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Peroxide cure study
in HCR silicone

Thermoplastic-silicone elastomer composites
production by multi-component injection molding

Polyfarnesene branched butyl rubber:
An efficient, sustainable processability solution

Substitutions for specialty bases
in medical silicones

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ACS Events, page 56

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Contents

Vol. 268, No. 3 June 2023

Features

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Departments

Substitutions for specialty bases in medical silicones

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The silicone shortage highlights the risk of overreliance upon a single supplier of specialty bases, especially when comparable off-the-shelf offsets do not exist. The techniques and approaches to modifying the properties of silicones are well known, but it is important to take a systematic approach regarding potential substitutions. This article describes how Specialty Silicone Products (SSP) identifies formulations with a specific combination of properties, and uses various fillers, initiators, cure mechanisms and other additives, such as functional polymers. Applications include USP Class VI medical silicones.

Initial trials

Initial trials for current work began with the addition of varying amounts of fillers, initiators and other additives. Plots showing the various properties as a function of loading are shown in figure 1 (Minusil, 5U quartz filler) and figure 2 (di(2,4-dichlorobenzoyl) peroxide or DCLBP initiator). The observed trends were neither new nor unexpected; however, the results helped established loadings that were used to target compound durometers of 50A.

Experimental details

Samples were formulated at the laboratory scale on either an 8" two-roll mill, or the combination of an 0.25 gallon laboratory scale dough mixer and an 8" two-roll mill. For highly filled formulations, the filler was combined with the silicone base in the dough mixer before catalysts and any additives were added to the two-roll mill. ASTM 6" by 6" test slabs were press cured at 177°C for 10 minutes and post-baked for 4 hours at 200°C, except for specific samples that used alternate peroxides requiring different press

Figure 1 - properties as a function of filler content using Minusil, 5U

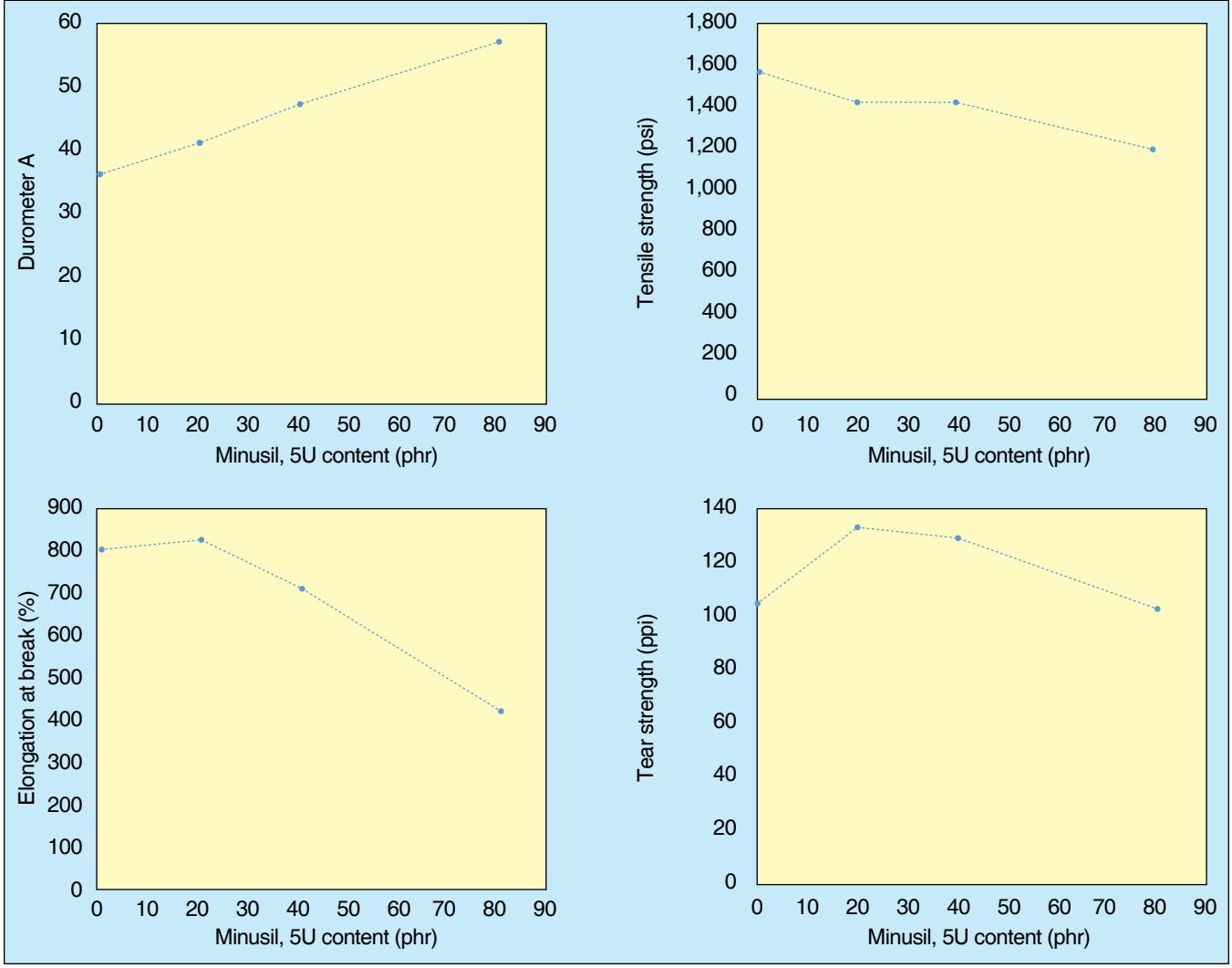
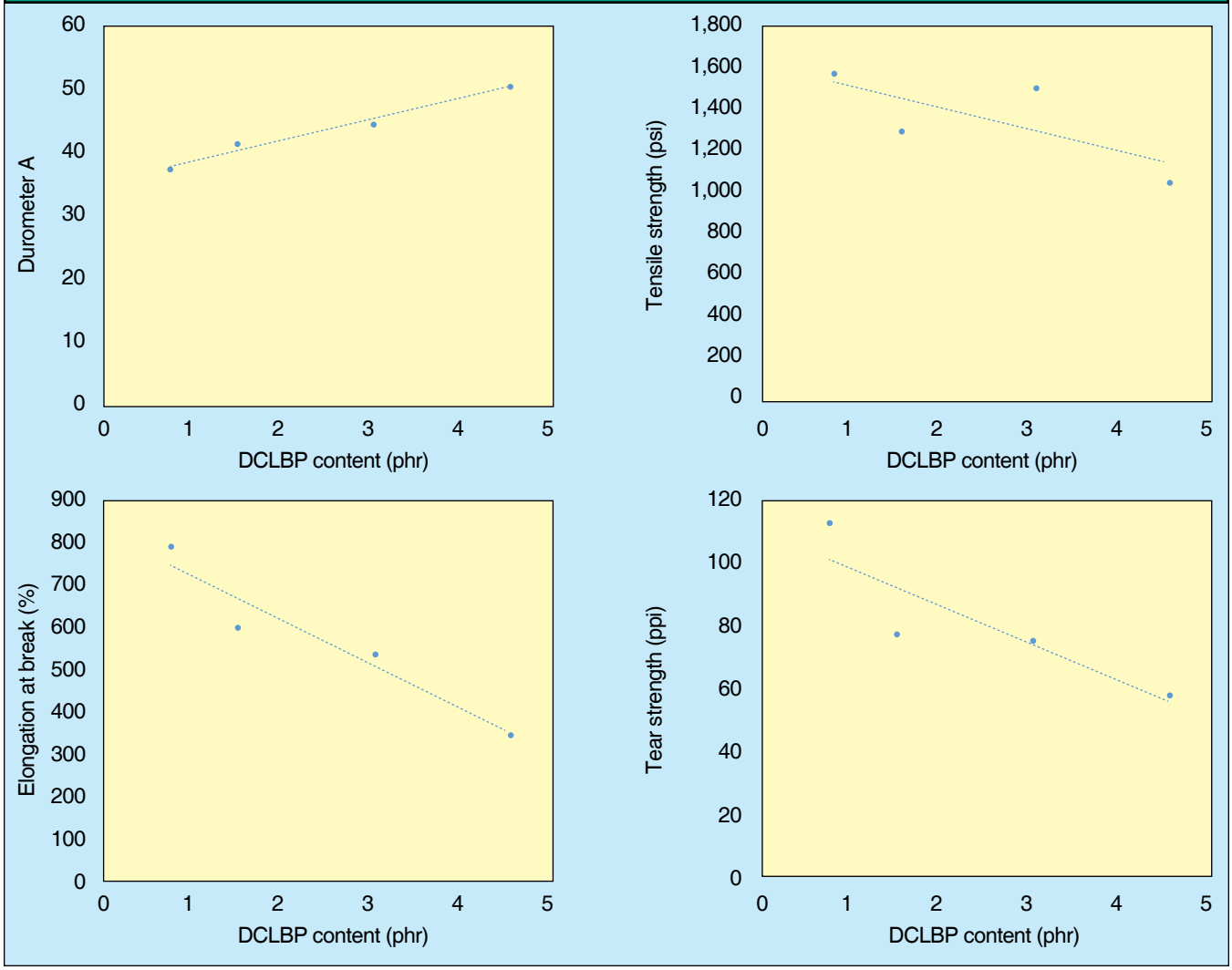


Figure 2 - properties as a function of initiator content using DCLBP



cure temperatures. Tested properties were selected from ASTM D2000 and other requirements. The tested properties were:

- Durometer A (ASTM D2240)
- Tensile strength, elongation at break and tensile stress at 50%, 100% and 200% elongation (ASTM D412)
- Tear strength (ASTM D624)
- Specific gravity (ASTM D792)
- Shrinkage after press cure and after post-bake; the shrinkage samples can be used to cut other samples for testing (internal test method SSP-55)
- Compression set as ply 22 hours at 175°C and as ply 70 hours at 150°C (ASTM D395)
- Heat aged 70 hours at 225°C to measure durometer change, tensile change, elongation change and weight loss (ASTM D573)
- Low temperature brittleness at -55°C, -60°C and -65°C (ASTM D2137)

The curing characteristics of all samples were measured using an Alpha Technologies ODR 1000 at 3° angular displacement and 350°F. The sample made with di(2,4-dichloro benzoyl)peroxide was tested at 240°F.

Sample details

All samples used a commercially available 40 durometer general purpose base, with the exception of the control sample, which also used the 60 durometer version of the base from the same series and same manufacturer to provide a 50 durometer baseline. Except where noted, all samples were cured using 1.7 phr 34% 2,5-dimethyl-2,5-di(t-butylperoxy)hexane (DBPH). Samples were press cured for 10 minutes at 177°C, and then post-cured for 4 hours at 200°C. Samples that were cured using di(2,4-dichloro benzoyl)peroxide used a 50 wt% paste and cure conditions of 10 minutes at

Table 1 - sample identifications and formulations used for the current work

Sample ID	*Formulation*
TS-03-016	Control
TS-03-011	53 phr Minusil, 5U
TS-03-014	35 phr Aktisil Q
AB-12-140	15 phr Celite 350
AB-12-144	3.5 phr HS-5 fumed silica
TS-03-019	Addition cured sample
AB-12-136	4.5 phr DCLBP paste
TS-03-022	5 phr high vinyl gum
AB-12-148	10 phr low vinyl gum

Table 2 - basic physical properties of the various samples

Sample ID	Tensile strength (psi)	Elongation at break (%)	Tensile stress at 100% elongation (psi)	Tear strength (ppi)
TS-03-016	1662	708	140	130
TS-03-011	1094	632	116	115
TS-03-014	1293	732	144	98
AB-12-140	1294	533	258	120
AB-12-144	1785	762	130	135
TS-03-019	1597	798	133	190
AB-12-136	1087	367	201	62
TS-03-022	1309	624	245	230
AB-12-148	1032	379	222	127

116°C. Addition cured samples used 1 phr of a commercially available HCR platinum catalyst blend and 0.4 phr of a low viscosity methyl hydrogen fluid.

Sample identifications and formulations are provided in table 1. For all of the formulations, the measured durometer A was 50 ± 2.

Results and discussion

Basic physical properties

Table 2 shows the samples' basic physical properties. For each property, the minimum and maximum observed values are shaded in gray. In the previous screening work that focused on how properties changed as the amount of a specific additive was changed, the properties measured were highly interdependent, as would be expected where the mechanism of the impact on the measured properties is the same because the same additive is always used. When the amount of quartz filler was increased, the durometer rose, and the tensile strength and elongation at break decreased (figure 1).

In those screening experiments with a single additive, each of the properties could not be varied independently. With the range of additives used in the current work, the trade-offs between the various properties were not as pronounced. Figure 3 plots the various physical properties from table 2 to show the breadth of the observed mechanical properties. The measured tensile strength varies about 700 psi, the elongation at break is about 430%, the tensile stress at 100% elongation varies about 130 psi, and the tear strength varies about 170 ppi. These broad ranges were obtained while maintaining a consistent durometer. The red dots represent the baseline material without modification.

The relative independence of the various physical properties is illustrated in some selected example regression plots in figure 4. This is of prime importance when formulating silicones to externally controlled specifications, or to legacy specifications that exist as a function of selecting a very specific specialty base when the part specifications were initially set.

Processing considerations

A key constraint of replacing existing materials in existing processes that is overlooked includes processing considerations such as scorch, cure time and shrinkage. A good materials solution will cause as little disruption as possible to existing tooling and processing conditions. Table 3 shows the linear shrinkage values and select ODR data for the various samples. With the exception of the alternate curing mechanisms (TS-03-019 and AB-12-136), there is no great impact on the scorch time, with the exception of the Aktisil Q filler. The overall cure time is extended by the addition of fumed silica (AB-12-144) and the two vinyl gums (TS-03-022 and AB-12-148).

For the gum containing samples, the increase in T90 is about 50%, suggesting that special attention will need to be paid to existing cycle times if such formulations are to be offered as replacements. However, the addition of gums has a relatively small impact on the shrinkage of cured parts; whereas the highly filled formulations, as would be expected, show significantly less shrinkage when compared to the control. This has implications for existing tooling, and illustrates why consideration of other properties outside of specified basic physical properties is key to formulating appropriate offsets.

Figure 3 - plot showing the range of measured physical properties from table 2

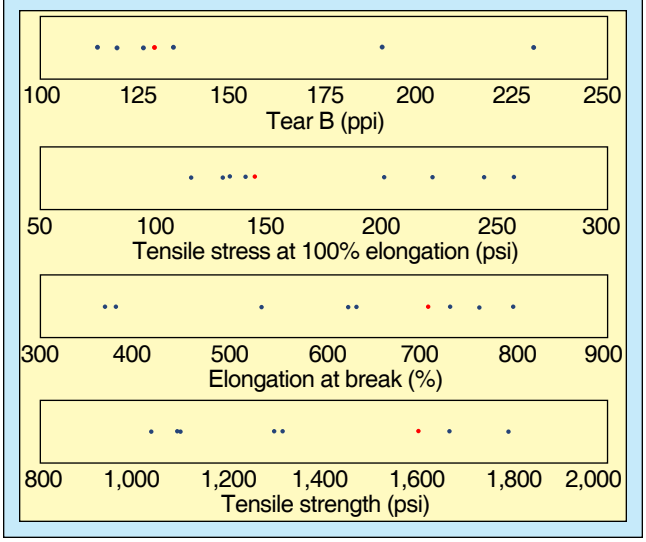


Table 3 - linear shrinkage and select ODR data for the various samples

Sample ID	Linear shrinkage on cure (%)	Linear shrinkage on post-cure (%)	TS2 (minutes)	T90 (minutes)
TS-03-016	3.8	4.0	0.94	2.33
TS-03-011	2.8	3.3	0.79	2.27
TS-03-014	3.2	3.3	0.55	2.02
AB-12-140	3.0	3.4	0.95	2.58
AB-12-144	3.5	3.9	0.93	2.85
TS-03-022	4.0	4.5	0.97	3.33
AB-12-148	3.7	4.3	1.07	3.51
TS-03-019	3.0	3.3	0.55	1.98
AB-12-136	1.9	3.0	0.41	1.95

Figure 4 - example linear regression plots illustrating the lack of dependence of some physical properties

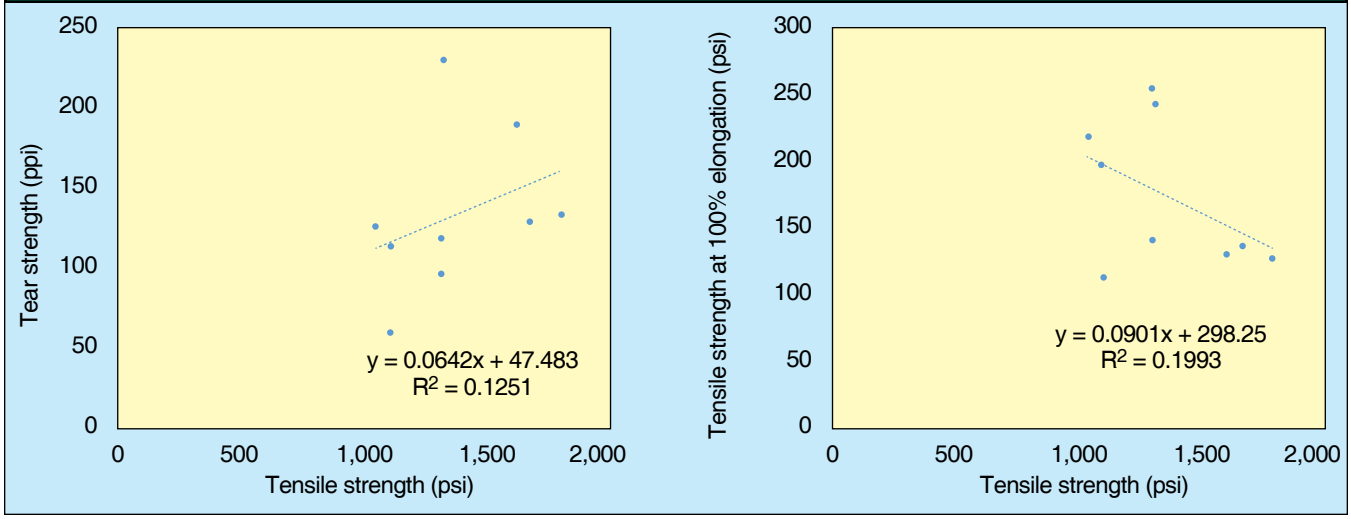


Table 4 - heat aged and compression set data for the various samples

Sample ID	*Heat aged 70 hours at 225°C*				*Compression set (%)*	
	Durometer change (points)	*Tensile change (%)*	*Elongation change (%)*	*Weight loss (%)*	*22 hours at 175°C*	*70 hours at 150°C*
TS-03-016	-5	-46	-41	5.4	32.3	23.2
TS-03-011	+4	-23	-32	0.9	27.4	28.0
TS-03-014	+3	-30	-17	1.1	22.1	12.7
AB-12-140	+2	-29	+24	1.4	21.2	16.9
AB-12-144	+4	-42	-24	1.0	25.7	30.6
TS-03-022	+24	-82	-97	2.5	28.3	28.1
AB-12-148	+21	-64.8	-87.9	1.9	17.2	20.8
TS-03-019	+7	-49	-58	1.4	33.1	34.5
AB-12-136	+10	-31.8	-56.7	1.2	69.3	65.0

The constraints of existing tooling and shrinkage can often be overlooked or perceived as less important than specifications around physical properties. However, this can lead to difficulties in the final testing and acceptance of custom compounds.

Application/environment properties

Specifications may include properties that are important to the performance of the part in the final application environment. Examples include compression set or heat aged properties. Table 4 shows heat aged property changes and compression set under two different conditions for the various tested formulations. Overall, the additions of Celite 350, Aktisil Q and the low vinyl gum resulted in the best compression set properties. The filled formulations (Minusil, 5U, Celite 350, Aktisil Q and fumed silica) had the best overall heat aged properties.

While the low vinyl gum had low compression set at both test temperatures, the heat aged properties were very poor. This difference in high temperature properties shows the importance of considering the impact of additives on the whole range of desired properties; and especially when some properties are not explicitly called out in specifications, but are still of vital importance to a product's end use. For example, an existing specialty base may have a low compression set, and this property is essential to the proper functioning of the final part; however, if the compression set is not defined as part of the specification, a custom compound could meet all of the specified requirements, but still be unsuitable for the final application.

Alternate curing mechanisms

Using a DCLBP type catalyst at very high loading results in a final material with poor physical properties. This is expected because of the high crosslink density that results from the chains' ability to become crosslinked at any point along their length, rather than only where there are available vinyl groups. The reduced physical properties may preclude the use of this formulation in many applications; however, there may be niche applications where the reduced shrinkage on curing makes the formulation attractive.

Controlling the network structure with functional gums

The primary interest in the addition of the vinyl bearing gums was to understand if the introduction of additional vinyl groups on flexible chains could impact the stiffness of the final rubber, independent of the durometer. Previous work with traditional fillers and oligomeric vinyl species resulted in formulations with higher tensile stress at 100% elongation, but also much higher durometers than the specifications called for. In the current work, it can be seen that the tensile stress at 100% elongation can be controlled with vinyl bearing gums.

An immediate application for this was in the replacement of a specialty base that had been experiencing significant supply issues, even after many other bases had seen increased availability. For the final application, the key requirements were

Table 5 - properties with and without the addition of a low vinyl gum to a platinum cured system for a customer application

Property	*Typical*	*SSP2390-55D*	*SSP2390-55D + 5 phr gum*	*Specification*
Durometer A	52	52	56	50-60
Tensile stress at 100% elongation (psi)	195	143	205	N/A
TS1 (minutes)	1.15	0.68	1.03	0.8

Table 6 - ODR data collected at 215°F for various formulations developed to meet the required processing conditions

Sample ID	*Notes*	*TS2 (minutes)*	*T90 (minutes)*
TR-02-122A	Standard catalyst	No cure	No cure
TR-02-122B	Commercial low temperature catalyst	0.91	5.66
SL-01-122	SSP low temperature catalyst	0.71	8.50
AB-04-006	Custom catalyst	2.65	6.87

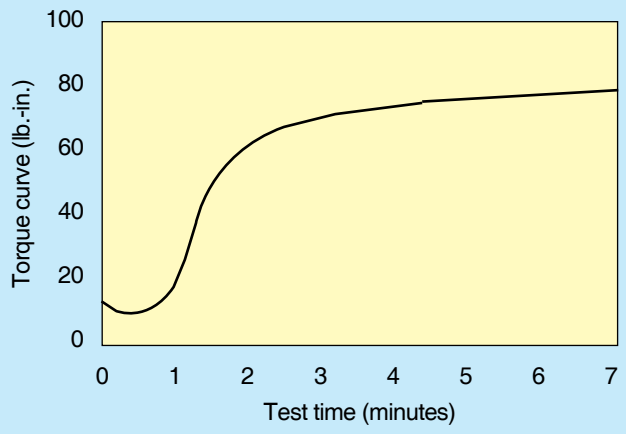
durometer (the specification is 50-60), tensile stress at 100% elongation (needs to match the existing material as closely as possible), TS1 time at 320°F (0.8 minutes, and preferably as close to the current material as possible in order to ensure adequate fill of the complex mold), and that the material be platinum cured.

The low vinyl gum was added to SSP's existing standard SSP2390-55D formulation (USP Class VI platinum cured one-part compound), resulting in the desired increase in the tensile stress at 100% elongation. The combination of the gum and a slight modification to the platinum catalyst also brought the TS1 into the appropriate range (table 5).

Conclusions on controlling mechanical properties

Understanding the breadth of accessible properties with various modifications to general purpose bases permits lower costs, more stable supply chains and the dual sourcing of bases to protect customers from supply issues that are associated with single sources. Some specifications require specialty bases that are among the most challenging to source during the recent shortages. The current work enables the displacement of specialty bases and their substitution with more flexible formulations. For example, some applications require high tensile strength and high tear strength. Both can be met through the addition of a high vinyl gum to a general purpose base, rather than sourcing a specialty base.

Figure 5 - example ODR curve for SSP2390-80D at 350°F



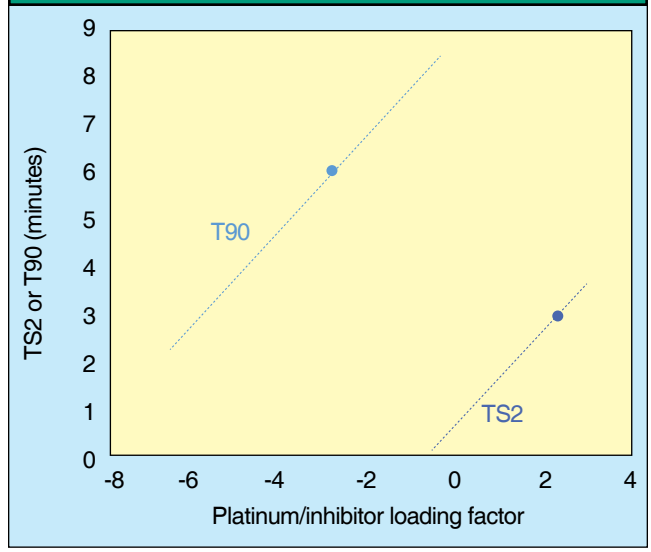
Case studies in custom compounds

80 durometer USP Class VI compound

In this application, the customer required an 80 durometer USP Class VI material that is overmolded onto a plastic insert. Because of part constraints and processing conditions, the customer specified a TS2 time of 2.5 to 3.5 minutes, and a T90 time of 5 to 7 minutes. SSP2390-80D is SSP's existing platinum cured USP Class VI 80 durometer material; however, this material is designed for much higher cure temperatures than those required by this application. Figure 5 shows an example ODR curve for SSP2390-80D collected at 350°F. The TS2 for this specific sample was 0.68 minutes, and the T90 was 3.40 minutes.

Switching to a commercially available low temperature platinum catalyst resulted in an acceptable T90, but a TS2 that was too fast. The internal SSP low temperature catalyst had a TS2 that was too fast and a T90 that was too long. Further work was then performed with custom mixed platinum catalysts made internally. A series of custom catalysts was made with varying platinum and inhibitor (diallyl maleate), and regression analysis was applied to the values of TS2 and T90 as a function

Figure 6 - fitted data for TS2 and T90 based on platinum and inhibitor loadings



of platinum and inhibitor loading. Applying the model to calculate the required platinum and inhibitor loadings revealed that 32 ppm of platinum and 0.72 wt% diallyl maleate would be required to attain the required cure conditions (figure 6).

While these values would theoretically provide the appropriate cure, the excessive addition of catalyst and inhibitor results in higher costs for the customer. The experiments were repeated with an alternate inhibitor (1-ethynyl-1-cyclohexanol), and the results of the final formulation that required approximately an order of magnitude lower addition of catalyst and inhibitor are shown as sample AB-04-006 in table 6. The final formulation was supplied to the customer as a two-part compound specifically designed for their manufacturing process and made with USP Class VI compliant bases.

Conclusions

Silicone compounders can mitigate the risks caused by over-reliance on specialty bases from a single supplier. By understanding the scope of accessible properties and making appropriate modifications to general purpose bases, compounders can protect customers from shortages. Although it can be challenging to find flexible formulations for some specialty bases, the benefits of dual sourcing include not just more stable supply chains, but also include lower costs.