Novel Strategy to Evaluate Platinum Photocatalysts for Hydrosilation-Curable Silicones

Melina Michailidis, John Leman PhD, Peter J. Bonitatibus Jr., PhD

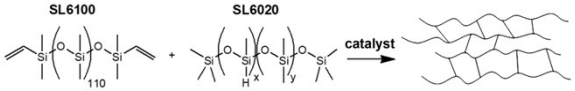
Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, Troy, NY 12180

1. Introduction

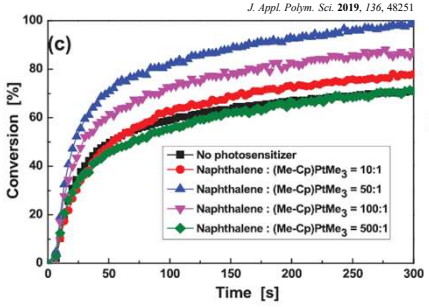
Release coatings are layers of cured silicone within pressure-sensitive adhesives (PSAs), like stamps and labels, that are applied to material backings to protect the adhesive component before use. Hydrosilation, a type of reaction leveraged in the manufacture of release coatings, involves addition of a silane (Si-H) across an olefin (ex. vinyl group) and typically requires high temperatures. Photopolymerization is a low-temperature crosslinking process that is being explored as an environmentally conscious alternative.

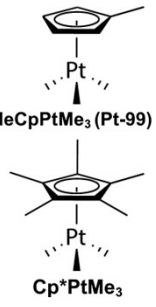
Eckberg, R.P. Photo-initiated addition cure silicone release coatings. Radtech: UV+EB 2020, Radtech Conference Proceeding, March 8-11, Disney Coronado Springs in Orlando, FL, USA.

Release coatings are commonly formed through Pt-catalyzed hydrosilation of hydrido- and vinyl-functionalized silicone fluids.



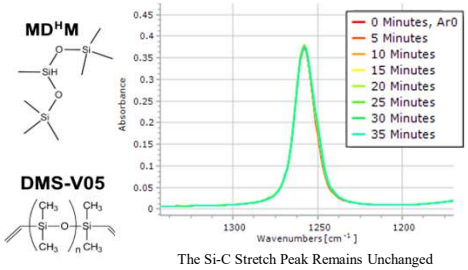
The authors of the plot below determined via RT-IR that, when incorporated into mixtures of the 3M catalyst (Pt-99) and silicone polymers PDMS-Vi and PMHS, some photosensitizers (ex. naphthalene) increased conversion and lowered the concentration of Pt required for photocuring. The Si-H stretching absorption band at 2165 cm^{-1} was chosen to monitor conversion, while the Si-O-Si vibration at 1060 cm^{-1} was used as an internal standard.



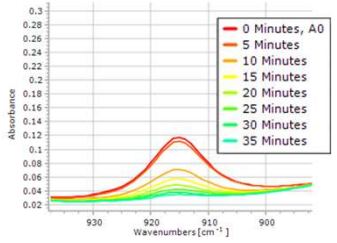


2. In-House Method

The photoactivated hydrosilation reaction was monitored via a novel ATR-FTIR strategy, enabling analysis of reaction kinetics in thin films. A "well" composed of six layers of electrical tape and one layer of double-sided tape with a hole punched through the stack was assembled and positioned to encircle the ATR crystal. A quartz microscope slide was placed on top to avoid evaporation of the sample contained by the well. Mixtures comprised of model silanes (MD^HM and DMS-V05), and Pt-catalysts ($MeCpPtMe_3$ and Cp^*PtMe_3; 500 ppm Pt) with and without naphthalene were irradiated at a fixed distance with 365 and 400 nm light using LED sources in darkness for 5 minutes. The disappearance of the Si-H bending absorption band at 915 cm^{-1} was followed, and referenced to the unchanging absorption band at 1260 cm^{-1} attributed to the Si-C stretching vibration. Plots were generated that feature percent conversion as a function of time.



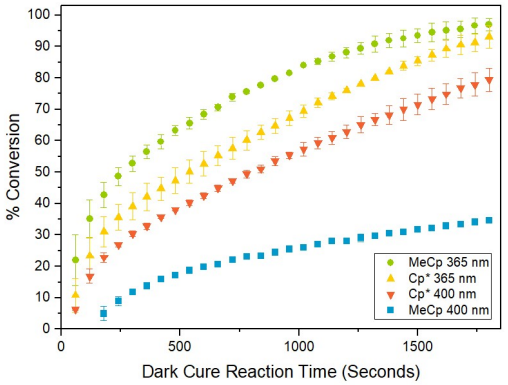
The Si-C Stretch Peak Remains Unchanged

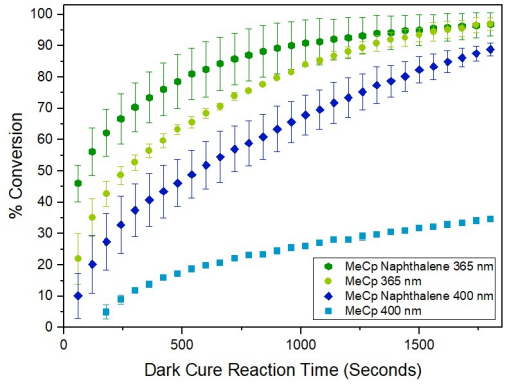


The Si-H Bend Peak Decreases as Hydride is Consumed

Catalyst	Experiment	$Rate_i$ ($\times 10^{-3}$ Ms^{-1})	k ($\times 10^{-3}$ s^{-1})	% Conversion
$MeCpPtMe_3$	365 nm, PS, 300s	3.01	1.98	96.8
$MeCpPtMe_3$	365 nm, PS, 150s	2.09	1.38	95.3
$MeCpPtMe_3$	365 nm, 300s	1.88	1.19	97.0
$MeCpPtMe_3$	400 nm, PS, 300s	1.14	0.791	88.9
$MeCpPtMe_3$	400 nm, 300s	0.417	0.108	34.7
Cp^*PtMe_3	365 nm, PS, 300s	1.39	1.00	96.0
Cp^*PtMe_3	365 nm, 300s	1.10	0.821	93.1
Cp^*PtMe_3	400 nm, 300s	0.864	0.627	79.4

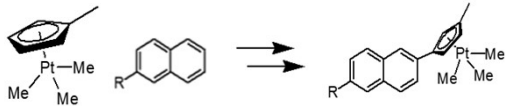
$$\text{Percent Conversion} = \left(\frac{\left(\frac{At}{Art}\right)-\left(\frac{Ao}{Aro}\right)}{\left(\frac{Ao}{Aro}\right)}\right)(100)$$

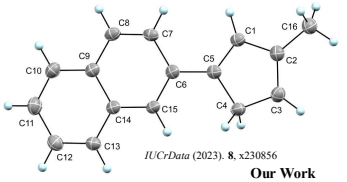




3. Future Work

Catalysts of the type $ArCpMePtMe_3$, where Ar = naphthyl, fluoronaphthyl, and methoxynaphthyl, are being investigated as they are hypothesized to accelerate photocatalytic curing due to the installment of ligands containing light-harvesting "antennas". Eco-inspired innovation of the curing process will produce novel Pt(IV) photocatalysts that can be evaluated against the current benchmark using this method.





IUCrData (2023). **8**, x230856

Our Work

Rensselaer