

Novel Means to Improving Low Temperature Mechanical Properties in a Silicone Elastomer

Charles Olsen Jr.¹, Brian Thornburg*², Erick Sharp³

(1) AB Specialty Silicones, Waukegan, IL; (2) Jamak Fabrication, Weatherford, TX; (3) ACE Products & Consulting, Ravenna, OH

Presented at the Fall 194th Technical Meeting of Rubber Division, ACS Louisville, KY
October 9 - 11 2018

ISSN: 1547-1977

* Speaker

ISSN: 1547-1977

Novel Means to Improving Low Temperature Mechanical Properties in a Silicone Elastomer

Charles Olsen Jr.¹, Brian Thornburg*², Erick Sharp³

(1) AB Specialty Silicones, Waukegan, IL; (2) Jamak Fabrication, Weatherford, TX; (3) ACE Products & Consulting, Ravenna, OH

ABSTRACT: Historically, high molecular weight phenyl substituted dimethyl siloxane polymers have been used to achieve good low temperature mechanical properties in silicone elastomers. We have found that improved low temperature properties can be achieved through incorporation of a low MW diphenyl dimethyl vinyl terminated copolymer into a conventional dimethyl gum. Heat aging properties of the modified polymer system were also evaluated in a commercial formulation.

Silicone elastomers are renowned for their performance in extreme environments. Because of their inherent molecular structure and very low glass transition temperature they remain flexible and exhibit elastomeric properties in both high and low temperature environments. Despite these remarkable attributes, dimethyl silicone elastomers, MQ and VMQ, suffer from an increase in modulus around -40°C. This increase in modulus negatively affects the sealing characteristics and dynamic properties of the rubber component. It has been shown that this increase in modulus is due to alignment of the dimethylsiloxane molecules in a quasi-crystalline fashion. In their efforts to overcome this mechanical property 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 (Ref. 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 (Ref 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 due to the free radical scavenging of the Pi delocalized electrons in the phenyl ring. Heat aging has been evaluated in this phenyl modified base.

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 such as Jamak. Examples include the Xiameter RBB-2060-XX base from Dow, ShinEtsu 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.

These commercial materials 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. There are inherent problems with this type of phenyl substitution. Due to 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 (Ref 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. 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 concept had been evaluated in unpublished work. 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 and 10%. In performance testing when compounded and cured the FVMQ - VMQ copolymer at 10% performed equivalent to a PVMQ commercial product in low temperature retraction, ASTM D139. The interesting result was that the FVMQ elastomer exhibited significantly less swell when exposed to testing fluid IRM 903 per ASTM D471.

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. They may be variously vinyl terminal, vinyl pendant or both depending on specific need of the formulation. These are synthesized using a re-equilibration process resulting in the final desired MW and phenyl content (Ref 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% up to about 42 Mol%. 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 % and 42% 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. phenyl substitution level of 1% and 3% 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.

Table of Andisil SF 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 CV designation refers to a stripped version of the base product.

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 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.

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

J244 is a proprietary base used for low-temperature seals. The base uses Andisil® AS 200 fumed silica as well as various treating agents including optionally a vinyl silane. In order to test the hypothesis the PVMQ gum was replaced with a portion of the Andisil SF in accordance with the following table.

Andisil® SF PVMQ test matrix

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

Loading rate; g/100g

The experiments were coded to simplify the interpretation of the results. Low phenyl content copolymer is more compatible with the dimethyl gum. Higher MW polymer contains less vinyl groups for an equivalent phenyl content.

The following variations on J244 base were prepared.

Cold mix

Iteration	Phenyl; MW		SG	Duro	Tensile	Elongation	Tear	Modulus	Modulus	Modulus	Plasticity	Flexibility
			1%									
1	LL	PD-2018-0023-001 (J244 Cold Mix w/ Andisil SF 1421 @ 1% Phenyl)	1.14	37	706	927	222	107	118	130	497	PASS
3	MH	PD-2018-0023-003 (J244 Cold Mix w/ Andisil SF 1721 @ 1% Phenyl)	1.13	44	1121	882	158	128	139	153	565	PASS
5	HL	PD-2018-0023-005 (J244 Cold Mix w/ Andisil SF 2430 CV @ 1% Phenyl)	1.14	35	635	988	206	134	137	141	557	PASS
7	HH	PD-2018-0023-007 (J244 Cold Mix w/ Andisil SF 9530 CV @ 1% Phenyl)	1.14	45	1343	910	160	147	158	170	555	PASS
			3%									
11	MH	PD-2018-0023-011 (J244 Cold Mix w/ Andisil SF 1721 @ 3% Phenyl)	1.14	33	666	946	215	131	137	144	425	PASS
13	HL	PD-2018-0023-013 (J244 Cold Mix w/ Andisil SF 2430 CV @ 3% Phenyl)	1.13	40	821	995	237	142	148	155	423	PASS
15	HH	PD-2018-0023-015 (J244 Cold Mix w/ Andisil SF 9530 CV @ 3% Phenyl)	1.14	45	1030	871	219	148	155	168	504	PASS

Hot mix also containing a vinyl silane.

Iteration	Phenyl; MW		SG	Duro	Tensile	Elongation	Tear	Modulus	Modulus	Modulus	Plasticity	Flexibility
			1%									
2	LL	PD-2018-0023-002 (-001 Hot Mix w/ 99012)	1.13	39	1221	822	176	129	155	193	340	PASS
4	MH	PD-2018-0023-004 (-003 Hot Mix w/ 99012)	1.14	45	1635	633	155	178	207	258	160	PASS
6	HL	PD-2018-0023-006 (-005 Hot Mix w/ 99012)	1.11	42	1260	625	138	159	187	227	143	PASS
8	HH	PD-2018-0023-008 (-007 Hot Mix w/ 99012)	1.13	46	1443	581	148	173	203	252	161	PASS
			3%									
Iteration	Phenyl; MW	Formulation PD# / Description	SG	Duro	Tensile	Elongation	Tear	25%	50%	100%	Plasticity	Cold
12	MH	PD-2018-0023-012 (-011 Hot Mix w/ 99012)	1.15	21	484	912	153	134	142	153	149	PASS
14	HL	PD-2018-0023-014 (-013 Hot Mix w/ 99012)	1.13	36	1083	814	156	141	160	185	152	pass
16	HH	PD-2018-0023-016 (-015 Hot Mix w/ 99012)	1.14	37	1316	801	147	135	160	191	161	pass

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

Discussion of hot and cold mix formulations

In the cold mixed experiments batches 1 and 5 the low molecular weight SF 1421 and SF 2430 both produced elastomers with relatively low strength. This may have been due to 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 due to 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 was also observed in sample batches 11 and 12. 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.

Effect of vinyl specific peroxide

To ensure the full reaction of all vinyl groups a third round of formulations were prepared and identified as J6230. These compared the effect of a DCBP to DCP. DCP is considered a vinyl specific peroxide. In addition, the specimens were post cured one hour at 400F. Platinum catalyzed addition cure systems may also be effective in formulating a compound which must efficiently incorporate the small MW polymer into the complete network. After an initial evaluation this cure chemistry was not pursued. Future work may explore the potential for this route.

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.

Iteration	Formulation PD# / Description	SG	Duro	Tensile	Elongation	Tear	Glass Transition Temp (°C)	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*
N/A	J6230-1 WHT Specification per P/N:	N/A	55-65	900 Min	200 Min	100 Min	-60 Max	N/A	N/A	N/A	N/A	No cracking
N/A	J6230-1 WHT Historical Data for Lot # C64121 (NVS 100.0 phenyl/vinyl)	1.37	58	947	434	119		72 (+14)	835 (-12%)	230 (-47%)	45%	
N/A	J6230-1 WHT Control - Lab Batch - Xiameter RBG-0931	1.35	47	1032	597	137	-115.5	70 (+20)	843 (-18%)	238 (-60%)	32-33%	PASS
N/A	PD-2017-0010-002 (NVS 75.25 phenyl / GP vinyl) - ref. J6230-1 WHT w/ Xiameter RBG-0931	1.35	54	1062	589	141	-115.2	71 (+17)	864 (-19%)	253 (-57%)	39-40%	PASS
N/A	PD-2017-0010-001 (NVS 25.75 phenyl / GP vinyl) - ref. J6230-1 WHT w/ Xiameter RBG-0931	1.33	56	1309	594	169		67 (+11)	924 (-29%)	303 (-49%)	50-51%	PASS
8	PD-2018-0015-008 (Pt 30:70 phenyl / HT vinyl) - ref. J6240-P WHT w/ Xiameter RBG-0931	1.15	55	1208	812	253		63 (+8)	870 (-28%)	269 (-47%)	47%	PASS
24	PD-2018-0015-024 (Pt 30:70 phenyl / HT vinyl) - ref. J6240-P WHT w/ Momentive GE SE54-2	1.16	54	1137	765	254		63 (+9)	679 (-40%)	215 (-72%)	41%	PASS
28	PD-2018-0015-028 (Pt 30:70 phenyl / GP & HT vinyl) - Momentive GE SE54-2	1.14	52	1368	932	258		64 (+12)	842 (-38%)	403 (-57%)	50%	PASS
15	PD-2018-0015-015 (Pt 50:50 phenyl / PS vinyl, extra filler, MR) - ABSS Andisil SF 9530 (3%)	1.18	59	1024	518	168		75 (+16)	735 (-28%)	228 (-56%)	59%	FAIL
25	PD-2018-0015-025 (Pt 50:50 phenyl / PS vinyl, extra filler) - ABSS Andisil SF 9530 (3%)	1.19	61	945	490	148						FAIL
26	PD-2018-0015-026 (Pt 70:30 phenyl / PS vinyl, extra filler) - ABSS Andisil SF 9530 (3%)	1.16	53	646	741	186						FAIL
27	PD-2018-0015-027 (Pt 70:30 phenyl / GP & HT vinyl) - ABSS Andisil SF 9530 (3%)	1.17	63	1001	747	231		69 (+6)	572 (-43%)	313 (-58%)	48%	FAIL
29	PD-2018-0015-029 (Pt 100:0 phenyl / vinyl) - ABSS Andisil SF 9530 (3%)	1.16	47	1197	754	226		67 (+20)	619 (-48%)	177 (-77%)	83%	PASS
32	PD-2018-0015-032 (Pt 100:0 phenyl / vinyl, 2x crosslinker) - ABSS Andisil SF 9530 (3%)	1.15	50	1092	700	234		71 (+21)	643 (-41%)	103 (-85%)	89%	PASS
30	PD-2018-0015-030 (NVS/NVS 100:0 phenyl / vinyl) - ABSS Andisil SF 9530 (3%)	1.19	54	1141	429	150		57 (+3)	701 (-39%)	357 (-14%)	28%	PASS
31	PD-2018-0015-031 (NVS/NVS 50:50 phenyl / GP vinyl) - ABSS Andisil SF 9530 (3%)	1.18	59	1455	511	166		61 (+2)	763 (-48%)	381 (-25%)	26%	PASS
34	PD-2018-0015-034 (NVS/NVS 30:70 phenyl / GP vinyl) - ABSS Andisil SF 9530 (3%)	1.18	59	1384	492	171		63 (+4)	697 (-50%)	294 (-40%)	13%	PASS

GP = General Purpose Silica Base
 HT = High Tear Strength Silica Base
 MR = Internal Mold Release
 NVS = Non-Vinyl-Specific Peroxide Cured
 PS = Precipitated Silica Base
 Pt = Platinum Cured
 VS = Vinyl-Specific Peroxide Cured

Iteration 34 of the second experimental design was selected for production trials. Mechanical properties and heat ageing data are highlighted below.

COMP#	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

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 crosslinks at the terminal vinyl groups. Additional crosslinks along the polymer chains are facilitated by the non-vinyl-specific peroxides included in the cure system. A production trial is planned to evaluate the PD-2018-0015-034 compound in a low temperature freezer door gasket application. It had excellent physical properties, heat aged properties, low temperature flexibility, and compression set with a lower cost and better availability than an equivalent compound incorporating a standard (i.e. off-the-shelf) phenyl silicone gum. We are hopeful that it will perform very well in the end-use application.

AUTHOR INFORMATION

Corresponding Author

Charles Olsen, AB Specialty Silicones; 3790 Sunset Ave., Waukegan, IL 60087

Notes

The authors declare no competing financial interests.

REFERENCES

(1) Polymer composition versus low temperature characteristics of polysiloxane elastomers

K. E. Polmanteer , M. J. Hunter

First published: January/February 1959

<https://doi.org/10.1002/app.1959.070010102>

(2) Suppression of Crystallization in Polydimethylsiloxanes and Chain Branching in Their Phenyl-Containing Copolymers

Alisa Zlatanic† , Dragana Radojcic†, Xianmei Wan†, Jamie M. Messman§, and Petar R. Dvornic*‡

†Kansas Polymer Research Center and ‡Department of Chemistry, Pittsburg State University, Pittsburg, Kansas 66762, United States

§ Honeywell Federal Manufacturing & Technologies LLC, Kansas City, Missouri 64147, United States

(3) Eur Urol 1981;7:85–88 (DOI:10.1159/000473186

Clinical Trial of a New Antigonadotropic Substance, 2,6-Cis-Diphenylhexamethylcyclotetrasiloxane, in Cancer of the Prostate

<https://onlinelibrary.wiley.com/doi/abs/10.1111/j.1600-0773.1975.tb03086.x>

(4) Monitoring of the Course of the Silanolate-Initiated Polymerization of Cyclic Siloxanes. A Mechanism for the Copolymerization of Dimethyl and Diphenyl Monomers

By: Zlatanic, Alisa; Radojcic, Dragana; Wan, Xianmei; Messman, Jamie M.; Dvornic, Petar R.

Source: Macromolecules (Washington, DC, United States), Volume: 51, Issue: 3, Pages: 895-905, Journal; Online Computer File,

2018, CODEN: MAMOBX, ISSN: 0024-9297, DOI: 10.1021/acs.macromol.7b02658

Company/Organization: Kansas Polymer Research Center and Department of Chemistry, Pittsburg State University, Pittsburg, KS, USA, 66762

Accession Number: 2018:208104, CAN 168:200193, CAPLUS

Publisher: American Chemical Society