UCRL--87613

DE82 015189

CONF-820642--2

UCRL- 87613
PREPRINT

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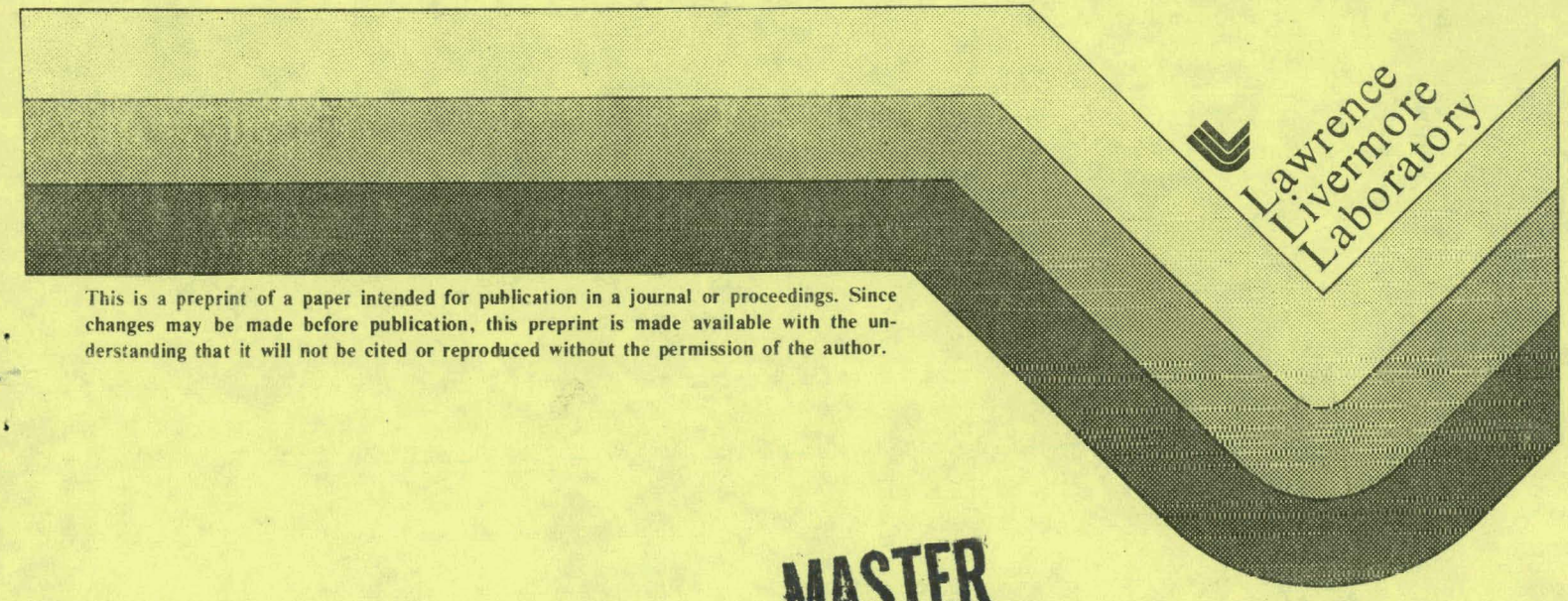
THIS PAPER WAS PREPARED FOR SUBMITTAL TO
JOWOG-28
KANSAS CITY, MISSOURI
JUNE 10-11, 1982

MAY 10, 1982



DISCLAIMER

SYNTHESIS AND CHARACTERIZATION OF A NEW SILICONE MULTIBLOCK POLYMER*

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* Work performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

CONTENTS

GLOSSARY

Banbury intensive mixer	Mixer produced by Farrel-Birmingham Co., Inc., Ansonia-Derby, Connecticut
Block Polymer	"Macromolecules comprised of chemically dissimilar, terminally connected segments."[1]
Cab-O-Sil MS7	Specific grade of fumed silicon dioxide made by the Cabot Corporation, Boston, Massachusetts.
Compression Set	The lack of recovery to free thickness a material incurs as a result of a load applied for a specified period of time.
Crepe Hardening	The process in which a filled polymer becomes excessively stiff, presumably through the interaction of functional groups on the polymer and the filler. This leads to high levels of bound polymers and long mill-softening times. In some cases this renders the polymer unprocessable.
DSC	Differential scanning calorimetry.
EEMCO rubber mill	Two-roll mill produced by Erie Engine and Mfg. Co., Erie, Pa.
GPC	Gel-permeation chromatography.
HiSil 233	A specific grade of precipitated silicon dioxide produced by Pittsburgh Plate Glass Industries, Inc., Chemical Division, Pittsburgh, Pa.
Haake Rotovisko	A rotary viscometer produced by Haake, Inc., Saddle Brook, New Jersey
L20	Designation for a silylamine intermediate used in the preparation of L60VB block polymer.
L60VB	Condensation-polymerized block silicone gum produced by LLNL.
L97KVB	Equilibrium-polymerized random silicone gum produced by LLNL.
LLNL	Lawrence Livermore National Laboratory, Livermore, California.

Load Retention	The ability of a material to resist stress in the form of an impressed weight.
Luperco 101XL	2,5-dimethyl-2,5-bis(t-butyl peroxy)hexane at 50% concentration is a curing agent produced by Lucidol Division, Pennwalt Corp., Buffalo, New York.
$\overline{M}_n$	Number average molecular weight from GPC measurements based on polystyrene equivalents.
$\overline{M}_w$	Weight-average molecular weight from GPC measurements based on polystyrene equivalents.
M60VB	Condensation-polymerized block silicone gum produced by McGhan-NuSil Corporation, Carpinteria, California.
M97KVB	Equilibrium-polymerized random silicone gum produced by McGhan-NuSil Corporation, Carpinteria, California.
MWD	Ratio of $\overline{M}_w/\overline{M}_n$. A measure of molecular weight distribution.
RP97	Equilibrium-polymerized random silicone gum produced by Rhone-Poulenc Chemical Co., Lakewood, New Jersey.
SE-54	Equilibrium-polymerized random silicone gum produced by General Electric Co., Waterford, New York.
T_g	Glass transition temperature.
TGA	Thermal gravimetric analysis
TMAS	Tetramethylammonium silanolate initiator
UCC	Union Carbide Corporation, New York, New York.
Y1587	Ethoxy-endblocked dimethylsilicone fluid produced by UCC. A processing aid for silicone gums.
Y- or L1668	Intermediate reinforced silicone gum produced by UCC (Y) or LLNL (L).
Y- or L3219	Heat stripped Y or L1668

Y- or L3223	Molding compound of Y- or L3219, temporary filler and curing agent or cellular silicone cushion produced from the molding compound. Nominal density of 0.63-0.65 g/cm^3 (M_g/M^3).
Y7005	A silanol endblocked polydimethylsiloxane of ca. 1600 M.Wt. supplied by UCC.

SYNOPSIS

The Lawrence Livermore National Laboratory (LLNL) has an active interest in the synthesis of new polysiloxanes as base polymers for cellular silicone materials. These elastomers have properties uniquely suited to very specific engineering requirements. While the polymers which we have prepared via random equilibration of various cyclic tetrasiloxanes[2] have adequate properties for certain applications, there is evidence to suggest that alternating block polysiloxanes prepared via condensation-polymerization techniques have properties more suited to our end uses as flexible foam materials (cushions). The synthetic sequence developed to prepare these materials involves reactions of functionally terminated (silylamino and silanol) polysiloxane oligomers to produce alternating multiblock (ABAB...) materials of high molecular weight. Dialkylamines are condensation byproducts in this reaction. The analysis and characterization of these multiblock polymers is reported. Since one of the oligomers is prepared in an equilibration reaction among several siloxane components, a significant degree of compositional flexibility is possible. An additional topic of discussion is the functional endcapping of these poly(dimethyl-diphenyl-methylvinyl) siloxane polymers with dimethylvinylsilyl groups. This termination provides a means of tying down polymer ends through peroxide crosslinking which very probably results in improved physical properties.

INTRODUCTION

Cellular silicone materials have been utilized for many years at LLNL as support materials, space fillers and shims. Due to a disruption in the commercial availability of these foams as well as the silica-filled molding compounds and base gums from which the foams are derived, we at LLNL have found it necessary to develop a silicone technology suited to our own needs. We have established both the synthesis capability for preparation of the base silicone elastomers and the requisite compounding expertise to convert gums to cellular materials.

The most crucial foam properties in our applications are low compression set, high load-retention and long service life. Our studies indicate that foams based on silicone elastomers which are alternating multiblock polymers have superior compression set properties to those foams that are based on standard random equilibration siloxane polymers, the preparation of which is described elsewhere.[2] Our synthesis of the former materials is based on sequential condensation reactions between functionally-terminated oligomers. The methods of reacting such functionally terminated oligomers (silanol/silanol,[3] silanol/silyl halide,[4] and silanol/silyl amine,[5] for example) are not new. The technique utilized here is based on the bulk reaction of amine-terminated and silanol-terminated siloxanes to yield regular, alternating multiblock polymers which serve as base elastomers in foam applications.

EXPERIMENTAL

Materials*

The cyclotetrasiloxanes (octamethyl, octaphenyl, and sym-tetramethyl-tetravinyl) were purchased from Silar Laboratories, Inc.; Y7005, a silanol-terminated polydimethylsiloxane fluid having a molecular weight of approximately 1600 was purchased from Union Carbide Corporation; 1,7-dichlorooctamethyltetrasiloxane, obtained from Petrarch Systems, Inc. was converted to 1,7-bis(dimethylamino)octamethyltetrasiloxane by reaction with dimethylamine and magnesium turnings according to the method of Creamer.[6] The oligomerization initiator, tetramethylammonium silanolate (TMAS), was prepared by the reaction of tetramethylammonium hydroxide with octamethyl-cyclotetrasiloxane.[7] The fumed silica, Cab-O-Sil MS-7, was obtained from Cabot Corporation, while the precipitated silica, Hi Sil 233 was supplied by PPG. The urea pore-forming reagent was purchased from Sherritt-Gordon Mines, Canada and the t-butyl per-2-methylbenzoate from Witco Corporation. The processing aid, Y1587, an ethoxy-endblocked polydimethyl-siloxane is marketed by Union Carbide Corporation.

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*The mention of firm names or trade products throughout this article does not imply that they are endorsed or recommended by the U. S. Department of Energy or the University of California over other firms or similar products not mentioned.

Oligomer Synthesis

In a typical preparation of an amine-terminated siloxane prepolymer (L20), 848.4g (2.860 mole, 56.6 wt. %) of octamethylcyclotetrasiloxane, 253g (0.319 mole, 16.9 wt. %) of octaphenylcyclotetrasiloxane, 23g (0.067 mole, 1.5 wt. %) of 2,4,6,8-tetramethyltetravinylcyclotetrasiloxane, and 376g (1.020 mole, 25 wt. %) of 1,7-bis(dimethylamino)octamethyltetrasiloxane were added to an oven-dried 2 liter resin kettle maintained under a dry argon blanket. The kettle had been equipped with the following oven-dried accessories which were assembled while hot under a dry argon stream: condenser, temperature controller, thermowell, and gas inlet adapter. The mixture was heated with stirring to 100°C and a total of 4.64g (0.31 wt. %) TMAS was added via syringe in three roughly equal portions, one hour apart. The polymerization was continued for two hours after the last portion of catalyst was added. The total reaction time was five hours. Finally, the kettle temperature was raised to 135°C for 30 min. to deactivate the TMAS. The reaction mixture was cooled and vacuum filtered under dry argon in a glove bag. According to proton nuclear magnetic resonance (pmr) analysis, the dimethylamino-terminated prepolymer had a molecular weight of 1514 (calc. 1477).

Polymerization

The bulk polymerization was carried out in a 1 gallon, steam-jacketed Baker Perkins sigma blade mixer at approximately 200°F. Before the reactants were placed in the mixer, it was dried by heating at 200°F for at least one hour while being purged with dry argon. The silanol-terminated polydimethylsiloxane (Y7005) was added to the mixer bowl and a clear plastic lid of Plexiglas^{R} (polymethylmethacrylate) with a Viton^{R} fluorocarbon gasket containing several closed ports was clamped in place. An addition funnel was

fitted on one port, and about 90% of the stoichiometric amount* of L20 (dimethylamino-terminated siloxane prepolymer) was added rapidly, consistent with maintaining a manageable level of foaming as dimethylamine was evolved. Another port permitted evolved dimethylamine to be diverted to an exhaust system, while a stream of dry argon was swept into the reactor through a third port.

The remaining L20 was added slowly, allowing for frequent determinations of the apparent viscosity by means of a Haake rotary viscometer. The spindle could be raised or lowered through a port in the cover. A one hole cork was fitted to the spindle so that air could be excluded from entering the reactor through the spindle port when the viscosity was not being determined. No attempt was made to determine an actual viscosity because of anticipated complications arising from differences in the in situ sample geometry depending upon mixer blade position, actual volume of reactants, spindle depth within the reaction mixture, etc. However, it was shown that a particular scale reading reproducibly corresponded to the desired $\overline{M}_w$ of 500,000 (GPC determination).

Once the stoichiometric equivalence point was reached, a three-fold molar excess of the endblocking reagent vinyldimethyl-N-methylacetamidosilane[8] was added. After an additional 15-30 minutes of mixing at 200°F, the product mass was washed three times with 1L portions of distilled water and then dried in a vacuum oven (80°C/29 in. Hg) for ca 16 hrs. to remove water and residual dimethylamine.

*Since the small amounts of atmospheric moisture encountered in handling operations affect the average molecular weight of the L20, the calculated condensation stoichiometry was checked by small scale screening reactions in which quantities of L-20 and Y7005 were mixed in different ratios in 4 dram screw cap glass vials under dry argon. The caps were loosely screwed on, and the vials placed in an oven at 100°C for 1 hour. The optimum stoichiometry was taken as that which resulted in the highest molecular weight gum.

RESULTS AND DISCUSSION

Synthesis

The major advantage of the preparative method described here is the smooth one-step synthesis of the amine-terminated block, block A. This is accomplished by the reaction of the octamethyl-, octaphenyl-, and tetramethyltetravinylsiloxanes, TMAS and 1,7-bis(dimethylamino)-tetrasiloxane at 100°C. The block size (molecular weight) is controlled by the relative amount of chain terminator (1,7-bis(dimethylamino)octamethyltetrasiloxane) added. The initiator is simply deactivated by increasing the reaction temperature to 135°C, where it decomposes into volatile, innocuous byproducts.[7] The product, block A, is a low molecular weight oligomer of randomly equilibrated siloxanes. Certain characteristics of the cured polymers can be controlled by varying the component ratios during the oligomer synthesis. For example, diphenylsiloxane units are incorporated to avoid crystallization[9] at low temperatures (<-40°C), while methylvinylsiloxane units provide vinyl sites at which crosslinking may occur through peroxide cure. By varying the vinyl concentration we may vary the cross link density, and, in turn, the compression set and load retention characteristics.

Block B is a commercially available silanol-terminated polydimethylsiloxane of about 1600 $\overline{M}_w$. Both blocks A and B are of approximately equivalent molecular weight so that the alternating blocks within the polymer are of roughly equal size.

The idealized synthesis pathways involved in the preparation of the oligomers are shown in equations (1) and (2).

$$(1)\quad \begin{matrix} CH_3 & CH_3 & CH_3 \\ ClSiO(SiO)_2 & SiCl & \\ CH_3 & CH_3 & CH_3 \end{matrix} + xs(CH_3)_2NH \xrightarrow{Mg} \underset{\underline{C}}{\begin{matrix} CH_3 & CH_3 & CH_3 \\ (CH_3)_2NSiO(SiO)_2 & SiN(CH_3)_2 & \\ CH_3 & CH_3 & CH_3 \end{matrix}} + MgCl_2 + H_2$$

(2) $$\underline{C} + x\left(\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}SiO\right)_4 + y\left(\begin{smallmatrix}C_6H_5\\ C_6H_5\end{smallmatrix}SiO\right)_4 + z\left(\begin{smallmatrix}CH_3\\ C_2H_3\end{smallmatrix}SiO\right)_4 \xrightarrow{TMAS}$$

$$(CH_3)_2N\overset{CH_3}{\underset{CH_3}{Si}}O\left[\left(\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}SiO\right)_{x+2}\left(\begin{smallmatrix}C_6H_5\\ C_6H_5\end{smallmatrix}SiO\right)_y\left(\begin{smallmatrix}CH_3\\ C_2H_3\end{smallmatrix}SiO\right)_z\right]_n\overset{CH_3}{\underset{CH_3}{Si}}N(CH_3)_2$$

$\underline{B}$

(where n, x, y, and z are integral numbers)

The polymerization and endcapping reactions are shown in equations (3) and (4), respectively.

(3) $$n\ HO\left(\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}SiO\right)_mH + n\ \underline{B} \xrightarrow{100°C} 2n\ HN(CH_3)_2 + HO(AB)_nOH$$

$\underline{A}$

(4) $$HO(AB)_n\ OH + CH_2{=}CH\overset{CH_3}{\underset{CH_3}{Si}}X \longrightarrow CH_2{=}CH\overset{CH_3}{\underset{CH_3}{Si}}O(AB)_nO\overset{CH_3}{\underset{CH_3}{Si}}CH{=}CH_2 + HN\overset{O}{\underset{CN_3}{C}}CH_3$$

$$X = -N(CH_3)COCH_3,\ -N(H)Si(CH_3)_2CH{=}CH_2$$

The presence and quantity of each type of organic group within the polymer was verified by means of continuous wave pmr spectroscopy. Gel permeation chromatography was used to characterize polysiloxane $\bar{M}_w$, $\bar{M}_n$ and polydispersity. The targets for this material were $\bar{M}_w$ of 500,000, a phenyl content of 9 wt.% (as $Si(C_6H_5)_2O$), a vinyl content of 0.7 wt.% (as $Si(CH_3)(CH{=}CH_2)O$) and vinyldimethylsilyl endcapping. These can be routinely attained.

Vinyl moieties were included in the end groups in order to facilitate incorporation of the polymer chain ends into the network during the crosslinking process. This is a means of countering the possibility that dangling chain segments may contribute to the compression set problem. A mechanism can be envisioned in which uncrosslinked dangling chain-ends become temporarily entangled during the proximity enforced upon them by compression of the cushion during test conditions.

Our approach was to react the silanol-terminated block polymers with vinyldimethyl-N-methyl-acetamidosilane or 1,3-divinyltetramethyldisilazane. Strict stoichimetric control is essential during polymerization because dialkylamine chain termination rather than silanol chain termination at the equivalence point would foil endblocking efforts. Hydrolysis of silylamine would lead to silanol endblocking during the wash step, and then to crepe hardening of the filled polymer system. This was, in fact, observed in one reaction sequence in which excess component A (equation 1) was added.

We have found that silanol endblocking can be assured in two ways: 1) as the stoichiometric equivalence point is approached (as indicated by a rapid increase in viscosity corresponding to a large increase in molecular weight), the silylamine prepolymer is added dropwise to avoid over-shooting the equivalence point; 2) when the desired viscosity is attained, an excess of water is added to hydrolyze any silylamine present and ensure silanol endblocking. Because of the operating temperature of a 90°C, any water added is a transient reactant, but excess endblocker is also subsequently added to ensure vinyl endblocking.

Because of the minute concentration (~0.01%) of vinyl introduced in this manner, and the difficulty in distinguishing it from pendant vinyl moieties substituted upon the elastomer backbone, it has not been possible thus far to obtain direct proof of vinyl endblocking.[10] Previously,[9c] endcapping was accomplished by reaction of the silanol-terminated polysiloxanes with N,N'-bis(trimethylsilyl)ethylenediamine to yield

ethylene diamine and trimethylsilyl-terminated polysiloxanes. Thorough washing of each of these polymers with water is mandatory to remove byproduct amines which could be responsible for reversion of polysiloxanes under conditions of confined heat,[11] for processing difficulties,[12] and also for bond cleavage in the cured foams.[13]

FORMULATION AND COMPOUNDING

The ultimate use for polysiloxane gums at LLNL is as base materials for elastomeric foams. The starting polysiloxane gums are reinforced with a silica filler of high surface area and activity, aged, heat stripped, catalyzed with a suitable peroxide such as t-butyl-per-2-methylbenzoate and temporarily filled with a water soluble pore former such as urea or ammonium chloride. The temporarily filled material is mold-cured to the desired shape. The filler is then washed from the crosslinked matrix with hot water leaving behind a cushion of density determined by the amount of temporary filler incorporated initially. Compression set data indicates these condensation block polysiloxanes have superior properties to cushions made from random polysiloxane polymers.

The gums were formulated using a standard LLNL formulation:

100 pts. gum;
32 pts. Cab-O-Sil MS-7 fumed silica (Cabot);
6 pts. Hi-Sil 233 precipitated silica (PPG);
10 pts. Y1587 processing aid (UCC).

The mixture was compounded in a Farrell-Banbury intensive mixer at 40 rpm for 6 min. and then milled for five minutes at 60°C and a surface speed of 25 fpm on a 6 inch two-roll mill, with a shear ratio of 1.2:1. After compounding, the formulation was bin aged for 28 days at room temperature. At the end of this period, the material was heat stripped for 18 hours at

177°C. The heat-stripped material (L3219) was then catalyzed with a vinyl specific peroxide, t-butyl-per-2-methylbenzoate. The catalyzed gum was then filled with the pore former and sheeted. The mold was charged with the molding compound, compression molded, and cured at 125° for 60 minutes. The cured part was washed for 16 hours in 90°C water, and then air dried for 16 hours at room temperature. The part was finally oven dried 4 hours at 150°C and then post cured 24 hours at 249°C.

CHARACTERIZATION AND TESTING

The polymers synthesized in this study were characterized by proton magnetic resonance (pmr) spectra, gel permeation chromatography (GPC), and thermal analyses (DSC and TGA). Table I summarizes results obtained for a variety of polymers, including: a) block polymers (L60VB - synthesized at LLNL; M60VB - synthesized at McGhan-NuSil Corp. under LLNL contract); b) random polymers (L97KVB - synthesized at LLNL; M97KVB - synthesized at McGhan-NuSil Corporation under LLNL contract; RP97 - a blend of random polymers synthesized at Rhone-Poulene Corporation; SE-54 - synthesized by General Electric Corporation).

The "VB" code refers to polymers which are vinyl endblocked; "K" refers to systems synthesized by using a potassium silanolate initiator.[2] These active silanolates are deactivated by milling 1 wt.% Cab-O-Sil MS-7 fumed silica into the gum to prevent polymer reversion. The General Electric and Rhone-Poulenc polymers are also presumably synthesized with either potassium silanolate or potassium hydroxide based on emission spectra analyses.[14] The TMAS used in the block polymer synthesis is deactivated by heating.

Except for the SE-54 gum, which is a relatively high phenyl, low vinyl content system, it can be seen that molecular composition does not vary widely within the group studied. Higher vinyl contents give rise to

higher crosslink density and thus to higher modulus foams. A systematic study of this and related structure-property relationships has been reported in a preliminary communication.[2] A fairly large range of molecular weights was synthesized, but this was found to have a small to negligible effect on properties. Significantly enhanced thermal stability as measured by TGA is demonstrated by the block polymer system. This is not unexpected, inasmuch as no ionic residius are introduced into the block polymer synthesis scheme to catalyze polymer reversion. The random polymers synthesized from potassium silanolates, however, suffer accelerated weight loss because of the presence of the metal salts.[15] This seems like a more plausible explanation for the observed differences in stability than one which invokes structural differences in the polymers. The GE and Rhone-Poulenc polymers demonstrate intermediate stability, possibly because: (1) metal silanolates were not used in their manufacture, (2) because they have been stablized or, (3) because they have been stripped to remove low molecular weight cyclic siloxanes during the manufacturing process, and therefore, suffer less weight loss at low temperature.

Table II contains examples of the rather large differences observed in compression set data for the various polymers studied. The block polymers are clearly superior to the commercially supplied random polymers, but only marginally better than the L97KVB system. This may indicate that vinyl endblocking is of critical importance in minimizing compression set since the commercial polymers are not believed to incorporate this feature. The trend is consistent in the two densities of foam examined. Compression set measurements were obtained in a confined-die test at 35% compression and 149°C for 24 hours.[16]

TABLE I. POLYMER CHARACTERIZATION

Polymer Type	H'NMR Ratios (Wt.%) CH_3 -SiO- CH_3	C_6H_5 -SiO- C_6H_5	C_2H_3 -SiO- CH_3	GPC $\bar{M}_n$	GPC $\bar{M}_w$	GPC MWD	DSC T_g(°C)	TGA -10Wt%(°C)	TGA -50Wt%
1. L60VB (Block) 154	26.09(89.98)	1.00(9.26)	0.0952(0.77)	181,000	476,000	2.62	-115	460	542
2. M60VB (Block)									
153	22.28(88.4)	1.00(10.7)	0.106(0.98)	99,000	457,000	4.60	-110	385	480
155	22.39(88.5)	1.00(10.6)	0.100(0.92)	139,000	442,000	3.18	-113	390	496
160-I	23.66(89.2)	1.00(10.1)	0.078(0.69)	151,000	419,000	2.77	-115	386	467
3. L97KVB (Random) 150	(89.7)	(9.6)	(0.7)	250,000	590,000	2.38	-106	218	430
4. M97KVB 158-III	24.67(89.58)	1.00(9.74)	0.080(0.68)	195,000	544,000	2.78	-115	190*	366
(random) 162	26.55(90.21)	1.00(9.11)	0.085(0.67)	308,000	698,000	2.26	-116	190*	423
163	25.43(89.82)	1.00(9.48)	0.085(0.70)	179,000	410,000	2.29	-118	302*	397
164	28.58(90.79)	1.00(8.52)	0.093(0.69)	192,000	514,000	2.67	-117	222*	362
5. RP97 (Random,blend)	27.83(90.73)	1.00(8.74)	0.070(0.53)	210,000	498,000	2.38	-114	333	473
6. SE-54 (Random) Lot JE167 115	15.99(85.43)	1.00(14.30)	0.0215(0.27)	289,000	656,000	2.28	-107	440	500

*1 wt.% Cas-O-Sil MS-7 fumed silica milled in

Table II. Compression Set Data for L3223* and L3260* Silicone Cushions

Cushion Type	Gum Type	% set 24 hour (Av, recovery)	Sx	C.V.%	n
L3223	SE-54 (random)	10.32	0.38	3.7	3
	RP-97 blend (random)	19.58	1.57	8.0	3
	L97KVB (random)	5.68	0.20	3.6	3
	L60VB (block)	3.84	0.29	7.6	3
L3260	SE-54 (random)	10.40	1.02	9.8	3
	L97KVB (random)	4.33	0.18	4.1	3
	L-60VB (block)	3.30	0.62	19.0	3

*These codes refer to the nominal densities of the cushions, which are controlled by the amount of leachable filler (in these cases urea) which is milled in during the formulation step; L-3223 is roughly 44% porosity (0.65g/cc) while L3260 is 60% porosity (0.50g/cc). Each slab is nominally 100 mil thick; urea was used as the pore-forming filler, and the curing agent was Esperox 497XL (t-Butyl-per-2-methylbenzoate). Further details relating to formulation and compression set determination are outlined elsewhere.[16]

ANALYSES

Both oligomers and polymers were routinely characterized by thermal analyses, gel permeation chromatography (GPC), and pmr spectra. The pmr spectra were obtained on 10 wt.% solutions in $CDCl_3$ using a Fourier transform Nicolet Magnetics Wide Bore 200 transform spectrometer operating at 200.071 MHz. Normally a 45 degree RF pulse (4 μsec) is used, along with a 3 sec. recycle time and 16,000 data points. The acquisition time is 2.72 sec., with a 3000 Hz spectral width. Between 100 and 1000 free induction decays are accumulated, depending on the sample.

The DSC analyses were obtained with a duPont Model 900 DSC module scanning from -120° to 20°C at 10°C per minute. The TGA analyses were performed on a Perkin-Elmer TGS2 thermal gravimetric system, scanning from 20°C to 600°C under dry nitrogen at a program rate of 5°C per minute.

A Gel Permeation Chromatograph, Waters Model 200, was used for determining the molecular weight averages and distributions in this study, with the following instrumental parameters and conditions:

Solvent:	Tetrahydrofuran, THF, inhibited with 0.025% butylated hydroxytoluene, degassed at 55°C, flow 1 ml/min.
Columns:	4 each, in series, 4-ft x 3/8-in Styragel (Waters) Linear 10^6 A exclusion limit.
Column Temperature:	Ambient, 21°C.
Detector:	Differential Refractometer
Calibration:	Waters Narrow Distribution Polystyrene Standards.
Data Reduction:	Linear Regression Calibration Curve for Polystyrene-Equivalent molecular weight averages, Computer-interactive data/computation methods.

CONCLUSIONS

It has been shown that L60VB, a multiblock silicone polymer can be clearly prepared in one step from prepolymers having designed compositions. These materials are processed to elastomeric foam cushions having low compression set and high thermal stability, which are superior to any other silicone cushion we have tested in these respects. This includes a comparison with elastomers having the same gross composition, but with a random arrangement of components along the polymer backbone.

ACKNOWLEDGMENTS

We gratefully acknowledge sample analyses performed by:

J. E. Clarkson	-	gas chromatography and gel permeation chromatography (GPC)
P. C. Crawford, G. Crossman, and B. M. McKinley	-	thermal analyses
J. Cupps	-	GPC
J. A. Happe	-	NMR

Discussions with Fred Smith who, along with Charles Creamer, worked on an early version of the block polymer at UCC are highly appreciated.

The Glossary was adapted inpart from the one contained in Reference 14.

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