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

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

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Summary

Stress relaxation properties of SiB-2 and poly(dimethyl siloxane) were compared in air and pure nitrogen. The effect of a protective filler system was also investigated for these materials. In addition, stress relaxation experiments were conducted on unfilled SiB-1 and SiB-1.5 in air only.

The crystalline structure of a special SiB-2 was investigated by X-ray techniques (courtesy of Olin), and by force-temperature experiments. The thermodynamic melting point of SiB-2 was found to be 66°C, and qualitative information was obtained on the crystallite size distribution.

The physical and mechanical properties of SiB-1 and a series of random copolymers of SiB-1 and SiB-2 were investigated by modulus-temperature and weight-loss experiments. SiB-1 and all the copolymer compositions investigated were found to have well-developed crystallinity. Thermal stability increased from SiB-2 to SiB-1, as expected.

The poly-*m*-carboranylenesiloxanes, better known as the SiB polymers, are of special interest because of their outstanding high-temperature properties. The first report *(1)* in this series was primarily concerned with a physical characterization of SiB-2. Stress relaxation, modulus-temperature, and volume-temperature techniques were employed to study the glass transition, T_g, and the melting point, T_m. The rubbery plateau region and maintenance of useful properties at elevated temperatures were primary points of emphasis.

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A second paper (2) reported thermal stability studies of elasto-
meric networks at high temperatures. Use was made of a very pure
nitrogen atmosphere. It was demonstrated that several polymers
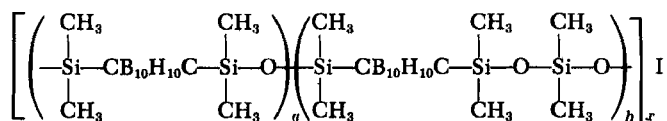exhibited unexpected stability under these conditions.

Much of the pertinent literature is discussed in Refs. 1 and 2.
However, attention is called to a comprehensive review paper on
SiB polymer synthesis and properties by Schroeder et al. (3), two
excellent discussions of carborane chemistry by Cotton and Wil-
kinson (4a) and Hawthorne (4b), and a thermal stability study by
Green and Mayes (4c).

The present work is concerned with three experiments: (1) com-
parison of several SiB polymers with poly(dimethyl siloxane) in
air and pure nitrogen at elevated temperatures by stress-relaxation
techniques, (2) the crystalline structure of SiB-2 as investigated by
X-ray and force-temperature methods, and (3) the physical and
mechanical properties of SiB-1 and a series of random copolymers
of SiB-1 and SiB-2 as investigated by modulus-temperature and
weight-loss studies. The present experiments will be compared to
past results where pertinent.

EXPERIMENTAL

Materials

Several types of SiB-2 panels were kindly supplied by Dr. H.
Schroeder of the Olin Mathieson Chemical Corporation, New
Haven, Conn. In addition, Olin Mathieson supplied unmolded
SiB-1 and random copolymers of SiB-1 and SiB-2 in powder form,
which were subsequently molded and cross-linked in these labora-
tories. The structure of the copolymers is as follows:

$$\left[\left(\begin{array}{c}CH_3\\|\\-Si-CB_{10}H_{10}C-\\|\\CH_3\end{array}\begin{array}{c}CH_3\\|\\Si-O\\|\\CH_3\end{array}\right)_n\left(\begin{array}{c}CH_3\\|\\Si-CB_{10}H_{10}C-\\|\\CH_3\end{array}\begin{array}{c}CH_3\\|\\Si-O-\\|\\CH_3\end{array}\begin{array}{c}CH_3\\|\\Si-O\\|\\CH_3\end{array}\right)_b\right]_x \quad I$$

The formulation of these materials is given in Table 1.

A pure gum poly(dimethyl siloxane) elastomer was kindly sup-
plied by Dr. A. C. Martellock of the General Electric Company,
Waterford, N.Y. The preparation of this material was outlined in
Ref. 2. Poly(dimethyl siloxane) is better known by the name sili-
cone rubber. All unfilled SiB polymers and silicone rubber samples
were extracted for 24 hr in acetone, ethyl acetate, or toluene before

TABLE 1

Description of SiB Polymers

Code	Sample	Formulation
#2-A and #2-B	Plain SiB-2	100 parts SiB-2(θCH = CH$_2$), 0.5 part DC-40 Press-molded 5 min at 300°C Postcured: 4 hr at 100°C 2 hr at 150°C 2 hr at 250°C
#2-C	Crystalline SiB-2	Similar to above
#393 and #394	Filled SiB-2	SiB-2(θCH = CH$_2$) 100 parts SiO$_2$ 37.5 parts Fe$_2$O$_3$ 5 parts DC-40 2 parts
$a/b = 1/0$	SiB-1	100 parts SiB-1(θCH = CH$_2$), 2 parts Dicup Press-molded 210°C, 25,000 psi, 30 min Postcured 2 hr at 275°C
$a/b = 3/1$	SiB-1.25	100 parts SiB-1.25 (θCH = CH$_2$) Heated air at 275°C for 2 hr
$a/b = 1/1$	SiB-1.50	100 parts SiB-1.5(θCH = CH$_2$), 2 parts Dicup Press-molded 235°C, 25,000 psi, 30 min
$a/b = 2/3$	SiB-1.60	100 parts SiB-1.6(θCH = CH$_2$), 2 parts Dicup Press-molded 250°C, 25,000 psi, 30 min Postcured in air 3 hr at 260°C
$a/b = 1/3$	SiB-1.75	100 parts SiB-1.75(θCH = CH$_2$), 2 parts Dicup Press-molded 300°C, 25,000 psi, 30 min

use. Samples were subsequently dried in a vacuum oven for 2 to 3 days. No trace of extracting agent could be found, and weight losses were usually under 2%.

Instrumental

All stress relaxation experiments were carried out either in a standard relaxometer (5a), or a standard relaxometer housed in an environmental chamber. The latter, equipped with calcium chloride–dried nitrogen of 99.996% purity pumped into the inner chamber, supplied a nitrogen atmosphere of superior quality (2). The

crystallite size distribution experiments also used the standard relaxometer, heating rates of approximately 1°C/10 min being employed.

The 10-sec modulus $G(10)$ was measured using a Clash-Berg (6), a standard Gehman, and a high-temperature modification (7). The usual rate of heating was 1–2°C/min.

RESULTS AND DISCUSSION

Stress Relaxation in Air and Nitrogen

Plain SiB-2, filled SiB-2, and plain silicone rubber were studied in air and nitrogen at elevated temperatures. In addition, SiB-1 and SiB-1.5 were studied in an air atmosphere only. These experiments should be considered together with those reported in Ref. 2, since plain silicone rubber measurements under nitrogen were reported therein; that work will be summarized below for comparison purposes.

The results of stress relaxation experiments on plain SiB-2 in pure nitrogen are shown in Fig. 1. The quantity $f(t)/f(0)$ represents the ratio of stress at time t to that at time zero. Also included in Fig. 1 is an observation in air at 261°C. These experiments show that SiB-2 retains about half its modulus after 24 hr at 323°C in the absence of oxygen. In air at 261°C, the material first rapidly relaxes, then oxidatively cross-links. [The rise in $f(t)/f(0)$ is caused by sample shrinkage due to cross-linking, not to the cross-linking itself.] Normal relaxation curves in air are not obtained above about 225°C. In Ref. 1 an "enriched" nitrogen atmosphere was employed. The present "pure" nitrogen atmosphere is significantly better, as can be seen by a simple comparison of the data.

The protective properties of the Fe_2O_3–SiO_2 filler system are illustrated in Fig. 2. Essentially no relaxation is observed in air below about 250°C, except for a small amount of physical relaxation. The maximum rate of stress decay is observed at about 267°C, a temperature at which the sample still remains surprisingly stable. Above this temperature, oxidative cross-linking becomes more important, becoming predominant above 300°C.

When protective filler and nitrogen are used in conjunction, the polymer retains $f(t)/f(0) = 0.87$ after 12 hr at 416°C. The simultaneous reduction of the effects of oxygen by protective filler and nitrogen appears greater than the effects of both separately. This is discussed further below.
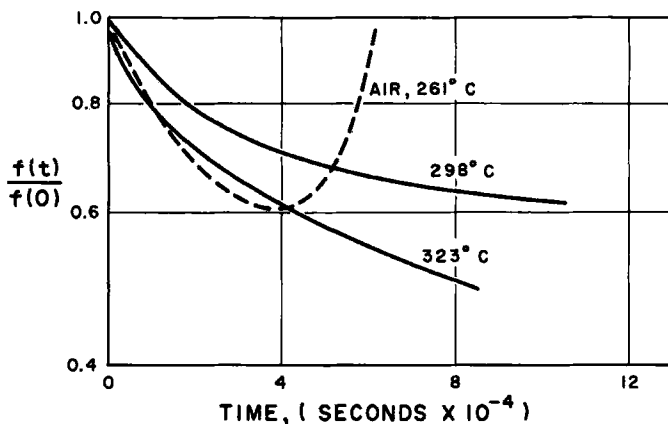
FIG. 1. Stress relaxation of unfilled SiB-2. Values at 298° and 323°C in pure nitrogen. Value at 261°C in air emphasizes effects of oxygen and/or water vapor.

The study of poly(dimethyl siloxane) stress relaxation in air is shown in Fig. 3. The corresponding values in pure nitrogen (2) yield similar results at temperatures some 50°C higher.

Both silicone rubber experiments yielded straight lines for In [$f(t)/f(0)$] vs. time concordant with an hypothesis of first-order kinetics and single-reaction mechanisms. Arrhenius plots yielded straight lines, from which apparent energies of activation were cal-
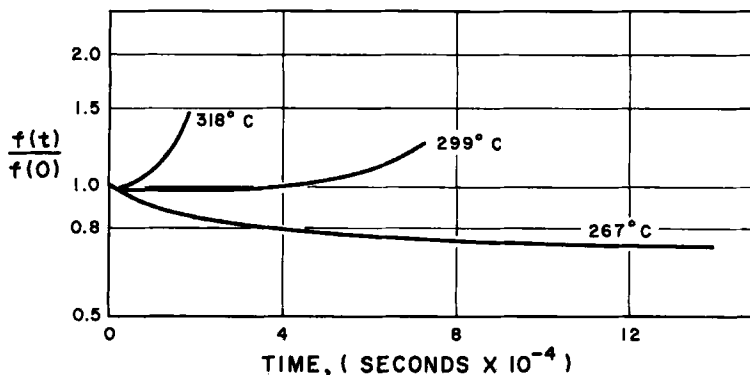
FIG. 2. Stress relaxation of filled SiB-2 in air. Below 260°C, little relaxation was observed. The maximum decrease in $f(t)/f(0)$ was found near 267°C. Above this temperature, sample shrinkage becomes important, and balances Si—O bond interchange at 299°C. Sample shrinkage, causing an apparent increase in $f(t)/f(0)$, predominates at 318°C and above.
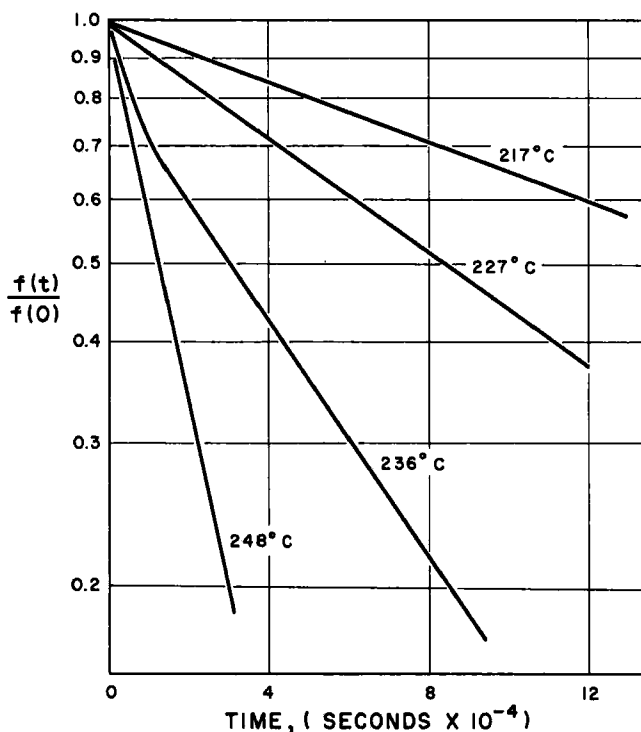
FIG. 3. Stress relaxation of silicone rubber in air. Note straight lines.

culated. The value for silicon rubber in air is 43 ± 5 kcal/mole, and
the value under nitrogen is 35 ± 5 kcal/mole (2).

The latter value probably represents the energy of activation of
the Si—O bond interchange (8,9) in the near absence of catalytic
materials. The mechanism of stress relaxation in air is unclear, but
it is well known that many materials catalyze the Si—O bond inter-

TABLE 2

Maximum Useful Temperatures (°C) of Elastomers for 24-Hr Exposures

Polymer	Air	Nitrogen
Plain SiB-2	260	325
Filled SiB-2	300	>416
Plain silicone rubber	230	280
SiB-1.5	275	—
SiB-1.0	285	—

change. Unfortunately, the question Are both experiments a measure of the same reaction? cannot be answered with the present data. The two apparent activation energies (above) might be the same, but the result is inconclusive. The differences between SiB-2 in air and nitrogen resemble the silicone rubber results, except that some curvature in the relaxation plots is observed.

Table 2 summarizes the results of the several experiments. Listed are the maximum temperatures at which the samples maintained at least $1/e = 0.368$ of their modulus or did not excessively cross-link through a 24-hr period. The "nitrogen" values are seen to be 50°C or more higher than "air" values, and the use of protective filler raises the useful limit of SiB-2 about 40°C. The maximum useful temperature of filled SiB-2 in nitrogen could not be ascertained, because risk of instrumental damage was apparent. Olin workers found SiB-2 chemically stable at 500°C (*10*).

Table 2 also illustrates the progressive increase in stability from SiB-2 through SiB-1.5 to SiB-1. It should be emphasized that these materials all had no filler or antioxidants.

Crystallinity in SiB-2

Olin scientists were able to prepare semicrystalline samples of SiB-2 with special techniques. These samples exhibit superior
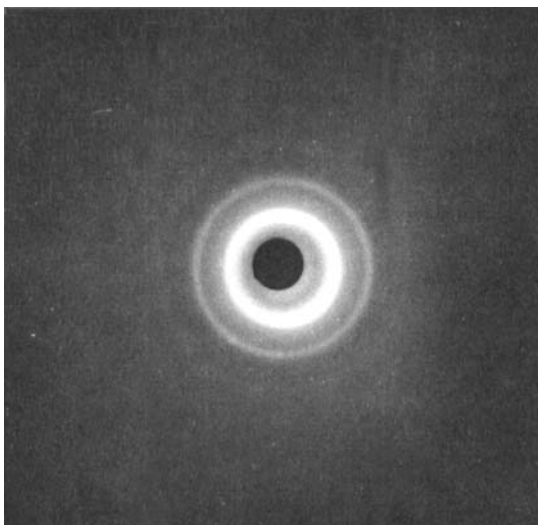

FIG. 4. X-ray photograph of crystalline SiB-2, courtesy of H. Schroeder, Olin.

TABLE 3

SiB-2 X-Ray Results[a]

Diffraction angle, 2θ	Relative intensity
25.4°	100
29.0°	100
43.0°	30
51.6°	5
56.8°	10
66.0°	5
68.4°	5

[a] X-ray photograph courtesy Hans Schroeder, Olin Research Center, New Haven, Conn.

mechanical properties at room temperature, elongations up to 720%, and tensiles to 460 psi (11).

A flat-plate X-ray photograph of this material is shown in Fig. 4, courtesy of Dr. H. Schroeder, Olin Research Center, New Haven, Conn. Copper $K\alpha$ radiation was employed for a 1-hr exposure on molded sheet. Diffraction angles and relative intensities are tabulated in Table 3.

Crystallite Size Distribution

Force-temperature studies were used to further characterize SiB-2 crystallinity. The samples were stretched to extension α at room temperature, time (overnight) was allowed to attain near-equilibrium conditions, and then the samples were heated as described above.

A typical result is shown in Fig. 5. Melting starts at room temperature, or just above, and finishes near 60°C. Above this temperature, a normal rubbery plateau is observed. The first derivative of Fig. 5 is shown in Fig. 6. Also included are two other values of α. Figure 6 is normalized by multiplication of the y axis by $100/(W_c - W_m)$, $W_c - W_m$ representing the crystalline minus melt forces.

The temperature at which crystallites melt is a function of their size (12), the smaller, or more imperfect crystallites melting at lower temperatures. Since decreasing modulus may be associated with decreasing crystallinity, Fig. 6 illustrates the following:
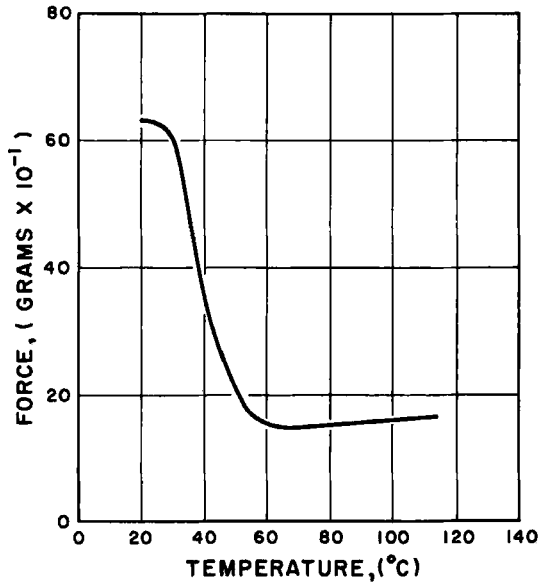
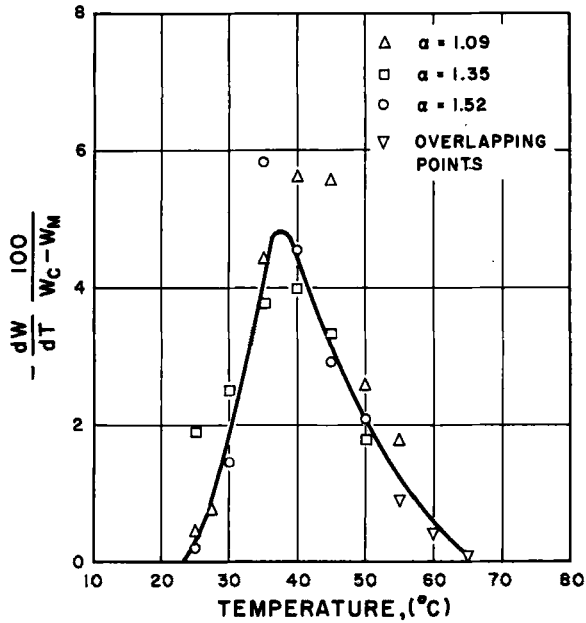**FIG. 5.** Force-temperature plot of crystalline SiB-2, $\alpha = 1.52$.

FIG. 6. Normalized first derivative plot of Fig. 5. Most abundant species of SiB-2 crystallites given by maximum.

1. A qualitative distribution of crystallite size, the maximum at 37°C probably representing the most abundant species.

2. The largest or most perfect crystallites melt at 66°C, which represents the thermodynamic melting point (13), T_m. Previously, crystallinity had been noted as an isolated case (1), with $T_m = 56°C$.

The above experiment "sees" only crystallites existing before initial stretch. Crystallites induced by stretching usually form with orientation in the direction of stretch, and actually tend to reduce force slightly. Volume-temperature, or dynamic measurements (12) in contrast, measure total crystallinity, preexisting plus induced. Thus, while total crystallinity and melting points are functions of extension (14), force-temperature studies measure only the initial population.

Thermoelastic Study

This experiment provides a powerful tool for evaluating the internal energy contribution to the elastic retractive force (15). The thermoelastic equation may be written (16)

$$\frac{f_e}{f} + \gamma\beta T = 1 - \frac{T}{f}\left(\frac{\partial f}{\partial T}\right)_{P,L} - \frac{\beta T}{\alpha^3 - 1} \tag{1}$$

where f_e is the internal energy fraction of the force f, β is the volume coefficient of expansion, T the absolute temperature, α the ratio of stretched to unstretched lengths, and γ a semiempirical constant (17), related to volume change on extension. All the parameters on the right may be evaluated by experiment, yielding $f_e/f + \gamma\beta T$.

Three considerations are important in the present study: (1) the sample be above T_m, (2) α be sufficiently high, and (3) thermodynamic equilibrium be attained. Owing to decreased sample tensile above T_m, these conditions were met only once. After reaching 120°C at $\alpha = 1.090$ (above), the sample was held at these conditions overnight to obtain thermodynamic equilibrium.

Thermoelastic measurements were made as before (16). The results are shown in Fig. 7. Owing to possible crystallization, data below about 70°C are of questionable validity. The general shape of the curve, however, is the same as observed for poly(dimethyl siloxane) and poly(ethyl acrylate) (16).

An important feature of Fig. 7 is the maximum exhibited at about 110°C, which represents the thermoelastic inversion point. The
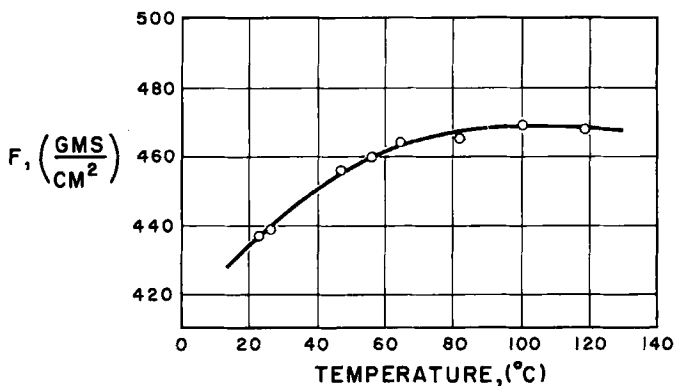
FIG. 7. Thermoelastic properties of SiB-2. Note thermoelastic inversion point near 110°C.

quantity $(\partial f/\partial T)_{P,L} = 0$, $\beta = 8.3 \times 10^{-4}$ (*1*), and $f_e/f + \gamma BT = -0.08$ was calculated.

Since the above was obtained from but a single experiment, a rather large ± error must be considered. Nonetheless, one conclusion may be reached: Amorphous SiB-2 behaves as an ordinary elastomer in that most of the retractive force is entropy-driven rather than originating in internal energy changes.

MODULUS-TEMPERATURE STUDIES ON SiB-1 AND COPOLYMERS OF SiB-1 AND SiB-2

The 10-sec modulus $3G(10)$ was determined in air between -60 and 400°C. Figure 8 shows a typical result for SiB-1.5. Figure 8 illustrates the three characteristic temperatures obtained for these materials: T_g, the glass transition temperature; T_m, the crystalline melting point; and T_{ox}, the temperature at which oxidative cross-linking becomes important. SiB-1 and all copolymer compositions tested were typical semicrystalline elastomers (*5b*).

Still referring to Fig. 8, below $T_g = 0°C$, SiB-1.5 is a hard glass. Between 0°C and $T_m = 185°C$, the polymer is in a leathery condition. In this temperature range the material might be expected to have good damping characteristics and may be useful to convert vibrational energy into heat. Above 185°C, SiB-1.5 is elastomeric. At $T_{ox} = 330°C$, the rate of oxidative cross-linking (*5c*) becomes rapid, and the sample hardens. Heating was continued up to 500°C.
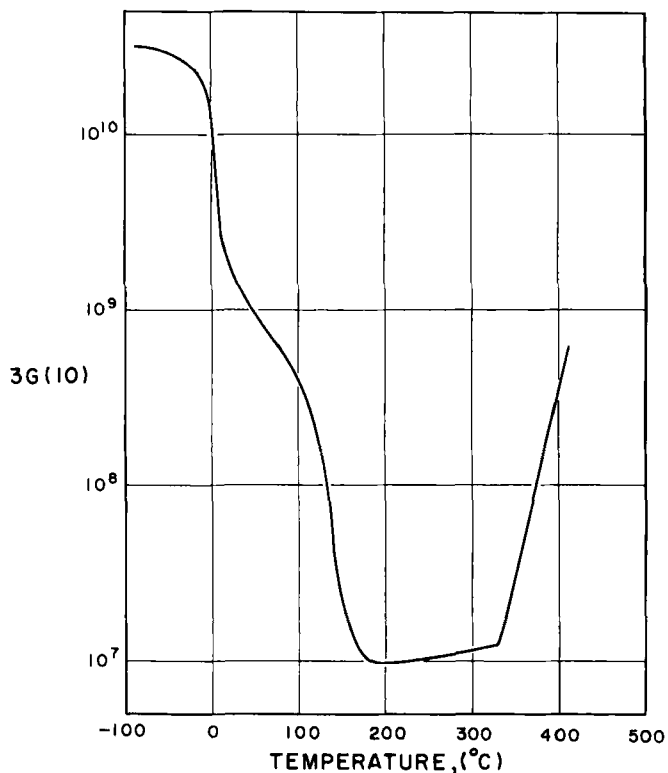
FIG. 8. Modulus temperature study of SiB-1.5. Note well-developed crystallinity, as indicated by flat hump between 50 and 150°C. $T_g = 0$°C, $T_m = 185$°C, and $T_{ox} = 330$°C for this polymer.

TABLE 4

Copolymer Transition Temperatures, °C

Polymer	T_g	T_m	T_{ox}
SiB-1	25	240	340
SiB-1.25	10	230	320
SiB-1.50	0	185	330
SiB-1.60	−5	170	355
SiB-1.75	−20	145	310
SiB-2	−30	66[a]	340

[a] SiB-2 as usually prepared by Olin is amorphous. Crystallinity is apparently caused by traces of SiB-1 (11).

TABLE 5

Weight-Change Studies of SiB Polymers in Air

	Property	SiB-1	SiB-1.5	SiB-2	Silicone rubber
After 70 min at 382°C	Weight loss	None	1%	1%	ca. 75%
	Color and mechanical	Nil change in color or properties	Darker, somewhat harder	Darker, slightly crazed	Becomes white powder
After 70 min at 504°C (after above)	Weight loss	1%	5%	9%	
	Color and mechanical	Yellow, brittle glass	Dark brown, brittle glass	Yellowed, cracked, weak rubber	

SiB-1.6 and below formed interesting glasslike structures under these conditions, while SiB-1.75 converted into a white powder.

Values of T_g, T_m, and T_{ox} are collected in Table 4. Also shown are the corresponding values for SiB-2 (*1*). The quantities T_g and T_m decrease progressively with increasing SiB number. However, T_{ox} remains constant, the observed variation perhaps depending on sample purity, heating rate, etc.

WEIGHT-LOSS STUDIES

SiB-1, SiB-1.5, SiB-2, and silicone rubber strips were weighed, heated to 382°C in air for 70 min, and reweighed. The same samples then were heated to 504°C for an additional 70 min, and weighed again. Resulting weight losses, together with obvious changes in color and mechanical properties, are shown in Table 5.

Several observations were made:

1. Silicone rubber completely decomposes in air at 382°C.

2. SiB-1 and SiB-1.5 form glasses at 504°C, with a slight retention of useful properties.

3. SiB-2 behaves in an intermediate manner between (1) and (2).

CONCLUSIONS

Within the framework of the above experiments, SiB-2 has significantly better high-temperature properties than its parent, silicone rubber. Under anaerobic conditions, filled SiB-2 has a long useful life at temperatures exceeding 400°C. SiB-1 and SiB-1.5 were

shown to be significantly more stable than SiB-2, which is expected because of increased carborane content (*3,4c*).

The present experiments, unfortunately, allow no conclusion to be drawn about the kinetic role of oxygen and water vapor in silicone rubber and SiB-2 stress relaxations. It is unclear whether the same reaction(s) are occurring in air and nitrogen, or what would be observed if still purer nitrogen atmospheres were to be employed.

The presence of moderate crystallinity definitely improves the elastomeric properties of SiB-2 near room temperature. The crystallites serve as pseudo-cross-link sites, and also exhibit filler properties. SiB-2 crystallites appear to have a distribution of sizes, as measured by force-temperature techniques. The melting point of the most perfect crystallites was 66°C.

The physical properties of.SiB-1 and random copolymers of SiB-1 and SiB-2 have been characterized by modulus-temperature studies. The glass transition of SiB-1 is near 25°C, and the crystalline portion of the polymer melts at 240°C, yielding a normal elastomer above this temperature. Above 335°C, oxidative crosslinking becomes important in an air atmosphere.

The several SiB copolymers all exhibited well-defined crystallinity, which is unusual (*5d*). The glass transition temperatures were shown to decrease in a regular manner from SiB-1 to SiB-2. This behavior is well known for other systems (*18*).

Acknowledgment

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Zusammenfassung

Die Spannungsrelaxationseigenschaften von SiB-2 und Poly(dimethylsiloxan) in Luft und Stickstoff werden miteinander verglichen. Ebenfalls untersucht wurde der Einfluss eines schützenden Füllmaterials in diesen Substanzen. Weiterhin wurden Spannungsrelaxationsmessungen mit ungefülltem SiB-1 und SiB-1.5 in Luft durchgeführt.

Die kristalline Struktur eines besonderen SiB-2 wurde röntgenographisch untersucht (durch Entgegenkommen von Olin) und mittels Kraft-Temperatur Experimenten. Der thermodynamische Schmelzpunkt von SiB-2 ergab sich bei 66°C und qualitative Aussagen wurden über die Grössenverteilung der Kristallite erhalten.

Die physikalischen und mechanischen Eigenschaften von SiB-1 und einer Reihe von statistischen Kopolymeren aus SiB-1 und SiB-2 wurden mittels Modul-Temperatur und Gewichtsverlustexperimenten untersucht. SiB-1 und alle untersuchten Kopolymeren hatten gut ausgebildete Kristallinität. Die thermische Stabilität erhöhte sich wie erwartet von SiB-2 zu SiB-1.

Résumé

On a comparé les propriétés de relachement de tension du SiB-2 et du poly(diméthyl siloxane) dans l'air et en atmosphère d'azote. On a aussi etudié l'effet protecteur d'un systeme de charge pour ces matériaux. On a en plus conduit des éssais de relachement de tension dans l'air seulement avec les SiB-1 et SiB-1.5 non-chargés.

On a etudié la structure cristalline d'un SiB-2 spécial à l'aide des rayons X (contribution gracieuse d'Olin) et par des expériences force-tempéra-

ture. Le point de fusion thérmodynamique de SiB-2 est 66°C; on a aussi obtenu des renseignements qualitatifs sur la distribution des tailles de cristallites.

On a etudié les propriétés physiques et méchaniques du SiB-1 et d'une série des copolymères desordonnés de SiB-1 et SiB-2 par des éssais de modulus-température et pertes de poids. On a trouve que SiB-1 et toutes les compositions copolymériques étudiées possèdent une cristallinité bien developée. La stabilité thermique augmente de SiB-2 à SiB-1, comme prévue.