

# Exactly Alternating Silarylene-Siloxane Polymers. V. Evaluation of the Mechanical Properties of Crosslinked Elastomers

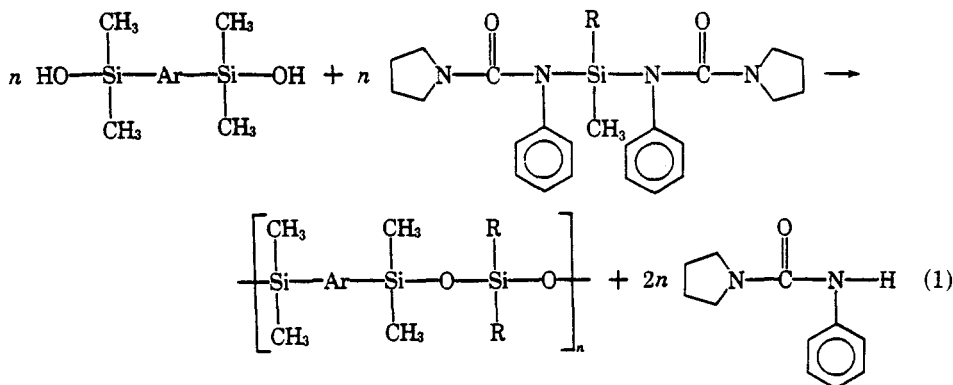
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## Synopsis

The search for technologically useful elastomers with good thermal stability at elevated temperatures combined with low temperature flexibility has led us and others to the preparation of a series of linear alternating silarylene-siloxane polymers. Because of the very favorable thermal stabilities of these polymers, a detailed study was made of methods for their vulcanization and for the evaluation of their mechanical properties. The results of these investigations are described, including mechanical properties of the vulcanizates both before and after heat aging and before and after immersion in different solvents, as well as their characteristics after prolonged and repeated extension.

## INTRODUCTION

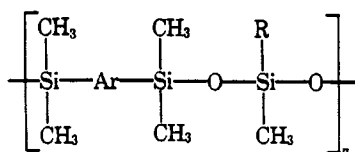
Silarylene-siloxane polymers, and among these especially the exactly alternating structures, have attracted considerable research attention for their unique combination of high thermal stability and pronounced low temperature flexibility.<sup>1-6</sup> However, there have been no extensive reports on their mechanical properties in relation to potential applications. Recently, a new method was developed in our laboratories to prepare high molecular weight, exactly alternating silarylene-siloxane polymers by a condensation polymerization reaction of arylenedisilanol and reactive, difunctional bisureidosilanes,<sup>5,7</sup> as follows:



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Using this method, we have prepared for evaluation 12 different homopolymers and copolymers, which can be represented by the general formula shown below and listed in Table I:



By this method 12 different homopolymers and copolymers were prepared as shown below and listed in Table I:

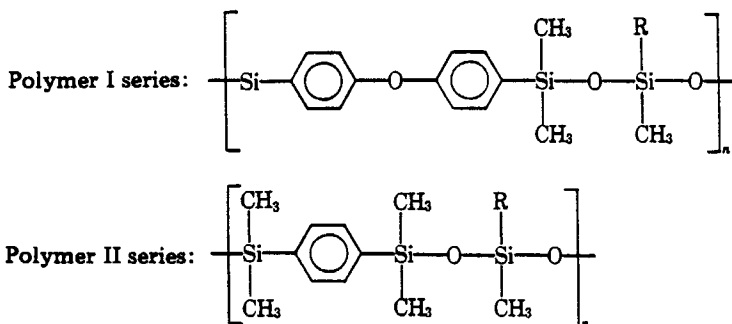


TABLE I  
Compositions of Exactly Alternating Silarylene-Siloxane Polymers Prepared for Evaluation as Vulcanized Elastomers

Polymer	Ar unit	Vinyl unit (mol %)	$\bar{M}_w^a$	$T_g^b$ (°C)
IA	<i>p</i> -phenylene (I)	0	132,000	-62
IB	<i>p</i> -phenylene (I)	5	119,000	-63
IC	<i>p</i> -phenylene (I)	7.5	126,000	-63
ID	<i>p</i> -phenylene (I)	100	199,000	-69
IIA	<i>p,p'</i> -diphenyl ether (II)	0	214,000	-24
IIB	<i>p,p'</i> -diphenyl ether (II)	5	74,000	-25
IIC	<i>p,p'</i> -diphenyl ether (II)	7.5	184,000	-25
IID	<i>p,p'</i> -diphenyl ether (II)	100	232,000	-34
IIIA	50:50 mol % mixture of I and II	0	163,000	-42
IIIB	50:50 mol % mixture of I and II	5	240,000	-43
IIIC	50:50 mol % mixture of I and II	7.5	165,000	-44
IIID	50:50 mol % mixture of I and II	100	219,000	-51

<sup>a</sup> As determined by GPC.<sup>6</sup>

<sup>b</sup> As determined by DSC.<sup>6</sup>

The letter designations applied to these polymers in Table I and the text are for the following siloxane compositions:

R	R in Polymers (mol %)			
	A	B	C	D
CH <sub>3</sub>	100	95	92.5	0
CH = CH <sub>2</sub>	0	5	7.5	100

In addition to the two homopolymer series, a series of random copolymers, polymer III, were prepared containing equimolar amounts of the two silarylene units from I and II.

Several formulation parameters were also found to be important in optimizing the properties of vulcanizates. These included the amount of filler, the type and amount of crosslinking agent, and the type and amount of antioxidant. Hence, considerable attention was devoted to the choice of the additives used in this work, on the basis of the considerations discussed below.

It is well known<sup>8</sup> that vulcanization of siloxane polymers may be brought about by a free-radical reaction based on the thermal decomposition of organic peroxides, and the ease with which polysiloxanes undergo this vulcanization depends on the type of pendant organic group in the polymer. It has been found that crosslinking is easiest through vinyl side groups, more difficult through methyl, and still more difficult through phenyl or nitrile groups.<sup>8</sup> Consequently, a less reactive peroxide such as dicumyl peroxide may initiate the crosslinking of vinyl-containing polysiloxanes, whereas only peroxides producing highly reactive radicals, such as benzoyl peroxide, can vulcanize methyl-containing polymers. Also, significantly higher efficiencies and smaller amounts of initiator are required in the former case to yield a constant crosslinking density in the vulcanizate, which in turn is determined by the concentration of vinyl groups present in a polymer. Based on these considerations, dicumyl peroxide was used in this work for vulcanization of the alternating silarylene-siloxane polymers containing vinyl units of Table I.

In order to increase the moduli and improve the ultimate mechanical properties of these vulcanized elastomers, including their tensile strength, tear resistance, and abrasion resistance, all of the polymers were compounded with 30 pph of a hydrophobic fumed silica filler. Tullanox 500 was used for this purpose because it has been pretreated with a trimethylsilylating agent so that most of the silanol surface groups were replaced with hydrophobic trimethylsilyl groups, thus preventing possible chemical reactions with the elastomer which could cause excessive crosslinking and unfavorable mechanical properties.<sup>9</sup>

Furthermore, in order to inhibit oxidation of these polymers during their use at elevated temperatures, it was necessary to add a suitable antioxidant into the formulation of the vulcanizates. Oxidation is a free-radical chain reaction, which probably occurs by direct attack on the methyl groups attached to the polymer backbone, and this reaction can increase the crosslink density of the elastomer during its thermal aging, causing severe changes in their original mechanical properties.<sup>10,11</sup> Ferric oxides have been found to be an effective antioxidant in silicone polymers, and their use can considerably extend the service life of such polymers by preventing drastic increases in tensile strength and decreases in elongation, which are usually observed after prolonged heat aging of iron-free silicon rubbers.<sup>11</sup> Even higher antioxidant efficiencies have been found for iron pentacarbonyl, which is soluble in many polysiloxanes, by Neal and Pines<sup>12</sup> and

by Peters and co-workers.<sup>11</sup> Consequently, in order to determine if the same was the case with exactly alternating silarylene-siloxane polymers, both types of antioxidants were tested in these investigations.

## SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

The main components of the polymer films prepared for these investigations were the hydrophobic filler, Tulanox 500, the peroxide and the antioxidant. These components were mixed together with the polymer, and the mixture was subjected to heat and pressure to form a film, which was then post-cured at higher temperatures before testing, as follows:

**Compounding of 5 and 7.5% vinyl-containing polymers:** To a weighed amount of polymer placed in a 100-mL Teflon beaker was added either 0.7 phr or 0.4 phr of dicumyl peroxide, for 5% or 7.5% vinyl containing polymer, respectively, followed by 30 phr of the filler and 3 phr of powdered  $\text{Fe}_2\text{O}_3$ . The mixture was homogenized by rolling between two 8 in. Teflon rods to form a dark, rust-colored material with the consistency of bread dough.

**Compounding of 100% vinyl-containing polymers:** In order to achieve more precise and homogeneous compounding of very small amounts of dicumyl peroxide, it was added in the form of a  $1.0 \times 10^{-4}$  g/10 mL chloroform stock solution. The amount of this solution required for 0.05 phr of peroxide was stirred for about 15 min with a weighed quantity of polymer in a 100-mL Teflon beaker using a Teflon-coated stirring bar, the solvent was evaporated in a vacuum oven held at room temperature, and filler and antioxidant were added and stirred in as described above.

**Compounding with  $\text{Fe}(\text{CO})_5$  as an antioxidant:** In a 100-mL, one-necked, round-bottomed flask equipped with a Teflon-coated stirring bar, serum cap, and nitrogen inlet and outlet, a weighed amount of polymer sample was dissolved in chloroform and inert atmosphere was established. The desired amount of the peroxide stock solution was added from a gas-tight syringe, and the mixture was stirred for about 15 min followed by addition of  $\text{Fe}(\text{CO})_5$ . The mixture was stirred for another 15 min, transferred to a 100-mL Teflon beaker and placed in a vacuum oven to evaporate the solvent. The filler was then added in the usual manner.

**Press cycle:** The film molding assembly used in these investigations was a sandwich structure which consisted of two 15 cm<sup>2</sup> pieces of heavy aluminum on the outer sides, two sheets of Teflon-coated aluminum foil with the Teflon side turned inwards on the inner sides, and an aluminum shim (approximately 10 mm thick with a 60.3 × 3.8 mm section cut out of the center) in the middle. The compounded polymer was placed in the mold, spread to uniformly fill the shim, and the assembly was closed and introduced into a Pasadena PH1 Press, in which the temperature was monitored by means of a thermometer affixed to each platen and controlled via a built-in thermistor. The press, which had been equilibrated to approximately 50°C, was closed and the pressure of 10,000 psi was applied and held for 20 min. The pressure was then decreased to 6,000 psi and the temperature raised to 125°C. These conditions were maintained for another 20 min followed by a second temperature rise to 150°C and held there for the final 30 min.

**Post-cure:** In order to remove any remaining peroxide decomposition

products, vulcanizates were subjected to a 24-h post-curing cycle in an oven at 180–200°C; then the rectangular test samples (40 × 3 × 0.15 mm) were cut out from the film obtained. Sample dimensions were measured using a Manostat Dial Type 6921 Caliper (accuracy ± 0.5 mm) and a Starrett Dial Micrometer (accuracy  $1 \times 10^{-2}$  mm).

**Heat aging:** For this purpose a Lindberg Heavy-Duty SB Type 167 Furnace was used in which a 25 × 70 mm Viton tube fitted with an air inlet and outlet was placed. Air was introduced through a trap held at ambient temperature, and the flow was maintained at a constant rate at all times. The furnace was allowed to equilibrate for at least 2 h before introduction of the samples, which were placed on small Viton coats. Heat aging was preceded by a second post-cure at 160°C for 24 h, which was performed in the furnace under the same air flow. The samples were removed as the furnace was allowed to reequilibrate at 200°C, and the samples were returned to the furnace and aged for 25, 50, and 150 h, respectively.

**Solvent resistance:** The amount of swelling which vulcanizates underwent in different solvents was determined in each case according to the standard methods described in ASTM D471-75. In a typical experiment, three samples cut from the pressed film were immersed in solvent for 168 h at 25°C. The length, width, and thickness of each sample was measured before and after the immersion period to the nearest 0.1 mm, and the percent change of volume was determined. The tensile tests were carried out in not less than 2 min and not more than 3 minutes after removal from solvent. All measurements and results reported herein are based on the unswollen cross-sectional area.

**Ambient temperature tensile tests:** Tensile tests were carried out using a Toyo Tensilon, Model Utm-II. The samples were stretched at a constant crosshead speed of  $6.67 \times 10^{-4}$  m/s, and the data obtained were processed by a computer program which yielded stress-strain values as well as their corresponding plots.<sup>13</sup> All the data reported herein for ultimate tensile strengths were based upon true stresses using the stressed cross-sectional area of the sample.

**Glass transition temperatures:** Glass transition temperatures of crosslinked vulcanizates were determined using a Perkin-Elmer DSC-2 at heating rates of 20°/min.

## RESULTS AND DISCUSSION

The major thrust of these investigations was directed towards the evaluation of polymers containing 5 and 7.5 mol % of vinyl groups pendant to the main chain, both for effectiveness of crosslinking by reaction with peroxides and for mechanical properties of the filled and vulcanized elastomers.

### Tensile Properties of Non-Heat-Aged Vulcanizates

The results obtained from tensile tests performed on non-heat-aged vulcanizates are shown in Tables II and III. It can be seen from the data in these tables that the vulcanizates containing soluble iron carbonyl as the antioxidant generally exhibited better tensile properties than those containing the powdered iron oxide antioxidant, so that an increase in tensile strength and elongation at break was observed in most cases when  $\text{Fe}(\text{CO})_5$  was used. For both antioxidants, however, the initial moduli were about the same.

TABLE II  
Mechanical Properties of Filled and Vulcanized Elastomers Prepared from Alternating  
Silylene-Siloxane Polymers of Table I with  $\text{Fe}(\text{CO})_5$  as Antioxidant<sup>a</sup>

Polymer	Initial modulus		Tensile strength		Elongation at break (%)
	(MPa)	(psi)	(MPa)	(psi)	
IB	1.6	240	1.9	270	51
IC	2.6	370	6.6	960	154
ID	5.2	750	4.0	580	11
IIB	1.9	270	1.8	260	54
IIC	3.9	560	6.7	970	99
IID	2.7	390	4.9	720	88
IIIB	3.0	440	8.0	1100	132
IIIC	4.2	600	4.3	620	78
IIID	11.0	1600	6.9	1000	17

<sup>a</sup> Composition of compounded elastomer in parts by weight: polymer 100, filler 30,  $\text{Fe}(\text{CO})_5$  0.25; the filler is "Tullanox 500," a powdered silica with a nominal particle size of 0.007  $\mu\text{m}$  and trimethylsiloxy surface groups.

The major exception to this comparison was with polymer IIB. This polymer, which had the lowest molecular weight of all (see Table I) had some compounding problems and formed films of poor quality, perhaps accounting for the discrepancy in the results obtained.

The mechanical properties of representative non-heat-aged vulcanizates in which  $\text{Fe}(\text{CO})_5$  was used as an antioxidant are given in Table II and Figures 1 and 2. As can be seen from Figure 1, in which behavior of the vulcanizates prepared from the copolymers containing 50:50 mol % mixtures of the two disilanol monomers is shown, the tensile strengths and initial moduli significantly increased while elongations at break correspondingly decreased with increasing vinyl content. The 100 mol % vinyl-substituted vulcanizates appeared very tough yet still were not too brittle to measure. However, when compared to the properties of commercial polysiloxanes<sup>8</sup> or even to silylene-siloxane polymers prepared previously by others,<sup>3</sup> which exhibited ultimate elongations of 100–400% for crosslinking degrees of about 1% or less, the values obtained for these alternating silylene-siloxane polymers suggest that 5% and 7.5% crosslinking degrees were perhaps too high for optimum elastomeric behavior.

TABLE III  
Mechanical Properties of Filled and Vulcanized Elastomer Prepared from Alternating  
Silylene-Siloxane Polymers of Table I with  $\text{Fe}_2\text{O}_3$  as Antioxidant<sup>a</sup>

Polymer	Initial modulus		Tensile strength		Elongation at break (%)	Tensile set (%)
	(MPa)	(psi)	(MPa)	(psi)		
IC	2.2	320	3.5	510	90	3.6
IIIB	1.6	230	2.6	380	86	1.6
IIC	3.6	520	4.7	680	80	1.3
IIIA	0.9	130	8.0	1160	332	1.5
IIIB	3.8	550	4.2	610	75	1.6
IIIC	4.8	700	6.2	900	79	3.8

<sup>a</sup> Composition of compounded elastomer in parts by weight: polymer 100, filler 30, powdered  $\text{Fe}_2\text{O}_3$ ; see the footnote of Table II for filler description.

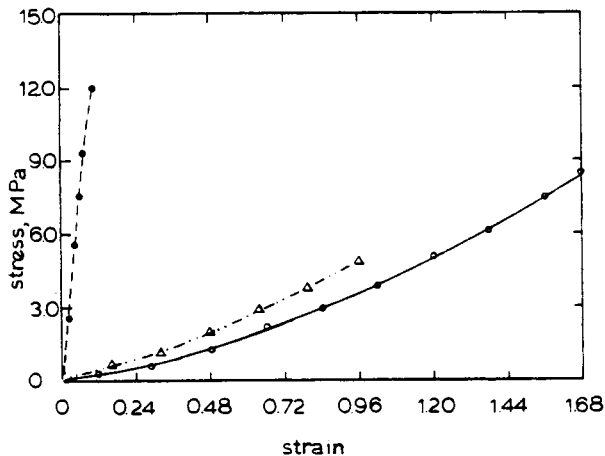


Fig. 1. Stress-strain curves for the group III polymers compounded with  $\text{Fe}(\text{CO})_5$ : (○) polymer IIIB (5 mol % vinyl groups); (△) polymer IIIC (7.5 mol % vinyl groups); (●) polymer IIID (100 mol % vinyl groups).

From the results obtained during these investigations it is difficult to deduce any regular effect of in-chain arylene groups on the mechanical properties. However, it appears that *p,p'*-diphenyl ether units, II, imparted higher tensile strength without significantly reducing elongation, but the best combination of these properties was achieved with 50:50 mol % copolymers of the two arylenes. This conclusion is illustrated for 7.5 mol % vinyl-containing polymers, IC, IIC, and IIIC, in Figure 2. In summary, therefore, the most desirable combination of properties was obtained from the polymer IIIB prepared from the mixture of two arylene disilanols and containing 5 mol % of vinyl groups. This sample showed a tensile strength of 1160 psi and an ultimate elongation of 132%.

Vulcanizates compounded with powdered  $\text{Fe}_2\text{O}_3$  showed mixed results, as listed in Table III. These results probably reflect an inferior homogenization

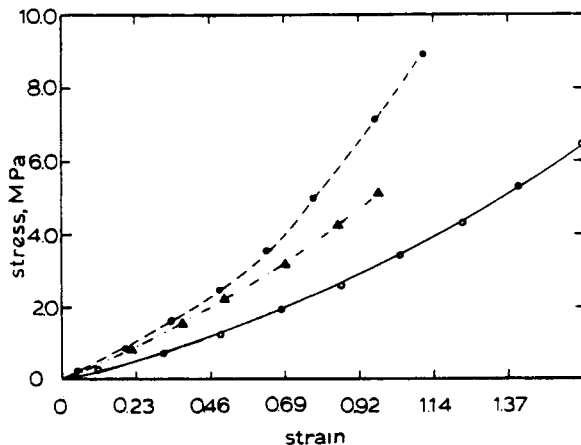


Fig. 2. Stress-strain curves for polymers containing 7.5 mol % vinyl units compounded with  $\text{Fe}(\text{CO})_5$ : (○) polymer IC; (●) polymer IIC; (▲) polymer IIIC.

compared to that achieved when the soluble antioxidant,  $\text{Fe}(\text{CO})_5$ , was used. That is, while polymers IIC, IIIB, and IIIC exhibited relatively high ultimate tensile strength of about 600–700 psi, polymer IC showed a relatively low value.

### Solvent Resistance

The resistance to various solvents is often a critical requirement for high performance elastomers. To evaluate this property for alternating silarylene–siloxane vulcanizates, by following the ASTM test method D471-75, vulcanized samples were immersed for 7 days at 25°C in water, benzene and Reference Fuel B (a 70/30 mixture of *iso*-octane and toluene). The percent swell was determined as described in the Experimental section. Those samples tested in water and in reference fuel B were also subjected to ultimate tensile strength evaluation before and after immersion, and the results obtained are shown in Tables IV and V.

It can be seen from the data in these tables that the vulcanizates swelled on the average about 10% in water, 200% in reference fuel B, and 210% in benzene. However, although the samples exhibited such large swelling in the organic media, their mechanical properties did not change very much, except for a slight decrease in tensile strength.

### Glass Transition Temperatures

Glass temperature data obtained by DSC measurements for both the as-prepared polymers<sup>6</sup> and the compounded and vulcanized elastomers are given in Table VI. It can be seen from the data in this table that the vulcanizates prepared from the *p*-phenylene-containing polymers, I, exhibited the lowest glass transition temperatures, and those from the *p,p'*-diphenyl ether polymers, II, were the highest. As expected, within each series the increasing vinyl unit content increased the glass transition temperature, but even the 100 mol % vinyl-containing polymers of groups I and III exhibited glass transition temperatures which were low enough for an acceptable elastomer.

An interesting trend was observed within each of the three groups. While vulcanization increased the glass transition temperatures of the 100 mol % vinyl polymers by about 10°C, little effect was observed on the 7.5 mol % vinyl polymers, and an unexpected decrease of  $T_g$  was observed for the 5 mol % vinyl-containing vulcanizates. No satisfactory explanation for this result has as yet been found.

TABLE IV  
Solvent Resistance for the Alternating Silarylene–Siloxane Polymers of Table III

Polymer	Percent swelling		
	H <sub>2</sub> O	Benzene	Reference fuel B
IC	9	225	236
IIB	8	225	196
IIC	17	211	139
IIIB	10	183	216
IIIC	2	212	196



TABLE V  
Resistance of Alternating Silarylene-Siloxane Vulcanizates of Table III to Water and to Reference Fuel B

Polymer	Properties after immersion in water <sup>a</sup>				Properties after immersion in reference fuel B <sup>a</sup>			
	Swell (%)	Initial modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Swell (%)	Initial modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
IC	9	4.6 (+110)	3.7 (+5)	58 (-35)	236	1.9 (-14)	3.0 (-16)	96 (+7)
IIB	8	2.2 (+38)	1.2 (-46)	57 (-34)	196	1.9 (+16)	1.7 (-35)	58 (-33)
IIC	17	7.4 (+110)	6.4 (+36)	64 (-20)	139	7.7 (+114)	6.4 (+94)	72 (-10)
IIIB	10	4.6 (+21)	7.3 (+74)	97 (+29)	216	3.8 (0)	3.9 (-7)	68 (-9)
IIIC	2	4.0 (-17)	4.0 (-35)	65 (-18)	196	2.9 (-40)	3.1 (-50)	59 (-25)

<sup>a</sup> After immersion for 7 days at 25°C; numbers in parentheses represent percent change in property.

TABLE VI  
Glass Transition Temperatures of As-Prepared and Vulcanized Alternating Silarylene-Siloxane Polymers from Table I

Polymer	Vinyl unit content (mol %)	$T_g$ of as-prepared polymer (°C)	$T_g$ of vulcanizate (°C)
IB	5	-63	-70
IC	7.5	-63	-59
ID	100	-69	-55
IIB	5	-25	-38
IIC	7.5	-25	-26
IID	100	-34	-27
IIIB	5	-43	-49
IIIC	7.5	-44	-42
IIID	100	-51	-40

### Stress-Relaxation and Second Cycle Loading

In order to evaluate the behavior of the alternating silarylene-siloxane vulcanizates during and after prolonged stress application, stress-relaxation and second cycle loading experiments were performed. The former were conducted by extending a sample to 30–70% of its initial length and maintaining it at that length for 10 min, after which the stress required to maintain the strain was measured. In no case was any significant change of stress observed as indicated by the data in Table VII.

The second cycle loading experiments were performed by extending vulcanizates to 50% of their initial length at a constant strain rate of  $0.036 \text{ s}^{-1}$ , suddenly releasing stress at this point, and then reapplying it to bring the sample back to 50% extension. Values for the initial moduli obtained for selected samples are shown in Table VIII, and a typical behavior is illustrated in Figure 3 for polymer IIIC, as an example. It can be seen from this table that, even after sustaining considerable stress in the first loading cycle, the alternating silarylene-siloxane vulcanizates did not develop enough internal fatigue to eventually cause a drop in moduli to any significant degree. This property may prove to be of uppermost engineering importance for specific applications of these materials.

### Heat Aging

Typical results of the heat-aging studies in air are given in Table IX and Figure 4, using as an example the data obtained for polymer IC, which was prepared from the *p*-phenylene disilanol and contained 5 mol % of vinyl groups. In general,

TABLE VII  
Stress Relaxation of Alternating Silarylene-Siloxane Vulcanizates of Table III

Polymer	Strain (%)	Extension time (min)	Initial stress (MPa)	Final stress (MPa)
IC	30		Sample failed in less than 2 min	
IIB	31	10	0.47	0.43
IIC	50	10	3.7	3.3
IIIB	70	10	3.1	2.6
IIIC	50	8.5	1.7	1.5

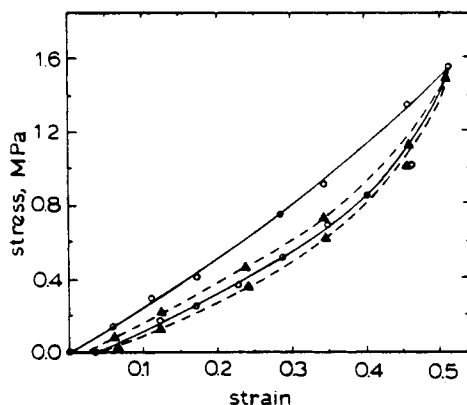


Fig. 3. Two-cycle loading of polymer IIIC: (○) first cycle; (▲) second cycle of extension and recovery.

expected, prolonged exposure to high temperatures decreased the tensile strength and elongation but increased the initial modulus. The second curing cycle had very little effect on the mechanical properties, indicating that no unreacted peroxide remained in the vulcanizates after heating from 24 h at 200°C. Although more extensive studies are in progress in our laboratory, a tentative

TABLE VIII  
Second Cycle Loading of Alternating Silarylene-Siloxane Vulcanizates of Tables II and III

Polymer	Strain (%)	Stress (MPa)	First cycle modulus (MPa)	Second cycle modulus (MPa)
<i>3.0 phr of powdered Fe<sub>2</sub>O<sub>3</sub></i>				
IC	34	1.5	3.2	3.6
IIB	38	0.8	1.8	1.9
IIC	50	3.9	6.2	5.7
IIIB	50	2.3	4.5	4.6
IIIC	50	1.5	2.5	2.5
<i>0.25 phr Fe(CO)<sub>5</sub></i>				
IC	46	1.5	2.7	2.3
IIC	50	2.3	3.5	4.1
IIIB	50	1.8	3.3	3.1

TABLE IX  
Heat Aging at 230°C in Air of the Vulcanizate of Polymer IC

Heat age (h)	Initial modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Tensile set (%)
0 <sup>a</sup>	2.2	3.5	90	3.6
0 <sup>b</sup>	2.6	6.6	150	—
0 <sup>c</sup>	2.6	3.8	84	0.6
25 <sup>c</sup>	2.7	3.2	80	0.7
50 <sup>c</sup>	3.6	4.0	68	0.9

<sup>a</sup> Two-cycle post-cure at 180–200°C for 24 h each cycle, Fe<sub>2</sub>O<sub>3</sub> antioxidant.

<sup>b</sup> Fe(CO)<sub>5</sub> antioxidant.

<sup>c</sup> One-cycle post-cure at 180–200°C for 24 h; Fe<sub>2</sub>O<sub>3</sub> antioxidant.

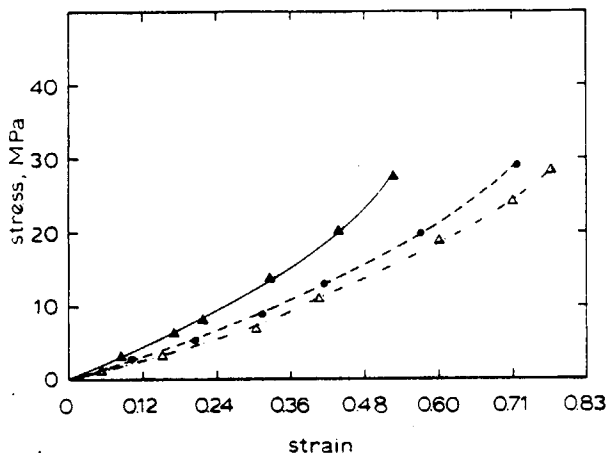


Fig. 4. Stress-strain curves of sample heat-aged at 230°C in air: Polymer IC with 3 phr of powdered  $\text{Fe}_2\text{O}_3$ : ( $\Delta$ ) 0 h; ( $\bullet$ ) 25 h; ( $\blacktriangle$ ) 50 h.

prolonged-use temperature of about 200°C in air appears to be possible for these materials.

### Effect of Molecular Weight on Vulcanizate Properties

As can be seen from Table I, most of the as-prepared polymers had weight average molecular weights ranging from 160,000 to 250,000 as determined by GPC.<sup>6</sup> However, there were exceptions, notably polymers IB and IC, with a molecular weight of about 120,000 and, most importantly, polymer IIB with a value of only 74,000. Consequently, although the  $\overline{M}_w/\overline{M}_n$  values for all of the polymers were very close to 2, it may be expected that the differences in the molecular weights of the samples could influence to some extent the variation in the values determined for certain mechanical properties. The magnitude of this effect, however, cannot be deduced on the basis of the present data and will require future attention.

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