Novel Energy Cured Mercapto Functional Silicone Q Resin Materials for 3D Printing.

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Abstract

Mercapto functional silicone-based Q resins are shown to be cross linked with vinyl silicone using UV light and photoinitiators. The materials are evaluated for physical properties and the best of these formulations are 3D printed looking for soft but printable resins.

Introduction

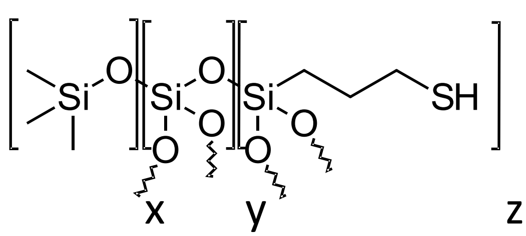
A series of mercapto functional silicone resins, with ultra-high cross-link density, are reacted with various vinyl silicones cured with UV light and photoinitiators. This reaction is well known and studied in the literature, our take on this is the use of these highly cross-linked reactive silicones.

The stoichiometry is first optimized using a rheometer screening for maximum G'. The reaction products are also prepared on the benchtop and mechanical properties are measured. Multiple structural and stoichiometric variables are evaluated for their affect on mechanical properties.

The best formulation is 3D printed as a proof of concept.

Experimental

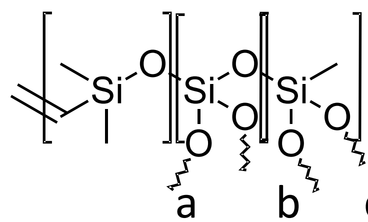
The first structures used in the study are shown in the Figure 1. We adhere herein to the widely used silicone industry MDTQ shorthand. In that shorthand, M indicates a trimethyl silyl group with one Si-O~ bond, i.e. a chain terminator. D, the chain extender, represents a dimethyl silyl group with two Si-O~ bonds. Finally, T and Q groups, which are cross-linking points, represent respectively a monomethyl silyl group with three Si-O~ bonds and a silyl group with four Si-O~ connections. Figure 1 shows the Mercapto functional MQT(SH) Silicone resin where "x" indicates the number of M groups; "z" the mercapto modified T groups and "y" the Q groups.



Designation	Q / T ratio (y/z)	Equivalent Weight	Viscosity (cPs)
SH 208	0%	208.0	215
SH208-10Q	10%	217.0	530
SH208-20Q	20%	220.3	1,350
SH208-30Q	30%	226.3	2,325
SH208-40Q	40%	231.6	12,300
SH208-50Q	50%	237.5	228,000

Figure 1. Mercapto Silicone Resin Structures.

Figure 2 shows another class of cross-linking silicone resin used in this study. These VTQ materials are vinyl functional to react with the mercapto radical formed in the reaction Conditions. Determining the ideal ratio of these MDTQ components as well as the stoichiometry of the two materials is a point of the study. Figure 2 also references 65K which is a difunctional high molecular weight silicone used as a chain extender or reactive diluent in the formulation. The VTQ compounds are diluted in this material for ease of handling.



Designation	a/b/c	Vinyl %	Viscosity (cPs)
Q83T30	100/83/30	1.84%	25,500
Q91T30	100/91/30	0.6262%	16,200
Q92T30	100/92/30	1.33%	18,000
Q93T30	100/93/30	1.88%	14,600
Q94T30	100/94/30	2.49%	14,000
Q92T50	100/92/50	1.41%	5,300
Q92	100/92/0	1.066%	55,000
Q93	100/93/0	1.62%	not measured
Q94	100/94/0	2.15%	64,500
Control 65K	na	0.060%	66,500
Alternate 65K	na	0.078%	66,600

Figure 2. Vinyl Silicone Resin Structures.

These experiments are 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 reacted volume is ~1 mL and the UV laser emits at 365 nm. The rheological properties including G', G'', tan (δ) and cure rate are analyzed and obtained by the TA Rheology Advantage software.

The reactions are repeated on the benchtop. Prepared by mixing a 50 gm sample using the requisite amounts into a plastic or paper cup. Stir the mixture until homogenous. Pour 50g mixture into a 6 x 6 inch mold and degas using the Lab-line vacuum chamber at -50 kPa for 5 minutes to remove air bubbles and then cure the mixture with Vogue Professional UV Lamp # ND362 for 10 minutes under a nitrogen blanket.

These 6x6 inch cured sheets are cut with ASTM D624 type C shape for tear strength measurement and ASTM D412 for tensile and elongation measurement. Bluehill 2 software is used according to the manufacturer's instructions for testing.

The general formulation is shown in Figure 3.

Ingredient	Amount (wt %)	Purpose
Mercaptosilicone	5-40%	Cross-linker
65K	50-70%	Extender
Vinyl silicone resin	15-25%	Softer Cross-Linker
TP0-L	0.6-0.7%	Photoinitiator

Figure 3. Formulation.

Variables evaluated in these experiments includes the stoichiometry of the MQT(SH); VTQ; and 65K components. We also delve deeply into the structural parameters of each component. Specifically, the ratios of the MQT groups and the degree of reactive groups on each polymer.

These formulations are expected to be soft, so we are targeting a 3D printable material with good tear strength, tensile strength, flexibility and elongation.

Results

In separate experiments, various amounts of analogous SH208 mercapto silicone resins with increasing amounts of Q groups are reacted with one VQ93T30 resin at various SH/VINYL stoichiometries. These are evaluated for maximum G' and mechanical properties. Figures 4-10 show these results.

Component	YL3-128A	YL3-128B	YL3-127F	YL3-128C	YL3-127E	YL3-127A	YL3-127B	YL3-127C
SH 208	11.41%	12.61%	13.77%	14.88%	16.97%	19.89%	21.48%	23.54%

65K	47.71%	47.07%	46.44%	45.84%	44.71%	43.15%	42.29%	41.18%
Q93T30	40.19%	39.65%	39.12%	38.62%	37.67%	36.35%	35.62%	34.69%
TPO-L	0.69%	0.67%	0.67%	0.65%	0.65%	0.62%	0.62%	0.60%
SH/VINYL ratio	1.88	2.11	2.34	2.56	2.99	3.63	4.00	4.50
Properties								
G' (Pa)	5.08E+05	5.70E+05	6.20E+05	5.31E+05	4.35E+05	2.96E+05	2.70E+05	2.09E+05
G" (Pa)	4.18E+04	4.55E+04	4.62E+04	4.03E+04	3.64E+04	2.95E+04	2.69E+04	2.44E+04
tan (delta)	0.082	0.080	0.074	0.076	0.084	0.099	0.100	0.117
Cure rate (Pa/s)	9.48E+04	1.48E+05	5.20E+05	2.88E+05	2.05E+05	1.14E+05	1.34E+05	1.38E+05
Appearance	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white

Figure 4: Optimization for SH 208 ratio.

Component	YL3-149A	YL3-146B	YL3-149B	YL3-150C
SH 208-10Q	13.56%	14.23%	14.87%	15.44%
65K	46.50%	46.13%	45.79%	45.48%
Q93T30	39.25%	38.96%	38.65%	38.41%
TPO-L	0.69%	0.67%	0.68%	0.66%
SH/VINYL ratio	2.21	2.33	2.46	2.57
Properties				
G' (Pa)	6.77E+05	6.92E+05	7.11E+05	6.89E+05
G" (Pa)	5.07E+04	5.14E+04	5.14E+04	4.89E+04
tan (delta)	0.075	0.074	0.072	0.071
Cure rate (Pa/s)	1.22E+05	1.26E+05	1.79E+05	1.41E+05
Appearance	Opaque white	Opaque white	Opaque white	Opaque white
Tensile Strength (kPa)	Not measured	3258.12	3167.24	Not measured
Elongation (%)		84.5	84.78	
Total Energy (J/m)		204.48	170.76	
Tear Strength (N/mm)		3.01	3.20	
Shore A Hardness		52	50	

Figure 5: Optimization for SH 208-10Q ratio.

Component	YL3-151A	-146C	-151B	-153B	-153D	-153E	-154B	-154A	YL3-153F
SH 208-20Q	13.81%	14.43%	15.05%	15.64%	16.52%	17.30%	18.02%	18.36%	20.27%

65K	46.41%	46.07%	45.74%	45.45%	44.98%	44.55%	44.15%	43.97%	42.95%
Q93T30	39.08%	38.80%	38.52%	38.23%	37.84%	37.48%	37.16%	37.00%	36.13%
TPO-L	0.70%	0.69%	0.69%	0.68%	0.67%	0.67%	0.66%	0.66%	0.64%
SH/VINYL ratio	2.22	2.34	2.46	2.57	2.75	2.90	3.05	3.12	3.53
Properties									
G' (Pa)	7.23E+05	7.53E+05	7.79E+05	7.61E+05	8.10E+05	8.13E+05	8.43E+05	7.39E+05	5.94E+05
G" (Pa)	5.47E+04	5.42E+04	5.67E+04	5.59E+04	5.77E+04	5.86E+04	5.95E+04	5.15E+04	4.16E+04
tan delta	0.076	0.072	0.073	0.073	0.071	0.072	0.071	0.070	0.070
Cure rate (Pa/s)	1.31E+05	1.28E+05	1.17E+05	1.57E+05	3.72E+05	1.81E+05	2.47E+05	1.95E+05	1.61E+05
Appearance	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white
Tensile Strength (kPa)	Not measured	3278.78	Not measured	Not measured	Not measured	Not measured	3006.54		
Elongation (%)		79.65					87.00		
Total Energy (J/m)		166.22					172.77		
Tear Strength (N/mm)		3.59					1.96		
Shore A Hardness		52					49		

Figure 6: Optimization for SH 208-20Q ratio.

Component	YL3-147A	YL3-160C	YL3-171B	YL3-171C
SH 208-30Q	14.75%	19.79%	24.75%	27.72%
65K	45.91%	46.66%	40.45%	38.86%
Q93T30	38.67%	32.89%	34.11%	32.77%
TPO-L	0.67%	0.66%	0.68%	0.66%
SH/VINYL ratio	2.34	3.66	4.44	5.18
Properties				
G' (Pa)	4.34E+05	6.31 E+05	7.36E+05	5.91E+05
G" (Pa)	4.53E+04	4.92 E+04	5.97E+04	5.01E+04

tan delta	0.104	0.078	0.081	0.085
Cure rate (Pa/s)	1.45E+05	1.56 E+05	1.51E+05	2.10E+05
Appearance	Opaque white	Opaque white	Opaque white	Opaque white
Tensile Strength (kPa)	2374.05	2533.29	Not measured	Not measured
Elongation (%)	68.59	93.22		
Total Energy (J/m)	117.93	161.53		
Tear Strength (N/mm)	3.59	2.82		
Shore A Hardness	51	41		

Figure 7: Optimization for SH 208-30Q ratio.

Component	**YL3-147B**	**YL3-159A**	**YL3-159B**	**YL3-159C**	**YL3-159D**	**YL3-160D**	**YL3-159E**
SH 208-40Q	15.03%	20.89%	24.77%	28.71%	32.83%	36.63%	40.00%
65K	45.82%	44.36%	42.18%	39.97%	37.66%	35.53%	33.64%
VQ93T30/VIN65K	38.49%	34.18%	32.50%	30.80%	29.02%	27.38%	25.92%
TPO-L	0.66%	0.58%	0.55%	0.52%	0.49%	0.46%	0.44%
SH/VINYL ratio	2.34	3.65	4.55	5.56	6.75	7.98	9.21
Properties							
G' (Pa)	8.55E+04	1.83E+05	3.86E+05	4.86E+05	5.18E+05	4.47E+05	4.47E+05
G" (Pa)	2.18E+04	3.09E+04	3.84E+04	4.23E+04	4.67E+04	4.16E+04	4.12E+04
tan delta	0.255	0.169	0.099	0.087	0.090	0.093	0.092
Cure rate (Pa/s)	1.28E+04	2.20E+04				9.47E+04	
Appearance	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white
Tensile Strength (kPa)	1888.26	Not measured	Not measured	Not measured	Not measured	Not measured	Not measured
Elongation (%)	103.72						
Total Energy (J/m)	122.78						
Tear Strength (N/mm)	2.01						
Shore A Hardness	39						

Figure 8: Optimization for SH 208-40Q ratio.

Component	**YL3-147C**	**YL3-148A**	**YL3-148B**	**YL3-148C**	**YL3-171E**	**YL3-171D**
SH 208-50Q	15.37%	23.39%	28.65%	34.74%	36.74%	40.86%
65K	45.58%	41.26%	38.42%	35.15%	33.79%	31.69%

VQ93T30/VIN65K	38.39%	34.76%	32.37%	29.61%	28.90%	26.82%
TPO-L	0.66%	0.60%	0.55%	0.51%	0.57%	0.63%
SH/VINYL ratio	2.34	3.93	5.17	6.85	7.42	8.89
Properties						
G' (Pa)	2.44E+04	1.01E+05	1.58E+05	2.11E+05	1.13E+05	1.16E+05
G" (Pa)	1.00E+04	3.60E+04	5.33E+04	6.48E+04	4.32E+04	4.19E+04
tan delta	0.411	0.355	0.337	0.308	0.381	0.360
Cure rate (Pa/s)	4.06E+03	1.15E+04	2.44E+04	2.89E+04	1.68E+04	1.74E+04
Appearance	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white	Opaque white
Tensile Strength (kPa)	162.22	Not measured	Not measured	Not measured	Not measured	Not measured
Elongation (%)	70.56					
Total Energy (J/m)	11.43					
Tear Strength (N/mm)	0.52					
Shore A Hardness	8					

Figure 9: Optimization for SH 208-50Q ratio.

Figures 4-9 show that SH/VINYL ratio and the degree of Q groups in SH208-xQ are very important variables. Notice in the case of SH208-50Q only the optimum SH/VINYL ratio gave workable material.

A summary of optimal SH/Vinyl ratios is shown in Figure 10. As we bring more Q groups into the resin stoichiometry, the needed ratio of SH/Vinyl for optimal reaction increases.

	SH 208	SH 208-10Q	SH 208-20Q	SH 208-30Q	SH 208-40Q	SH 208-50Q
Optimal SH/VINYL ratio	2.33	2.46	3.05	4.44	6.75	6.85

Figure 10: Optimized SH/Vinyl ratios for SH 208 to SH 208-50Q.

Having established the optimum SH/VINYL ratio of 2.33 for the SH 208/65K/Q93T30 system, we next sought to show the effect of the Q groups directly. We repeated these experiments with the constant SH/VINYL ratio=2.33. Rheological and mechanical data are tabulated in Figure 11.

Component	SH 208	SH 208-10Q	SH 208-20Q	SH 208-30Q	SH 208-40Q	SH 208-50Q
SH 208 series	13.76%	14.23%	14.43%	14.75%	15.03%	15.37%
65K	46.44%	46.13%	46.07%	45.91%	45.82%	45.58%
Q93T30	39.12%	38.96%	38.80%	38.67%	38.49%	38.39%
TPO-L	0.67%	0.67%	0.69%	0.67%	0.66%	0.66%

SH/VINYL ratio	2.33	2.33	2.34	2.34	2.34	2.34
Properties						
G' (Pa)	6.65E+05	6.92E+05	7.53E+05	4.34E+05	8.55E+04	2.44E+04
G" (Pa)	4.75E+04	5.14E+04	5.42E+04	4.53E+04	2.18E+04	1.00E+04
tan delta	0.071	0.074	0.072	0.104	0.255	0.411
Cure rate (Pa/s)	1.62E+05	1.26E+05	1.28E+05	1.45E+05	1.28E+04	4.06E+03
Appearance	opaque white	opaque white	opaque white	opaque white	opaque white	opaque white
Tensile Strength (kPa)	2438.66	3258.12	3278.78	2374.05	1888.26	162.22
Elongation (%)	79.18	84.50	79.65	68.59	103.72	70.56
Total Energy (J/m)	128.10	204.48	166.22	117.93	122.78	11.43
Tear Strength (N/mm)	2.78	3.01	3.59	3.59	2.01	0.52
Shore A Hardness	48	52	52	51	39	8
Note	poor tear strength				poor tear strength, soft, undercured	poor tear strength, very soft, undercured

Figure 11. SH/VINYL ratio set to 2.33

Cured samples prepared with SH 208-10Q and 20Q have better storage modulus, tensile strength, tear strength and Shore A hardness compared to the sample prepared with SH 208. This shows that introducing 10% to 20% Q group into the vinyl MT resin improves cross-linking and tear strength.

The storage moduli for SH208-40Q and -50Q samples are lessened. Indicating that these two samples are under-cured and weakly crosslinked at SH/VINYL ratio=2.33. the tensile strength is particularly affected in SH208-40Q and -50Q. Although previously data suggested a SH/VINYL ratio of 2.33 is sufficient (Figure 4), the under-cured samples indicate that more mercaptosilicone needs to be added into the system to make a properly cured sample. The storage modulus drop in SH 208-40Q and -50Q experiments could also indicate that the larger amounts of the bulky Q groups are creating steric problems for the reaction.

Although SH 208-10Q and 20Q samples give reasonable tensile strength of about 3 MPa, all of the samples in shown Figure 11 have poor toughness. All samples break upon twisting.

Because Figure 11 suggests that SH/VINYL ratio =2.33 may not be the optimal ratio for all of the mercaptosilicone resins, a SH/VINYL ratio study is performed on all samples by adding more mercaptosilicone to adjust SH/VINYL ratio. Rheological and mechanical data of optimal SH/VINYL ratio and % increase data are tabulated in Figure 12.

	-10Q	delta	-20Q	delta	-30Q	delta.	-40Q	delta	-50Q	delta
SH/VINYL ratio	2.46	5%	3.05	30%	4.44	90%	6.75	189%	6.85	193%
Tensile Strength (kPa)	3167.24	-3%	3006.54	-8%	Not Measured					
Elongation (%)	84.78	0%	87	9%	Not Measured					
Total Energy (J/m)	170.76	-16%	172.77	4%	Not Measured					
Tear Strength (N/mm)	3.2	6%	1.96	-45%	Not Measured					
Shore A Hardness	50	-4%	49	-6%	Not Measured					
G' (Pa)	7.11E+05	3%	8.43E+05	12%	7.36E+05	69%	5.18E+05	507%	2.11E+05	762%
G" (Pa)	5.14E+04	0%	5.95E+04	10%	5.97E+04	32%	4.67E+04	114%	6.48E+04	546%
tan delta	0.072	-3%	0.071	-2%	0.081	-22%	0.09	-65%	0.308	-25%
Cure rate (Pa/s)	1.79E+05	42%	2.47E+05	93%	1.51E+05	4%	8.24E+04	544%	2.89E+04	612%
Note					poor tear strength					

Figure 12. Rheological and mechanical data for SH 208-10Q to 50Q at optimal SH/VINYL ratio

Optimizing the SH/Vinyl ratio did give the maximum storage moduli. Notice that the G' of the sample with SH/VINYL = 3.05 increases by 12%. This shows that a greater SH/VINYL ratio is required in the MQT(SH) samples with more Q groups. In comparison to data measured at SH/VINYL=2.33, the G', G" and cure rate all increased at the optimal SH/VINYL ratio. The G' for SH 208-40Q and SH 208-50Q samples at these optimal SH/vinyl ratios are greater than 105 Pa and this indicates the sample is now properly cured.

Figures 11-12 shows that the sample toughness is not dictated by the amount of MQT(SH) (mercaptosilicone) in the formulation. Adjusting for optimal SH/VINYL ratio does not improve tensile strength, tear strength and Shore A hardness in SH 208-10Q and SH 208-20Q samples.

Also, increasing the SH/VINYL ratio does not always give a better storage modulus than the control Silmer SH 208 (with no Q group). Based on the rheological data measured at the optimal SH/VINYL ratio, adding up to 30% Q group on the MQT(SH) resin improves storage modulus and cure rate whereas any excess Q group reduces cure rate and crosslinking perhaps as a result of steric hindrance.

We next examine the amount of 65K. Recall that this diluent is also reactive and affects the final properties. In the following data, we add more 65K to the some of the formulations just examined and note the effect.

Component	-10Q w/+10% 65K		-20Qw/+5% 65K		-30Q w/+5% 65K	
SH 208-xQ	12.24%		16.44%		17.96%	
65K	55.81%		49.23%		51.71%	
VQ93T30/VIN65K	31.26%		33.67%		29.84%	
TPO-L	0.69%		0.67%		0.49%	
SH/VINYL ratio	2.46		3.05		3.63	
Property		**delta**		**delta**		**delta**
Tensile Strength (kPa)	2495.98	-21%	2450.47	-18%	2898.85	14%
Elongation (%)	122.1	44%	97.1	12%	130.64	40%
Total Energy (J/m)	209.75	23%	162.97	-6%	283.56	76%
Tear Strength (N/mm)	3.27	2%	2.67	36%	3.92	39%
Shore A Hardness	38	-24%	42	-14%	40	-2%
G' (Pa)	3.62E+05	-49%	5.40E+05	-36%	4.70E+05	-25%
G" (Pa)	2.49E+04	-52%	3.76E+04	-37%	3.66E+04	-26%
tan delta	0.069	-4%	0.07	-1%	0.078	0%
Cure rate (Pa/s)	1.35E+05	-25%	5.54E+04	-78%	1.21E+05	-22%
Appearance			more flexible			

Figure 13. Impact of adding 5-10% more 65K reactive diluent

Figure 13 shows that elongation, tear strength and twistability are all improved after adding 5-10 wt% more 65K. However, this does reduce hardness, tensile strength, storage modulus and cure rate. Thus, for tear strength and toughness improvement, no more than 5% linear high MW vinyl terminated siloxane (65K) can be tolerated.

Among the three samples compared, SH 208-30Q gives the highest tensile strength, elongation, total energy and tear strength after adding 5% more 65K.

Next, we examine the VTQ resin. This is the vinyl functional component that reacts with the mercapto groups. We look first at the M(V)/Q ratio. Two different VTQ samples VQ83T30 and VQ93T30 are evaluated in SH 208-30Q/VTQ/VIN system for rheological and mechanical properties. VQ83T30 has a M/Q ratio of 0.8:1 and VQ93T30 has a M/Q ratio of 0.9:1. In other words, more Q groups are present in VQ83T30. Both of these are evaluated at a SH/VINYL ratio of 3.63.

Component	M/Q=0.9	M/Q=0.8	M/Q=0.8 + 5 wt% 65K
SH 208-30Q	17.96%	17.60%	15.81%
65K	51.71%	52.09%	57.07%
VQT83-30/VIN65K	0.00%	29.80%	26.51%
VQ93T30/VIN65K	29.84%	0.00%	0.00%

TPO-L	0.49%	0.51%	0.62%	
Property				Delta
SH/VINYL ratio	3.63	3.63	3.62	0%
Tensile Strength (kPa)	2898.85	2587.3	3186.03	-23%
Elongation (%)	130.64	85.5	148.51	-74%
Total Energy (J/m)	283.56	149.77	387.83	-159%
Tear Strength (N/mm)	3.92	4.32	4.63	-7%
Shore A Hardness	40	49	42	14%
G' (Pa)	4.70E+05	5.97E+05	4.39E+05	26%
G" (Pa)	3.66E+04	3.60E+04	2.82E+04	22%
tan delta	0.078	0.06	0.064	-7%
Cure rate (Pa/s)	1.21E+05	1.73E+05	4.04E+04	77%
Appearance	very flexible, leaves no marks after twisting.	very flexible, leaves no marks after twisting.	very flexible, maybe marks after twisting	

Figure 14. Impact of M/Q ratio in VTQ component on 208-30Q

Figure 14 suggests that VQ83T30 has greater tear strength, hardness, storage modulus and cure rate than VQ93T30. The M/Q=0.8 material gives a more crosslinked and tougher resin than M/Q=0.9. However, it also gives less tensile strength, elongation, total energy under the area in comparison to VQ93T30. Similar to the results when changes were made to the MQT(SH) component, these formulations are improved by adding 5 wt% of 65K. This is expected when adding a chain extender.

We next evaluated the vinyl content in the 65K for SH/VTQ/VIN system. We prepared to different 65K products. The difference between these two batches is vinyl contents of 0.060% and 0.078% vinyl respectively. These were evaluated using the SH 208-30Q and VQT83-30 resins.

Component	**0.060% vinyl**	**0.078% vinyl**
SH 208-30Q	20.84%	21.04%
65K (0.060% vinyl)	42.64%	0.00%
65K (0.078% vinyl)	0.00%	42.50%
VQT83-30/65K	35.92%	35.86%
TPO-L	0.61%	0.60%
SH/VINYL ratio	3.63	3.63
Tensile Strength (kPa)	3571.56	4037.85
Elongation (%)	73.71	84.8
Total Energy (J/m)	209.13	238.75
Tear Strength (N/mm)	3.46	5.11
Shore A Hardness	59	57
G' (Pa)	1.05E+06	1.09E+06
G" (Pa)	7.46E+04	6.54E+04
tan delta	0.071	0.06

Cure rate (Pa/s)	1.83E+05	1.76E+05
Appearance	tears easily	very flexible, good twist

Figure 15. Impact of vinyl content in 65K component on 208-30Q

It is shown in Figure 15 that that higher vinyl content 0.075% 65K gives better tensile strength, tear strength and twist. The sample prepared with lower vinyl (0.060%) 65K (11906018) breaks immediately upon twisting whereas the 0.075% formula withstands a good twist.

Next we examine the vinyl content in the VTQ resin. Four analogous VTQ resins based on VQxT30 with different vinyl contents are evaluated in SH/VTQ/VIN system for rheological and mechanical properties. These samples have the same amount of T group and M/Q ratio. They are designated VQ91T30 (0.63% vinyl, 16200 cps); VQ92T30 (1.33%, 18000 cps); VQ93T30 (1.88%, 14600 cps); and VQ94T30 (2.49%, 14000 cps).

Component	VTQ 0.626% Vinyl	VTQ 1.33% Vinyl	VTQ 1.88% Vinyl	VTQ 2.49% Vinyl
SH 208-20Q	8.12%	12.44%	14.43%	16.53%
65K	25.87%	39.67%	46.07%	49.09%
VQxT30	65.31%	47.20%	38.80%	33.75%
TPO-L	0.71%	0.70%	0.69%	0.63%
SH/VINYL ratio	2.35	2.34	2.34	2.33
Properties				
Tensile Strength (kPa)	1924.43	4923.25	3278.78	not measured
Elongation (%)	113.88	95.8	79.65	
Total Energy (J/m)	115.58	248.89	166.22	
Tear Strength (N/mm)	3.12	3.54	3.59	
Shore A Hardness	27	46	52	
G' (Pa)	1.63E+05	4.61E+05	7.53E+05	7.73E+05
G" (Pa)	2.70E+04	4.67E+04	5.42E+04	4.47E+04
tan delta	0.166	0.101	0.072	0.058
Cure rate (Pa/s)	3.57E+04	8.04E+04	1.28E+05	2.79E+05

Figure 16. Impact of vinyl content in VTQ component on 208-20Q

It is observed in Figure 16 that as vinyl content increases in VTQ resin, storage modulus, tear strength, hardness and cure rate increase whereas elongation decreases. This indicates as expected that higher vinyl content in the VTQ resin results in higher crosslinking.

Hardness and tensile strength data indicate that VQ91T30 is too weak because of its low vinyl functionality. Hardness and tear strength data suggest VQ93T30 is the best among these 4 VTQ samples tested. Both VQ93T30 and VQ94T30 samples give good toughness and twist.

The above formulations were evaluated with more 65K than optimum to maximize tear strength. Recall that tear strength improves as 65K extender is increased. The summary of these improved preparations is shown in Figure 17 where 1.88% and 2.49% vinyl examples were improved by adjusting the SH/VINYL content.

Component	VTQ 0.626% Vinyl	VTQ 1.33% Vinyl	VTQ 1.88% Vinyl	VTQ 2.49% Vinyl
SH 208-20Q	8.12%	12.44%	13.14%	13.27%
65K	25.87%	39.67%	**51.13%**	**59.03%**
VQxT30	65.31%	47.20%	35.06%	27.12%
TPO-L	0.71%	0.70%	0.68%	0.59%
SH/VINYL ratio	2.35	2.34	2.34	2.29
Properties				
Tensile Strength (kPa)	1924.43	4923.25	3594.64	2861.09
Elongation (%)	113.88	95.8	108.63	128.49
Total Energy (J/m)	115.58	248.89	288.86	301.43
Tear Strength (N/mm)	3.12	3.54	**5.26**	**4.54**
Shore A Hardness	27	46	48	45
G' (Pa)	1.63E+05	4.61E+05	4.83E+05	5.11E+05
G" (Pa)	2.70E+04	4.67E+04	3.65E+04	3.00E+04
tan delta	0.166	0.101	0.076	0.059
Cure rate (Pa/s)	3.57E+04	8.04E+04	8.33E+04	2.30E+05
Appearance	soft	firm with okay tear	firm with good tear	firm with okay tear

Figure 17. Impact of vinyl content in VTQ component on SH208-20Q – maximal tear strength

The effect of the amount of T groups in VTQ resin is also studied in SH/VTQ/VIN system for better tear strength and toughness. These three samples have the same vinyl content in VQ but different amounts of T/Q groups from 0 to 50%.

Component	VQ92T0	VQ92T30	VQ92T30 +5% xs 65K	VQ92T50 +5% xs 65K
SH 208-20Q	10.15%	12.44%	11.25%	11.56%
65K	41.09%	39.67%	45.40%	46.52%
VQ92Tx	48.07%	47.20%	42.71%	41.24%
TPO-L	0.70%	0.70%	0.63%	0.68%
Properties				
SH/VINYL ratio	2.32	2.34	2.32	2.33
Tensile Strength (kPa)	5524.11	4923.25	4293.6	2816.47
Elongation (%)	87	95.8	111.49	105.43
Total Energy (J/m)	284.75	248.89	288.53	163.51
Tear Strength (N/mm)	4.9	3.54	3.46	3.17
Shore A Hardness	58	46	44	31
G' (Pa)	9.14E+05	4.61E+05	4.25E+05	2.22E+05

G" (Pa)	7.28E+04	4.67E+04	3.56E+04	1.68E+04
tan delta	0.08	0.101	0.084	0.076
Cure rate (Pa/s)	3.19E+05	8.04E+04	1.06E+05	5.27E+04
Appearance	Tough. Can be twisted. Elongation and tensile are better than numbers show b/c dogbones did not break at the center.	Firm, can be twisted without break	Break after twisting	Soft, break upon twisting

Figure 18. Impact of T group in VTQ component on SH208-20Q.

Figure 18 shows that the VTQ resin with 0 T groups gives the best rheological and mechanical properties. This is a tough material with excellent tear strength at 4.9 N/mm, fast cure rate and moderate hardness. The other samples also indicate that introducing T group to the VQ resin lowers both mechanical and rheological properties. This is likely again a steric hindrance effect. However, T groups are useful as an aid for viscous material, because including T groups in the VTQ resin lowers the viscosity.

Next, we evaluate the effect of vinyl content in VQ resin without T groups. We prepare three VQ resins which the same M/Q ratio and with slightly different ratios of V/Q . VQ92(1.07% vinyl); VQ93(1.62% vinyl); VQ94 (2.15% vinyl). Reaction with SH208-30Q is the basis for the evaluation.

Component	**1.07% vinyl**	**1.62% vinyl**	**2.15% vinyl**
SH 208-30Q	10.56%	14.88%	18.54%
65K	54.86%	52.33%	49.97%
VQx	33.82%	32.02%	30.74%
TPO-L	0.76%	0.77%	0.75%
Properties			
SH/VINYL ratio	3.21	3.23	3.21
Tensile Strength (kPa)	3957.38	1642.08	2907.32
Elongation (%)	156.51	65.09	75.2
Total Energy (J/m)	550.25	79.41	185.8
Tear Strength (N/mm)	6.95	3.8	4.84
Shore A Hardness	44	50	56
G' (Pa)	4.71E+05	7.20E+05	1.26E+06
G" (Pa)	3.47E+04	4.35E+04	6.90E+04
tan delta	0.074	0.06	0.055
Cure rate (Pa/s)	1.21E+05	1.70E+05	1.84E+05
Appearance	Very tough material, very flexible, white opaque	breaks upon twisting	breaks upon twisting

Figure 19. Impact of vinyl content in VQ component on SH208-30Q

Figure 19 shows that Silmer VQ92 (1.07% vinyl) gives the best tear strength, 6.95 N/mm, among all samples tested in this project. This formulation also has excellent elongation, good tensile strength and suitable hardness for 3D UV printing.

It is also observed that higher vinyl content in VQ gives greater hardness, storage modulus and cure rate.

We are able to do UV cured 3D printing with the VQ92 (1.07% vinyl) formulation show in the first column of Figure 19. The materials were whit, opaque with good mechanical properties. Additional optimization of this formula especially to improve breakage of the additive part, is our next step.

Conclusion

Regarding the VQT(SH) resin, the lower amounts of Q groups give good performance, using more Q than the SH 208-30Q results in decreased properties. SH 208-20Q and SH 208-3Q gave the best properties.

Regarding the VTQ resin, M/Q ratios of 0.8 are better than 0.9. We did not explore the boundary of this trend, i.e. would M/Q of 0.7 be even better. In our experience this M/Q ratio is not stable enough for commercial use.

Introducing T groups in the VTQ resin provides lower viscosity as intended, but hardness and toughness suffer quickly. In fact, the VQ (T=0) resins performed the best – independent of viscosity considerations.

The stoichiometry of SH/vinyl is a critical parameter. Too much VQ resin can hurt properties. For the VQT(SH) resins specified above, up to about 17% VQ resin is positive, beyond that properties are lost.

Regarding the 65K, divinylsilicone chain extender, increasing the amount of this product gives elongation and tear strength improvements but this comes with a large reduction of hardness and tensile strength. No more than 5% excess is recommended.

Increasing the vinyl content of the 65K gave improved tensile strength, tear strength and flexibility.

We did isolate an optimum formulation for 3D printing and were able to print multiple additive parts with good properties. We used an UltiMaker 2+ FMD from Sturctra3D for 3D printing of the SH formulations due to the relatively high viscosity. This is a thermal cured printer so we attached a UV lamp to the print head to effect UV curing.