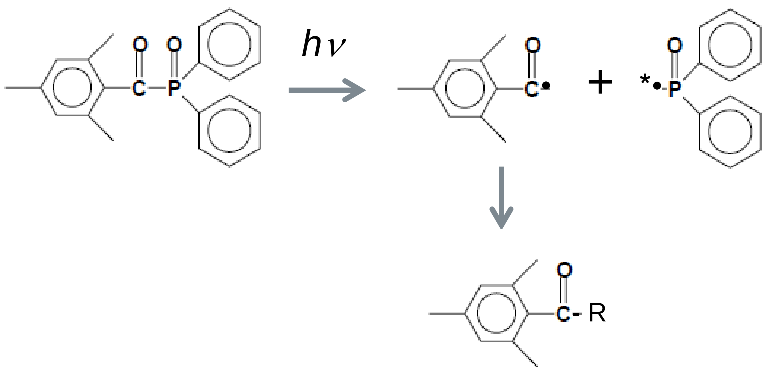
independent of viscosity

dependent of viscosity

Consumption of TPO: Summary

- (Unexpected) Mechanism 2
- Increased absorption between 320-365nm) implies reaction intermediate being formed
  - Presumed to be carbonyl containing group, given increased absorption band



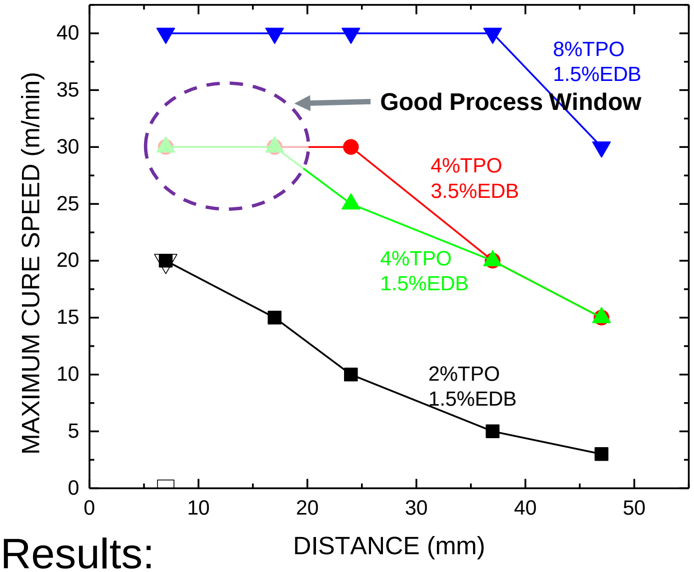


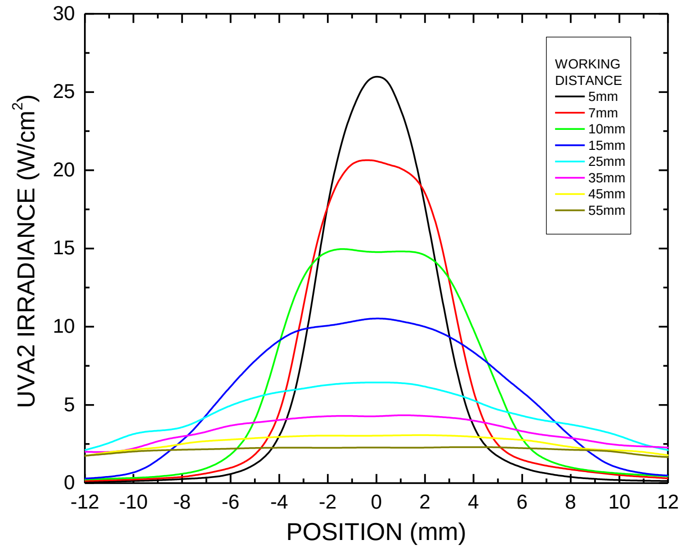
short λ absorption

GC-MS on similar formulation showed significant amounts of unreacted TPO and TPO byproducts such as tri-methyl benzoic acid

Additives (LED irradiation)

- 60/40/TPO mixtures with
  - 1.5% ITX co-PhI
  - EDB amine-based synergist





Results:

- Much higher maximum cure speeds possible (with higher TPO)
- Peak power more important at lower TPO concentrations
- Addition of synergist is helpful
- (4% TPO + 1.5% EDB) appears to be the best compromise

Wrap up

- Several clear coat formulations and their curing kinetics were studied as a function of various TPO concentration when exposed to a monochromatic LED source (395 nm) and a broad band UV source
- No correlations were observed between the surface tackiness and associated double bond conversion
- Higher concentrations of TPO generally resulted in better cure when judged by surface tackiness
- In all cases, a minimum of two passes were needed to achieve good cure
- For higher HDDA concentration high intensity (25 W/cm2) LED lamps performed better than the broad band Hg lamps with lower intensity (4-6 W/cm2)
- This was attributed to the higher intensity

Wrap up

- Inconsistent TPO were observed at lower viscosity, possibly due to increased diffusion and monomers
- TPO absorption studies indicated evaluation of two independent reactions
- Increased absorption at shorter wavelength indicated formations of reaction intermediate (carbonyl containing group)
- More thorough investigation needs to be conducted for further understanding

Thank you