# OVERCOMING CHALLENGES OF LED IN GRAPHIC ARTS APPLICATIONS

## 2018 Radtech

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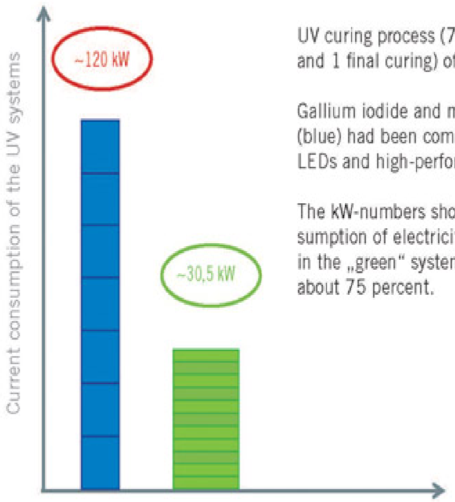
# INDUSTRY EVOLUTION FROM UV LAMP TO LED

- **Market value of UV LEDs for the curing application continuing to grow[1]**
  - **Estimated 2016~2021 growth US$81M to US$195M**
  - **Market penetration forecasted to reach 50~60% by 2020**
- **Technical/Economic/Environmental advantages to LED**

- **~75% Lower power consumption**




UV curing process (7 steps incl. 2 grinding stations and 1 final curing) of a parquet flooring:

Gallium iodide and mercury medium pressure lamps (blue) had been compared with a combination of UV LEDs and high-performance UVC lamps (green).

The kW-numbers show the difference in the consumption of electricity which is significantly lower in the „green" system. There is an energy saving of about 75 percent.

- **No warm up, fast start-up**
- **Appropriate for temperature sensitive substrates**
- **Environmentally friendlier**
  - **No ozone production**
  - **Longer lifetime**
  - **No Hg concerns (Hg Arc Lamps)**

1. https://www.packworld.com/article/material-type/polymers/forecast-flexible-food-packaging-2021



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# LED INDUSTRY CHALLENGE

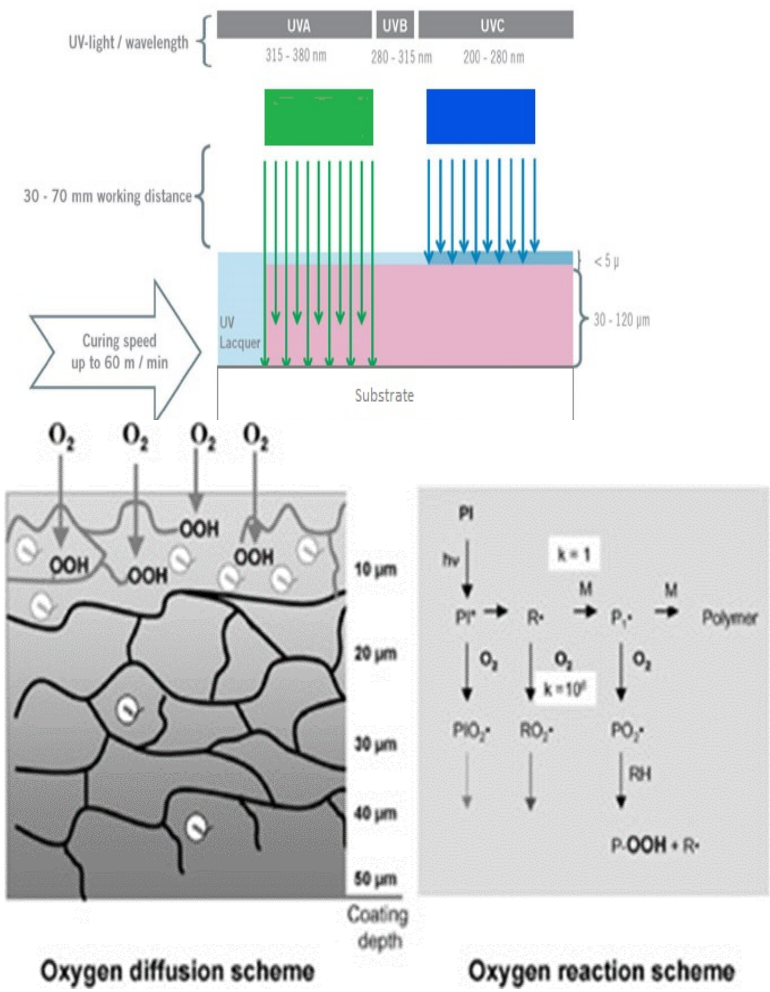
→ **Narrow wavelength emission reduced to 365nm,395nm,405nm**

→ **Reduction in surface curing**

- **Due to oxygen inhibition**
- **200-280nm best for surface cure**

→ **~5um at surface remains uncured**

- **Peroxy radicals form when oxygen reacts with free radicals**
- **Oxygen terminates PI and acrylate radicals**
- **Exacerbated in thin films, $O_2$ continually diffuses**




UV Coatings: Basics, Recent Developments and New Applications, Chapter 7. Reinholds Schwalm, Elsevier 2007.



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# STRATEGIES FOR COUNTERING OXYGEN INHIBITION

→ **Mechanical solutions**

- Nitrogen inert
- Ensure maximum distance of LED is < 2cm  to substrate

→ **Optimize photo-initiator selection and concentration**

- Match PI absorbance with LED transmission
- Excess PI can also inhibit cure, ladder study to confirm loadings

→ **Practical guide for chemistry based solutions**

- Increase formulation reactivity
- Optimize double bond concentration
- Reduce glass transition effect
- Hydrogen donors for peroxy radical conversion
  - Thiols > Amines > Ethers
  - Dr. Jon Scholte, "Thiolene Chemistry, past and progress" presentation Tue 5/8/18

# ANALYTICAL TECHNIQUES: MEASURING REACTIVITY

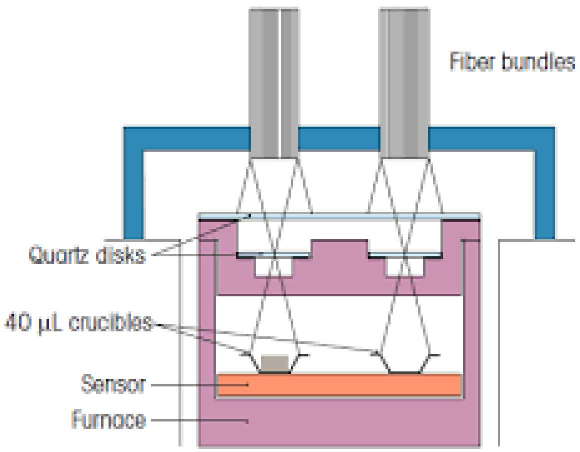
→ **Heat is generated during polymerization**

→ **(ΔH) Enthalpy, can be quantified using Photo-Differential Scanning Calorimeter (DSC)**

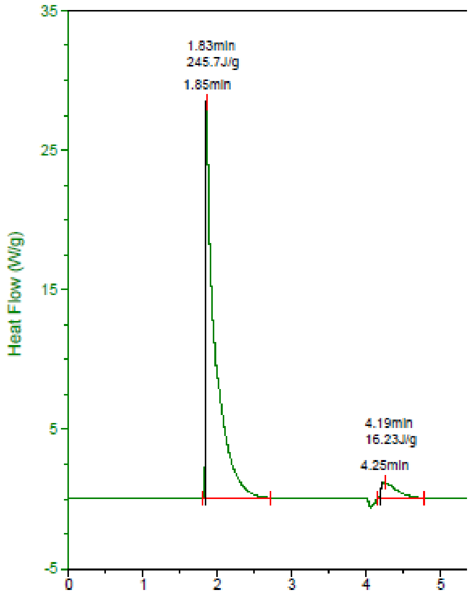
→ **Sensors below crucibles detect and measure heat changes**

- **Empty crucible serves as control**
- **LED/UV focused over samples**
- **Exposure typically pulsed ~5-10 sec**

→ **Sum of integrated peak(s) give J/g**




Cross-section of the optical system and the DSC furnace






https://polymerinnovationblog.com/uv-curing-thermosets-part-14-using-uv-dsc-monitor-curing-1/

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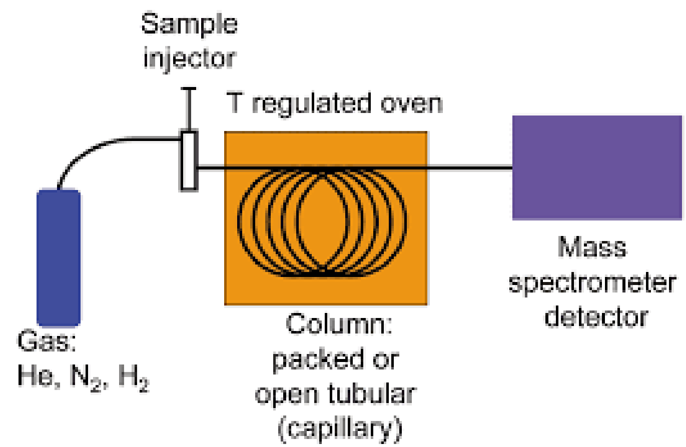
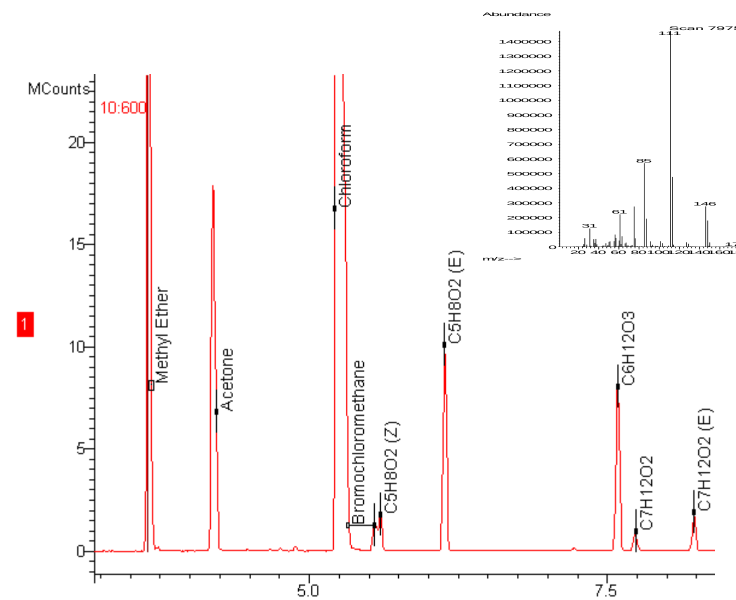
# ANALYTICAL TECHNIQUES: RESIDUAL MONOMER

- **Residual, unreacted monomer left post cure indicates degree of conversion**
- **Residual monomer quantification by GC-Mass Spectrometry**
  - **Cured samples immersed in solvent**
  - **Extract injected, monomers elucidated and quantified using GC/MS**
- **Limitations on MW for Gas Chromatography (~550 m/z)**
  - **Analytes must be volatile**



# REACTIVITY & CONVERSION STUDY

- Evaluated low & high molecular weight polyester & polyurethane acrylates
  - 2f LMW PEA
  - 6f HMW PEA
  - 6f LMW PUA
  - 2f HMW PUA
  - 16f PEA Hyper Branched PEA
- Increasing molecular weight and functionality monomers
- Effects of ethoxylation in light blue

| Monomer | Dendrimer PEA Wt% | High MW PEA Wt% | Low MW PEA Wt% | Low MW UA Wt% | Low MW UA Wt% |
|---|---|---|---|---|---|
| PhEA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| HDDA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| TCDMDA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| TMPTA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| PETA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| DI-PETA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| (3EO)TMPTA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| (9EO) TMPTA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| PI (50/50 TPO/BAPO) | 5 | 5 | 5 | 5 | 5 |

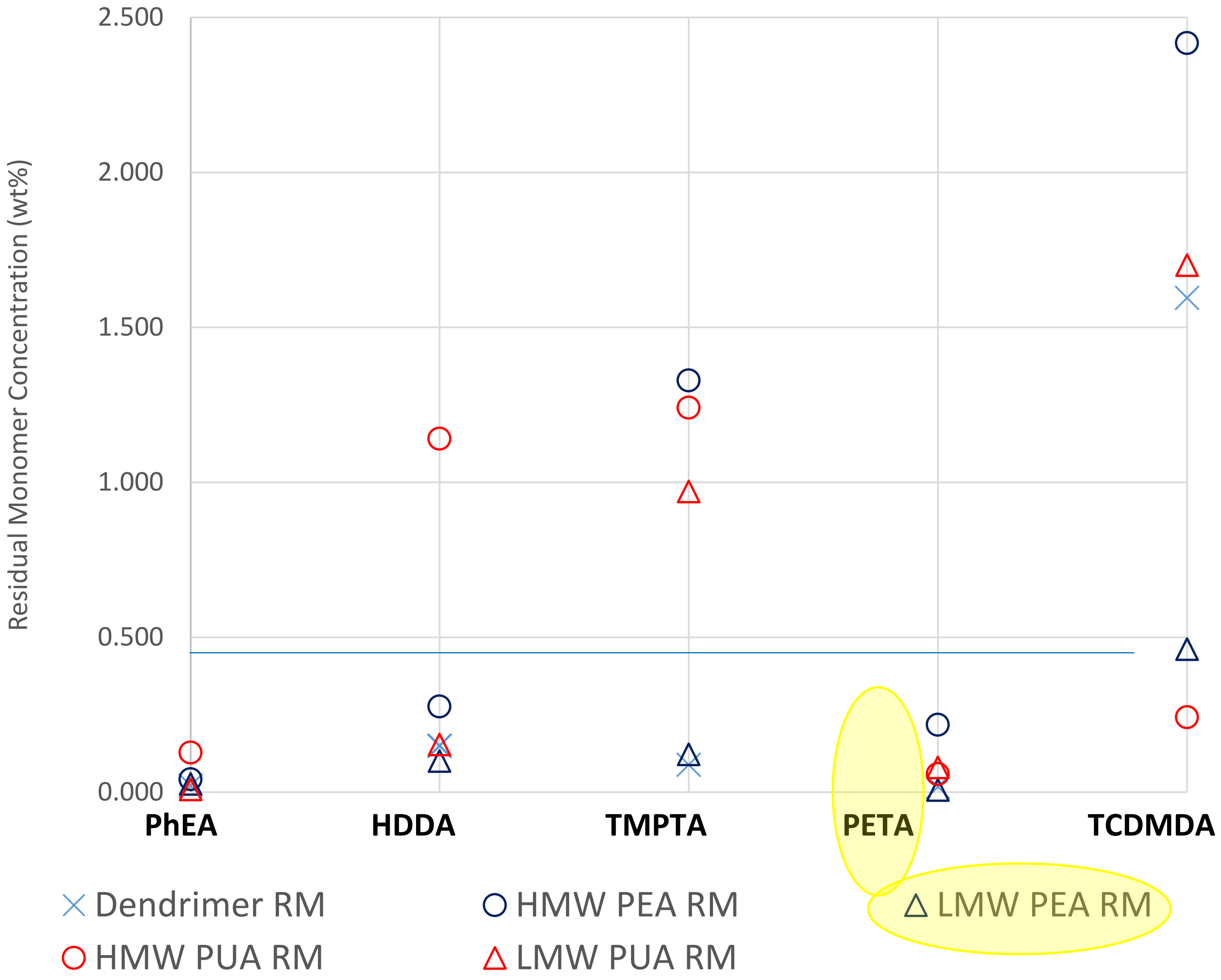
# INCREASE REACTIVITY THROUGH FUNCTIONALITY

- ($C_{db}$), Total double bond concentration is important [2]
  - PETA > Di-PETA
- ($C_{db}$) mol/L = $f_m(d_m/MW_m)$
  - f = # of acrylate functionality
  - $d_m$= density(g/mL)
  - $MW_m$ = molecular weight (g/mol)
- Residual monomer results confirm PETA had highest conversion
  - Lowest TMPTA and TCDMDA
  - Additional properties at work!

| f | 1 | 2 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Monomer | PhEA | TCDMDA | HDDA | TMPTA | PETA | DI-PETA |
| | [$C_{db}$] mol/L | [$C_{db}$] mol/L | [$C_{db}$] mol/L | [$C_{db}$] mol/L | [$C_{db}$] mol/L | [$C_{db}$] mol/L |
| NEAT Monomer | 5.8 | 7.2 | 8.9 | 11 | 13 | 11 |
| Dendimer PEA | 6.0 | 7.2 | 8.5 | 9.9 | 12 | 10 |
| Low MW PEA | 5.4 | 6.5 | 7.9 | 9.3 | 12 | 9.3 |
| High MW PEA | 5.2 | 6.3 | 7.7 | 9.1 | 11 | 9.1 |
| Low MW UA | 6.2 | 7.3 | 8.7 | 10 | 12 | 10 |
| High MW UA | 5.4 | 6.5 | 7.9 | 9.2 | 11 | 9.3 |

2. *Polish Journal of Chemical Technology, 16, **3**, 51 —Po l5. 5J,. 1C0h.2em47.8 T/pejccht-.,2 0V1o4l.- 01065, 0No. 3, 2014 51*

# RESIDUAL MONOMER: CLOSER LOOK

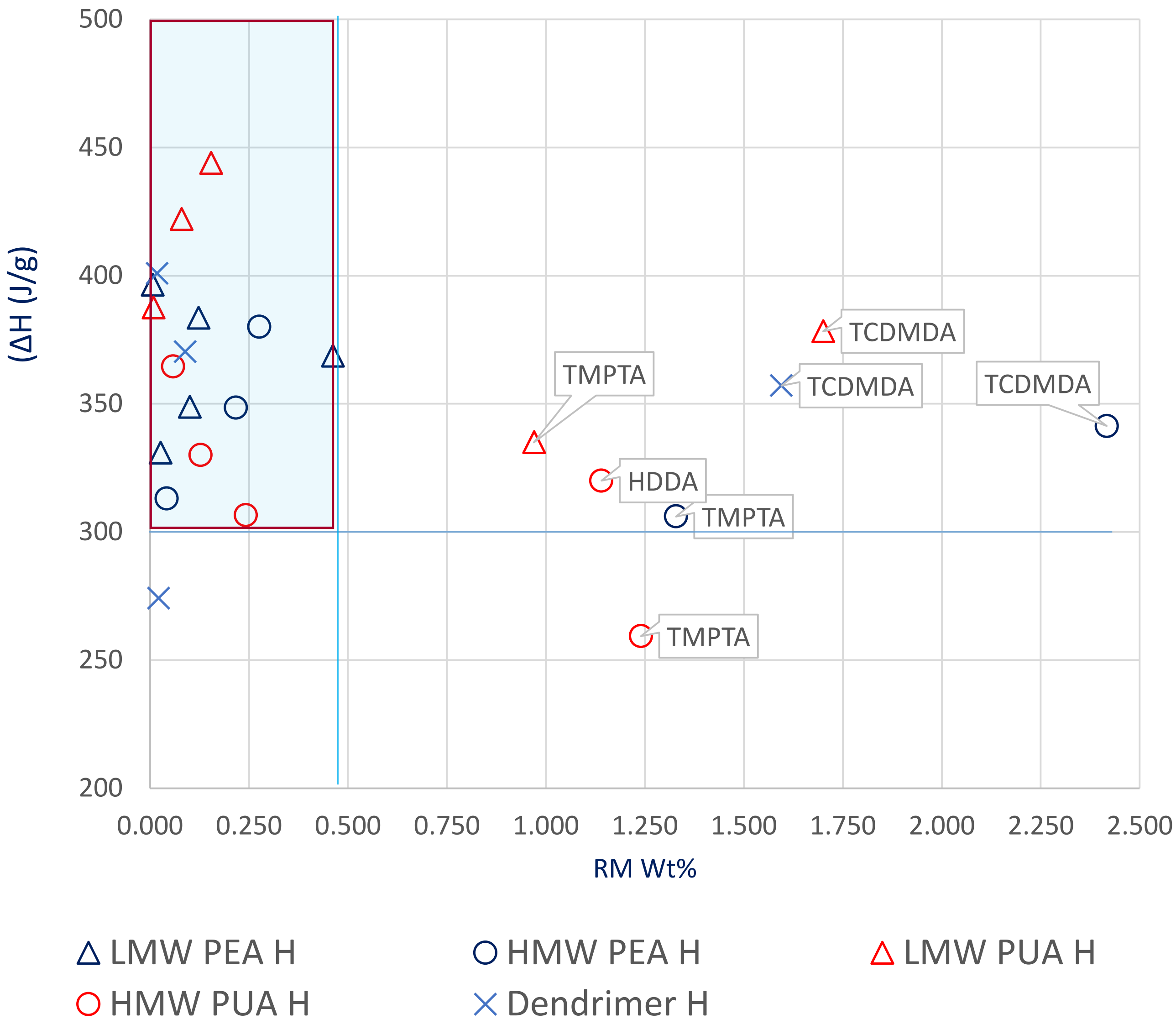



**RM sample preparation**

- #6 Wire rod draw down on Al
- Cure speed 50 fpm X 2
- 395nm LED
- LED Power 12W/cm$^2$
- 0.2g sample to 5mL acetone 24hr extraction
- 10 ppm Quantification Limit
- Varian Ion Trap GC/MS

*Di-PETA not included in residual monomer analysis

# RESIDUAL MONOMER VERSUS HEAT OF REACTION (J/g)




→ **Liquid samples for photo-DSC analysis**

- **10-15 mg sample**
- **35°C isothermal**
- **385nm pulse 10s, 3-5X**
- **ΔH area under curve(s)**
- **LED-DSC Power 9W/cm$^2$**

# OBSERVATIONS ON INCREASING REACTIVITY

→ **Majority of residual monomer results <0.3% (Wt.)**

- Analysis did not include acrylated or inert impurities

→ **Majority of heat of reaction for formulations with low residual monomer >300 J/g**

- LMW PEA diluted in PETA lowest at 10 ppm

→ **High residual monomers outliers included formulations with TCDMDA, TMPTA**

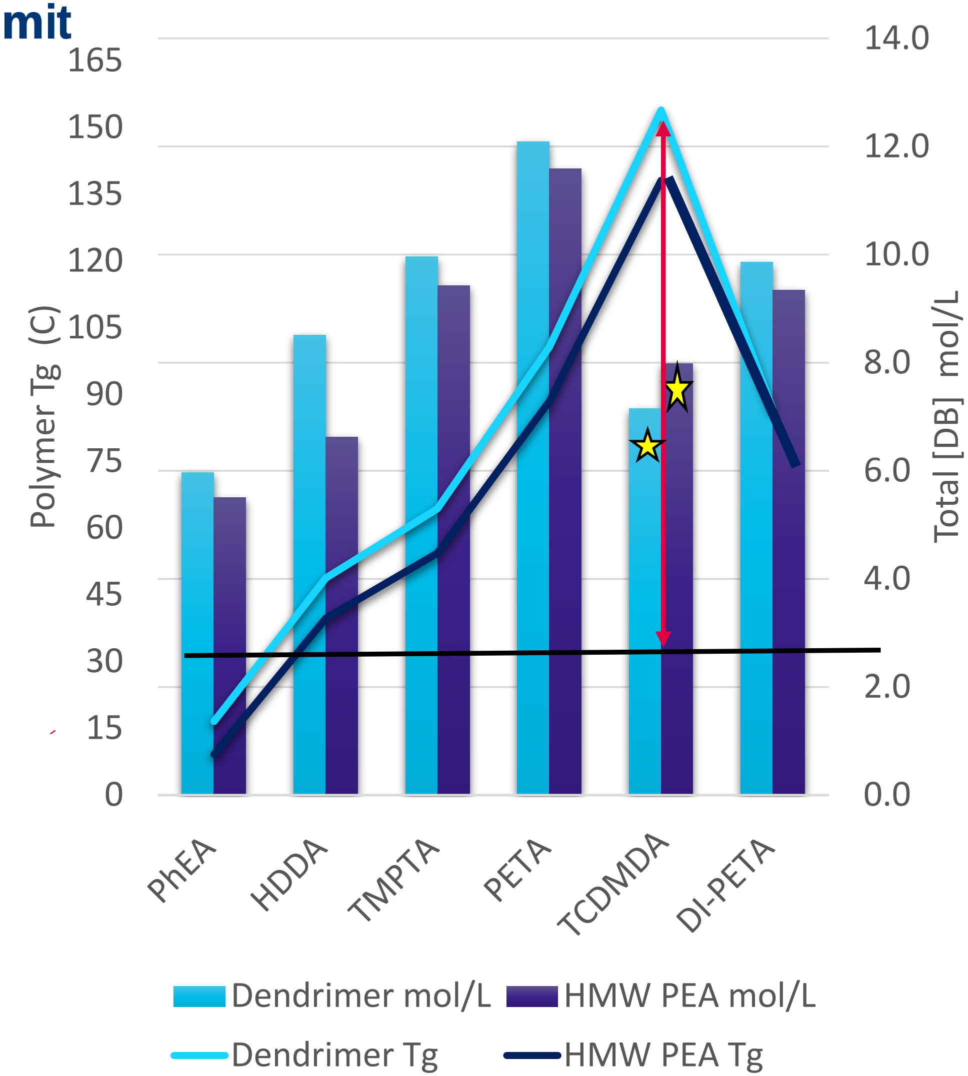
- Also had >300 J/g

→ ***Caveat emptor!***

- Great screening tool
- Need additional data to better differentiate products for LED

# INVESTIGATING EFFECT OF $T_G$: POLYESTER ACRYLATE

- **Products with high glass transitions limit molecule mobility**
  - **Faster path to vitrification**
- **TCDMDA combination of high Tg and low $C_{db}$**
  - **Good indicator of slower cure**
- **PETA $C_{db}$ compensates for Tg effect**
  - **Verified by residual monomer**
- **PhEA exhibited great conversion**
  - **Tg below (close-to)ambient cure temperature**
  - **>0.04 %(Wt) residual monomer**



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# INVESTIGATING EFFECT OF TG: POLYURETHANE ACRYLATE

→ **Exaggerated Tg effect for TCDMDA**

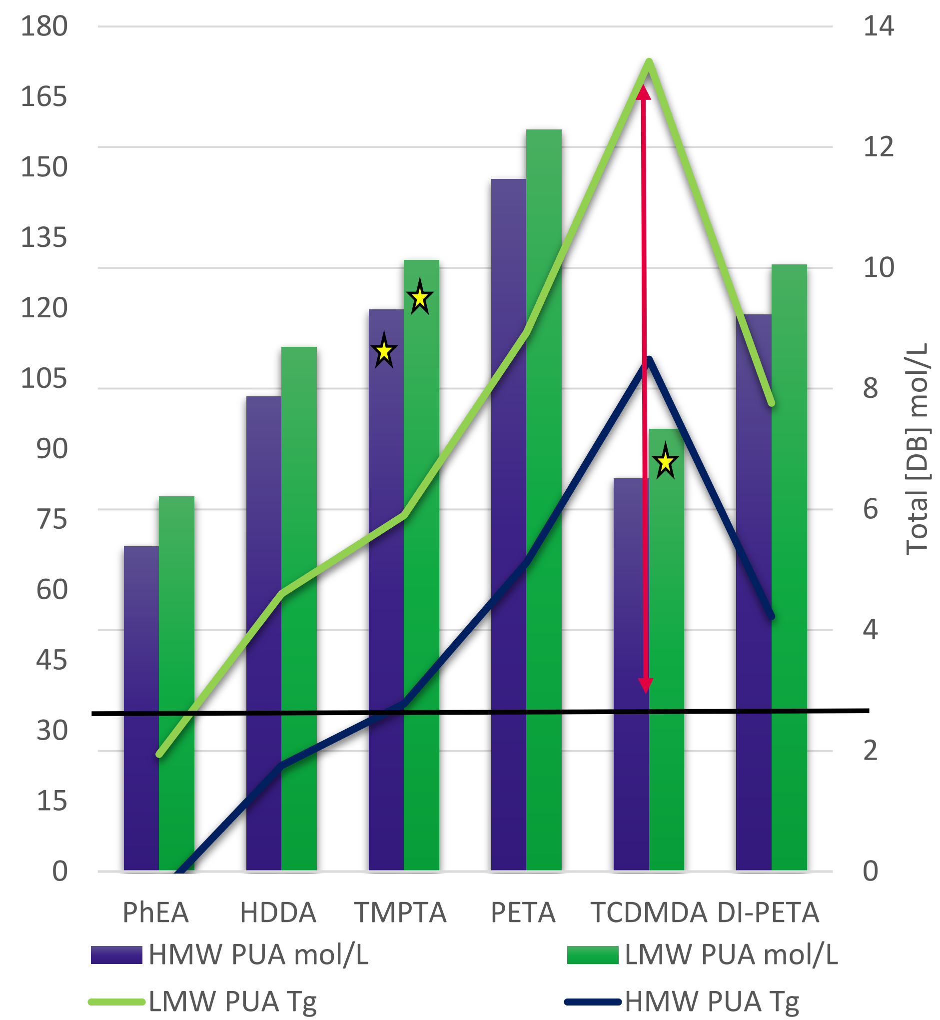
- **High Tg, (6f) LMW PUA combination dramatically slowed reaction (< 270 J/g)**

→ **TMPTA**

- **Expected poor performance from high Tg LMW PUA**
- **Potential issue with high initial viscosity HMW PUA**

→ **PhEA**

- **>0.13%(Wt) residual monomer**



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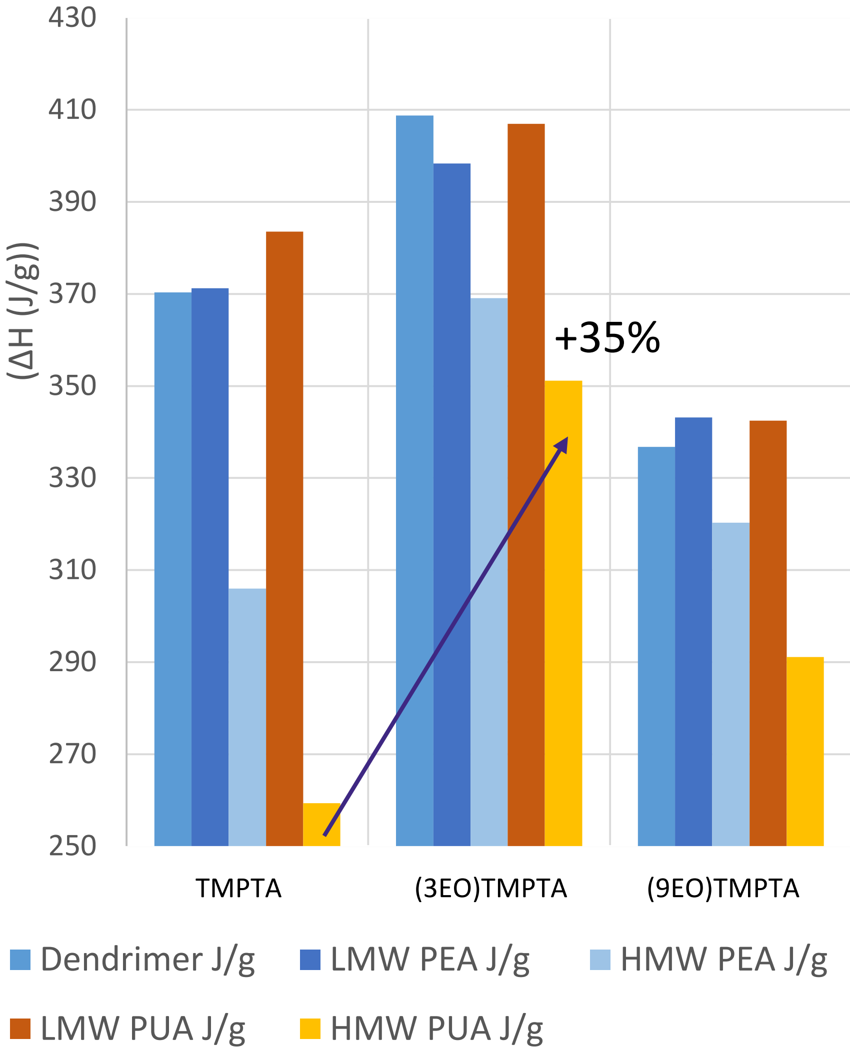
# HEAT OF REACTION (J/g) & ETHOXYLATION




| Monomer | Dendrimer PEA Wt% | High MW PEA Wt% | Low MW PEA Wt% | Low MW UA Wt% | Low MW UA Wt% |
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| (3EO)TMPTA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| (9EO) TMPTA | 75/20 | 75/20 | 75/20 | 75/20 | 75/20 |
| PI (50/50 TPO/BAPO) | 5 | 5 | 5 | 5 | 5 |

→ **(3EO)TMPTA increases reactivity**

- **Increases seen in all formulations**
- **~35% increase for the HMW PUA**

→ **(9EO)TMPTA no significant improvement**

- **More EO, not necessarily better, diminished double bond concentratio**


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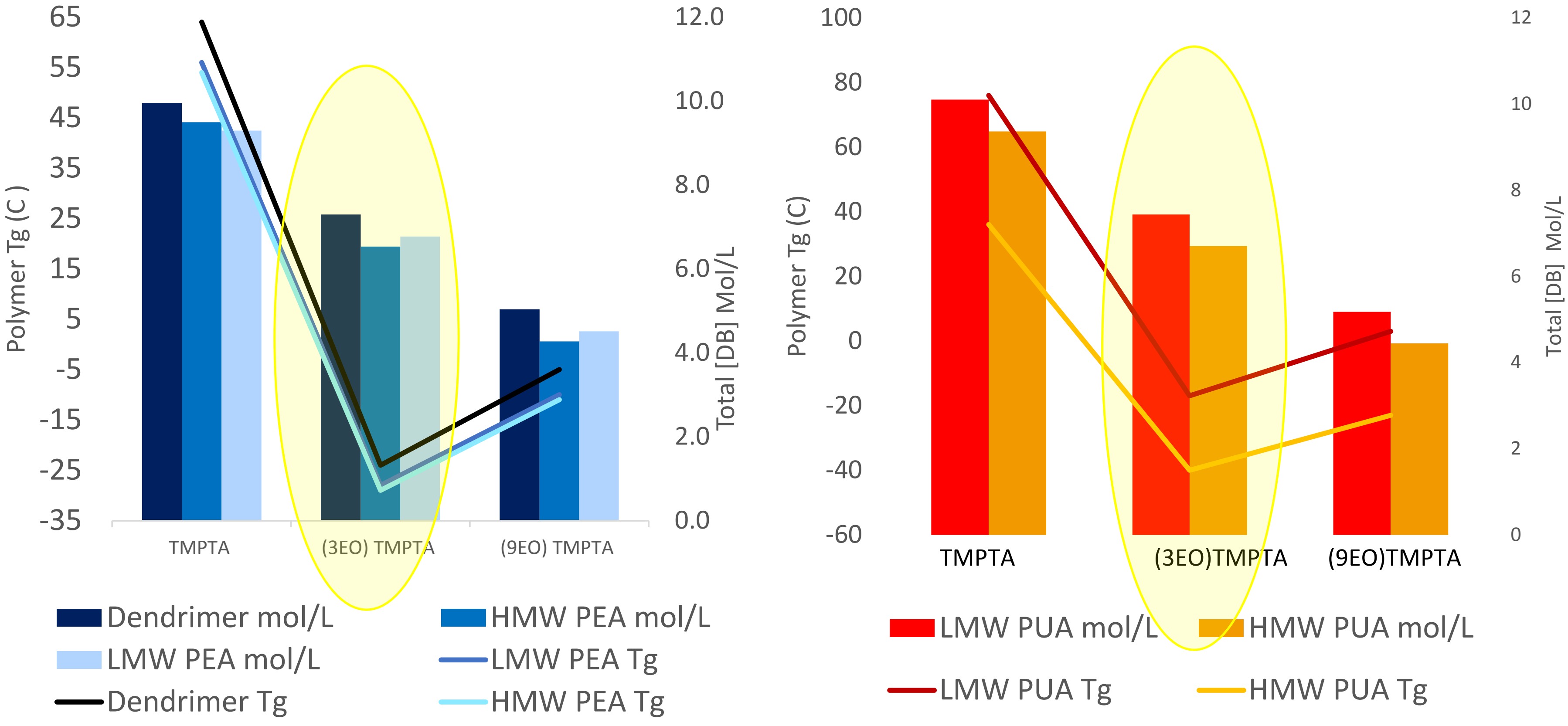
# EFFECT OF $T_G$ VERSUS $[C_{DB}]$ & ETHOXYLATION

## → Trend of highest reactivity remains consistent

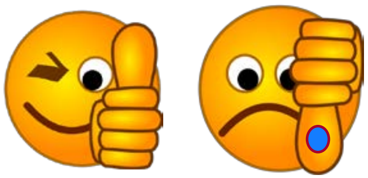
- **Optimize double bond concentration**
- **Reduced polymer glass transition**



# FLEXO INK FORMULATIONS: ACRYLATED AMINES/POLYTHIOLS

→ **Industry recognized "Thumb Twist" to evaluate surface cure quality**

- **Convenient**
- **Subjective**

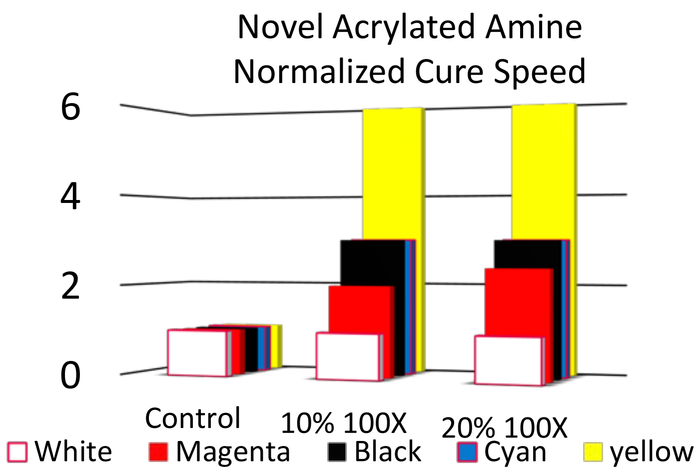


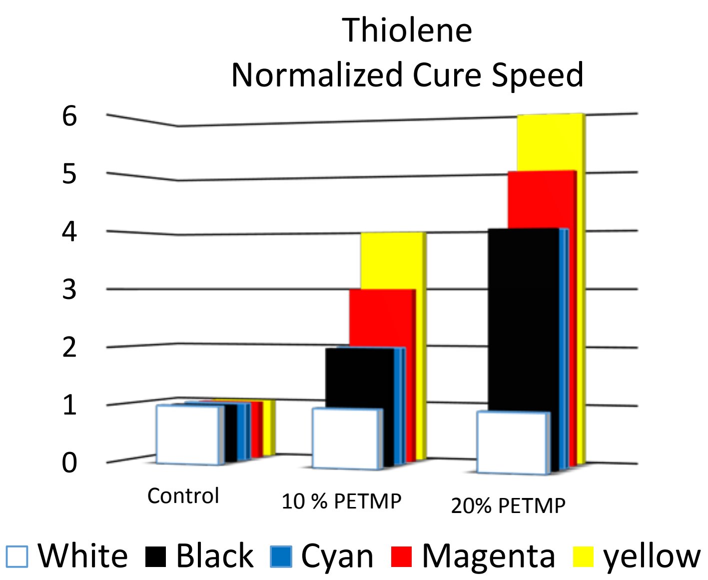
→ **Amine modified PEA increased cure speed (fpm)**

- **10-20% loadings cured 2-6x's the belt speed**

→ **PETMP cure speed at 20% PETMP loading**

- **2 -6 x's cure speed, color dependent**
- **Stability issues at high loadings**




Base Formualtion: Equal Parts of 4f Polyester, PO NPGDA & Di Penta Tetra Acrylate, ~15% pigment loadings
LED Peak Irradience 12W/cm2 ,395nm Note: White cured at max line speed (500 fpm)



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# CONCLUSIONS

→ **Photo-DSC convenient instrument for evaluating heat of reaction**

- Need additional data to better differentiate products for LED
- Much more power analytical tool when in parallel residual monomer

→ **Practical ways to boost formulation reactivity**

- Optimize double bond concentration
- Balance functionality with molecular weight of the system
- Balance high/low glass transition materials

→ **Optimize base formulation before adding hydrogen donors**

- Ethoxylation is least efficient ( Thiols > Amines > Ethers), had positive contribution

# THANK YOU FOR YOUR ATTENTION
# QUESTIONS?



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