SPECIAL REPORT — **Silicone**

Improving low temperature properties in a silicone elastomer

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Executive summary

This article describes the investigation and commercialization of a specific compound intended for a cryogenic seal application. A hypothesis to account for the improvement in low-temperature performance is discussed and extended to other potential chemistries and applications.

It is well known in the elastomers industry that dimethyl silicone elastomers exhibit a dramatic increase in their modulus at temperatures at about -40°C.

Historically, phenyl substituted dimethyl siloxane polymers (PVMQ) have been used to achieve consistent mechanical properties in silicone elastomers at these low temperatures.

We have found that improved low temperature properties can be achieved through incorporation of a medium viscosity, vinyl terminated diphenyl dimethyl copolymer into a conventional vinyl dimethyl gum (VMQ). This modified VMQ gum was combined with filler and processed into a low temperature base.

The low temperature base was combined with additional VMQ high consistency rubber base and catalyst for molding into test articles and finished seals.

The effect on the mechanical properties were assessed for a range of viscosities of the vinyl diphenyl dimethyl copolymer, for the degree of phenyl substitution on the copolymer, for the base processing and catalyst choices for the compound.

Elastomers based on silicone polymers, MQ and VMQ, are widely used in industrial, aerospace and medical applications where, among other attributes, they retain their performance characteristics under both very low and very high temperature conditions. One challenge to using these materials at low temperature is a change in the mechanical properties at about -40°C. At this temperature the modulus of a typical silicone elastomer increases significantly.

It has been shown that this increase in modulus is because of alignment of the dimethylsiloxane molecules in a quasi-crystalline fashion. In their efforts to overcome this mechanical property

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limitation, scientists at General Electric, Dow Corning and others developed a lightly substituted silicone copolymer in which the presence of a randomly distributed organic group would help prevent this crystallization from occurring.[1] Much as the presence of salt lowers the freezing point of ordinary water, the presence of the bulkier sidechains slows or prevents the formation of ordered structures in the silicone elastomer.[2] A second benefit from introducing phenyl groups into the polymer network is an increase in heat stability. It has been suggested that this is because of the free radical scavenging of the Pi delocalized electrons in the phenyl ring. Heat aging has been evaluated in this phenyl modified base.

This change in properties impacts the proper function of the component, whether it be a static gasket in an aircraft window or dynamic door sealing in a cryogenic freezer. A common solution to this involves using phenylmethyl dimethyl copolymers, PVMQ, as the starting polymer in the elastomer. The sidechains on the backbone polymer reduce the tendency to crystallize and allow the silicone elastomer to maintain flexibility throughout the useful temperature range.

This study explored an alternative route to introducing the phenyl side chain into the elastomer. Incorporating a low molecular weight vinyl terminal diphenyl dimethyl copolymer into a high molecular weight VMQ polymer compound allows for control of the phenyl content in the final compound very precisely and tailors the mechanical properties to the specific application. When properly compounded, an example compound of this modified elastomer maintained its flexibility down to at least -86°C.

There are a wide range of possibilities for incorporating higher or lower levels of diphenyl dimethyl copolymer and further impacting both the low temperature as well as the high temperature properties. The success of this approach also suggests the possibility for incorporating other functional sidechains into VMQ polymers, which may impart a variety of unique characteristics. Some ideas for future exploration include vinyl trifluoropropyl methyl dimethyl copolymers, which may also be capable of lowering the functional use temperature while possibly changing the surface energy of the elastomer.

Background

For a variety of reasons, the use of the phenyl side chain became the preferred option for improving the mechanical properties of silicone elastomers when required to perform at temperatures at or below -40°C. As defined by ASTM D 1418, rubber nomenclature PVMQ presently refers to vinyl, dimethyl silicone elastomers containing some percentage of phenyl side groups. Commercial products available today include gums from the primary basic producers and bases from other compounders. Some manufacturers blend their own bases and compounds for their internal use such as Jamak Fabrication. Examples include the Xiameter RBB-2060-XX base from Dow, Shin-Etsu KE 5006 U, Jamak J244 and others. The silicone rubber base can be manufactured from PVMQ gum such as Xiameter RBG-0931 from Dow or SE54-2 from Momentive.

The PVMQ gums are copolymers of dimethyl silicone and phenyl methyl silicone and include vinyl functionality for curing. Vinyl is present at the terminal ends, as pendant groups or both depending on the specific grade of gum. The low temperature bases may include blends with VMQ polymers.

There are inherent problems with this type of phenyl substitution. Because of the phenyl methyl functionality there are issues of toxicological management associated with minor impurities, which are formed during the manufacturing process. The impurity of most concern is 2,6-cis-Diphenylhexamethylcyclotetrasiloxane (2,6 Cis). This impurity has been shown to have dramatic negative effects on fertility in rats and mice and was variously considered a candidate for a male contraceptive drug and a treatment for cancer of the prostate.[3] In order to overcome both supply challenges and toxicological issues associated with commercial PVMQ gum and base, efforts were initiated to develop a functional alternative.

Hypothesis

A hypothesis was proposed that a low molecular weight vinyl terminal phenyl methyl polymer could be co-cured with conventional dimethyl vinyl polymer. It was expected that the presence of the bulky sidechains would create sufficient disruption that the cured elastomer would not experience the crystallization transition experienced by VMQ elastomers. Thus the elastomer would remain flexible at low temperature. The presence of the phenyl group would also impart better high temperature stability.

This hypothesis had been evaluated in another potential application. In this experiment vinyl terminal dimethyl fluoro methyl silicone copolymers and hydride terminal dimethyl fluoro methyl silicone copolymers were prepared. The degree of substitution with the fluoro group was evaluated at 5 percent and 10 percent. In performance testing when compounded and cured the FVMQ-VMQ copolymer at 10 percent performed equivalent to a PVMQ commercial product in low temperature retraction, ASTM D139. The in-

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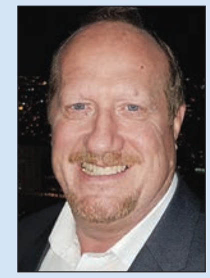
Fig. 1: Table of Andisil vinyl terminal diphenyl dimethyl copolymers.

PRODUCT NAME	PHENYL CONTENT	REFRACTIVE INDEX @25 °C	VISCOSITY
Andisil® SF 1421	3.0 Mole%	1.4150	1,100 cSt
Andisil® SF 2421 CV **	3.0 Mole%	1.4185	1,100 cSt
Andisil® SF 1721	7.0 Mole%	1.4240	7,000 cSt
Andisil® SF 2430 CV **	13.0 Mole%	1.4635	1,550 cSt
Andisil® SF 9530 CV **	13.0 Mole%	1.4635	10,000 cSt
Andisil® SF 2450 CV **	29.0 Mole%	1.5165	625 cSt
Andisil® SF 6550 CV **	29.0 Mole%	1.5165	7,000 cSt
Andisil® SF 2465 CV **	42.0 Mole%	1.5400	2,500 cSt
Andisil® SF 4565 CV **	42.0 Mole%	1.5400	4,500 cSt

The authors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Charles Olsen holds a bachelor of chemical engineering from the University of Washington and a masters of science in technology management from the Howe School of Management at Stevens Institute. Olsen has worked in silicone technology and business for more than 25 years. Prior to that, he spent seven years working in materials and processing for the NASA space shuttle program at Thiokol.

As director of technology for AB Specialty Silicones he is now leading the firm's new initiative into the addition cured silicone high consistency rubber marketplace.

Brian Thornburg earned his bachelor of science degree in chemical engineering with a specialization in polymer engineering and minors in chemistry and mathematics from The University of Akron. Thornburg has served the rubber industry for more than 20 years in various roles in engineering, laboratory and manufacturing management.

As director of product development at Jamak Fabrication in Weatherford, Texas, Thornburg is focused on developing new materials, products and technologies for revenue growth. He is responsible for managing the technical services group, research and development laboratory, quality assurance laboratory, and metrology.

Erick Sharp is the founder and CEO of ACE Products & Consulting. Sharp founded ACE, a laboratory and technical services provider, in 2015. He has 16 years of rubber industry experience holding key roles within Lauren International, Edgetech UK and Portage Precision Polymers.

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teresting result was that the FVMQ elastomer exhibited significantly less swell when exposed to testing fluid IRM 903 per ASTM D471.

Practical challenges

Low molecular weight PVMQ and VMQ polymers are immiscible in one another. In fact nonfunctional phenyl dimethyl copolymers are used as self bleed additives for specialized applications such as connector seals. The approach to avoiding the phase separation of the phenyl component was to select a PVMQ copolymer with sufficient phenyl content to be effective in modifying the low temperature flexibility but not so high that it would form a separate phase either prior to or during the cure.

Once the compound is cured, it's assumed that the polymer network would prevent further phase separation. The long-term stability of the cured compound will be tested as part of the continued evaluation of these materials.

Results

Evaluation of diphenyl dimethyl copolymer stability

For practical considerations, a series of commercial vinyl terminal PVMQ products from the Andisil SF line were evaluated. Andisil phenyl methyl vinyl polymers consist of copolymers of dimethyl siloxane and diphenyl siloxane (**Fig. 1**). They may be variously vinyl terminal, vinyl pendant or both depending on the specific need of the formulation. These are synthesized using a re-equilibration process resulting in the final desired MW and phenyl content.[4] These materials are available in a variety of degrees of substitution of the phenyl content. The phenyl concentration of the commercial products ranges from about 3 Mol percent up to about 42 Mol percent. A range of viscosities from about 1000 cSt up to about 10,000 cSt are commercially available.

Preliminary work was performed assessing the compatibility of these polymers with dimethyl polymer. The 29 percent and 42 percent phenyl substituted polymer blended with dimethyl polymer appeared hazy and nearly opaque suggested a highly incompatible two phase mixture which would make it difficult to co-cure the polymers.

Four diphenyl containing vinyl terminal copolymers were selected. Two different viscosity ranges were chosen, representing a higher and lower molecular weight. Molecular weight is not routinely measured as part of the quality acceptance testing. It is important to point out that the viscosity does increase with increasing phenyl content and so can only approximately represent the molecular weight of the polymer. A phenyl substitution level of 1 percent and 3 percent was selected for evaluation in an example base, J244. Andisil SF 1421, SF 1721, SF 2430 and SF 9530 diphenyl dimethyl vinyl polymers were selected for evaluation. The target phenyl level is the percent of diphenyl in the final base composition. The phenyl molpercent is the amount of phenyl in the vinyl diphenyl dimethyl copolymer, and the approximate viscosity represents a measure of the molecular weight of the phenyl copolymer. The low molecular weight copolymer would not be practical at 3 percent loading level (**Table 1**). It was also decided that an intermediate 2 percent phenyl level would not be evaluated.

Evaluation of the effect of cure mechanisms on compound

To evaluate the effect of the phenyl methyl substitution on the low temperature performance, it was necessary to prepare a silicone rubber base incorporating these polymers. A commercial base known as J244 was selected as a starting point. This extrusion base is intended for use in low-temperature seals. J244 contains PVMQ to maintain good sealing properties at temperatures as low as -86°C. J244 is manufactured in-house at Jamak Fabrication for internal use.

J244 is a proprietary base used for low-temperature seals. In order to test the hypothesis, the PVMQ gum was replaced with a portion of the Andisil SF vinyl diphenyl dimethyl polymer (**Table 1**).

Table 1: Andisil SF PVMQ test matrix.

	Viscosity cSt. (MW)		Target Phenyl level %		
Phenyl Mol %	L 1000	H 10000	1%	2%	3%
3	SF 1421		33	67	100
7		SF 1721	15	28	43
13	SF 2430	SF 9530	7.7	15	23
				g/100g	

In addition to the substitution of the Andisil SF for the PVMQ gum, two different base manufacture processes were evaluated.

- Process 1: In the first instance each batch of the base was cold mixed with the amount and type of the Andisil SF vinyl diphenyl dimethyl copolymer (**Table 1**).
- Process 2: In the second instance each batch of the base was hot mixed with the inclusion of a vinyl silane along with the same level of and type of vinyl diphenyl dimethyl copolymer as in the cold mix.

In order to evaluate mechanical properties, the base was cured with a non-vinyl specific peroxide, DCBP.

Discussion

In the cold mixed experiment batches, the low molecular weight SF 1421 and SF 2430 both produced elastomers with relatively low strength. This may have been because of unreacted terminal vinyl groups. Because of its low MW, the SF 1421 and SF 2430 polymers delivered more vinyl groups into the formulation than an equivalent phenyl group loading when compared to the higher MW polymer SF 9530.

It was hypothesized that because of the use of non-vinyl specific peroxide not all of the small MW phenyl polymer was fully incorporated into the elastomer network. Chain ends, which were not able to participate in the full network, would tend to reduce hardness, increase elongation and drop the tensile properties.

This also was observed in sample batches incorporating the high molecular weight copolymer with the intermediate phenyl concentration of 7 percent. Even though the SF 1721 had a higher MW, the increased loading required to achieve the desired phenyl content resulted in unreacted vinyl, leading to poor mechanical properties.

In order to ensure complete reaction of all vinyl groups, including in the copolymer additive a blend of vinyl specific and non-vinyl specific cure systems were evaluated. These included both a blend of vinyl specific and non-vinyl specific peroxides as well as an addition cure platinum catalyzed cure system.

The selected base can be described as a blend of vinyl-terminated polydimethylsiloxane (PDMS) gum and vinyl-terminated polydiphenyldimethylsiloxane (phenyl silicone) fluid hot mixed with fumed silica, a process aid, and a coupling agent for in-situ treatment of the filler.

This base is then blended with conventional VMQ base to create a final compound for extrusion.

A second experimental design was performed using the blended peroxide system. In this compound mechanical properties and heat aging data are highlighted below.

Utilizing a peroxide cure system incorporating a vinyl-specific peroxide was key to unlocking the potential of this project by forming a true co-polymer between the PDMS gum and phenyl silicone fluid. These homopolymer dimethyl siloxane and the copolymer diphenyl dimethyl siloxane are connected by cross-links at the terminal vinyl groups.

Up to this point the commercially produced Andisil SF 9530 CV have been used as the vinyl copolymer of choice. Because of the selection of a high temperature base manufacturing process and the efficiency of the batch stripping process at AB Specialty Silicones, a new product was created—Andisil SF 6030—which did not undergo the high vacuum wiped film evaporator stripping process needed to achieve a "controlled volatility" CV designation.

The most recent commercial production of phenyl base and compound for internal use at Jamak has been based on Andisil SF 6030.

Based on the success of the vinyl specific evaluation, the platinum catalyzed addition cure system was also evaluated.

All compounds incorporating the diphenyl dimethyl copolymer pass the -86°C low temperature flexibility test with the platinum catalyzed version exhibiting the best mechanical properties.

J244 specification and historical data:

Formulation PD# / Description	SG	Duro	Tensile	Elongation	Tear	Plasticity	Cold
J244 Specification	1.11-1.17	35-45	800 Min	350 Min	60 Min	Record	No cracking
J244 Historical Data - Lot # BN16937	1.15	40	1054	582	97	188	
Control - J244 w/ H110-0 vinyl gum - 0% Phenyl) - Cold Mix	1.12	43	1244	803	148	557	PASS
Control - J244 w/ H110-0 vinyl gum - 0% Phenyl) - Hot Mix w/ 99012	1.13	45	1521	566	149	152	PASS

CMPD #	SG	Duro	Tensile	Elongation	Tear	Heat Aged 70 h @ 450°F Hardness D	Heat Aged 70 h @ 450°F Tensile D	Heat Aged 70 h @ 450°F Elong. D	Comp. Set 22 h @ 350°F	Cold Flexibility 24 h @ -86°C *
J6230	1.18	59	1384	492	171	63 (+4)	697 (-50%)	294 (-40%)	13%	PASS

Description	SG	Duro	Tensile (psi)	Elongation (%)	Tear (pli)	Plasticity	Cold Flexibility 24 h @ -86°C *
ABSS Andisil SF 6030 – platinum compound	1.15	60	1606	743	262	211	pass

Conclusions

There are a number of benefits to using a relatively low molecular weight vinyl functional copolymer as a way to modify the properties of VMQ base. In this particular development project, the functional requirements of the elastomer were met while lowering the cost and improving mechanical properties.

Using this approach also allows a broad range of different compounds to be prepared using the same basic starting materials by altering the ratio between the copolymer in the VMQ gum. Future work also will include more detail thermal analysis of these compounds by ACE Products and Consulting using advanced methods such as differential scanning calorimetry.

This study concludes that this approach can also be extended to other vinyl containing functional materials for modification of VMQ gum. The use of vinyl trifluoropropyl dimethyl copolymers may provide interesting surface properties or possibly better oil resistance in low temperature compounds. Use of a copolymer containing a high percentage of pendant vinyl groups such as Andisil VDM 65,000 may be able to provide additional toughness and improve mechanical characteristics, to take the place of a high vinyl VMQ gum.

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