Novel Acrylated Urethane Silicone Polymers and Formulations to Increase Elongation in 3D Printing Resins.

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ABSTRACT

In condensation cured systems, reactive silicones provide up to 300 % elongation, but in energy cured acrylate systems, the reactive silicones typically give low elongation of only 5%. The new materials have shown elongation as high as 45%.

To increase the flexibility and elongation of silicone acrylate resins, we have explored both a formulated and modified polymer approach to include both urethane and silicone polymers into the matrix. These will be cured under UV and SLA 3D printed (UV Laser) conditions and their physical and mechanical properties will be evaluated in the context of SLA 3D printing.

INTRODUCTION

Being a silicone company, we generally approach problems by developing and evaluating new silicone polymers. We have shown in past papers that elongation, flexibility, chemical resistance and low temperature impact resistance are improved with the inclusion of silicones into cured organic resin systems [1].

Typically, toughness is significantly increased and maximized at an ideal use level. Hardness is decreased with increasing silicone content. These general learnings tend to cross systems, but we have noticed an aberration with elongation. In condensation cured systems, elongation is typically about 300% for pure silicone resins. For silicone/ organic hybrid resins systems we see elongation of around 100% [1].

However, we repeatedly observe that for UV cured acrylated silicones the elongation is as low as a few percent. We believe this is due to the different curing mechanism of acrylate moieties. The silicone is incorporated as cross-sections of the main polymer chain rather than becoming part of the main chain as it does in epoxy, polyester and similar condensation cured polymer systems.

To explain this better, consider the reaction of a di-functional silicone into a condensation cured polymer as exemplified in Figure 1 with an elementary di-epoxy/ diol scheme. When R_2 = hydroxyalkyl silicone, the resultant polymer includes the highly flexible, low T_g (soft) silicone polymer in the main chain. It therefore makes sense that much of the silicones inherent flexibility is passed through to the hybrid polymer network.

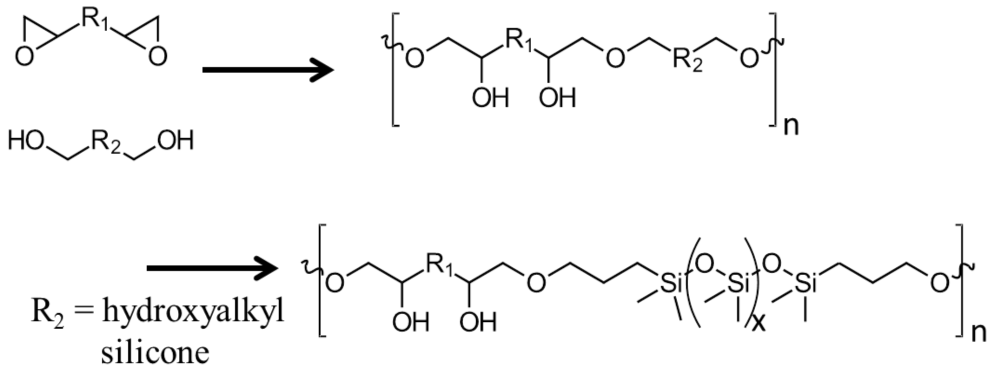

Figure 1: Silicone modified epoxy resin

We have done this reaction many times with epoxies and with polyesters and other condensation type polymers. Elongation is typically increased by about 100% as shown in Figure 2. This slide from our 2015 Waterborne Symposium presentation [2] shows elongation as a function of percent silicone (x axis) in an epoxy/ silicone hybrid polymer. Notice also that the total energy to break is dramatically increased over the organic polymer alone reaching a maximum before dropping off.

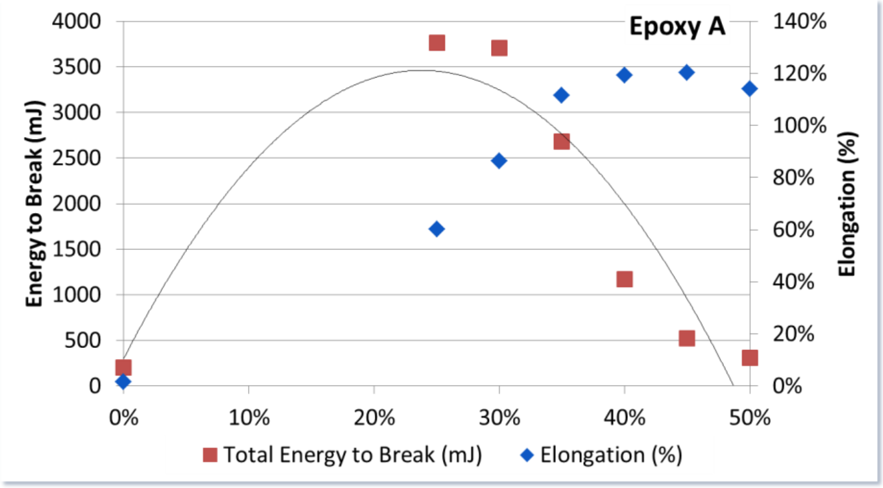

Figure 2: Elongation in epoxy silicone hybrids

Conversely with free-radical polymerization, exemplified in Figure 3 using an elementary acrylate cure, reaction occurs at the olefin only. This effectively builds the main chain but the silicone is not incorporated into the backbone but rather is pendant to it. If one further envisions a di-functional alkyl acrylate silicone, it would react at both ends, giving some silicone cross-polymerization between the main chains. We believe this is the source of the moderate elongation which we see in UV or free radical cured formulations when reacting acrylate silicones and organic acrylate resins.

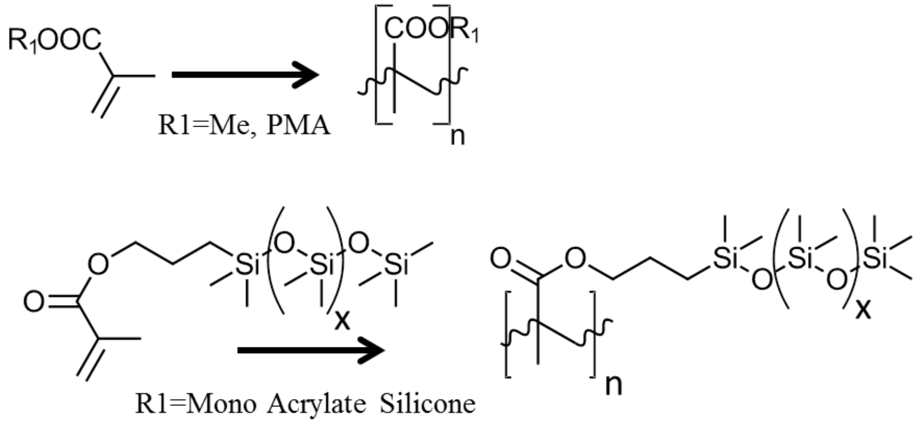

Figure 3: Acrylate polymerization

EXPERIMENTATION

Viscosity Measurement

Viscosity was measured using Brookfield Viscometer Model# DV-III. Each test sample was collected and placed into the viscometer. For each sample, the RPM of the motor was set at speeds of 5, 7, and 9 rpm. An average of these values was reported as the final viscosity measurement in units of centipoise (cP).

Rheological Properties Measurement

The rheological properties of G', G'' and Tan δ of each test sample was also measured using a TA Rheometer AR-G2 equipped with 150 mW/cm^2 LED UV lamp. A sample was collected and placed into a rheometer which used UV or thermal curing to measure the rheological properties of G', G'', and Tan δ.

Tensile Strength and Elongation

The dumbbell samples for the INSTRON measurements were prepared by pouring the liquid formula into a Teflon mold and heating at 110°C for 30 minutes. Once the dumbbells were molded and cooled to room temperature, they were measured for tensile strength and elongation properties using the INSTRON 1122 and ASTM D412 Die C standard test method.

In the case of the 3D printed formulation, the dumbbell was printed using Pegasus Touch 3D Printer from Full Spectrum Laser with RetinaCreate ASTM D412 Type C program. Approximately, 130g of each sample was collected and poured into the vat which was to be inserted into the 3D printer. It was ensured that motor homing and appropriate levelling was established before initiating the device. Using the 3D printer program, two dog-bone shapes were created which were then collected and placed under a UV lamp with nitrogen gas for 30 minutes to ensure compete cure.

Hardness Measurement

After tensile strength and elongation measurements were collected, the dumbbell samples were collected and hardness was measured using a Type A or D Durometer. Three hardness measurements were collected and the average was reported as the final value.

Formulation

The formulations are very basic, unoptimized formulations which are designed to show differences in the silicone products evaluated not necessarily to meet any particular property.

Silicone Structures

A new class of acrylated silicone urethane has been developed. Di-functional linear silicones modified with organic isocyanate functional groups on the termini were reacted with di-functional linear silicones modified with organic hydroxyl groups. Both of these NCO and OH di-functional silicones are available commercially from Siltech.

The reaction scheme is shown in Figure 4. An excess of dihydroxyl functional polymer is used to keep the value of z low and to provide terminal OH groups (R=H). This polymer is then acrylated to make R=acrylate.

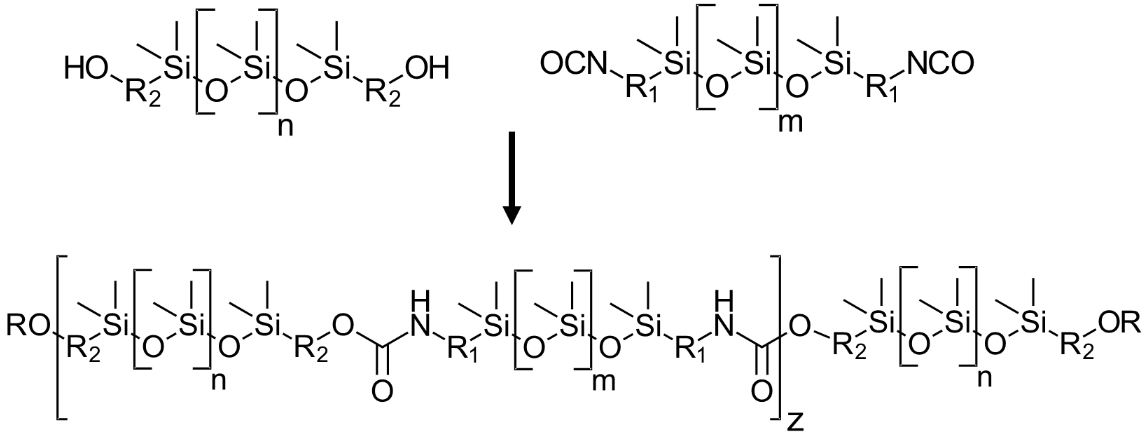

Figure 4: Novel Silicone Urethane Hybrid Polymers

The four structures used in this work and their base properties are shown in Table 1. The value of m was held constant and n was varied from 10 to 25 and 50. In the fourth structure, labeled UACR Di-1010, n is equal to 10 but the R_2 was modified to increase solubility.

Table 1 Novel PU Silicones

Silmer UACR	**UACR Di-10**	**UACR Di-1010**	**UACR Di-25**	**UACR Di-50**
Appearance, 23°C	Solid. Melts at~ 40°C	Clear to hazy liquid	White pasty liquid	White pasty liquid
Viscosity, 23°C	Solid	65,500 cps	50,000 cps	128,000 cps

RESULTS

The four hybrid silicones were evaluated in acrylate functional resins, AME 6001 T-25 and AME 6001 INF-35 from Ashland Chemical. In these very tough resins, the extension is small but one sees improvement with increasing use levels of the products. Likewise, the hardening increases as the use level goes up.

The formulation is shown in Table 2 and the results are shown in Table 3 and Table 4.

Table 2: Formulation with acrylate functional resins.

Ingredient	Control	1%	2.5%	5%	9%
Hybrid Silicone	0.00%	0.97%	2.40%	4.69%	8.96%
Resin	98.36%	97.40%	96.00%	93.75%	89.55%
DMA	0.15%	0.15%	0.14%	0.14%	0.13%
MEKP	1.48%	1.46%	1.44%	1.41%	1.34%
Dabco T-12	0.02%	0.02%	0.01%	0.01%	0.01%
total	100.00%	100.00%	100.00%	100.00%	100.00%

Table 3: Results with AME 6001 T-25

		Liquid Clarity	**Solid Clarity**	**Average Tensile Strength (kPa)**	**Max Tensile Strength (kPa)**	**Average Extension (%)**	**Max Extension (%)**	**Average Energy/ Thickness (J/m)**	**Tear Strength (N/M)**	**Flexure Stress (mPa)**	**Flexure Strain (%)**	**Bending Modulus (mPa)**	**Hardness (Shore D)**
Control		clear	clear	8129	10773	1.3	1.3	very low	12.9	35.2	4.5	2130	48
UACR Di-10	1%	hazy	hazy	11700	12523	2.6	3.6	very low	26.0	58.4	3.9	1739	48
	2.5%	opaque	opaque	10482	10878	1.9	2.6	very low	29.3	64.9	7.0	1786	52
	5%	opaque	opaque	9797	10185	1.8	2.1	very low	29.8	69.3	6.0	1719	55
	9%	opaque	opaque	9028	10071	1.6	2.0	very low	29.7	77.0	5.5	1700	55
UACR Di-25	1%	hazy	hazy	13775	17026	3.2	4.5	very low	19.8	64.6	5.3	1569	52
	2.5%	opaque	opaque	10189	13189	1.9	1.9	very low	31.9	85.3	5.5	1893	55
	5%	opaque	opaque	9428	12365	1.6	1.7	very low	26.7	73.5	6.0	2122	58
	9%	opaque	opaque	7251	9045	1.4	1.5	very low	24.7	59.6	6.6	1340	60
UACR Di-50	1%	opaque	opaque	13794	22621	1.6	2.0	very low	23.2	55.2	4.9	2154	45
	2.5%	opaque	opaque	12705	12808	1.9	2.0	very low	53.2	52.5	5.2	1730	46
	5%	opaque	opaque	11058	12338	1.6	1.6	very low	52.7	51.3	5.3	1431	48
	9%	opaque	opaque	10190	10607	1.5	1.6	very low	50.6	50.8	5.6	1340	50
UACR Di-1010	1%	clear	clear	3874	4962	0.8	0.9	very low	20.4	48.9	4.8	1243	46
	2.5%	clear	clear	5001	6765	1.0	1.2	very low	36.3	88.3	8.6	1625	49
	5%	clear	clear	5134	6935	1.5	1.6	very low	25.9	90.8	8.2	1664	52
	9%	clear	clear	6963	8142	1.5	1.7	very low	22.8	91.3	7.4	1793	53

Table 4: Results with AME 6001 INF-35

		Liquid Clarity	Solid Clarity	Average Tensile Strength (kPa)	Max Tensile Strength (kPa)	Average Extension (%)	Max Extension (%)	Average Energy/ Thickness (J/m)	Tear Strength (N/M)	Flexure Stress (mPa)	Flexure Strain (%)	Bending Modulus (mPa)	Hardness (Shore D)
Control		clear	clear	5351	5362	0.96	1.09	very low	12.0	49.4	4.1	2130	51
UACR Di-10	1%	translucent		6664	6739	1.66	1.73	very low	20.6	70.7	5.1	1648	50
	2.5%	hazy	hazy	8390	10605	1.66	2.04	very low	27.0	74.4	7.9	1341	52
	5%	hazy	hazy	9334	10776	1.59	1.60	very low	30.4	64.2	7.6	1124	53
	9%	opaque	opaque	11178	13564	1.68	1.81	very low	34.6	60.3	7.6	1120	55
UACR Di-25	1%	translucent		5394	5464	1.42	1.58	very low	17.8	67.5	6.2	1910	53
	2.5%	opaque	opaque	5543	5863	1.35	1.35	very low	18.2	62.8	6.2	1852	54
	5%	opaque	opaque	6876	8468	1.34	1.34	very low	18.6	53.6	6.2	1506	55
	9%	opaque	opaque	7656	9757	1.34	1.34	very low	21.2	43.5	6.1	911	56
UACR Di-50	1%	opaque	opaque	4714	4848	1.54	1.7	very low	20.4	73.7	4.1	2352	40
	2.5%	opaque	opaque	7660	9371	1.68	1.77	very low	26.1	61.8	5.2	1447	45
	5%	opaque	opaque	7919	11964	1.78	1.78	very low	27.0	53.0	5.1	1364	46
	9%	opaque	opaque	9438	14624	1.8	2.1	very low	32.3	47.4	5.0	1095	47
UACR Di-1010	1%	clear	clear	3980	4129	1.15	1.23	very low	22.5	45.8	6.5	1425	51
	2.5%	clear	clear	4511	5118	1.47	1.59	very low	25.6	67.4	6.7	1329	53
	5%	clear	clear	7427	7569	1.96	2.25	very low	33.5	71.9	6.8	1321	55
	9%	clear	clear	11751	12117	2.05	2.53	very low	33.1	62.9	7.2	1095	61

In a different type of system, which we designed to be very flexible for 3D printing, we compared three of these new materials to two standard acrylate functional silicone polyether products. This in house [3] developed formulation uses Laromer resins from BASF and SR833S from Sartomer. The formulation is shown in Table 5 and the results in Table 6.

Table 5: Formulation of UV cured 3D printer example.

Ingredient	Level
Silicone	17.62%
UA 9072	30.84%
UA 9033	28.63%
UA 19T	0.00%
V-Cap	20.93%
TBCH	0.00%
SR833S	0.00%
TPO-L	1.98%
Total	100.00%

Table 6: Results for of UV cured 3D printer formulation.

	Viscosity (cPs)	G' (MPa)	G" (MPa)	Tan Delta	Cure Rate (kPa/s)	Hardness Shore A	Ave Tensile Strength (kPa)	Max Tensile Strength (kPa)	Average Elongation (%)	Max Elongation (%)	Average Unit Energy (J/m)	Max Unit Energy (J/m)	Tear Strength (N.mm)	Clarity (1-10)
UACR Di-10	4333	8.13	3.21	0.39	52	85	7599	8695	27.3	27.4	293	311	35.2	9
UACR Di-50	5700	5.02	1.67	0.33	34	80	6211	6620	37.6	45.3	321	356	48.3	2
UACR Di-1010	4710	6.05	2.1	0.35	44	82	5512	5512	46.1	46.1	309	309	26.1	5
ACR D208	1095	18.76	7.02	0.37	197	85	2837	2837	10.2	10.2	39	39	31.6	9
ACR E608	1400	11.12	1.9	0.17	77	40	9450	9450	18.9	18.9	224	224	31.3	6

CONCLUSIONS

The new products are high in molecular weight and not entirely soluble in the systems, as shown by the clarity results. While some interesting results are shown, the materials are difficult to work with in normal coatings systems and do not provide exceptional results.

The tensile strength of the AME 6001 INF-35 resin is significantly improved with the hybrid silicone urethane materials. This is maximized with the UACR Di-1010 at the highest use level. The other AME resin only shows this increase in tensile strength with the UACR Di-1010.

Both of these resins also show a significant increase in tear strength. In the INF-35 there is a clear dose response, but in the T-25 the effect is seen at low levels and holds as usage level is increased. The hybrid polymers work similarly with the exception that the UACR Di-50 shows a strong advantage in tear strength with the T-25 resin.

Surprisingly, hardness seems to be increased with the use of the hybrid polymers which is the opposite of what is normally seen. The magnitude of the effect is small enough that it may not be significantly different from the control. However, another and perhaps more interesting way to state this is that hardness is not reduced as it is with other reactive silicones.

Elongation appears to be improved with the new polymers and shows a dose response. However, these resins are designed to minimize extension and the effect is again so small that it is unconvincing.

Finally examining the 3D printed formulation, which we spent significant effort optimizing for maximum elongation [3] achieving 10-20%. Recall condensation cured systems provide about 100% elongation. All three of the hybrid polymers evaluated in this system showed much higher elongation than the reactive silicone controls. The UACR Di-1010 gave 46% elongation which we are very satisifed with for a free-radical system.

Hardness and strength seem to be retained with these new products in this system as well.

REFERENCES

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