Acrylated Silicones Suitable for SLA 3D Printing

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Abstract
Two types of acrylated silicones will be cured under UV and SLA 3D printed (UV Laser) conditions. They will be cured with organic acrylated polymers. Their physical and mechanical properties will be evaluated in the context of SLA 3D printing.

Introduction

In the last few years, 3D printing has been getting a lot of interest and press. 3D printing has seen commercial success in Healthcare[i], Aerospace, Jewelry, and other niches.

The two major types of 3D printing use respectively heat from a laser to melt the resins or UV light from a laser to cure the resin. In coatings we would call these processes thermoplastic and “radiation cured” approaches.

The thermoplastic types are often called FDM (Fused Deposition Modeling) or SLS (Selective Laser Sintering). The former uses a wide variety of thermoplastics and is the type available today for hobbyists or the DIY market.

The UV cured printers, generically termed SLA, are able to deliver much more detail to a printed article than the thermoset type. This fact often makes them the preferred approach.

One big barrier today to large scale adoption of 3D printing techniques on commercial manufacturing scales is the materials. Although, the SLS type can use ceramics or metals to make more durable materials, most of the market is made from plastics. These materials do not always have the strength, elongation, tensile strength, etc. for the application.

In this paper, we explore the ability of UV cured acrylate functional silicones to modify the properties of existing UV cured resins. Silicones increase flexibility and impact resistance, while often sacrificing hardness.

Experimental and Methodology:

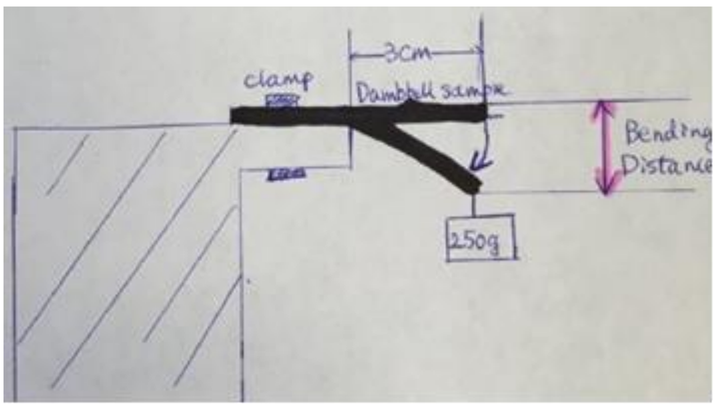
The overall design is to evaluate multiple acrylate functional silicones at 0-40% use levels, mainly in 10% increments, in several UV cured 3D printing resin systems. These were printed into a standard dumbbell shape using either ASTMD638_specmen.stl or RetinaCreate

ASTM D412 Type C programs with an SLA 3D Printer, Pegasus Touch, purchased from FSL3D. Said dumbbell was evaluated for mechanical properties with an Instron 1122.

Some properties were evaluated from inspection and scored from 1-5. For example, Tackiness was evaluated this way with 5 being the tackiest.

For more practical evaluation of the flexibility, we also performed a bending test where deformation is measured at a given extension and weight. One end of the dumbbell sample was fastened on bench top with 3 cm overhang. A 250 grams weight was hung on the edge of the dumbbell sample. The bending distance was measured vertically from the end of the bending dumbbell to the horizontal line of the bench. See Figure 1.

Figure 1: Bending test



The silicones used were linear, di-functional materials and pendant multifunctional materials. The linear materials are expected to increase elongation and flexibility and the multi-functional materials are expected to increase cross-link density to help hardness and strength. See Table 1 for details.

Table 1: Acrylated silicone information:

Name	Type	Equivalent Weight
Lin 650	Linear Di-functional	650
Lin 1000	Linear Di-functional	1000
Lin 1200	Linear Di-functional	1200
Lin 2500	Linear Di-functional	2500
Pen 300	Multi-Functional	300
Pen 600	Multi-Functional	600
Pen 1000	Multi-Functional	1000

We prepared Soft Formulation 1, a relatively soft material, according to Table 2. Hard Formulation 1 was an in-house prepared proprietary formulation. Hard Formulation 2 was the resin as supplied by 3D printer manufacturer FSL3D

Table 2

	5%	10%	20%	30%
Sartomer CN 991	8.40%	7.96%	7.07%	6.18%
Laromer UA-9072	47.08%	44.58%	39.61%	34.64%
Laromer LR-8887	34.40%	32.57%	28.94%	25.31%
Sartomer SR833S	3.91%	3.70%	3.29%	2.88%
Silicone Acrylate	5.00%	10.04%	20.07%	30.10%
TPO	1.04%	0.98%	0.87%	0.76%
Silmer ACR Di-10	0.17%	0.17%	0.15%	0.13%
Total	100.00%	100.00%	100.00%	100.00%

Results:

In the soft formulation 1, which is relatively soft and tacky, the inclusion of reactive silicones has a strong impact on several mechanical properties. Referring to Chart 1, the linear di-functional materials provide a strong increase in flexibility. The highest molecular weight version of this, Lin 2500, increases tackiness as well. The one multifunctional material evaluated in this test increases flexibility and significantly reduces tackiness.

One can see in Charts 2 and 3, that the maximum energy, which correlates to strength, is highest for the linear, di-functional material with an equivalent weight of 1000 gm/mol. Elongation is improved in all but is maximized for the highest equivalent weight material, Lin 2500.

Chart 1: Flexibility and Tack in Soft Formulation 1

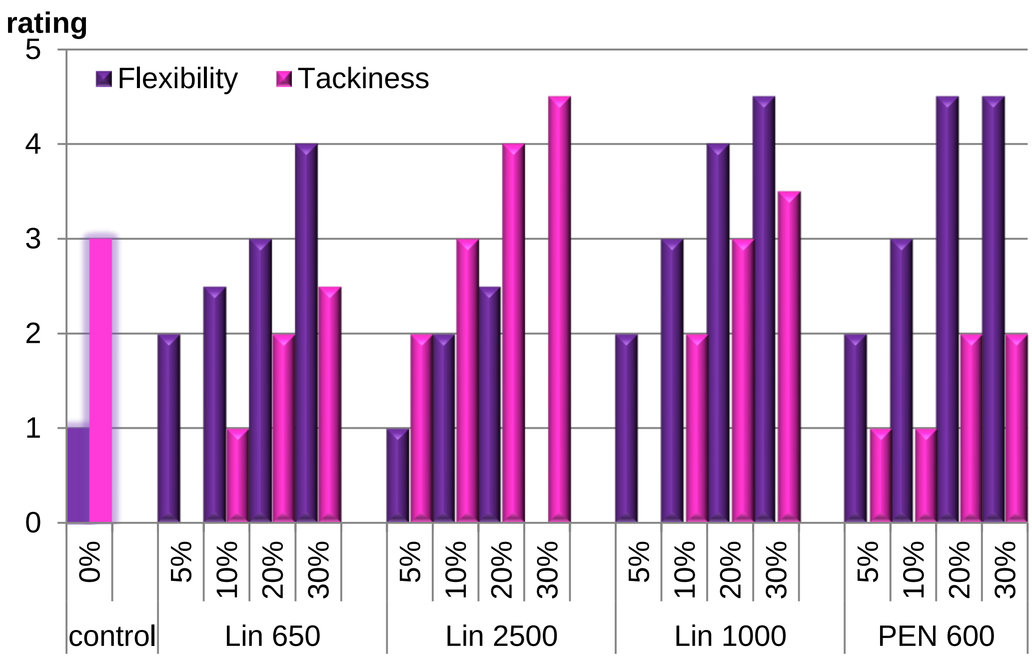


Chart 2: Elongation and Strain in Soft Formulation1

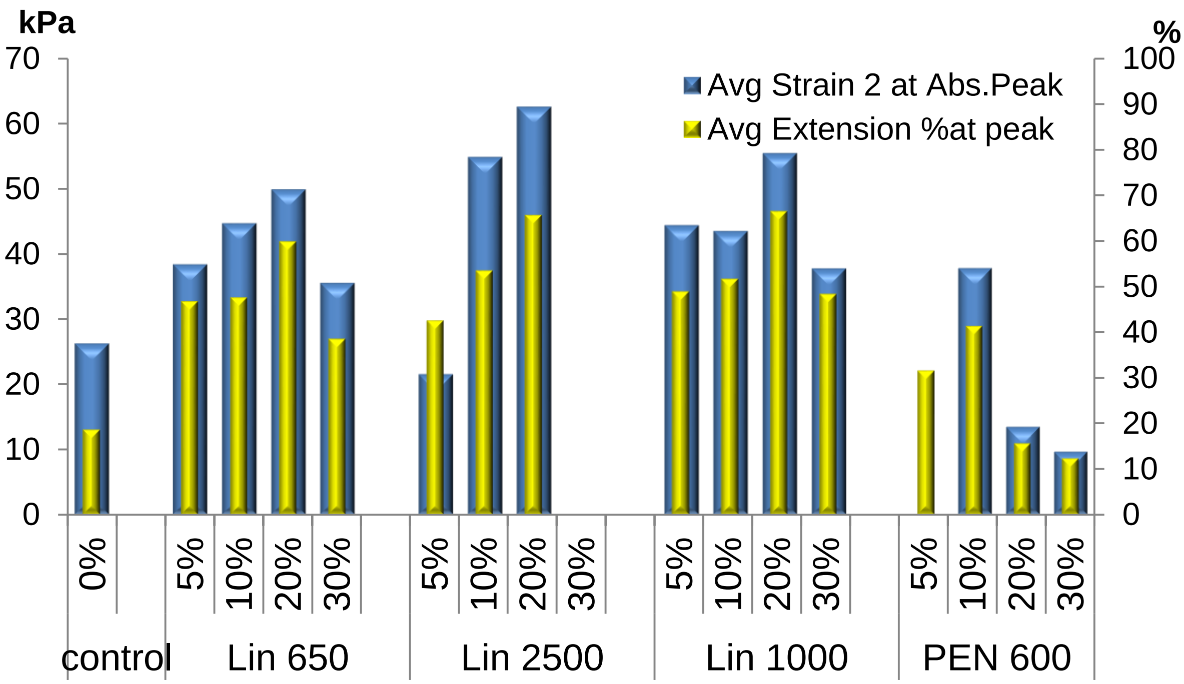
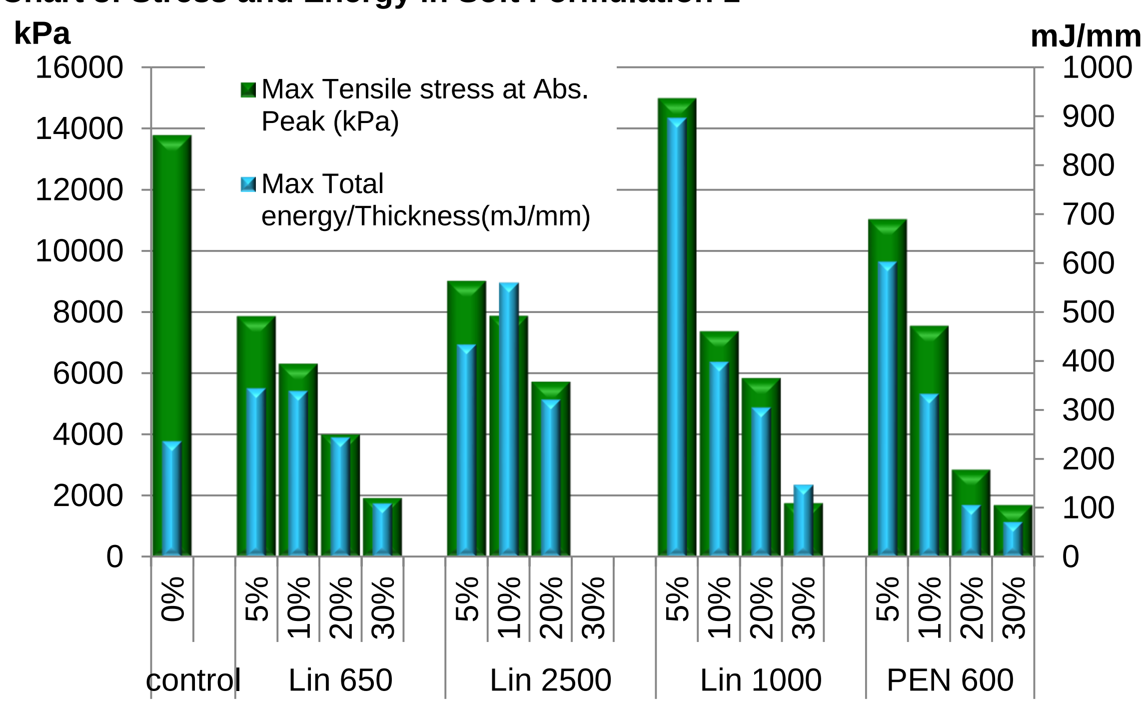


Chart 3: Stress and Energy in Soft Formulation 1



Next we screened several acrylated silicones in hard formulation 1, an in-house formula. This formulation is so hard that the control without silicone is too brittle to be measured. All of these improved flexibility. Charts 4 and 5.

Chart 4: Tensile Strength in Hard Formulation 1

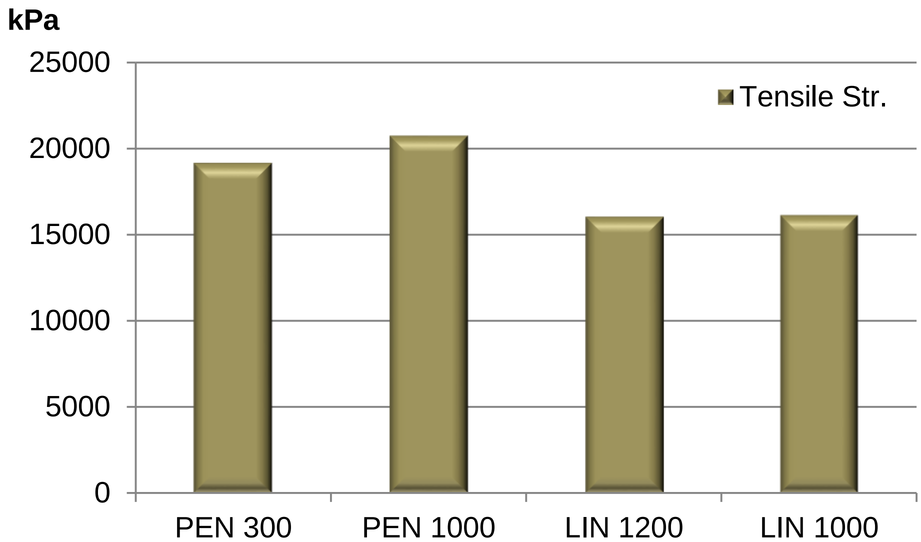
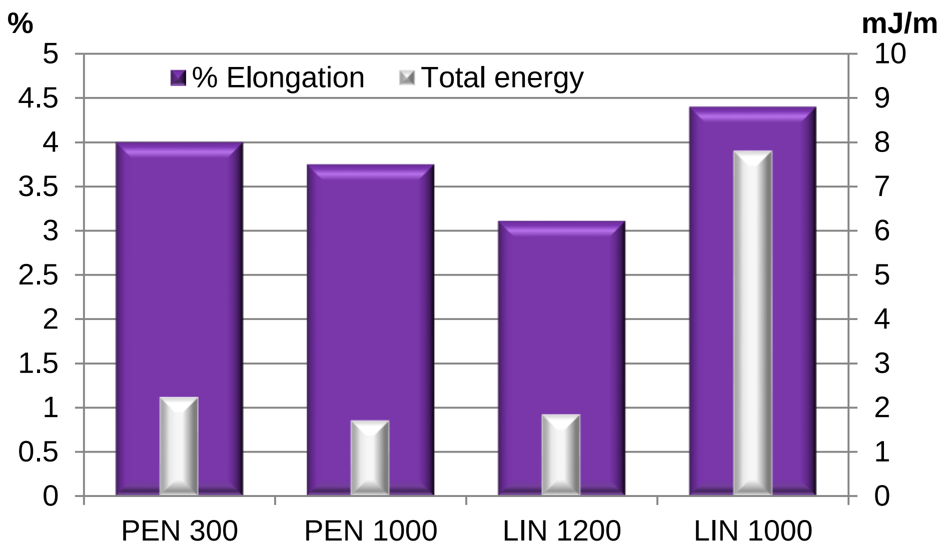


Chart 5: Elongation and Energy in Hard Formulation 1



In a harder, commercial formulation supplied from the printer manufacturer, one silicone which is multi-functional and has an equivalent weight of 300 is assessed at five use levels. In this simplistic example, one can readily see that as more silicone is used, hardness and strength are lost but elongation and flexibility are replaced. Charts 6 and 7 review the data for this hard formulation 2.

Chart 6: Elongation and Bending in Hard Formulation 2

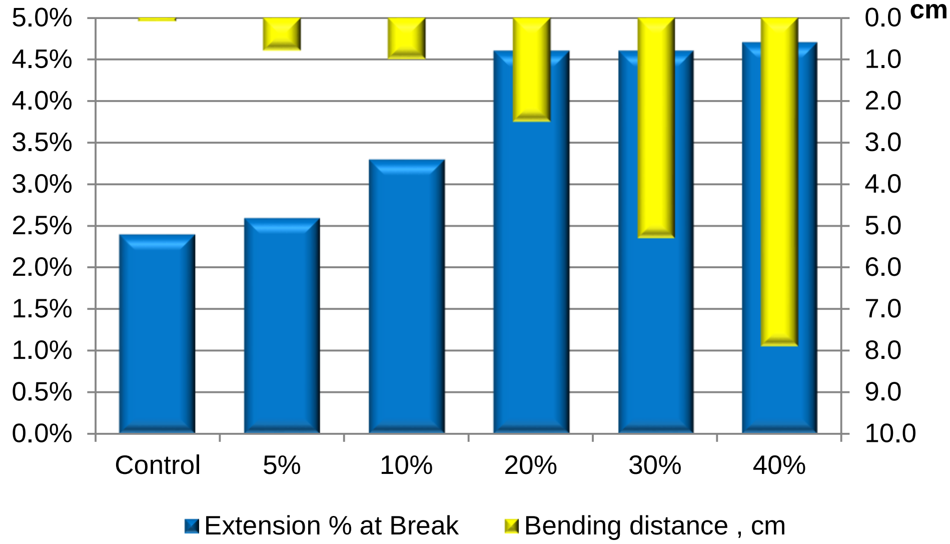
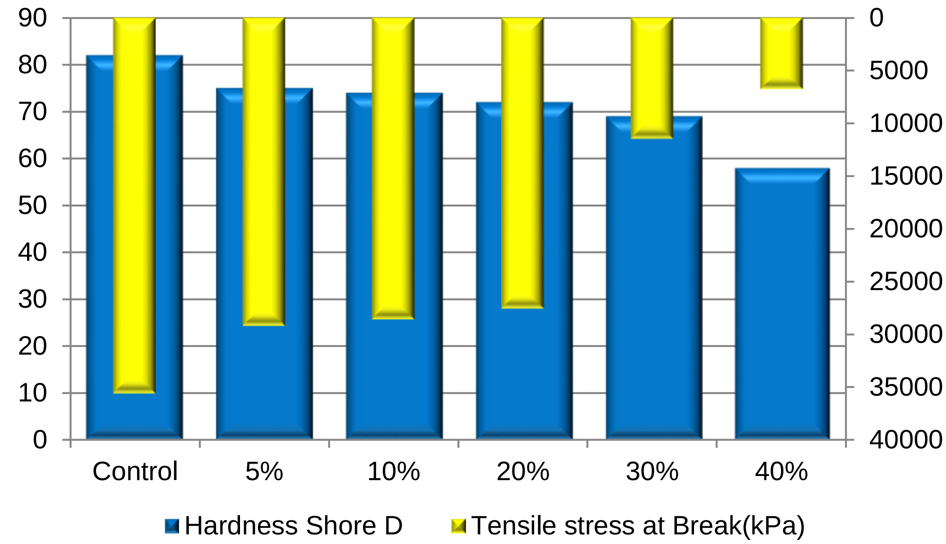


Chart 7: Stress and Hardness in Hard Formulation 2



The same commercial system hard formulation 2 was used to screen three silicones at 3 levels. Charts 8 and 9.

Chart 8: Stress and Hardness vs. Use Level in Hard Formulation 2

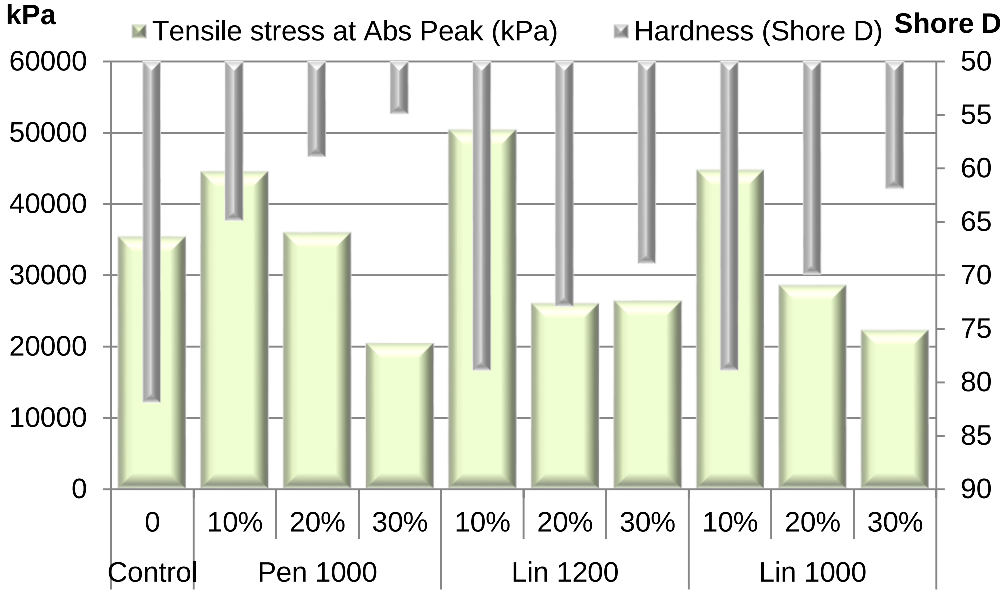
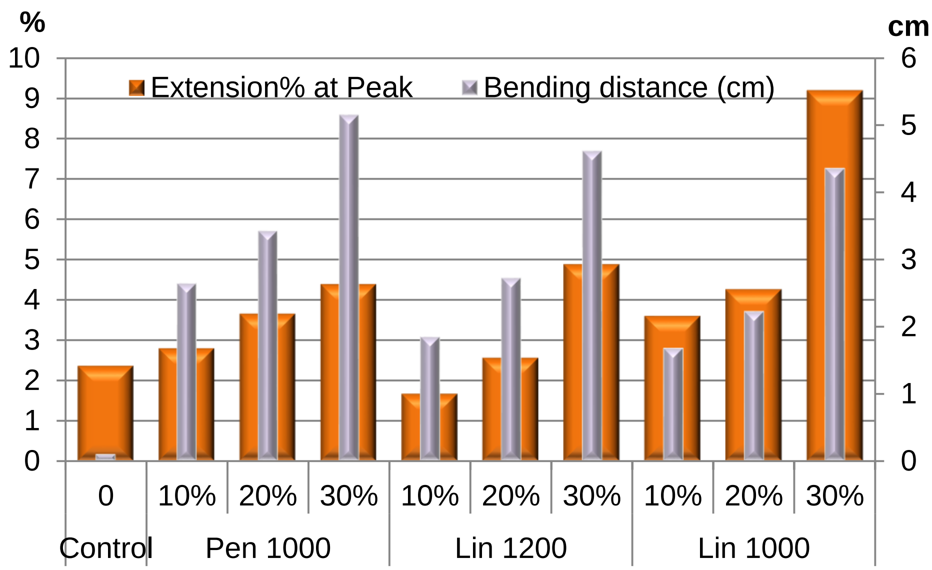


Chart 9: Elongation and Bending vs. Use Level in Hard Formulation 2



Summary

These early 3D resin formulation attempts were either too soft or too tacky to obtain proper readings. This is why in some cases we report maximum values and in others average values. However the trends we see are consistent with what we have seen when reacting these silicones in other contexts[ii]

The introduction of acrylated silicones into these 3D printing resins causes an increase in elongation and flexibility as measured with an Instron and bending test. The energy and strength are also increased.

Hardness is lost in these examples. We have been able to offset this loss of hardness in other systems by using the silicone as a cross linker.[iii]

Dose response is strong and linear in the cases of elongation and hardness. In the case of breaking strength or toughness we have seen this dose response curve to have a maximum value[iv], which we see in many of the examples herein.

The results we are most comfortable with are those with the commercial resin as the base. This system gave data that was very reliable and consistent with the expected effects.

Future work will focus on better formulated systems and exploring cross-linked silicone systems to maintain hardness while increasing flexibility and impact resistance.

References:

[i] http://www.eos.info/press/customer_case_studies/fhc

[ii] Ruckle,R.E., Cheung,S.T.; *Properties of Silicone Modified UV Cured Acrylate and Epoxy Coatings Films*. Proceedings of Waterborne Symposium, **2013**

[iii] Ruckle,R.E., Cheung,S.T.; *A Structure Property Study of Epoxy Resins Reacted with Epoxy Silicones*. Proceedings of Sampetech, **2015**

[iv] Ruckle,R.E., Cheung,S.T.; *Properties of Silicone Modified UV-Cured Acrylate and Epoxy Coatings Films*. UV/EB Technology **2015** issue 1, pp 34-43