

NOVEL SILICONE MATERIALS PROVIDE A SECONDARY CURE FOR ENERGY-CURED SILICONE ACRYLATES

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Secondary Cure

Your X-RAY showed a broken rib, but we fixed it with Photoshop



I oppose **medical marijuana**
Because it's a gateway drug,
But I'd be happy to refill
your **OxyContin**.



It's **FDA APPROVED**,
which means it's
100% safe!



Secondary Cure

Doc: You'll soon be at peace

Man: I'm dying?

Doc: No your wife is



Why Use Energy Curing

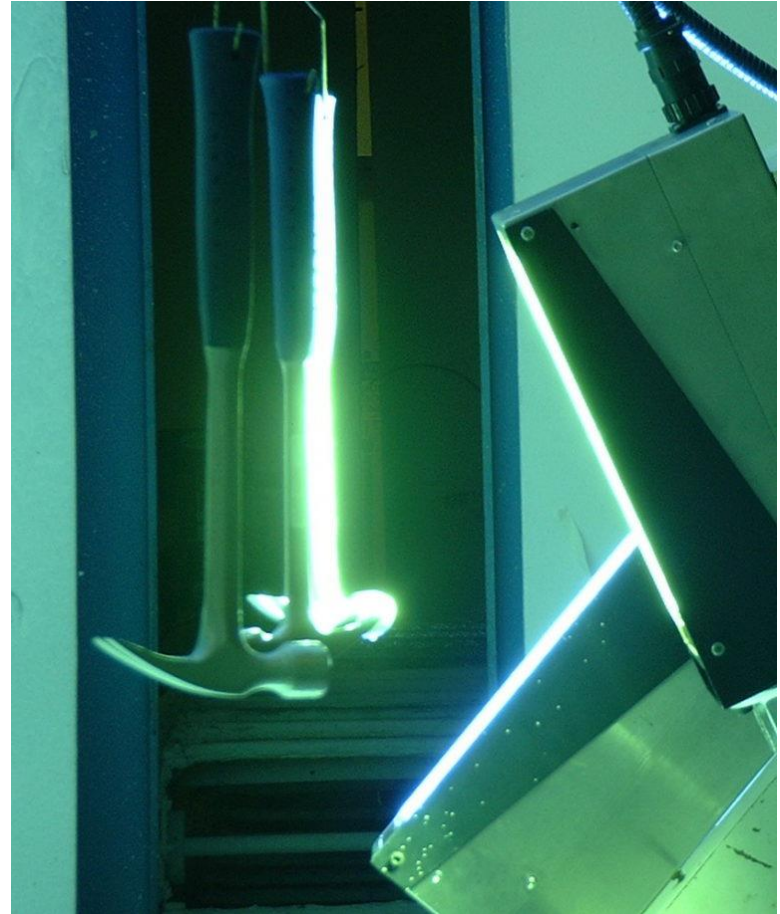
- Energy Savings and Improved Productivity: Web line speeds of 1,000 ft/min. are common and the product is immediately ready for testing and shipment.
- Suited for Sensitive Substrates: Most systems do not contain any water or solvent. In addition, the process provides total control of the cure temperature making it ideal for application on heat sensitive substrates.
- Environmentally and User Friendly: Compositions are typically solvent-free so emissions and flammability are not a concern.

Source: radtech.org

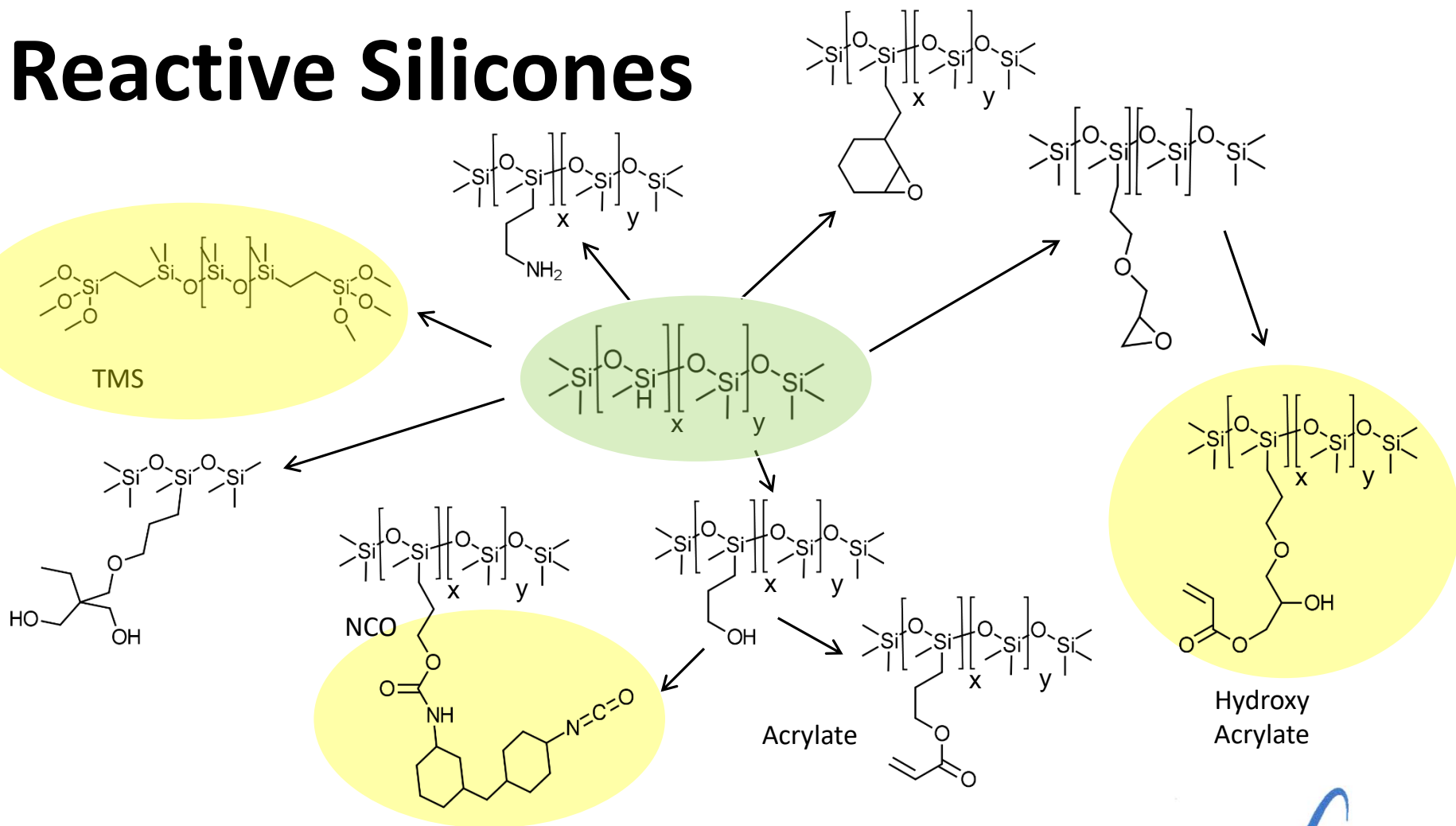


Secondary Cure (Energy Curing)

- Mainly developed for shadow curing of 3-dimensional goods.
- Can also improve the properties.
- Often called Dual Cure
- Typically secondary cure is a condensation type



Reactive Silicones



Experimental

These experiments were conducted in a TA Instruments AR-G2 SN 10G4421 Rheometer with a UV reactive chamber.

The rheological properties including G' , G'' , $\tan(\delta)$ and cure rate are analyzed and obtained by the TA Rheology Advantage software.



Modulus

- G' or storage modulus measures the stored energy or elastic portion. Higher G' indicates more X-linking and more hardness.
- G'' or elastic modulus measures the heat lost or viscous portion. Higher G'' indicates more stiffness
- $\tan(\delta)$ is the damping modulus, also the ratio of G''/G' . $\tan(\delta) > 1$ indicates a liquid.
- Increased values are seen as an indication of curing in thermoset systems



Experimental

The reactions were repeated on the benchtop and the films compared by drawdown on aluminum Q panel with #10 rod.

First cured with a benchtop UV light then further cured at ambient conditions.

A number of properties were measured before and after the condensation cure step to understand the impact of secondary cure.



Experimental

Coefficient of Friction - COF (or Slip) and tape peel force are measured with ChemInstruments Coefficient of Friction -500. (Test speed: 15 cm/min; travel length: 15 cm; sled weight: 200 grams and sled surface which is covered with ASTM-specified rubber).

Static and Kinetic coefficients of friction are read directly from the equipment.



Experimental

Tape peel force is measured with a 12" Tesa 7475 (1" wide PSA) or 12" BRB tape (2" wide SBS PSA). The tape is applied on the coated panel at a 45° angle with a wooden applicator.

The 1st peel force is measured by peeling the 6" tape with ChemInstruments 500 at an angle of 180° and peel rate of 60 cm/min.

The 2nd peel force is measured by applying the tape on the same area and performed the same test as in the 1st run. The peel force in grams is directly obtained from the equipment.



Experimental

Silicone transfer is measured by contacting the coated aluminum with a silicone liner and drawing a red marker on the liner to see if any silicone transfers. The results are qualitatively rated from 0 (worst) to 10 (best).



Experimental

Stain resistance test is conducted according to Chemical and Stain Spot Resistance Test Method. 2 mL of each of the stain is placed and covered with a watch glass.

Left in contact for 24 hours, washed with a sponge and clean water and dried.

Report the degree of stain removal: 2 very strong, 4 considerable, 6 moderate, 8 slight, and 10 no change.

The following were used: Old English Lemon Oil, Vegetable Oil, Salad Dressing , Soy Sauce, Red Wine, Vinegar, IPA, MEK, Acetone, and Colour Dye.



Experimental

Mar resistance is measured using a Sutherland 2000 Ink Rub Tester - Dry Rub method with the following settings:

100 rubs, 84 rpm stroke speed. Rubs are done using a 4 lb test block which is attached with a 2"x 4" nylon scrubbing pad.

The mar resistance rating is determined by visual inspection of surface defects, slip and the percentage change in gloss reading before and after the rubbing test.

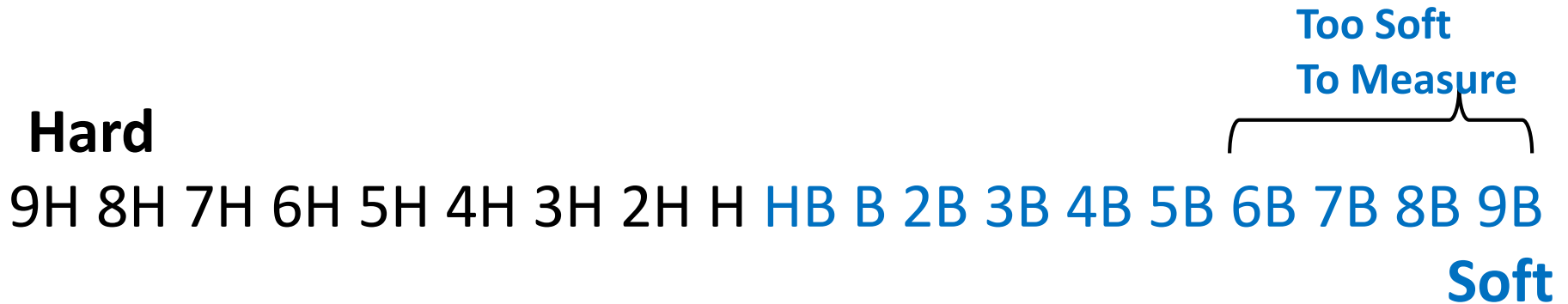
10 is the best and 0 is the worst.



Experimental

Contact angle is measured using KRUSS GH11 Mobile Drop tester and D.I. water. The contact angle of the droplet is read from the instrument.

Film Hardness is measured using the Pencil Hardness Tester ASTM D 3363.



Basic Formulation

Ingredient	Amount (when x=50)	Purpose
OH ACR type	~47.50%	Energy Cure
TMS or NCO type	~47.50%	Secondary Cure
DBTDL	0.25%	Condensation Catalyst
Darocur 1173	4.75%	Photoinitiator

Ratio of 95% components is adjusted to keep molar ratio at 1.1



Control with Monomer

3-(triethoxysilyl) propyl isocyanate.

	Modulus	First Cure	Seven Days Cure
Control, x=10	G' (pa)	$1.89 \cdot 10^6$	Too Brittle
	G''(pa)	$1.69 \cdot 10^4$	
	Tan delta	0.0091	
Control, x=50	G' (pa)	$7.45 \cdot 10^5$	$2.78 \cdot 10^7$
	G''(pa)	$4.23 \cdot 10^3$	$4.23 \cdot 10^5$
	Tan delta	0.0059	0.039



TMS System

	Modulus	First cure	Seven Days Cure
TMS, x=10	G' (pa)	$6.51 \cdot 10^5$	$1.34 \cdot 10^6$
	G''(pa)	$2.73 \cdot 10^3$	$8.32 \cdot 10^3$
	Tan delta	0.0048	0.0063
TMS, x=50	G' (pa)	$9.08 \cdot 10^4$	$2.42 \cdot 10^7$
	G''(pa)	$3.18 \cdot 10^2$	$1.52 \cdot 10^6$
	Tan delta	0.004	0.062



NCO System

	Modulus	First cure	Overnight cure	Seven Days Cure
NCO, x=10	G' (pa)	$6.33 \cdot 10^5$	na	$2.79 \cdot 10^6$
	G''(pa)	$9.19 \cdot 10^3$		$5.43 \cdot 10^5$
	Tan delta	0.0146		0.195
NCO, x=50	G' (pa)	$2.58 \cdot 10^5$	$5.37 \cdot 10^5$	$1.08 \cdot 10^7$
	G''(pa)	$3.62 \cdot 10^3$	$3.14 \cdot 10^4$	$4.23 \cdot 10^5$
	Tan delta	0.0141	0.0587	0.0392



Changes in Moduli

	TMS x=10	TMS x=50	NCO x=10	NCO x=50
G' (Pa) first cure	$6.51 \cdot 10^5$	$9.08 \cdot 10^4$	$6.33 \cdot 10^5$	$2.58 \cdot 10^5$
G' (Pa) seven days	$1.34 \cdot 10^6$	$2.42 \cdot 10^7$	$2.79 \cdot 10^6$	$1.08 \cdot 10^7$
G' change (%)	106%	26,561%	341%	4086%
G'' (Pa) first cure	$2.73 \cdot 10^3$	$3.19 \cdot 10^2$	$9.19 \cdot 10^3$	$3.62 \cdot 10^3$
G'' (Pa) seven days	$8.32 \cdot 10^3$	$1.52 \cdot 10^6$	$5.43 \cdot 10^5$	$4.23 \cdot 10^5$
G'' change (%)	205%	476,389%	5,809%	11,585%
Tan delta first cure	0.0048	0.004	0.015	0.014
Tan delta seven day	0.0063	0.063	0.195	0.0392
Tan delta change (%)	31%	1,660%	1,238%	180%



Panels

- Very excited with the large changes in moduli, we decided to drawdown some Q panels and test meaningful properties.
- Increased G' and G'' should translate to hardness



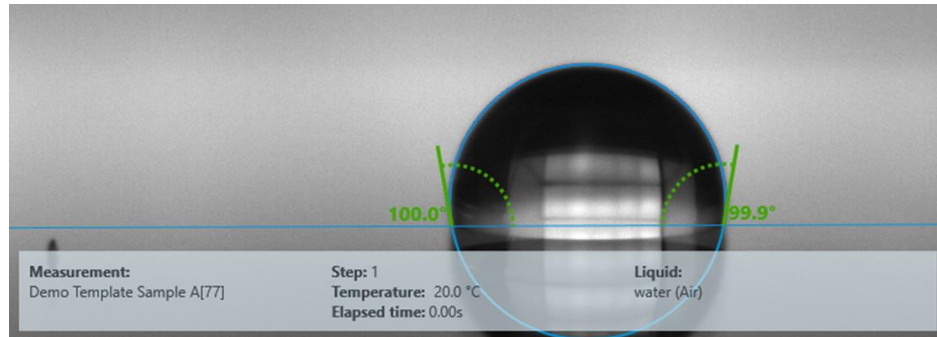
Q-Panels

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Appearance	smooth			
Pencil Hardness first cure	2B	<6B	2B	<6B
Pencil Hardness seven day	7H	HB	>9H	<6B
Contact Angle (°) first cure	86.3	89.3	99.8	105
Contact Angle (°) seven day	87.8	97.3	97.1	98.4
Change contact angle (%)	1.7%	9.0%	-2.7%	-6.2%
Gloss first cure	160.3	160	160.7	164.3
Gloss seven day	153	156	156	161
Change in gloss (%)	-4.6%	-2.8%	-3.2%	-2.0%

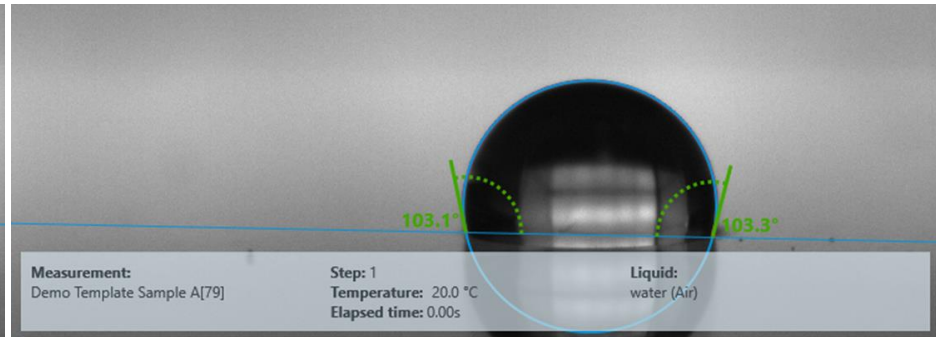
Improvement in pencil hardness and contact angle esp. with TMS



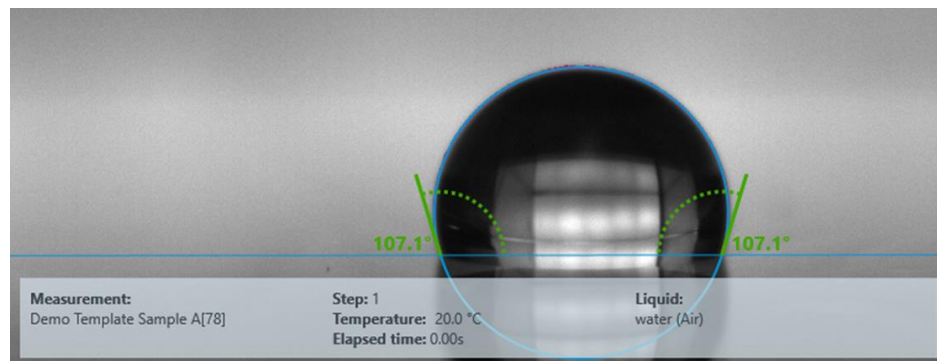
Contact angle increase: from secondary cure or from TMS?



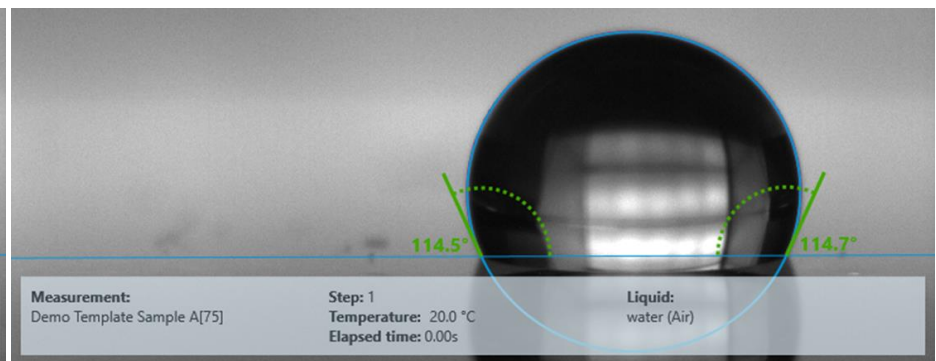
TMS, X=0 angle 100° on glass



TMS, X=10 angle 103°



TMS, X=50 angle 107°



TMS, X=400 angle 115°



Surface Properties

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Tesa release (N/m) first cure	0.468	0.39	5.302	0.858
Tesa release (N/m) seven day	1.715	0.624	13.879	1.559
Change in tesa release (%)	267%	60%	162%	82%
BRB release (N/m) first cure	0.156	0.117	5.341	0.312
BRB release (N/m) seven day	0.624	0.273	30.526	0.507
Change in BRB release (%)	300%	133%	472%	63%
Slip (Static CoF) first cure	2.032	2.817	1.043	3.726
Slip (Static CoF) seven day	1.844	3.236	1.073	3.696
Change in Static CoF (%)	-9%	15%	3%	-1%
Slip (Kinetic CoF) first cure	1.453	2.567	0.64	3.177
Slip (Kinetic CoF) seven day	1.372	3.14	1.184	3.369
Change in Kinetic CoF(%)	-6%	22%	85%	6%

Tape release force and COF are increased
Surface energy increases



Transfer and Resist

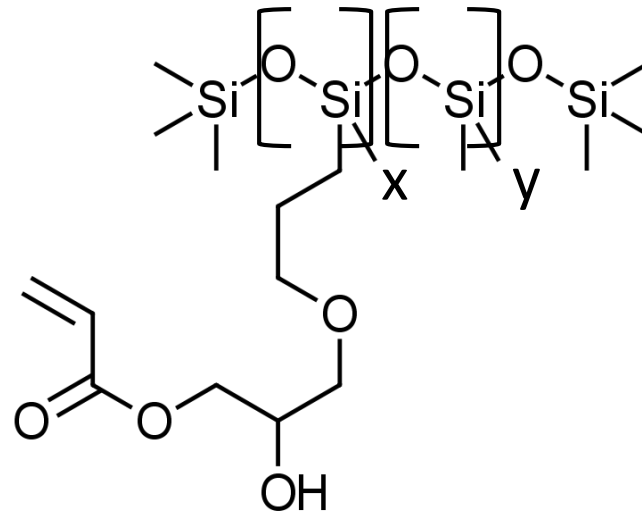
Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Silicone transfer first cure	4	4	4	2
Silicone transfer seven day	8	6	8	2
Stain resistance first cure	2	2	2	2
Stain resistance seven day	2	2	2	2
Mar resistance first cure	2	2	8	2
Mar resistance seven day	2	6	6	2
Rub resistance first cure	>100	>100	>100	Peel off at 6
Rub resistance seven day	>100	>100	>100	Peel off at 6

Improvement in transfer properties.



More formulated/ X-linked commercial release product

- Composition is complex and trade secret
- ..but X-linkers like the one shown here are used for a harder coating



More Formulated/X-linked System

	TMS x=10	TMS x=50	NCO x=10	NCO x=50
G' (Pa) first cure	$8.58 \cdot 10^4$	$3.64 \cdot 10^4$	$2,21 \cdot 10^5$	$5.62 \cdot 10^3$
G' (Pa) seven days	$2.02 \cdot 10^6$	$2.76 \cdot 10^6$	$7.22 \cdot 10^7$	$6.84 \cdot 10^6$
G' change (%)	2,254%	7,482%	32,570%	121,608%
G'' (Pa) first cure	$1.08 \cdot 10^3$	$5.26 \cdot 10^2$	$5.54 \cdot 10^3$	$7.29 \cdot 10^2$
G'' (Pa) seven days	$6.10 \cdot 10^4$	$1.79 \cdot 10^5$	$2.64 \cdot 10^7$	$5.01 \cdot 10^5$
G'' change (%)	5,548%	33,930%	476,434%	68,624%
Tan delta first cure	0.013	0.014	0.025	0.13
Tan delta seven day	0.03	0.065	0.365	0.073
Tan delta change (%)	131%	364%	1,360%	-44%



Q-Panels Formulated System

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Appearance	smooth			
Pencil Hardness first cure	<6B	6B	<6B	<6B
Pencil Hardness seven day	4H	6H	<6B	<6B
Contact Angle (°) first cure	99.6	101.7	107.7	115.3
Contact Angle (°) seven day	101.1	100.9	102.5	103.4
Change contact angle (%)	1.7%	-0.8%	-4.9%	-10.4%
Gloss first cure	151	163.3	68.9	72
Gloss seven day	147	165	70	59
Change in gloss (%)	-2.6%	1.1%	2.3%	-18.3%

Improvement in hardness for TMS
NCO too soft to measure



Surface Properties formulated

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Tesa release (N/m) first cure	0.624	0.624	0.936	0.624
Tesa release (N/m) seven day	0.78	0.546	0.858	0.858
Change in tesa release (%)	25%	-13%	-8%	38%
BRB release (N/m) first cure	0.429	0.507	0.936	0.312
BRB release (N/m) seven day	0.468	0.234	0.546	0.507
Change in BRB release (%)	9%	-54%	-42%	63%
Slip (Static CoF) first cure	3.614	3.625	4.855	3.896
Slip (Static CoF) seven day	2.865	3.168	4.903	4.434
Change in Static CoF (%)	-21%	-13%	1%	14%
Slip (Kinetic CoF) first cure	3.422	3.289	3.141	2.873
Slip (Kinetic CoF) seven day	2.852	3.164	3.465	3.585
Change in Kinetic CoF(%)	-17%	-4%	10%	25%

Better results on surface energy



Transfer and Resist Formulated

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Silicone transfer first cure	8	8	2	2
Silicone transfer seven day	2	2	2	2
Stain resistance first cure	10	10	4	4
Stain resistance seven day	10	6	6	10
Mar resistance first cure	6	6	4	6
Mar resistance seven day	8	6	4	4
Rub resistance first cure	>100	>100	>100	>100
Rub resistance seven day	>100	>100	>100	>100



New Tetra Functional X-Linker

	TMS x=10	NCO x=10
G' (Pa) first cure	6.75*10 ⁵	8.54*10 ⁵
G' (Pa) seven days	1.59*10 ⁷	7.52*10 ⁶
G' change (%)	2256%	781%
G'' (Pa) first cure	2.42*10 ⁴	6.58*10 ⁴
G'' (Pa) seven days	1.00*10 ⁶	9.44*10 ⁵
G'' change (%)	4032%	1335%
Tan delta first cure	0.036	0.077
Tan delta seven day	0.063	0.126
Tan delta change (%)	76%	63%
Pencil Hardness first cure	<6B	<6B
Pencil Hardness seven day	4H	4H



Conclusions

- Based on moduli which increase by orders of magnitude, the secondary cure occurs.
- The pencil hardness results, especially with the TMS polymers, support the increase in G' data.
- Surface and release properties are strongly affected.
- It is important to choose the right material to emphasize the benefit of the secondary cure





Thank
You