

Elastomeric and Mechanical Properties of Poly-*m*-carboranylenesiloxanes

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Synopsis

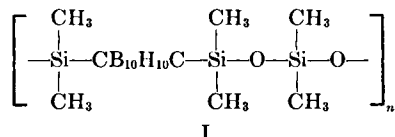
A new high-temperature elastomer, SiB-2, has been investigated by stress relaxation, modulus-temperature, and volume-temperature techniques. SiB-2 was found to be more stable than a related elastomer, radiation-cured silicone rubber, having about twice as long a chemical relaxation time at 250°C. Possible mechanisms to account for this increased stability are discussed. At low temperatures, T_g for SiB-2 was estimated at -34°C., which compares well with $T_i = -30^\circ\text{C}$. for this polymer. By comparison, SiB-3 has $T_i = -60^\circ\text{C}$., while phenyl-modified SiB-4 was found to have $T_i = -25^\circ\text{C}$. T_m for SiB-2 was estimated to be + 56°C.

INTRODUCTION

The need for new high-temperature elastomers is very great, for both military and industrial uses. Among the most important high-temperature elastomers currently in use are the silicone rubbers, their useful temperature range extending to near 250°C.¹⁻³

Continued syntheses of new silicones have led to the incorporation of *m*-carborane in the siloxane backbone.⁴ The *m*-carborane nucleus^{6,7} is known to be stable at high temperatures,^{6,8} and the carboranes in general have been described as electron-deficient, "superaromatic" systems.⁹ It was hoped that this new derivative might be stable at very high temperatures.

The present investigation is concerned with the physical and mechanical properties of the poly-*m*-carboranylenesiloxanes, especially that of SiB-2, which has the structure I.



This and related SiB structures are discussed in detail by Heying et al.^{4,5}

EXPERIMENTAL

Several types of SiB-2 panels were kindly supplied by Dr. H. Schroeder of the Olin Mathieson Chemical Corporation, New Haven, Connecticut.

TABLE I
Sample Designation of SiB-2 Polymers

Sample	Formulation
A	No cure, no filler
B	1.5% benzoyl peroxide, no filler
C	1.5% benzoyl peroxide, 25% Cab-o-Sil
D	2.0% benzoyl peroxide, no filler
E	SiB(- Θ -CH=CH ₂) (See structure II below) 100 parts, SiO ₂ 37.5 parts, Fe ₂ O ₃ 5 parts, DC-40 2 parts.

Their formulation is described in Table I. In addition, smaller amounts of SiB-3 and phenyl-modified SiB-4 were supplied for comparison purposes.

Stress relaxation measurements were made on a standard relaxometer,^{10a} and a high-temperature modification of this instrument. The latter is surrounded by an electric furnace capable of maintaining 500°C. Measurement of the 10-sec. modulus $G(10)$ was made using both a standard Gehman¹¹ and a high-temperature modification¹² similar to the above. For torsion moduli greater than 5×10^9 dyne/cm.², a Clash-Berg¹³ Torsion stiffness tester was utilized. Clash-Berg data in the glassy region were combined with Gehman measurements to construct the modulus-temperature curves. The usual heating rate for these experiments was 1°C./min.

Thermal expansion coefficients above and below the glass transition temperature were determined for SiB-2 by displacement measurements. The sample was weighed in density-calibrated Dow-Corning silicone oil as a function of temperature by a Mettler balance. After several hours immersion in silicone oil, the weight gain of SiB-2 was approximately 2%.

RESULTS AND DISCUSSION

Mechanical Experiments

Combined Gehman and Clash-Berg data for SiB-2 samples A, B, and C are shown in Figure 1. Particular points of interest are as follows.

(1) The modulus in the glassy region is close to 3×10^{10} dyne/cm.² for all these samples. This is a usual finding.

(2) The inflection temperature^{10b} T_i , defined as the temperature at which $3G(10) = 1 \times 10^9$ dyne/cm.², is -30°C. The inflection temperature is closely related to the glass transition temperature T_g .

(3) Sample A, which has not been crosslinked, shows no well-defined rubbery plateau. This property is characteristic of many polymers, silicones in particular.² Samples B and C show normal rubbery plateaus for crosslinked polymers, the difference between them being attributable to the effects of the filler, which raises the modulus of the system.

Using these techniques, T_i for SiB-3 was found to be -60°C., while the phenyl-modified SiB-4 had $T_i = -25^\circ\text{C}$. The high value reported for

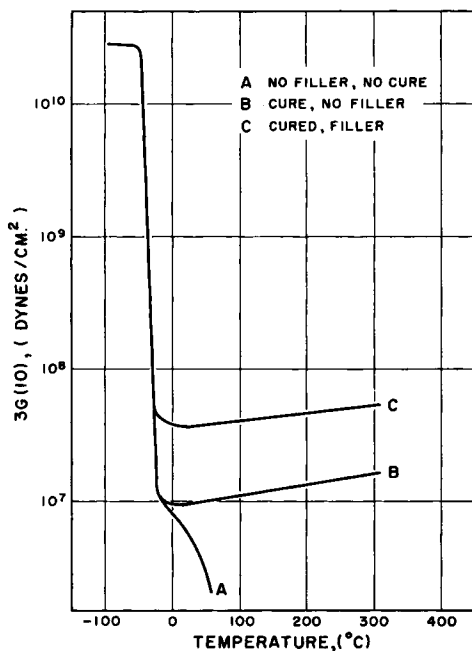


Fig. 1. Log modulus vs. temperature plots for samples A, B, and C showing changes in modulus caused by cure and filler.

this last measurement was probably caused by the substitution of phenyl for methyl groups in the polymer.

At temperatures above 300°C. chemical changes occur in SiB-2 samples, as shown in Figure 2 (Sample D). The effect noted is probably due to crosslinking, which raises the modulus of the samples. The nitrogen atmosphere employed, however, should probably be called a nitrogen-enriched atmosphere. No attempt was made to measure the residual oxygen. The Olin workers^{4,5} have found that SiB-2 is stable up to 500°C. in an inert atmosphere. After the steep rise in $3G(10)$ noted, the samples broke. Simple inspection showed them to be hard and brittle, with only residual elastic properties remaining. Extraction of the sample with acetone to remove residual benzoyl peroxide, or more rapid heating did little if anything to increase the elastic range. From Figure 2 the upper limits of usefulness of SiB-2 are 340°C. in air and 380°C. in the nitrogen atmosphere employed.

The high temperature resistance to oxidative crosslinking can be considerably improved by the addition of a small amount of Ionox, a commercial antioxidant.* Incorporation of approximately 1.8% of this material by weight produced a sample stable to 432°C. in the nitrogen atmosphere. This is approximately 50°C. higher than available otherwise.

* Ionox is 1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene and is sold by the Shell Chemical Company.

Above this temperature, the modulus increased rapidly, as with the other samples.

Figure 3 illustrates the effect of temperature on the relaxation modulus

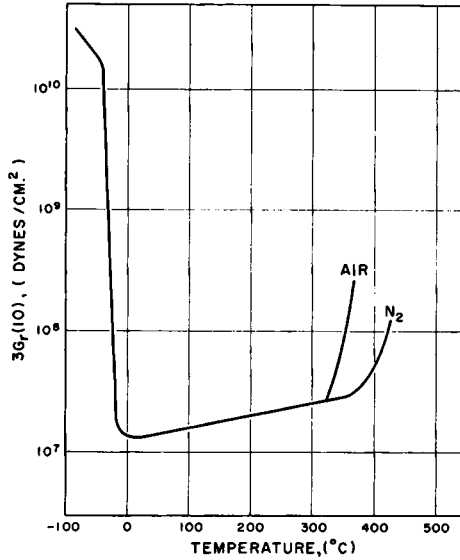


Fig. 2. Effect of air and nitrogen atmospheres on SiB-2 modulus values for sample D.

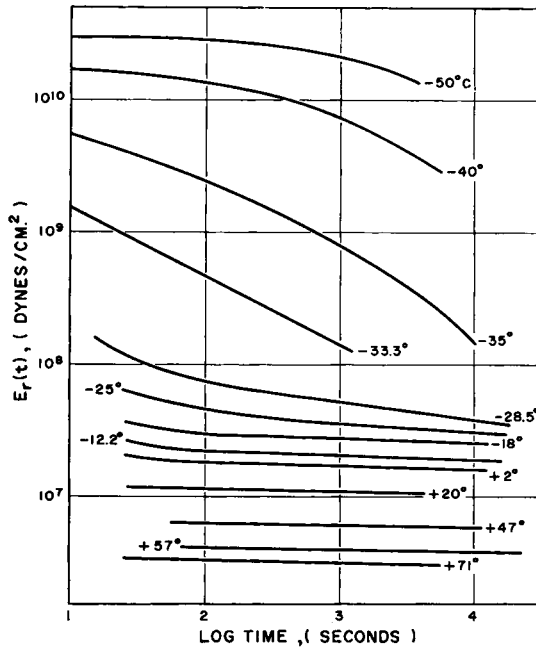


Fig. 3. Sample A stress relaxation at low temperatures. Log modulus vs. log time. Lowest four temperatures converted from creep data.

of sample A through the glass transition region. Above 71°C. this sample forms holes and tears. The lowest four temperatures represent data converted from creep measurements.¹⁴ Samples B and C show similar effects, but the samples are stable to much higher temperatures, and the stress relaxations above T_g show the rubbery plateau effect.

A master curve^{15,16} was constructed for sample A, using the time-temperature superposition principle¹⁷ with -25°C . as the reference temperature. This curve, corrected for proportionality of modulus to absolute temperature, is shown in Figure 4. This graph illustrates the theoretically

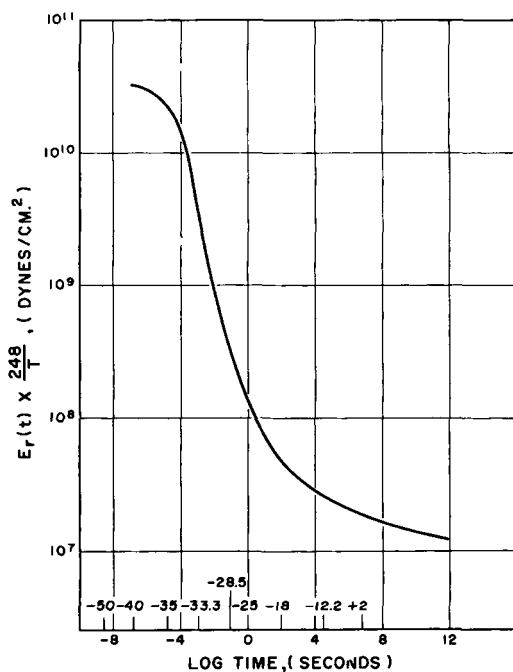


Fig. 4. Master curve for sample A. Log modulus, corrected for temperature effects vs. log time.

predicted relaxation modulus over twenty decades of time, as would be observed at -25°C . The characteristic slope^{10a,18} n for this polymer, deduced from Figure 4, was found to be $1/2$, which suggests that the backbone chain is stiff, and/or intermolecular interactions do not play a very significant role in the transition. The parameter n is defined as the negative slope of the master curve at the inflection point.

An attempt was made to fit Figure 4 by the WLF equation.¹⁹ Unfortunately, the fit was only very approximate. A possible reason for this discrepancy is the slight crystallinity found for this polymer (see below). The WLF equation was designed to fit linear amorphous polymers.

Chemical Relaxation Studies

For crosslinked polymers, stress relaxation at high temperatures may be used as a measure of the kinetics of chemical change. For polydimethylsiloxane, Si—O bond interchange reactions^{20,21} are thought to be responsible for the observed relaxation. Figure 5 compares present data of acetone-extracted sample D with radiation-cured polydimethylsiloxane²⁰ and ordinary filled silicone rubber.²² It is observed that SiB-2 is considerably more stable than ordinary silicone rubber and somewhat more stable than the radiation-cured preparation. Comparison of Figure 7 of Osthoff et

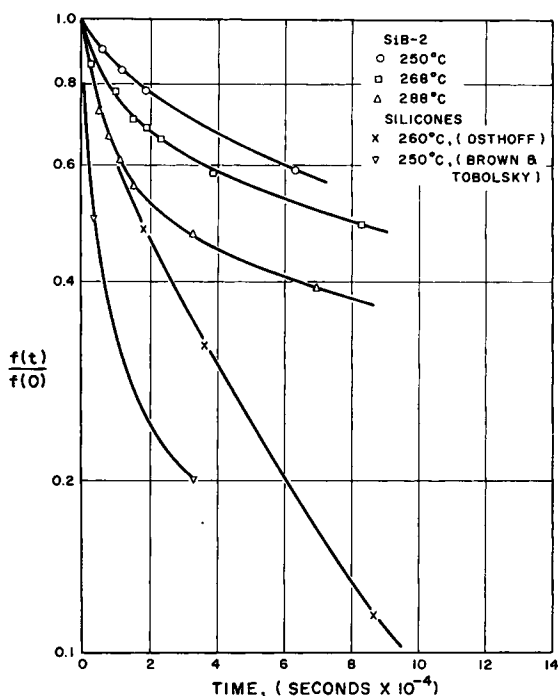


Fig. 5. Stress relaxation of sample D at high temperatures compared to two types of silicone rubber.^{18,20} Log reduced stress vs. time.

al.²⁰ with Figure 5 shows that SiB-2 stress relaxation curves fall about 30°C. higher on stress-time plots than those for the radiation-cured silicone. In Figure 5, the ratio $f(t)/f(0)$ represents the stress at time t divided by the stress at time zero.

Intermittent stress relaxations^{10a} were also run at 268 and 307°C. Intermittent relaxation studies measure both scission and crosslinking whereas continuous stress relaxation measures only scission. The data obtained at the lower temperature indicated no substantial change with time, which suggests that the plot at that temperature in Figure 5 is valid. The intermittent stress-time plot at 307°C., however, showed considerable increase

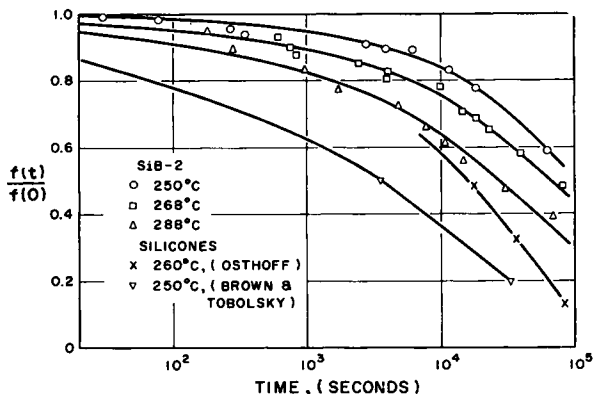


Fig. 6. Same data as Fig. 5, plotted as reduced stress vs. log time to facilitate estimation of τ_{ch} .

of stress. Values of $f(t)/f(0)$ greater than unity may be interpreted as an increasing crosslinking density with time. At higher temperatures, the continuous stress relaxation plot goes through a definite minimum, as was observed by Brown,²² because of very extensive crosslinking.

The data in Figure 5 were replotted on an $f(t)/f(0)$ versus log time scale as shown in Figure 6. This type of plot facilitated the estimation of τ_{ch} , the chemical relaxation time,^{10c} defined as the time necessary for the $f(t)/f(0)$ value to drop to $1/e = 0.368$. From Figure 6 and ref. 18 the values shown in Table II were estimated. The value of τ_{ch} obtained by Turner and Lewis²³ is also included for comparison. These workers used a filled, commercial type preparation, which represents one of the most stable silicone rubbers mentioned in the literature.

A word should be said about the τ_{ch} values in Table II. If one takes this value as an arbitrary limit to the useful life of the polymer at 250°C. in certain types of service, then SiB-2 should last twice as long as the irradiated silicone rubber and twenty times as long as some of the commercial formulations of silicone rubber.

Chemical stress relaxation studies were also carried out on a filled derivative of SiB-2, sample E. This material contains occasional *o*-carborane

TABLE II
Relaxation Times at 250°C.

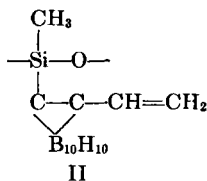
τ_{ch}	Polymer
1.9×10^5	SiB-2
8.6×10^4	Silicone ^a
8.0×10^3	Silicone ^b
1.6×10^5	Silicone ^c

^a Data of Osthoff et al.²⁰

^b Data of Brown.²²

^c Data of Turner and Lewis.²³

nuclei as the crosslinking sites in addition to the *m*-carborane nuclei. Its structure is^{4,5} II,



which after curing yields a structure similar to the methylvinylsilicone elastomers in current use. The results are shown in Figure 7 for air and an enriched nitrogen atmosphere.

It is observed that these samples are highly resistant to stress relaxation. This may be attributable^{4,5} in part to the protective properties of Fe_2O_3 .

Determination of T_g and T_m

Volume-temperature studies were carried out on sample A. From the known weights of the dry and immersed sample and the density of the oil, Figure 8 was constructed. The value of T_g was found to be -34°C ., as evidenced by the change in the slope of the V_{sp} versus T plot at this temperature. The volume expansion coefficients above and below T_g were estimated to be $8.3 \times 10^{-4}/^\circ\text{C}$. and $4.3 \times 10^{-4}/^\circ\text{C}$., respectively. The value of -34°C . for T_g compares well with $T_i = -30^\circ\text{C}$. mentioned above.

The Olin workers^{4,5} reported SiB-2 to be slightly crystalline. Figure 8 shows a small but definite melting transition near 56°C . This value is in fair agreement with the empirical rule^{10d} stating that for an unsymmetrical polymer $3/2 T_g \cong T_m$. This slight crystallinity, however, can account for the relatively small change in $E_r(t)$ versus time noted above T_g in Figure 3.

The counterpart transition properties of silicone rubber^{24,25} are as follows: $T_g = -123^\circ\text{C}$., $T_m = -60^\circ\text{C}$., $\beta_g = 2.7 \times 10^{-4}$, and $\beta_R = 12 \times 10^{-4}$. As more carborane units are added to the siloxane chain backbone, both T_g and T_m are raised. Table III summarizes these changes. A higher value of T_g , of course, means that the SiB polymers cannot be used at temperatures as low as the silicone rubbers.

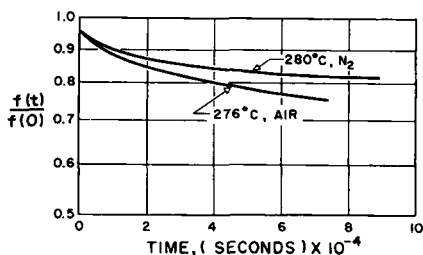


Fig. 7. Stress relaxation of sample E in air and enriched nitrogen atmospheres.

TABLE III
 T_g and T_m Values

Polymer	T_g , °C.	T_m , °C.
Silicone rubber	-123	-60
SiB-3	-60	—
SiB-2	-34	+56

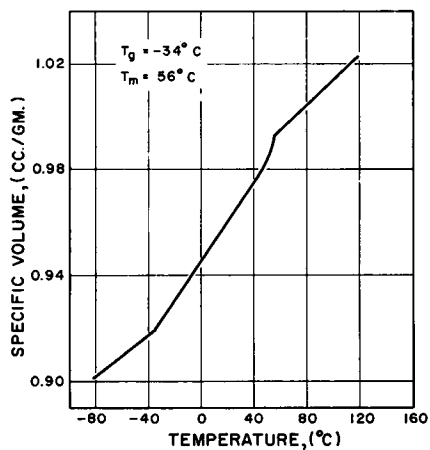


Fig. 8. Specific volume-temperature plot for Sample A.

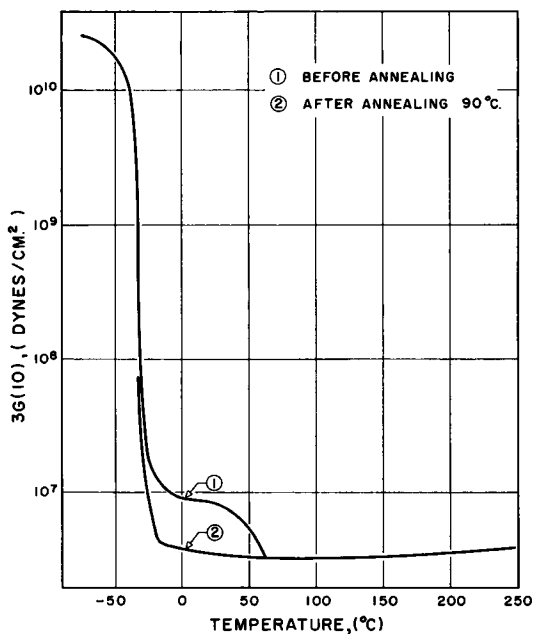


Fig. 9. SiB-2, Sample A, modulus-temperature curve: (1) original sample; (2) after annealing at 90°C. Note slight crosslinking as indicated by rubbery-plateau, and crystalline melting at 60°C.

The effect of this crystallinity was noted in one other experiment, as shown in Figure 9. This sample, a slightly crosslinked version of sample A, apparently was somewhat more crystalline than other preparations. Two distinct rubbery plateau regions are noted, above and below an apparent melting temperature of 66°C. After annealing at 90°C., retesting showed no trace of crystallinity. By using the relation^{10e}

$$f(O) = N(O)kT[(L/L_u)^2 - L_u/L] \quad (1)$$

where $f(O)$ is the stress immediately after stretching from length L_u to length L , k is Boltzmann's constant, and T the absolute temperature, the number of effective network chains per cubic centimeter, $N(O)$, may be calculated. For sample D, $N(O)$ was estimated to be 7.4×10^{19} . If all of the benzoyl peroxide reacted to form crosslinks at the rate of one crosslink per molecule, 12×10^{19} network chains/cm.³ would have been produced. A crosslinking efficiency of 60% may therefore be estimated. This value is in accord with those for other systems.²⁶ A similar result was obtained for sample B.

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Résumé

Un nouvel élastomère résistant aux hautes températures, SiB-2, a été étudié par les méthodes de relaxation à l'étirement, module-température et volume-température. Le SiB-2 était plus stable qu'un élastomère apparenté, un caoutchouc de silicone irradié, ayant approximativement un temps de relaxation double à 250°C. Un mécanisme possible pour rendre compte de cette stabilité accrue est discuté. Aux basses températures, T_g du SiB-2 était située à -34°C , ce qui peut être comparé avantageusement avec $T_i = -60^\circ\text{C}$, pour ce polymère. Par comparaison, SiB-3 à une température $T_i = -60^\circ\text{C}$, alors que le SiB-4 modifié présente une $T_i = -25^\circ\text{C}$. T_m du SiB-2 était égale à $+56^\circ\text{C}$.

Zusammenfassung

Ein neues Hochtemperatur-Elastomeres, SiB-2, wurde mittels Spannungsrelaxations-, Modul-Temperatur- und Volum-Temperaturverfahren untersucht. SiB-2 erwies sich als stabiler als ein verwandtes Polymeres, strahlungs-vulkanisierter Silikonkautschuk, und besass eine mehr als doppelt so hohe chemische Relaxationszeit bei 250°C . Mögliche Mechanismen für die Erhöhung der Stabilität werden diskutiert. Bei niedrigen Temperaturen wurde T_g für SiB-2 zu -34°C bestimmt, was gut einem $T_i = -30^\circ\text{C}$ für dieses Polymere entspricht. Vergleichsweise ist für SiB-3 $T_i = -60^\circ\text{C}$, während phenyl-modifiziertes SiB-4 ein $T_i = -25^\circ\text{C}$ besitzt. T_m wurde für SiB-2 zu $+56^\circ\text{C}$ bestimmt.

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