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

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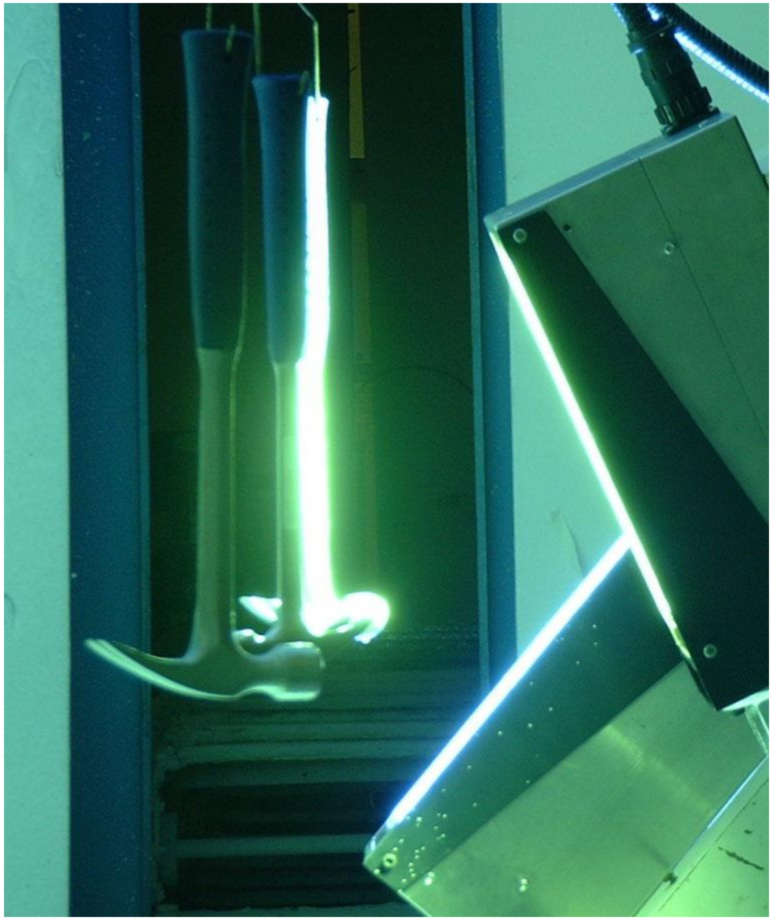
# Hypothesis

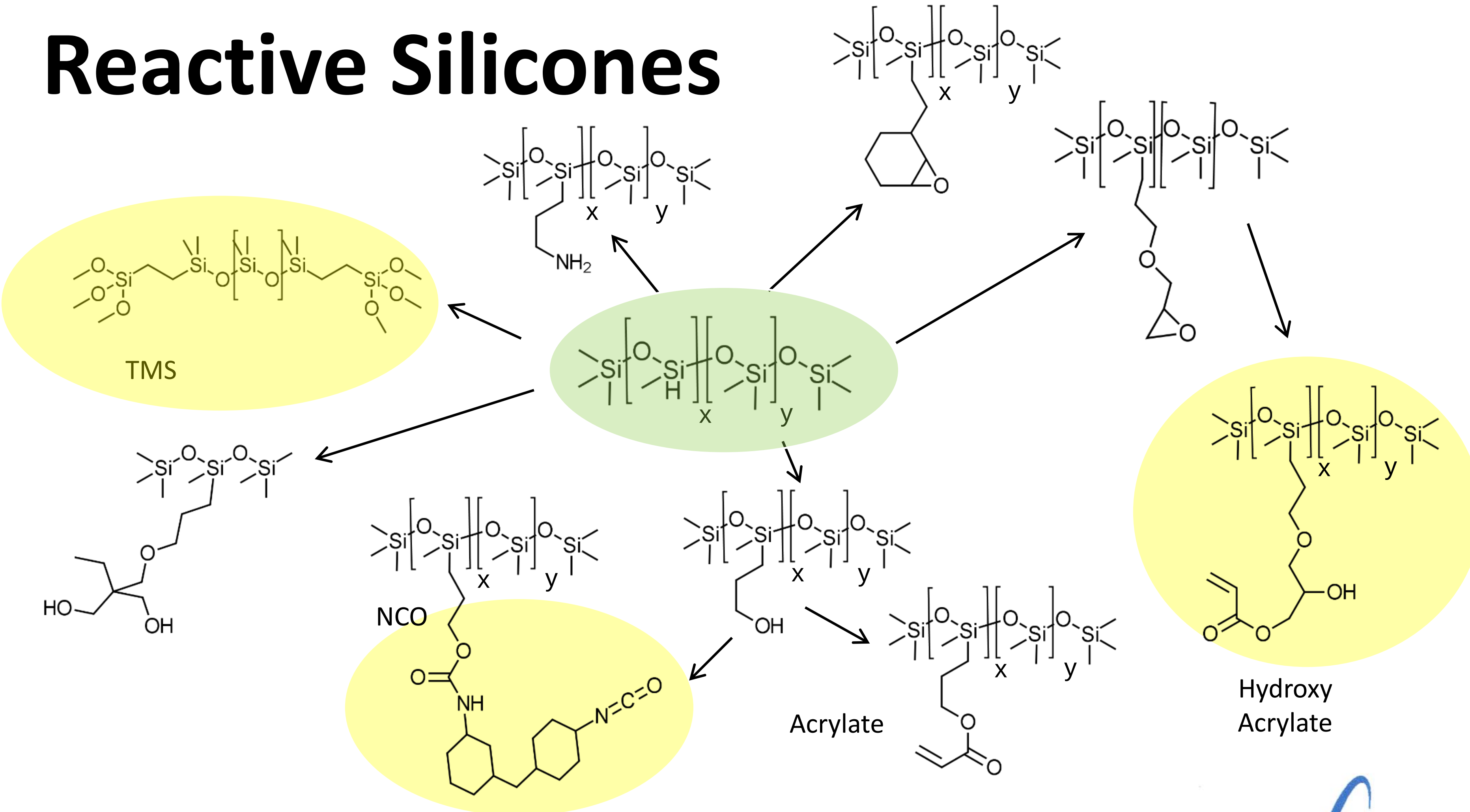
A silicone polymer with difunctional electrophilic groups can provide a secondary cure to UV cured OH functional acrylate silicones

# Secondary Cure (Energy Curing)

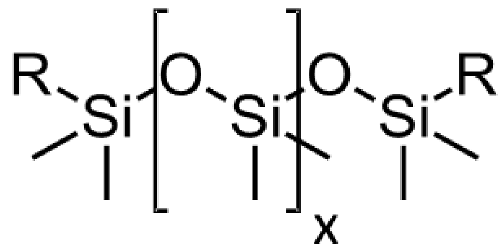
- Mainly developed for shadow curing of 3-dimensional goods.
- Can also improve the properties.
- Often called Dual Cure
- Typically secondary cure is a condensation type



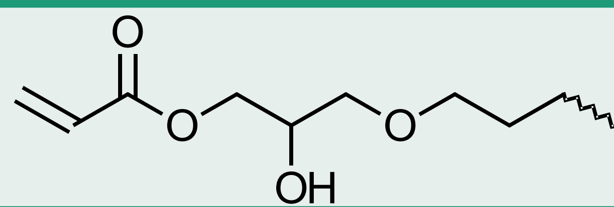
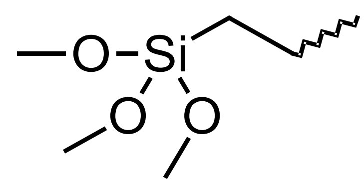
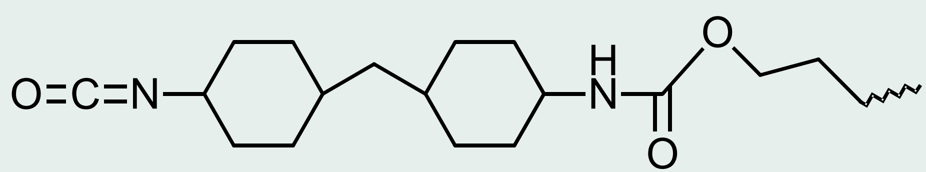
# Reactive Silicones



# Structures Evaluated



X=10, X=50

| Name | R-Group |
|---|---|
| **OH ACR** |  |
| **TMS** |  |
| **NCO** |  |

# 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 (δ) 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 (δ) is the damping modulus, also the ratio of G''/G'.  Tan (δ)>1 indicates a liquid.
- Increased values are seen as an indication of curing in thermoset or photoset 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.

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# 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.

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# 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.

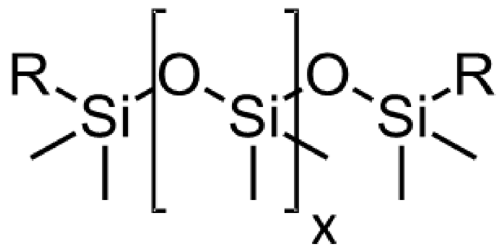
Too Soft
To Measure

**Hard**

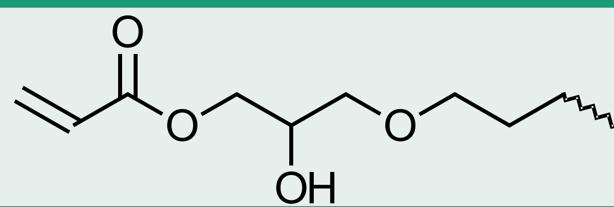
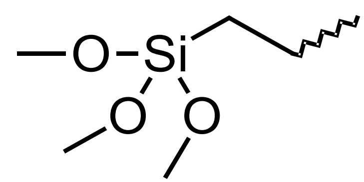
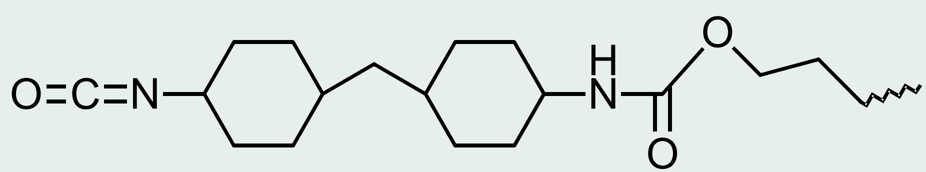
9H 8H 7H 6H 5H 4H 3H 2H H HB B 2B 3B 4B 5B 6B 7B 8B 9B

**Soft**

# Structures Evaluated




X=10, X=50

| Name | R-Group |
| --- | --- |
| **OH ACR** |   |
| **TMS** |   |
| **NCO** |   |

# 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

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# Control with Monomer

## 3-(triethoxysily) propyl isocyanate.

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

# NCO System

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

# TMS System

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

# Changes in Moduli

| | TMS x=10 | TMS x=50 | NCO x=10 | NCO x=50 |
|---|---|---|---|---|
| G' (Pa) first cure | $6.51*10^5$ | $9.08*10^4$ | $6.33*10^5$ | $2.58*10^5$ |
| G' (Pa) seven days | $1.34*10^6$ | $2.42*10^7$ | $2.79*10^6$ | $1.08*10^7$ |
| G' change (%) | 106% | 26,561% | 341% | 4086% |
| G'' (Pa) first cure | $2.73*10^3$ | $3.19*10^2$ | $9.19*10^3$ | $3.62*10^3$ |
| G'' (Pa) seven days | $8.32*10^3$ | $1.52*10^6$ | $5.43*10^5$ | $4.23*10^5$ |
| 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% |

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# Panels

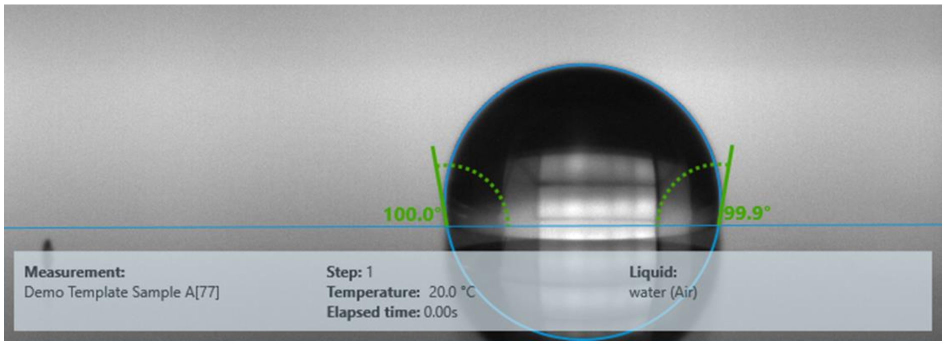
- Very excited with the large changes in moduli, we decided to drawdown some Q panels and test meaningful properties.
- Increased G' and G'' should translate to hardness

# Q-Panels

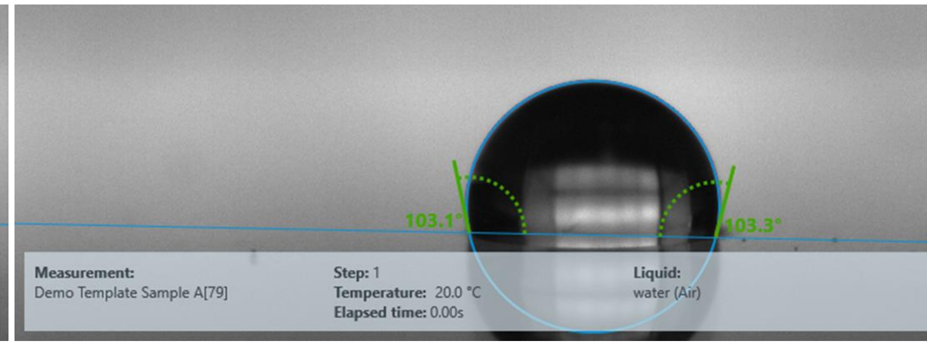
| Property | TMS x=10 | TMS x=50 | NCO x=10 | NCO x=50 |
|---|---|---|---|---|
| Appearance | smooth | | | |
| Pencil Hardness first cure | 2B | <6B | 2B | <6B |
| Pencil Hardness seven day | 7H | HB | >9H | <6B |
| Contact Angle (°) first cure | 86.3 | 89.3 | 99.8 | 105 |
| Contact Angle (°) seven day | 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

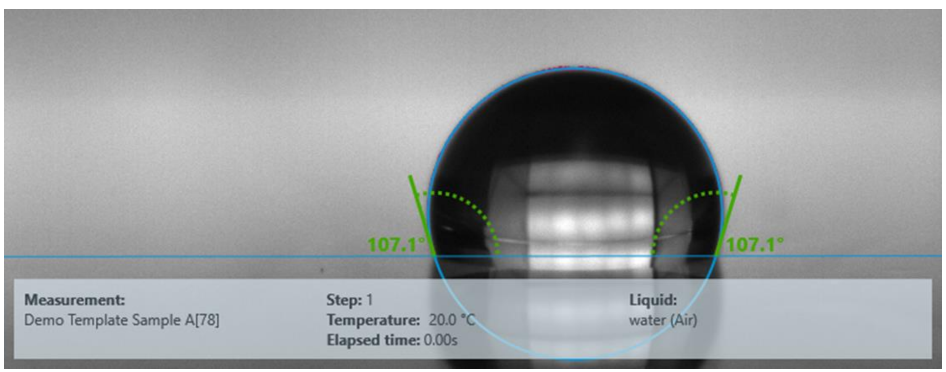
# Contact angle increase: from secondary cure or from TMS?



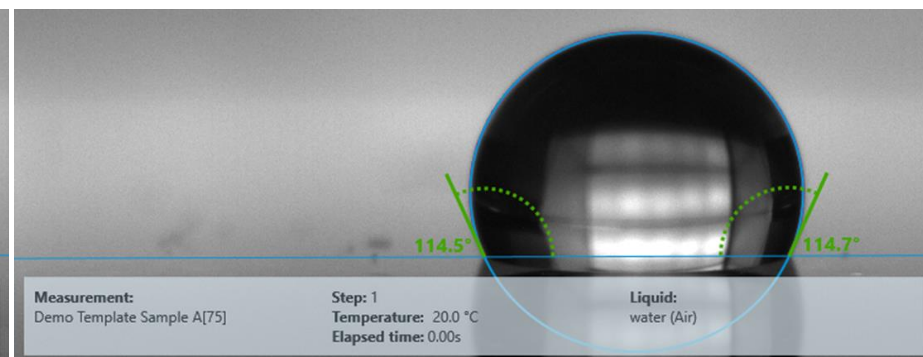

TMS, X=0 angle 100° on glass




TMS, X=10 angle 103°




TMS, X=50 angle 107°




TMS, X=400 angle 115°

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# 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 increase or reactive sites?

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# 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.

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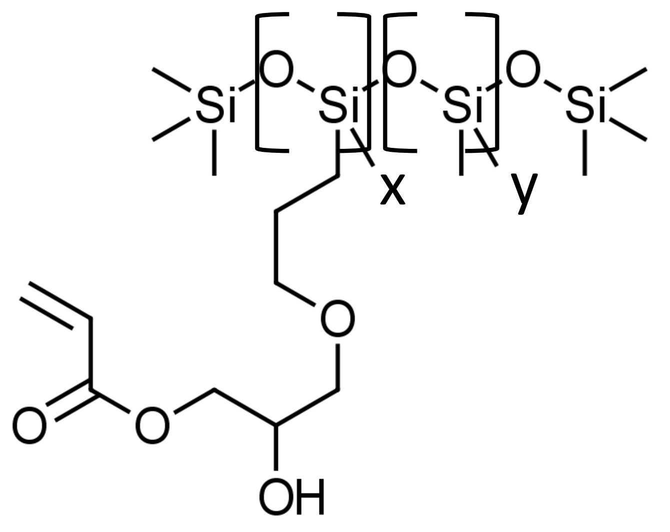
# More formulated/ X-linked commercial release product

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

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# More Formulated/X-linked System

| | TMS x=10 | TMS x=50 | NCO x=10 | NCO x=50 |
|---|---|---|---|---|
| G' (Pa) first cure | $8.58*10^4$ | $3.64*10^4$ | $2,21*10^5$ | $5.62*10^3$ |
| G' (Pa) seven days | $2.02*10^6$ | $2.76*10^6$ | $7.22*10^7$ | $6.84*10^6$ |
| G' change (%) | 2,254% | 7,482% | 32,570% | 121,608% |
| G'' (Pa) first cure | $1.08*10^3$ | $5.26*10^2$ | $5.54*10^3$ | $7.29*10^2$ |
| G'' (Pa) seven days | $6.10*10^4$ | $1.79*10^5$ | $2.64*10^7$ | $5.01*10^5$ |
| 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% |

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# 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

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# 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 |

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# 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 affected but maybe not in predictable ways.
- It is important to choose the right material to emphasize the benefit of the secondary cure


Thank
You