

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

¹Bob, Ruckle and ²Tom-Seung, Cheung

Siltech Corporation

Toronto, ON Canada

¹Robert@siltech.com, ²Tom@siltech.com

Abstract

Two unique condensation curable silicones, with trimethoxy silyl and isocyanate moieties are evaluated. When formulated with energy cured hydroxyl and acrylate dual functional silicones, these materials exhibit increased shear modulus and rigidity, developing over time even in ambient conditions.

Introduction

The use of secondary cure pathways in energy cured systems has been practiced for many years. In these systems, a condensation cure mechanism is included in the coating design in addition to the energy cured moieties. Whether a “cure” for shadowing or to improve overall film properties, this technique is well demonstrated.

We wanted to explore the usefulness of some of our unique silicones as secondary cure components. We will look at polymers with either trialkoxy silane groups or isocyanato functionality appended to the silicone backbone. We will also use in the formulation silicone polymers with both hydroxyl and acrylate groups. The former will react along the secondary condensation pathway and the acrylate functionality will polymerize in response to light.

Experimental

The salient structures used in the study are shown in the Figure 1. The value of x is either 10 or 50. The acrylate functionality of the OH ACR materials will react with the photoinitiator, starting a free radical reaction which will polymerize the double bonds of the acrylate group. This reaction will be initiated by radiation and some of the film properties will develop very quickly from this energy cured reaction.

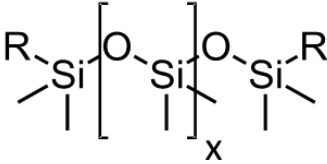
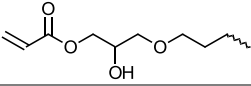
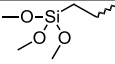
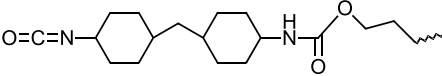
Structure	Name	R-Group
	OH ACR	
	TMS	
	NCO	

Figure 1. Structures.

After the quick energy cure, the hydroxyl group of the OH ACR will still be available to react with the silane of the TMS containing polymers or the isocyanate of the NCO designated polymers. This condensation reaction will occur slowly overnight and even over several days in our experiments, altering the film properties. The maximum moduli were typically obtained after three days but not overnight. We report all the data at seven days cure.

These experiments will be conducted in a TA Instruments AR-G2 SN 10G4421 Rheometer with a UV reactive chamber. The geometry is set to 20 mm disposable plate and procedure set to UV fast with the thickness of 1000 μm . The rheological properties including G' , G'' , $\tan(\delta)$ and cure rate are analyzed and obtained by the TA Rheology Advantage software.

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

Gloss is measured with BYK-Gardner 60 micro-glossmeter before and after mar resistance test. The value is directly recorded from the micro-glossmeter.

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. 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. Care is taken to ensure good contact between the tape and the substrate. One end of a stainless steel string is attached to the transducer and another end is fastened onto the tape with 2" Scotch tape. 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.

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).

Stain resistance test is conducted according to Chemical and Strain Spot Resistance Test Method The coated Q panel is placed in a horizontal position, 2 mL of each of the stainant is placed on the surface and covered with a watch glass. The following stainants are used: Old English Lemon Oil, Vegetable Oil, Salad Dressing , Soy Sauce, Red Wine, Vinegar, IPA, MEK, Acetone, and Colour Dye.

The stain is left in contact with the film for 24 hours and then the surface is washed with a sponge and clear water and dried with a clean cloth. Report all results and the degree of stain

removal from 2-10 using the criteria for degree of change: 2 very strong, 4 considerable, 6 moderate, 8 slight, and 10 no change.

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.

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.

The general formulation is shown in Figure 2. The exact weights of the energy and secondary cured polymers was adjusted slightly to achieve the desired molar ratios of 5-10% excess of TMS or NCO over OH.

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

Figure 2. Formulation.

Results

A control experiment was done with OH ACR types, both x=10 and x=50, reacted with 3-(triethoxysilyl) propyl isocyanate. This non-polymeric material contains both NCO and TMS groups and should give a secondary cure if the concept works.

Figure 3 shows the moduli and tan delta values right after cure and after 24 hours. With x=10 the materials were very brittle and we have little confidence in the rheometer data. The experiment with the OH ACR type where x=50 is reacted with the secondary cure monomer shows an increase in the moduli of about 2 orders of magnitude. This shows additional curing is indeed occurring over days.

	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

Figure 3: Monomer Control

The chart in Figure 4 is printed directly from the rheometer. It shows the increase of G' with time for the control, x=50 reaction. The red line shows the first 900 seconds when the modulus increases dramatically from the UV cured reaction. The blue line shows the condensation secondary cure occurs quickly in the overnight time frame maximizing the modulus.

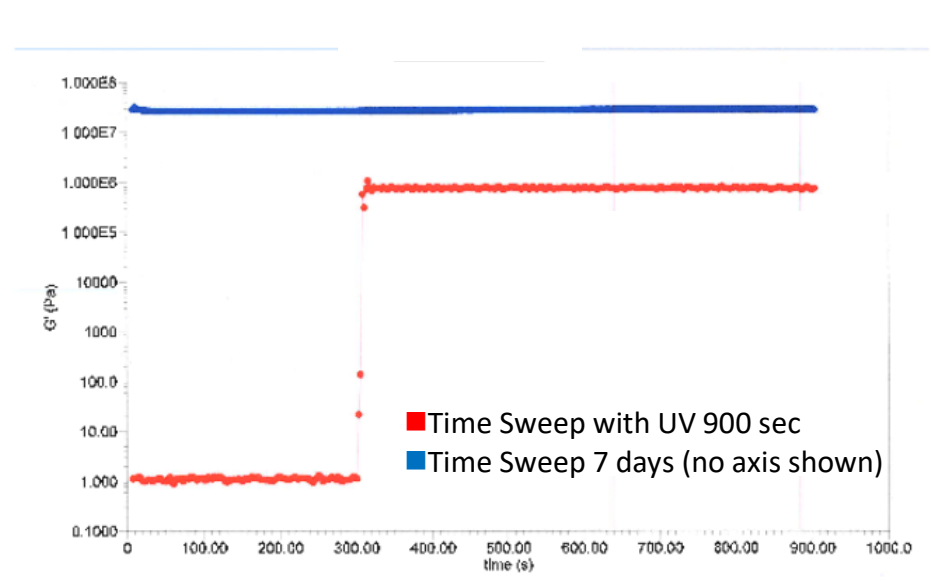


Figure 4. G' from Rheometer.

The experiments with the TMS functional silicone polymers are shown in Figure 5. Here the data are reported after the energy cure and then at seven days of ambient cure for both x=10 and x=50 systems. While an improvement is seen in x=10 system, an especially large increase in moduli for the x=50 polymers is seen over the seven days.

	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

Figure 5. Silane Cured System.

For the NCO designated isocyanate functional silicones, the data are shown in Figure 6. Again, the longer duration cure for the x=50 polymers gives very dramatic increases in properties. We are showing the overnight cure data to demonstrate that this secondary cure is taking days to maximize the properties.

	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

Figure 6. Isocyanate Cured System.

Figure 7 provides percent changes in the moduli. It is in effect, a summary of the impact on mechanical properties. Both the TMS and NCO secondary cure mechanisms seem to show more efficacy in the x=50 polymer systems.

	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%

Figure 7. Changes in Moduli.

The film properties such as hardness, contact angle and gloss are shown in Figure 8.

Property	TMS x=10	TMS x=50	NCO x=10	NCO x=50
Appearance	smooth	smooth	smooth	smooth
Pencil Hardness (6B to 9H) 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 (%)	1.70%	9.00%	-2.70%	-6.20%
Gloss first cure	160.3	160	160.7	164.3
Gloss seven day	153	156	156	161
Change in gloss (%)	-4.60%	-2.80%	-3.20%	-2.00%

Figure 8. Film Properties.

Surface energy based properties are summarized in Figure 9. The more cross-linked systems such as TMS x=50 show lesser release but greater slip properties. They may show improved mar properties, unfortunately one cannot see an improvement in rub resistance since they are all >100 rubs.

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%
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	>101	>100	>100	Peel off at 6

Figure 9. Film Surface Properties.

Discussion

There is clearly an impact of secondary cure which manifests over several days. The TMS reactive groups seem to be more effective than the NCO, although both are impactful.

Not surprisingly the amount of cross-linking to the x=10 system is too much for the low molecular weight of these polymers, resulting in brittle coatings. The polymer lengths of x=50 seem to have enough flexibility and space to give improved properties.

Although very large increases in G' and G'' are seen with the rheometer the changes in film properties were not as dramatic. We were gratified by the pencil hardness increases with the TMS system which validates the increased G' data.

The appearance of the films was not altered but we did see a small reduction in gloss after the secondary cure. We did see movement in the contact angle with the TMS derivatives increasing contact angle somewhat and the NCO functional polymers reducing it. We did not

examine similar systems which could not undergo secondary cure to rule out oxidation or other aging phenomena of the surface for this loss of gloss and change in contact angle.

With surface properties we did see significant increases in silicone transfer resistance and mar resistance. The big difference was slip and in particular release properties. The secondary cure gave surfaces that are much higher in surface energy.

Conclusion

In conclusion, we believe we have demonstrated that a secondary, condensation cure has occurred in these systems. This conclusion is largely defended by the changes in moduli in the rheometric experiments, but some impact on the film properties, particularly pencil hardness supports the conclusion as well.

In a more real-world optimized coating, the impact on properties could be very useful.